

CRYSTALLOGRAPHIC STUDIES OF ORGANOMETALLIC AND
COORDINATION COMPOUNDS

A thesis submitted for the degree of
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by

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SUMMARY

The theory of X-ray diffraction by single crystals, and some topics in crystal structure analysis are discussed. The crystal structures of six metal complexes have been determined from diffractometer and photographic data. The complexes are:

- (i) 1:1 Cis-trans(1,5) cyclodecadiene-silver nitrate,
 $C_{10}H_{16} \cdot AgNO_3$.
- (ii) Tetramethylammonium bis(isothiocyanato)- μ -tetrakis (acetato)dicopper(II), $[(CH_3)_4N]_2 [Cu(CH_3CO_2)_2NCS]_2$.
- (iii) Tetramethylammonium bis(isothiocyanato)- μ -tetrakis (formato)dicopper(II), $[(CH_3)_4N]_2 [Cu(HCO_2)_2NCS]_2$.
- (iv) Trimeric diacetatopalladium(II), $[Pd(CH_3CO_2)_2]_3$.
- (v) Propylpentamminerhodium(III) Perchlorate, $[Rh(NH_3)_5 C_3H_7] (ClO_4)_2$.
- (vi) Hexafluoropropylpentamminerhodium(III) Perchlorate, $[Rh(NH_3)_5 C_3F_6H] (ClO_4)_2$.

(i) has a polymeric type of structure in which the olefin is coordinated via its cis and trans double bonds to two silver ions, at $Ag^+ - C=C$ (mid-point) distances of 2.37 Å (cis) and 2.35 Å (trans). The conformation of the diolefin ring accounts for its ready cyclisation to substituted cis-decalins, and the enhanced reactivity of the trans double bond is accounted for in terms of considerable sp^2-sp^2 torsional strain.

(ii) and (iii) are isomorphous, and have dimeric structures essentially similar to that of cupric acetate monohydrate. In the acetato complex the Cu...Cu separation is 2.647 Å ($\sigma = 0.003$ Å), and in the formato complex it is 2.710 Å ($\sigma = 0.002$ Å), while magnetic susceptibility measurements indicate that the formato complex exhibits substantially greater spin coupling between the copper atoms. This suggests that metal-metal bonding may play only an insignificant role in

determining the magnetic properties of these, and related copper(II) carboxylate dimers.

(iv) has a novel trimeric structure, of approximate symmetry $\bar{6}m2$ (D_{3h}), in which each palladium atom is joined to the other two by double acetate bridges. The long Pd...Pd distances, 3.105 - 3.204($\sigma = 0.001\text{\AA}$)^o show there to be no metal-metal bonding.

(v) and (vi) are isomorphous: in both complexes the rhodium atom has the expected octahedral coordination, with a σ -bonded alkyl or fluoroalkyl group on one side, and an ammine group on the other side of a square plane containing four ammine groups and a central rhodium atom. The propyl ligand has a strong trans-influence, demonstrated by a relative lengthening of 0.183 $\text{\AA}$ (23 σ)^o in the trans Rh-N bond, while the hexafluoropropyl group exerts a much smaller trans-influence, 0.086 $\text{\AA}$ (8 σ)^o. However, both ligands are strongly trans labilising in solution, and this suggests that kinetic factors may operate in the fluoropropyl complex, arising from the π -acceptor properties of the $-\text{C}_3\text{F}_6\text{H}$ group.

A more detailed abstract is given at the beginning of the appropriate chapter.

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dedicated
to
my parents

CONTENTS

<u>Chapter 1</u> :	Theoretical Background	8
<u>Chapter 2</u> :	Crystal Structure Analysis	35
<u>Chapter 3</u> :	The Crystal Structure of 1:1 Cis-trans (1,5) cyclodecadiene-silver nitrate	60
<u>Chapter 4</u> :	The Crystal Structures of Tetramethyl- ammonium bis(isothiocyanato)- μ -tetrakis (acetato)dicopper(II) and Tetramethyl- ammonium bis(isothiocyanato)- μ -tetrakis (formato)dicopper(II) : a discussion of antiferromagnetism in copper(II) carboxylate dimers	95
<u>Chapter 5</u> :	The Crystal Structure of Trimeric diacetatopalladium(II)	135
<u>Chapter 6</u> :	The Crystal Structures of Propylpentam- minerhodium(III) Perchlorate and Hexafluoropropylpentamminerhodium(III) Perchlorate : structural trans-influence in d^6 octahedral complexes.	178
<u>Appendix</u> :	Publications	214

"The intolerable wrestle
With words and meanings!"

.....T.S. Eliot.

CHAPTER 1

Theoretical Background

In this chapter a necessarily brief and incomplete account is presented of the interaction of X-rays with crystals.

1.1 Nature and Properties of X-rays

X-rays are penetrating electromagnetic radiations of wavelengths ca. $0.1 - 100 \text{ \AA}$ emitted when a beam of high speed electrons collides with the surface of a solid. Two types of spectra are emitted.

Continuous (White) Radiation: This is radiation emitted by an electron as it is decelerated by multiple collisions with atoms of the target matter. Its wavelength distribution depends on the accelerating voltage. Emission starts abruptly at a minimum wavelength, λ_0 (the Duane-Hunt Limit), corresponding to the kinetic energy of the electron being absorbed in a single collision. Thereafter its intensity rises to a maximum at ca. $3/2\lambda_0$ and then falls more gradually with increasing wavelength.

Characteristic Radiation: This is radiation of discrete wavelengths emitted when an atom reverts to the ground state following ionisation in an inner shell. In particular, at energies of ca. 10keV electrons may be ejected from the innermost (K) shell by collisions. The ionised atom is extremely unstable and the K shell vacancy is filled rapidly by the descent of an electron from the next higher shell (L) or next but one (M), and energy is emitted as electromagnetic radiation in the X-ray region. These radiations are termed K_α and K_β respectively. Under high resolution the α and β lines are seen to consist of closely

spaced pairs of transitions α_1, α_2 and β_1, β_2 since there are two sublevels differing slightly in energy, from which an electron may descend. A very useful radiation is CuK_α , whose properties are summarised below:

CuK_α $\text{K}_{\alpha 1}$ $\lambda = 1.54051$, $\text{K}_{\alpha 2}$ $\lambda = 1.54433$ $\text{\AA}$

Excitation Voltage 8.98 kV

Operating Conditions: Fine focus 32 - 40 kV, 16 - 25 mA

1.2 Absorption and Filtering

Absorption of monochromatic X-radiation follows the law

$$I = I_0 \exp(-\mu t) \quad 1.1$$

where I is the transmitted intensity, I_0 the incident intensity, μ the linear absorption coefficient for the wavelength, and t the thickness of material traversed.

If μ is plotted against λ for a given element, the result is a series of curves of the type $\mu \approx k\lambda^3$, connected by sharp jumps (Fig 1.1). These discontinuities are absorption edges and occur at wavelengths where the incident X-ray photon is sufficiently energetic to eject an electron from an atomic orbital. In particular the K absorption edge lies slightly to the short wavelength side of the K_β lines for that element. The absorption edge shifts to longer wavelengths with decreasing atomic number. Thus in general the element of atomic number $(Z-1)$ has an absorption edge between the characteristic K_α and K_β lines for the element Z . This has important consequences in choosing selective filters for reducing the intensity of the undesirable K_β lines, with a much smaller loss in the K_α (Fig. 1.1)

By selecting a filter material one or two atomic numbers lower still the K_α line may be removed as well. This is the basis of the Balanced Filter Method¹, which may be

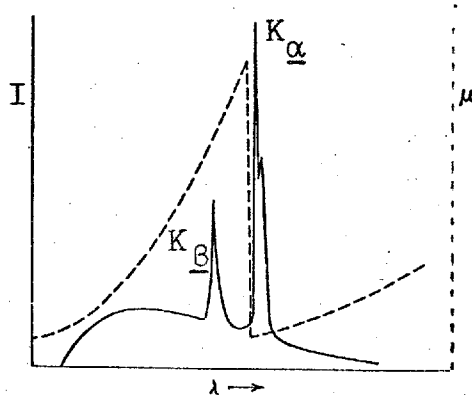


Figure 1.1

The effect of a β -filter

I X-ray spectrum showing characteristic peaks.

μ linear absorption coefficient of β -filter.

Table 1.1 The Seven Crystal Systems

Crystal System	Parameters	Lattice Symmetry
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	$\bar{1}$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$; $\beta \neq 90^\circ$	$2/m$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	mmm
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	$4/mmm$
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	$\bar{3}m$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$	$6/mmm$
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	$m\bar{3}m$

$\neq$ implies no necessary equality

used to give an accurate assessment of the white radiation background. Another method of obtaining monochromatic radiation is to use a Crystal Monochromator², although this results in a serious loss in intensity of the primary beam.

1.3 Lattices and Crystals

A lattice is a three dimensional array of points or motifs all having parallel orientations and identical environments. Adjacent lattice points may be joined up to form a parallelepiped, and the whole lattice may be regarded as made up by translations of this parallelepiped, or unitcell, along its three principle directions.

In a similar way a crystal is made up of unitcells stacked regularly in three dimensions. This fact was first suggested by the regularity of the external forms of crystals, and was later confirmed by quantitative studies of their interfacial angles, and later still by the first diffraction experiments with crystals³.

1.4 Crystal Systems and Symmetry

There are seven crystal systems based on unitcells of different shapes. These are summarised in Table 1.1. For any lattice the unitcell may be chosen in an infinity of ways, although practically it is important to choose a cell which conforms to the symmetry of the lattice.

The symmetry operations which occur in crystals are 1,2,3,4 and 6 fold rotations, inversion through a centre, and reflection in a plane. Other types of operations result from combinations of these elements amongst themselves, and with the translational operations of the lattice. It has been shown⁴ that 230 Space Groups result when these symmetry elements are combined fully within the seven crystal systems.

Thus any crystal belongs to one of the 230 Space Groups.

1.5 Scattering of Radiation

According to classical theory electrons are set into forced oscillation by incident electromagnetic radiation. The oscillating charge then re-emits radiation which is coherent with the incident radiation. Thus each electron becomes a source of secondary wavelets, and the wave observed in a given direction is the resultant of the waves scattered by all the electrons of the object.

Because of their relatively greater mass atomic nuclei are not set into oscillation by X-rays to any appreciable extent. They do not, therefore, contribute to the scattering of X-rays. Of course other mechanisms occur for the scattering of X-rays by electrons!- Compton Scattering and Fluorescence. Compton Scattering gives rise to incoherent radiation and merely contributes to the background intensity. The effects of Fluorescence are more subtle and will be considered in a later section.

Consider a beam of monochromatic X-rays falling on a body of non-uniform electron density. The scattered wave at B can be written with respect to the wave at A (Fig. 1.2) as

$$\rho(\underline{r})dV \exp \frac{2\pi i}{\lambda} |\underline{r}| (\cos \psi - \cos \varphi) \quad 1.2$$

where the vector $\vec{AB}$ is denoted by $\underline{r}$ and B is contained in the volume element dV , with electron density $\rho(\underline{r})$. The total scattered wave is given by the integral over the volume of the body

$$\int \rho(\underline{r}) \exp \frac{2\pi i}{\lambda} |\underline{r}| (\cos \psi - \cos \varphi) dV \quad 1.3$$

Defining vectors $\underline{s}_1$ and $\underline{s}_2$ of length $1/\lambda$ along the incident

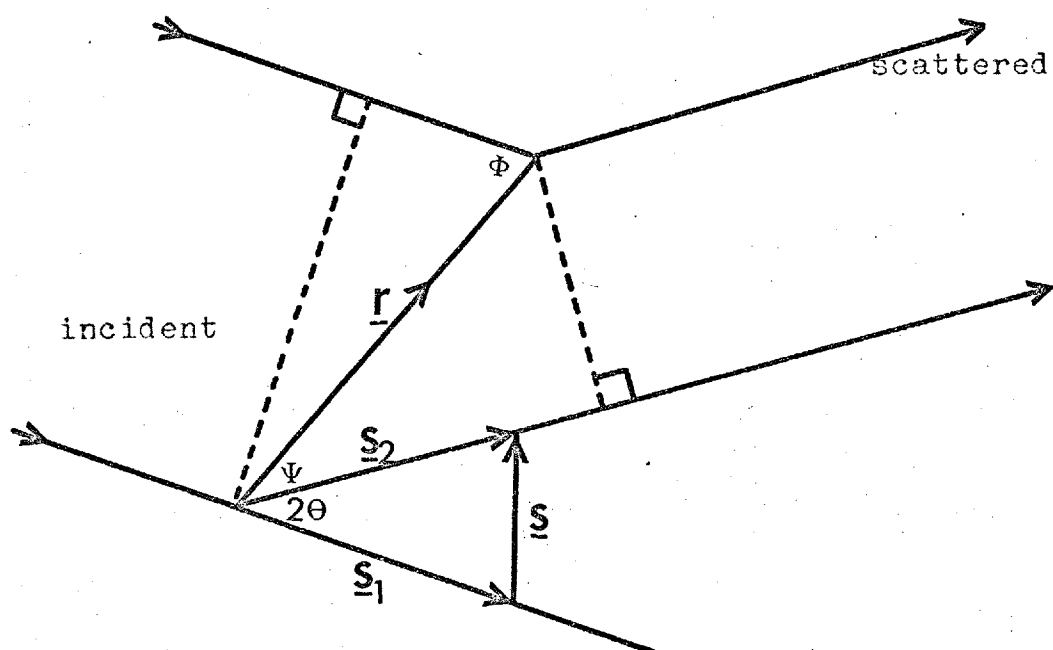


Figure 1.2

and scattered beam directions, then

$$\underline{r} \cdot \underline{s}_1 = \frac{|\underline{r}| \cos \varphi}{\lambda} \quad 1.4$$

$$\underline{r} \cdot \underline{s}_2 = \frac{|\underline{r}| \cos \psi}{\lambda} \quad 1.5$$

the total scattered wave then becomes

$$\int \rho(\underline{r}) \exp 2\pi i \underline{r} \cdot (\underline{s}_1 - \underline{s}_2) dV \quad 1.6$$

or

$$G(\underline{s}) = \int \rho(\underline{r}) \exp 2\pi i \underline{r} \cdot \underline{s} dV \quad 1.7$$

where the vector $\underline{s} = (\underline{s}_1 - \underline{s}_2)$, and has a length of $2\sin\theta/\lambda$ and its direction is the bisector of the angle between the incident and scattered beams

Thus the important result follows that the amplitude of the scattered wave, $G(\underline{s})$, is given by the Fourier Transform⁵ of the electron density.

1.6 Scattering by a Free Atom

For an atom of atomic number Z the wave scattered will be the resultant of the wavelets from its Z electrons. Thus

$$f(\underline{s}) = \int_V \rho(\underline{r}) \exp 2\pi i \underline{r} \cdot \underline{s} dV \quad 1.8$$

It is generally assumed that the electron density, $\rho(\underline{r})$ has spherical symmetry, and is thus a function only of the distance x from the nucleus. Equation 1.8 may then be re-written

$$f(|\underline{s}|) = \frac{2}{|\underline{s}|} \int_0^\infty \rho(x) \sin(2\pi s x) x dx \quad 1.9$$

The quantity $f(|\underline{s}|)$ is known as the Atomic Scattering Factor, and for a given atom type is a function only of $\sin\theta/\lambda$ (under the assumption of spherical symmetry). In practice, values of $f(|\underline{s}|)$ are tabulated⁶ for the common atom types, using varying degrees of sophistication in the

quantum mechanical calculation of $\rho(x)$.

1.7 Diffraction by a Single Crystal

If there are N atoms in the unitcell, each with positions defined by the fractional components (x_n, y_n, z_n) from the origin parallel to the crystallographic axes, then

$$\underline{r}_n = \underline{a}x_n + \underline{b}y_n + \underline{c}z_n \quad 1.10$$

and the wave scattered by the n th. atom, with respect to the hypothetical wave at the origin may be written

$$f_n \exp 2\pi i \underline{r}_n \cdot \underline{s} \quad 1.11$$

where f_n is the Atomic Scattering Factor for the n th. atom. The result for the unitcell is obtained by summing over the N atoms - assuming that the electron density is everywhere zero except in the vicinity of an atom.

$$G_u(\underline{s}) = \sum_{n=1}^N f_n \exp 2\pi i \underline{r}_n \cdot \underline{s} \quad 1.12$$

Lattice related atoms in the crystal may be designated by the ends of vectors of the form $u\underline{a} + v\underline{b} + w\underline{c} + \underline{r}_n$, where u, v, w are integers. The total transform for the crystal is therefore

$$G_t(\underline{s}) = \sum_{u=0}^{U-1} \sum_{v=0}^{V-1} \sum_{w=0}^{W-1} G_u(\underline{s}) \quad 1.13$$

for a crystal composed of UVW unitcells.

Each of the summations in 1.13 is of the form

$$\sum_{t=0}^{T-1} = (1 + \exp 2\pi i \underline{a} \cdot \underline{s} \dots + \exp 2\pi i t \underline{a} \cdot \underline{s} \dots + \exp 2\pi i T \underline{a} \cdot \underline{s}) \quad 1.14$$

$$= \frac{1 - \exp 2\pi i T \underline{a} \cdot \underline{s}}{1 - \exp 2\pi i \underline{a} \cdot \underline{s}} \quad 1.15$$

which reduces to

$$\sum_{t=0}^{T-1} = \frac{\sin T \pi \underline{a} \cdot \underline{s}}{\sin \pi \underline{a} \cdot \underline{s}} \quad 1.16$$

Its value is T when $\underline{a} \cdot \underline{s}$ is an integer, but is negligible otherwise.

Therefore $G_t(\underline{s})$ may be written

$$G_t(\underline{s}) = G_u(\underline{s}) \left(\frac{\sin U\pi \underline{a} \cdot \underline{s}}{\sin \pi \underline{a} \cdot \underline{s}} \right) \left(\frac{\sin V\pi \underline{b} \cdot \underline{s}}{\sin \pi \underline{b} \cdot \underline{s}} \right) \left(\frac{\sin W\pi \underline{c} \cdot \underline{s}}{\sin \pi \underline{c} \cdot \underline{s}} \right) \quad 1.17$$

Thus $G_t(\underline{s})$ is zero unless $\underline{a} \cdot \underline{s}$, $\underline{b} \cdot \underline{s}$, $\underline{c} \cdot \underline{s}$ simultaneously have integer values - h , k , l , say. i.e.

$$G_t(\underline{s}) = 0 \quad \text{in general} \quad 1.18$$

$$\text{and } G_t(\underline{s}) = UVWG_u(\underline{s}) \quad 1.19$$

$$\text{when } \underline{a} \cdot \underline{s} = h \quad 1.20$$

$$\underline{b} \cdot \underline{s} = k \quad 1.21$$

$$\underline{c} \cdot \underline{s} = l \quad 1.22$$

The conditions for non-zero $G_t(\underline{s})$ are the Laue equations. Thus the total diffracted amplitude for the crystal is directly proportional to the Fourier Transform of the unitcell contents, at points in Reciprocal Space defined by the integers h , k , l , but is negligible elsewhere

1.8 Bragg's Law

The Laue equations are of fundamental importance in diffraction theory, but are not very instructive as to the geometric nature of diffraction by crystals. W.L.Bragg⁷ gave the process of diffraction a simple physical interpretation by identifying the integers h , k , l as the Miller Indices of the lattice planes. Re-casting equations 1.20 - 22 in the form

$$\frac{\underline{a} \cdot \underline{s}}{h} = 1 \quad 1.23$$

$$\frac{\underline{b} \cdot \underline{s}}{k} = 1 \quad 1.24$$

$$\frac{\underline{c} \cdot \underline{s}}{l} = 1 \quad 1.25$$

and subtracting 1.24 from 1.23

$$\left(\frac{a}{h} - \frac{b}{k}\right) \cdot \underline{s} = 0 \quad 1.26$$

Thus the vector $\underline{s}$ is perpendicular to the vector $\left(\frac{a}{h} - \frac{b}{k}\right)$, which is in the plane hkl (Fig 1.3). By a similar argument $\underline{s}$ is also perpendicular to $\left(\frac{c}{l} - \frac{a}{h}\right)$ and $\left(\frac{c}{l} - \frac{b}{k}\right)$, and thus $\underline{s}$ must be perpendicular to the parametral plane hkl .

The d spacing of the hkl planes is given by the perpendicular distance of the plane hkl from the origin, and is thus the projection of $\frac{a}{h}$, $\frac{b}{k}$ or $\frac{c}{l}$ on $\underline{s}$. i.e

$$d_{hkl} = \frac{\frac{a \cdot \underline{s}}{h}}{|\underline{s}|} \quad 1.27$$

But from 1.23 $\frac{a \cdot \underline{s}}{h} = 1$, and $\underline{s} = 2 \frac{\sin \theta}{\lambda}$. Thus

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad 1.28$$

or,

$$2d_{hkl} \sin \theta = \lambda \quad 1.29$$

which is Bragg's law. The factor n which appears in some statements of Bragg's law - giving the number of wavelengths path difference between successive planes in the family - has been absorbed into the indices hkl . Thus these indices may contain a common factor, and there is always one wavelength path difference between the origin plane and the hkl plane of the family of parallel planes.

Thus Bragg, having noted that the vector $\underline{s}$ bisects the incident and scattered beams, and by relating the integers h , k and l with the Miller Indices of a lattice plane, was able to compare the process of diffraction with "reflection" at a parallel stack of planes (Fig 1.4). However, in contrast to normal reflection a reflected beam is only observed at discrete values of θ given by 1.29.

This was a very important result since it enabled early workers to interpret, for the first time, their complex experimental results on the diffraction of X-rays

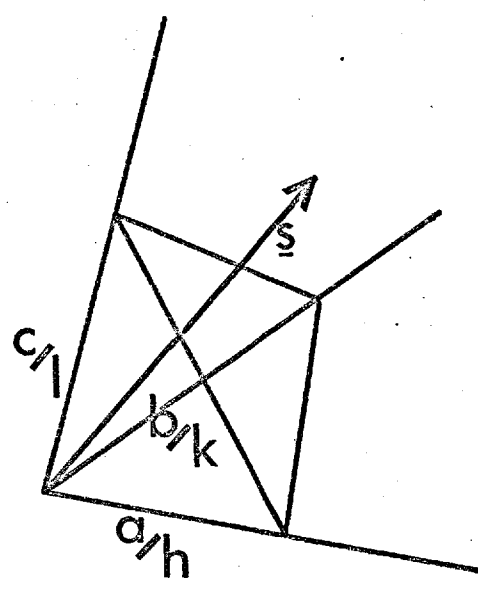


Figure 1.3

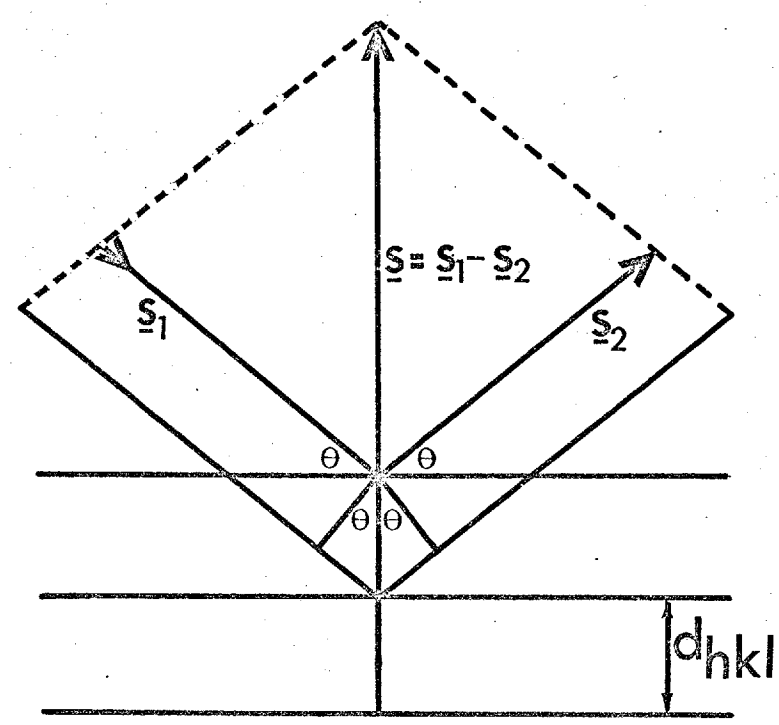


Figure 1.4

Relationship between the plane (hkl) and the vector $\underline{s}$.

by crystals. As such it must rank as one of the greatest advances in science in the twentieth century.

1.9 The Reciprocal Lattice

Bragg's law may be regarded as a physical method of solving Laue's equations. Mathematical solutions lead to the abstraction of the Reciprocal Lattice, which is the basis of all modern methods of X-ray diffraction. 1.20 states that the projection of $\underline{s}$ on $\underline{a}$ is constant for a fixed value of h . Thus the ends of the vectors $\underline{s}$ which satisfy 1.20 lie on a plane perpendicular to $\underline{a}$. If h is zero the plane passes through the origin. If h is unity it makes a certain intercept on $\underline{a}$; if $h = 2$ it makes double the intercept, and so on. Thus a set of parallel planes of constant spacing is set up, each plane corresponding to a particular value of h . Similarly, sets of equi-spaced planes will also be set up perpendicular to $\underline{b}$ and $\underline{c}$, respectively. The intersections of these planes represent the end points of vectors which satisfy the Laue equations simultaneously. These intersections define a lattice of points which is called the Reciprocal Lattice.

The unitcell of this lattice is defined by three non-coplanar vectors, $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$, and each point in the lattice is defined by h , k and l . To relate these vectors to those of the real cell, we note that $\underline{a}^*$ is the vector defined by the intersection of planes perpendicular to $\underline{b}$ and $\underline{c}$ respectively. Thus

$$\underline{a}^* = p(\underline{b} \times \underline{c}) \quad 1.30$$

$$\underline{b}^* = q(\underline{c} \times \underline{a}) \quad 1.31$$

$$\underline{c}^* = r(\underline{a} \times \underline{b}) \quad 1.32$$

where p , q and r are constants

$$\text{Then, } \underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^* \quad 1.33$$

$$\text{but } h = a.s \quad 1.20$$

$$= a.(h\underline{p}(\underline{bxc}) + k\underline{q}(\underline{cxa}) + l\underline{r}(\underline{axb})) \quad 1.34$$

$$= h\underline{pa}.\underline{bxc} \quad 1.35$$

since $\underline{a}.\underline{cxa}$, $\underline{a}.\underline{axb} = 0$

$$\text{i.e. } l = \underline{pa}.\underline{bxc} \quad 1.36$$

$$\text{or } p = \frac{1}{\underline{a}.\underline{bxc}} = \frac{1}{V} \quad 1.37$$

where V is the volume of the real cell.

Similarly it may be shown that

$$q = r = \frac{1}{V} \quad 1.38$$

$$\text{Thus } \underline{a}^* = \underline{bxc}/V \quad 1.39$$

$$\underline{b}^* = \underline{cxa}/V \quad 1.40$$

$$\underline{c}^* = \underline{axb}/V \quad 1.41$$

When combined with Bragg's Law the Reciprocal Lattice provides a powerful tool for the observation and interpretation of diffraction patterns, namely the Reflection or Ewald⁸ sphere.

1.10 The Structure Factor

The amplitude of scattering, $G_u(\underline{s})$, at a reciprocal lattice point is termed the structure factor at that point, denoted by F_{hkl} . Combining 1.12 and 1.10

$$F_{hkl} = \sum_{n=1}^N f_n \exp 2\pi i (x_n \underline{a}.s + y_n \underline{b}.s + z_n \underline{c}.s) \quad 1.42$$

and for a diffraction maximum to be observable (1.20)

$$F_{hkl} = \sum_{n=1}^N f_n \exp 2\pi i (hx_n + ky_n + lz_n) \quad 1.43$$

$$= \sum_{n=1}^N f_n \cos 2\pi (hx_n + ky_n + lz_n) + i \sum_{n=1}^N f_n \sin 2\pi (hx_n + ky_n + lz_n) \quad 1.44$$

which may be written

$$F_{hkl} = A_{hkl} + iB_{hkl} = |F_{hkl}| \exp(i\phi_{hkl}) \quad 1.45$$

For a centrosymmetric structure, having a centre of symmetry at the origin, the sine term vanishes and 1.45 reduces to

$$F_{hkl} = A_{hkl} \quad 1.46$$

$$\text{i.e. } \varphi_{hkl} = 0 \text{ or } \pi \quad 1.47$$

This is evident since the summation may be carried out over pairs of atoms at $\underline{r}_n$ and $\underline{r}_n'$, related by

$$\underline{r}_n' = -x_n \underline{a} - y_n \underline{b} - z_n \underline{c} \quad 1.48$$

noting that $\sin(\varphi) = -\sin(-\varphi)$ for all φ

For a non-centrosymmetric structure the structure factors are complex, and the intensity of diffraction is given by

$$I = A^2 + B^2 \quad 1.49$$

Since only the intensities are observable in a diffraction experiment, all phase information is lost, and this gives rise to the celebrated "Phase Problem" of Crystallography.

It should be noted that 1.42 results from considering the electron density distribution in the unitcell to consist of discrete, spherical atoms. A more fundamentally correct relation (though far less convenient computationally) is of the form

$$F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z) \exp 2\pi i(hx+ky+lz) dx dy dz \quad 1.50$$

the factor V appearing since we are dealing with the fractional co-ordinates x, y, z .

1.11 The Temperature Factor

The above equations were derived for stationary atoms, but in real structures atoms absorb thermal energy and set up normal modes of vibration. Since the frequency of the incident radiation is far greater than that of the atomic modes the intensity of scattering of a photon is determined by the instantaneous positions of the atoms. The observed intensity, however, corresponds to a great number of photons and is determined by the average positions of the atoms: the average being taken over all unitcells at the same instant.

As such the observed intensity is always smaller than that given by 1.44, since the vibrations destroy the perfect periodicity of the lattice.

If the restoring force on an atom is assumed to be proportional to its displacement, the probability that its centre lies within the volume element $dx_1 dx_2 dx_3$ is given by⁹ $P(x_1 x_2 x_3) dx_1 dx_2 dx_3$, where

$$P(x_1 x_2 x_3) = ((2\pi)^{3/2} u_1 u_2 u_3)^{-1} \exp\left(-\frac{x_1^2}{2u_1^2} - \frac{x_2^2}{2u_2^2} - \frac{x_3^2}{2u_3^2}\right) \quad 1.51$$

In this expression u_1 is the root mean square displacement in the x_1 direction etc., and the axes x_1, x_2, x_3 are orthogonal. In general these axes bear no relation to the crystallographic axes, although symmetry may impose certain restrictions.

The effect on the diffracted intensity is obtained by multiplying the scattering factor for the stationary atom by the Fourier transform of the probability distribution¹⁰ i.e.

$$f = f_0 \exp(-2\pi^2 (u_1^2 s_1^2 + u_2^2 s_2^2 + u_3^2 s_3^2)) \quad 1.52$$

where s_1, s_2, s_3 are the projections of the reciprocal lattice vector on the axes x_1, x_2, x_3 respectively.

If the forces acting on an atom are Isotropic,

$$u^2 = u_1^2 = u_2^2 = u_3^2 \quad 1.53$$

and 1.52 reduces to

$$f = f_0 \exp(-2\pi^2 u^2 s^2) \quad 1.54$$

$$= f_0 \exp\left(-\frac{8\pi^2 u^2 \sin^2 \theta}{\lambda^2}\right) \quad 1.55$$

This is usually written

$$f = f_0 \exp\left(-\frac{B \sin^2 \theta}{\lambda^2}\right) \quad 1.56$$

where B is the Isotropic Temperature Factor, and is related to the root mean square amplitude of vibration u of the

atom by

$$B = 8\pi^2 u^2 \quad 1.57$$

If the forces on an atom are harmonic but anisotropic, the centre is constrained to lie within an ellipsoidal volume. 1.52 may be written

$$f = f_0 \exp -2\pi^2 ((\underline{u}_1 \cdot \underline{s})^2 + (\underline{u}_2 \cdot \underline{s})^2 + (\underline{u}_3 \cdot \underline{s})^2) \quad 1.58$$

This may be expanded to

$$f = f_0 \exp -2\pi^2 (\underline{U}_{11} h^2 \underline{a}^{*2} + \underline{U}_{22} k^2 \underline{b}^{*2} + \underline{U}_{33} l^2 \underline{c}^{*2} + 2\underline{U}_{12} hka^* \underline{b}^* + 2\underline{U}_{13} hla^* \underline{c}^* + 2\underline{U}_{23} klb^* \underline{c}^*) \quad 1.59$$

where the $\underline{U}_{ij}$ are elements of a symmetric tensor, referred to the reciprocal axes of the crystal

$$\underline{U} = \begin{pmatrix} \underline{U}_{11} & \underline{U}_{12} & \underline{U}_{13} \\ \underline{U}_{12} & \underline{U}_{22} & \underline{U}_{23} \\ \underline{U}_{13} & \underline{U}_{23} & \underline{U}_{33} \end{pmatrix} \quad 1.60$$

Thus in the general case six parameters characterise the thermal ellipsoid and its orientation. The parameters may be determined from X-ray diffraction data, and from them the mean square displacements $\underline{u}_1^2$, $\underline{u}_2^2$, $\underline{u}_3^2$ may be calculated. The anisotropic temperature factor may also be expressed as

$$f = f_0 \exp -1/4 (\underline{B}_{11} h^2 \underline{a}^{*2} + \underline{B}_{22} k^2 \underline{b}^{*2} + \underline{B}_{33} l^2 \underline{c}^{*2} + 2\underline{B}_{12} hka^* \underline{b}^* + 2\underline{B}_{13} hla^* \underline{c}^* + 2\underline{B}_{23} klb^* \underline{c}^*) \quad 1.61$$

$$\text{or } f = f_0 \exp - (\underline{\beta}_{11} h^2 + \underline{\beta}_{22} k^2 + \underline{\beta}_{33} l^2 + 2\underline{\beta}_{12} hk + 2\underline{\beta}_{13} hl + 2\underline{\beta}_{23} kl) \quad 1.62$$

from which the relationships between the various types of coefficient may be deduced.

Thermal vibration also gives rise to another scattering mechanism - whereby the wavelength of the radiation is modified by exchange of one or more quanta of lattice vibrational energy (phonons). This effect is known as Thermal Diffuse Scattering, and in general is disregarded in structural analysis, although occasionally it conveys

structural information^{10b}.

1.12 Corrections to Intensity

Several corrections must be applied to an experimentally observed intensity before it may be related to the structure factor via 1.49.

The Polarisation Factor: According to classical theory the intensity of electromagnetic radiation is proportional to the square of the electric vector. In an unpolarised X-ray beam the electric vector assumes all directions with time in a direction perpendicular to the direction of propagation. It is convenient therefore to resolve the time-averaged electric vector ϵ , into the equal components ϵ_1 and ϵ_2 in directions respectively parallel and perpendicular to the plane containing the incident, normal and reflected ray (Fig.1.5). While it can be seen that the ϵ_2 component makes a constant contribution to the reflected intensity, the parallel component is reduced by a factor of $\cos 2\theta$. The reflected beam is partially polarised, being richer in the component ϵ_2 . The total intensity is given by

$$I = I_1 + I_2 \quad 1.63$$

$$= \frac{1}{2}I_0 + \frac{1}{2}I_0 \cos^2 2\theta \quad 1.64$$

Where I_0 is the unpolarised incident intensity. i.e.

$$I = \frac{I_0(1 + \cos^2 2\theta)}{2} \quad 1.65$$

The factor $\frac{1 + \cos^2 2\theta}{2}$ is known as the Polarisation Factor. As such it is not an instrumental constant, since its value depends only on θ . However, when using a crystal monochromator allowance must be made for the fact that the incident beam is also partially polarised.

The Lorentz Factor: This is a geometrical factor which arises in moving crystal methods because the time required

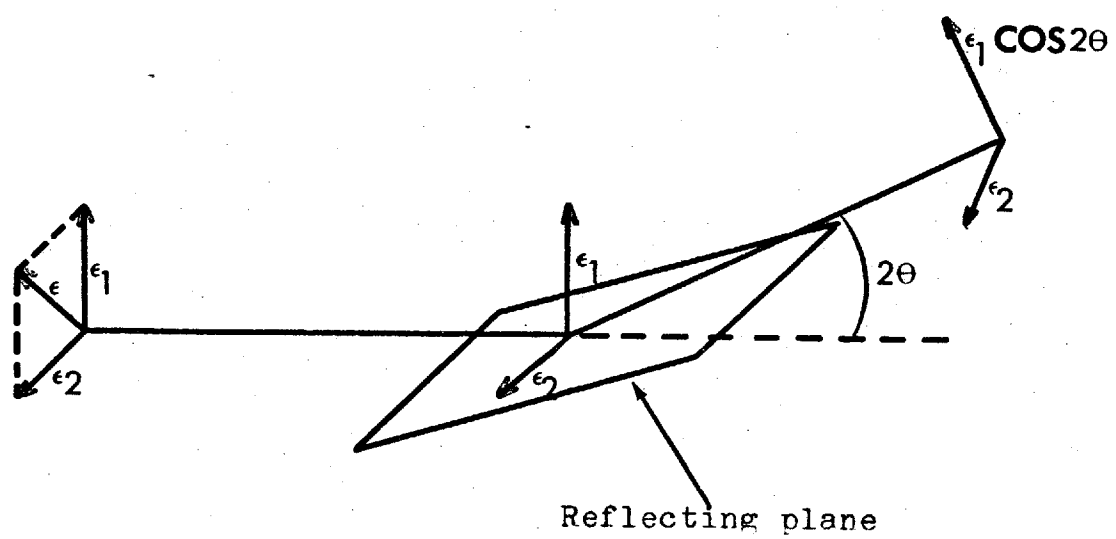


Figure 1.5

for a reciprocal lattice point to pass through the reflecting position is not constant throughout reciprocal space, but varies with the position of the point, and the direction in which it approaches the sphere. In general, reciprocal lattice points whose velocity components normal to the reflection sphere are small, spend relatively longer in the reflecting position and thus their observed intensities are enhanced. It is therefore necessary to correct all observed intensities to the same velocity component normal to the sphere of reflection.

For this purpose it is usual to define the Lorentz Factor, L , as

$$L = \frac{\omega}{v} \quad 1.66$$

where ω is the angular velocity of the crystal, and v is the normal velocity component.

The evaluation of 1.66 depends on the experimental technique used. For the two types of method used throughout this work L is given by¹¹

Equi-inclination Weissenberg Method:

$$L = \frac{1}{2\cos\theta(\sin^2\theta - \sin^2\mu)^{1/2}} \quad 1.67$$

where μ is the equi-inclination angle

Diffractometer, $\theta - 2\theta$ scan

$$L = \frac{1}{\sin 2\theta} \quad 1.68$$

The Multiplicity Factor: By some instrumental methods it is not possible to resolve certain reflections $h_1k_1l_1$, $h_2k_2l_2$ etc. As a consequence the diffracted intensity is given by

$$I_{\text{total}} = I_{h_1k_1l_1} + I_{h_2k_2l_2} + I_{h_mk_ml_m} \quad 1.69$$

If these reflections are equivalent by symmetry, this becomes

$$I_{\text{total}} = mI_{hkl} \quad 1.70$$

where m is the multiplicity factor. For both the Weissenberg and diffractometer methods m is unity.

Absorption: Absorption of monochromatic radiation follows the law (Section 1.2)

$$I = I_0 \exp -\mu t \quad 1.1$$

μ is given by

$$\mu = \rho \sum_{i=1}^N p_i \mu_{mi} \quad 1.71$$

where p_i is the fraction by weight of the i th element, μ_{mi} its mass absorption coefficient, and ρ the density of the material.

For a crystal bathed in a homogeneous X-ray beam, the transmission factor, T_{hkl} is given by

$$T_{hkl} = \frac{1}{V} \int_0^V \exp(-\mu(t_1 + t_2)) dV \quad 1.72$$

where t_1 is the path length of the incident ray inside the crystal, and t_2 that of the diffracted ray.

In general it is not possible to evaluate 1.72 directly. This evaluation is simplified considerably if the crystal is ground to the shape of a sphere or cylinder, and values of T_{hkl} are tabulated in these cases for various values of θ in "International Tables for X-ray Crystallography" Vol II. However, the case most frequently of interest is that of the arbitrarily shaped crystal. Provided that the shape of the crystal may be described in terms of plane faces, and that there are no re-entrant angles between faces, the calculation of T_{hkl} is possible, although extremely laborious. Two main methods exist for this calculation: the Numerical Integration technique developed by Busing and Levy¹², and the Analytical method of de Meulenaer and Tompa¹³.

The Numerical Integration method has been used for all the structures herein, and will be discussed in some detail.

Gaussian integration is used, whereby the integral is approximated by the weighted sum of terms

$$\int_a^b g(x)dx \approx (b-a) \sum_{i=1}^m R_i g(x_i) \quad 1.73$$

where

$$x_i = a + (b-a)u_i \quad 1.74$$

R and u are fractional constants depending only on m , so chosen to make the difference between the integral and the summation a minimum. Their values are available¹⁴ up to $m=32$. For three dimensional integration 1.73 is replaced by a triple sum, with upper values of m_1, m_2, m_3 respectively.

In practice a grid of sampling points is set up within the crystal, and the limits of integration are found by solving for the intersections of bounding faces. The volume of the crystal is also calculated during this stage. Then, for each reflection the function $\exp(-\mu(t_{1ijk} + t_{2ijk}))$ is evaluated for each grid point, and the transmission factor is obtained as the weighted sum over all the points.

The vector analysis method of Coppens et al.¹⁵ is used to calculate the ray paths t_{1ijk}, t_{2ijk} for each sampling point. The components of the incident and diffracted rays along the crystallographic axes are found, and used to calculate the intersections of these rays with the bounding faces of the crystal (produced if necessary). The distances of the sampling point from all these points of intersection are found, and the incident ray path length, t_{1ijk} , is simply the smallest distance of the set (in a direction anti-parallel to that of the incident ray). This process essentially selects which face of the crystal the incident ray actually traverses. A similar process is used to evaluate the path length of the diffracted ray.

The analytical method uses a formula derived¹³ for

the transmission factor of a tetrahedron, which can be evaluated exactly. The crystal, which is assumed to be a convex polyhedron, is subdivided into a number of tetrahedra and the transmission factor obtained by summing over all the tetrahedra.

An excellent review of the relative merits of these methods is given by Coppens et al.¹⁶ Briefly, the analytical method gives exact results, while the numerical method approximate ones. However, the precision of the numerical method may approach that of the analytical method if a large enough number of grid points is used. The numerical method is generally most suitable - provided the sampling grid is chosen carefully from a number of trial runs. However, for strongly absorbing specimens (>90%) the computing time may become excessive, owing to the large number of grid points required for accuracy. The analytical method may then be used with advantage.

Extinction: This is a process whereby the beam traversing a crystal suffers attenuation in addition to the ordinary absorption effect, when the crystal is oriented to give a Bragg reflection. Darwin, who made the first theoretical study of extinction¹⁷ realised that two main processes operated, and termed them Primary and Secondary Extinction.

Primary Extinction: Inside a crystal, a reflected ray satisfies the Bragg requirements to be reflected back into the path of the direct beam. Classical theory shows that a phase change of $\pi/2$ occurs on each reflection, and thus the twice reflected ray differs in phase by π from the primary ray, and destructive interference results. The same situation occurs for rays which have been reflected n and $(n-2)$ times respectively. In particular the once reflected

and thrice reflected rays interfere to attenuate the reflected ray.

If this process continues for a large number of planes of the stack, the attenuation is severe, and Darwin showed that in such a case the intensity of the reflected ray should be proportional to $|F_{hkl}|$ and not $|F_{hkl}|^2$. However, early investigations showed that the majority of crystals did in fact give $I \propto |F_{hkl}|^2$, and this led Darwin to the concept of the Imperfect, or Mosaic crystal - which has since proved to be remarkably accurate. According to this model, crystals are composed of perfect domains, which diffract the beam coherently, but which are so small that primary extinction is negligible.

Secondary Extinction: In the process of Bragg reflection the primary beam is weakened since some of its energy is diverted into the diffracted beam. Thus mosaic blocks near to the surface "shield" parallel blocks within the crystal from the primary beam, and the buried blocks do not fully contribute to the diffraction process. This secondary extinction effect is most pronounced for very strong reflections, where the diffracted intensity is a significant fraction of the primary beam, and for crystals in which the mosaic blocks lie closely parallel, since the shielding is more effective in this case.

Extinction of both types is characterised by a systematic tendency for $|F_{obs}|$ to be less than $|F_{calc}|$ (equation 1.44), among the strongest reflections. Correction for primary extinction is difficult, since it depends ultimately on the size of the perfect domains. Fortunately most crystals approximate quite well to the Ideally Imperfect model, or may be persuaded to do so on thermal

shock treatment. A theoretical correction, to a first approximation, exists for secondary extinction. Zachariasen¹⁸ has shown that the effect may be accounted for by modifying the absorption coefficient

$$\mu_{\text{eff}} = \mu + g(P_2/P_1^2)Q \quad 1.75$$

where P_n is a polarisation factor $= (1 + \cos^{2n} 2\theta)/2$ for an unpolarised incident beam. Q is the absolute integrated intensity per unit volume, and g is the Secondary Extinction Coefficient. This gives an expression for the corrected structure factor

$$F_{\text{corr}} = F_{\text{obs}}(1 + c\beta_{2\theta}I_0) \quad 1.76$$

where I_0 is the observed intensity on an arbitrary scale, c is a parameter related to g , to be adjusted, and $\beta_{2\theta}$ is given by

$$\beta_{2\theta} = \frac{2(1 + \cos^4 2\theta).A'(2\theta)}{(1 + \cos^2 2\theta)^2} \quad 1.77$$

where

$$A'(2\theta) = \frac{\int (t_1 + t_2)/V \cdot \exp(-\mu(t_1 + t_2)) dV}{\left(\int \frac{1}{V} \exp(-\mu(t_1 + t_2)) dV\right)^2} \quad 1.78$$

and may be calculated for a crystal of arbitrary shape during the calculation of the transmission factor, T_{hkl} . The value of c may be found either by a least squares procedure, substituting F_{calc} for F_{corr} ¹⁹ in the reflections thought to be suffering from extinction, or better by including c as a variable in the least squares refinement procedure.²⁰

Thus in terms of the corrections enumerated above,

$$|F_0|^2 = s(LP)^{-1}T_{hkl}^{-1}I_0 \quad 1.79$$

and

$$F_{\text{corr}} = F_0(1 + c\beta_{2\theta}I_0) \quad 1.76$$

where s is a scale factor to be adjusted.

In this work, no corrections for secondary extinction have been applied. Reflections thought to be suffering from extinction were merely removed in the later stages of refinement.

1.13 Anomalous Scattering

In the treatment of the structure factor (Sect. 1.10), it was assumed that the atomic scattering factors were real quantities. However, this assumption is not valid when the wavelength of the radiation lies near to an absorption edge of any of the atoms. In this case an anomalous phase change occurs, and the scattering factor for the atom concerned becomes complex. Thus

$$f_{\text{anom}} = f_0 + \delta f' + i\delta f'' \quad 1.80$$

For a centrosymmetric crystal in the presence of anomalous scattering, the structure factors become complex, although Friedel's law still holds (i.e. $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$). However, for a non-centrosymmetric crystal, Friedel's law no longer holds and this has important consequences in determining the absolute configurations of optically active molecules.²¹

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CHAPTER 2

Crystal Structure Analysis

Some topics in Crystal Structure Analysis are presented as a preface to the experimental section of this work.

2.1 Fourier Synthesis

Since the electron density in a crystal is periodic in three dimensions, it may be expressed as a three-dimensional Fourier series. The electron density at any point on a line parallel to $\underline{a}$ may be written as

$$\sum_h C_h \cos(2\pi hx - \delta_h) \quad 2.1$$

Considering the periodicity parallel to $\underline{b}$, each coefficient C_h may be expanded as

$$\sum_k C_{hk} \cos(2\pi ky - \delta_k) \quad 2.2$$

and thus the electron density $\rho(xyz)$ is given by

$$\rho(xyz) = \sum_h \sum_k \sum_l C_{hkl} \cos(2\pi hx - \delta_h) \cos(2\pi ky - \delta_k) \cos(2\pi lz - \delta_l) \quad 2.3$$

This expression may be simplified by the use of Complex Exponential notation, and by incorporating the phase angles δ into the (complex) coefficients $C(hkl)$. Thus

$$\rho(xyz) = \sum_h \sum_{-\infty}^{\infty} \sum_l C(hkl) \exp(-2\pi i(hx + ky + lz)) \quad 2.4$$

To evaluate the coefficients $C(hkl)$ we may use the orthogonality property of periodic complex exponential functions. Multiplying throughout by $\exp(2\pi i(h'x + k'y + l'z))$ and integrating with respect to x, y, z over ranges 0 to 1,

all terms of the series vanish, except that having $h = h'$,
 $k = k'$, $l = l'$, thus

$$\int_0^1 \int_0^1 \int_0^1 \rho(xyz) \exp 2\pi i (h'x + k'y + l'z) dx dy dz = C(h'k'l') \quad 2.5$$

Comparing with 1.50

$$F_{hkl} = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \exp 2\pi i (hx + ky + lz) dx dy dz$$

it is apparent that

$$C(hkl) = F_{hkl}/V \quad 2.6$$

Thus,

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{\mathbf{k}} \sum_{\ell} F_{hkl} \exp -2\pi i (hx + ky + lz) \quad 2.7$$

Evaluation of $\rho(xyz)$ is, of course, the ultimate aim of X-ray crystallography. However, before 2.7 may be employed, one must be able to derive the phases of the F_{hkl} terms - since only their moduli are accessible experimentally.

Since the electron density is everywhere real (in the absence of anomalous scattering: section 1.13) an important consequence of 2.7 is that

$$F_{\bar{h}\bar{k}\bar{l}} = F_{hkl}^* \quad 2.8$$

$$\text{or, } |F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| \quad 2.9$$

Patterson's Fourier Series: In 1934 A.L. Patterson¹ showed that the phase problem might be circumvented by deriving a Fourier series with coefficients equal to $|F_{hkl}|^2$. He showed that this gave a vectorial representation of the structure, independently of phase information. Consider the function

$$P(uvw) = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \rho(x+u, y+v, z+w) dx dy dz \quad 2.10$$

From 2.7

$$\begin{aligned}
 P(uvw) = & V \iiint \left(\sum_{hkl} \frac{F_{hkl}}{V} \cdot \exp(-2\pi i(hx+ky+lz)) \right) \\
 & \times \left(\sum_{h'k'l'} \frac{F_{h'k'l'}}{V} \cdot \exp(-2\pi i(h'(x+u) + k'(y+v) \right. \\
 & \quad \left. + l'(z+w))) \right) dx dy dz
 \end{aligned} \tag{2.11}$$

Using the orthogonality property product terms vanish unless $h=-h'$, $k=-k'$, $l=-l'$, and in this case $F_{hkl} = F_{h'k'l'}^*$.

$$P(uvw) = \frac{1}{V} \sum_{hkl} |F_{hkl}|^2 \exp(-2\pi i(hu+kv+lw)) \tag{2.12}$$

$$= \frac{1}{V} \sum_{hkl} |F_{hkl}|^2 \cos 2\pi(hu+kv+lw) \tag{2.13}$$

since the sine terms cancel in pairs.

$P(uvw)$ has a simple interpretation: at a point (uvw) its value is equal to the sum of the products of the electron densities at points $(x_a+y_b+z_c)$ and $((x+u)a + (y+v)b + (z+w)c)$. Thus its magnitude will be appreciable only when $(ua+vb+wc)$ coincides with an interatomic vector. This synthesis is most useful for a structure containing a heavy atom. The Patterson in this case will appear as a set of heavy atom vector peaks superimposed on a background of smaller peaks. The position of the heavy atom in the unitcell may then be deduced, and a reasonable approximation to the phases of the F_{hkl} terms may be obtained. By computing a conventional Fourier synthesis using the observed structure factor amplitudes with the phases calculated on the basis of the heavy-atom position, the structure is often revealed immediately.

Equation 2.7 shows that the electron density in a crystal may be expanded as an infinite Fourier series. In practice only a finite number of orders may be observed - those reciprocal lattice points lying within the limiting sphere of radius $2/\lambda$. This number of terms may be reduced further by thermal attenuation, and these effects lead to series termination errors. As a result Fourier maps often show atoms surrounded by prominent diffraction rings. This effect may be avoided by calculating a Difference synthesis in which the Fourier coefficients are taken as $F_o - F_c$. Since both the F_o and F_c syntheses are subject to the same series termination errors, these errors are eliminated from the Difference synthesis.

2.2 Direct Methods

This name applies to a class of methods whereby attempts are made to derive the phases of the structure factors directly i.e independently of any structural information or model. These methods first made an appearance in the form of inequality relationships among the structure factors^{2,3} arising from the positivity of the electron density.

2.2.1 Inequalities among the Structure Factors

Harker-Kasper Inequalities: In discussing inequalities it is useful to introduce the Unitary Structure Factor, defined as

$$U_{\underline{h}} = F_{\underline{h}} / \sum_{j=1}^N f_j \quad 2.14$$

where $\underline{h}$ denotes the reciprocal lattice point with indices hkl , and f_j is a generalised formfactor, incorporating the effects of thermal motion (equation 1.56).

It is convenient to assume that all atoms in the structure

have unitary scattering factors,

$$n_i = f_i / \sum_{j=1}^N f_j \quad 2.15$$

Since the f curves for medium heavy atoms all have approximately the same shape, the effect of division by $\sum f_j$ is to cancel out the reduction of scattering amplitude with increasing $\sin\theta/\lambda$, due to finite atomic size, and thus to replace the real atoms by "point scatterers".

For a centrosymmetric crystal therefore

$$U_{\underline{h}} = \sum_{j=1}^N n_j \cos 2\pi \underline{r}_j \cdot \underline{h} \quad 2.16$$

Using the Cauchy inequality

$$\left| \sum_{j=1}^N a_j b_j \right|^2 \leq \left(\sum_{j=1}^N |a_j|^2 \right) \left(\sum_{j=1}^N |b_j|^2 \right) \quad 2.17$$

with $a_j = (n_j)^{1/2}$, $b_j = (n_j)^{1/2} \cos 2\pi \underline{r}_j \cdot \underline{h}$

$$U_{\underline{h}}^2 \leq \left(\sum n_j \right) \left(\sum n_j \cos^2 2\pi \underline{r}_j \cdot \underline{h} \right) \quad 2.18$$

$$U_{\underline{h}}^2 \leq \frac{1}{2} \left(\sum n_j (1 + \cos 2\pi 2\underline{h} \cdot \underline{r}_j) \right) \quad 2.19$$

$$\text{i.e. } U_{\underline{h}}^2 \leq \frac{1}{2} (1 + U_{2\underline{h}}) \quad 2.20$$

since $\sum_{j=1}^N n_j = 1$

$U_{2\underline{h}}$ is of course a structure factor whose indices are all even. Its phase does not therefore depend on choice of origin and it is thus termed a Structure Invariant. Under certain circumstances 220 may be used to show that the sign of a Structure Invariant is positive.

e.g. if $|U_{\underline{h}}| = 0.6$ and $|U_{2\underline{h}}| = 0.5$

then $U_{\underline{h}}^2 = 0.36$, $1/2(1 + U_{2\underline{h}}) = 1/2(1 + 0.5s(2\underline{h}))$

The inequality cannot be satisfied unless $s(2\underline{h})$ is positive.

Other inequality relationships may be found by considering the space group symmetry operations. If the crystal has a twofold axis so that atoms occur in pairs at x, y, z and $\bar{x}, \bar{y}, \bar{z}$ the unitary structure factor becomes

$$U_{hkl} = 2 \sum_{j=1}^N n_j \exp 2\pi i k y_j \cdot \cos 2\pi (h x_j + l z_j) \quad 2.21$$

by taking

$$a_j = (n_j)^{1/2} \exp 2\pi i k y_j \quad 2.22$$

and

$$b_j = (2n_j)^{1/2} \cos 2\pi (h x_j + l z_j) \quad 2.23$$

we find

$$U_{hkl}^2 \leq \frac{1}{2} (1 + U_{2h,0,2l}) \quad 2.24$$

which may be used to give a positive sign to the invariant $U_{2h,0,2l}$.

Similarly, a twofold screw axis gives

$$U_{hkl}^2 \leq \frac{1}{2} (1 + (-1)^k U_{2h,0,2l}) \quad 2.25$$

which may be used to establish either a positive or negative sign.

So far the inequalities have enabled signs of invariants to be determined under certain circumstances. To extend the process to more general reflections we may consider, for the centrosymmetric crystal,

$$U_{\underline{h}} + U_{\underline{h}'} = 2 \sum_{j=1}^N n_j \cos 2\pi \frac{\underline{h} + \underline{h}'}{2} \cdot \underline{r}_j \cos 2\pi \frac{\underline{h} - \underline{h}'}{2} \cdot \underline{r}_j \quad 2.26$$

which leads to

$$(U_{\underline{h}} + U_{\underline{h}'})^2 \leq (1 + U_{\underline{h} + \underline{h}'}) (1 + U_{\underline{h} - \underline{h}'}) \quad 2.27$$

The presence of higher symmetry may lead to more powerful inequality relationships.

Matrix Inequalities: Hauptman and Karle³ have derived a set of inequalities, valid for all spacegroups, based on the positivity criterion. The first three of these are

$$F_{000} \geq 0 \quad 2.28$$

$$|F_{hkl}| \leq F_{000} \quad 2.29$$

$$\left| F_{h_1+h_2, k_1+k_2, l_1+l_2} - \frac{F_{h_1 k_1 l_1} F_{h_2 k_2 l_2}}{F_{000}} \right| \leq \frac{\left| \begin{array}{cc} F_{000} & F_{h_1 k_1 l_1} \\ F_{h_1 k_1 l_1} & F_{000} \end{array} \right|^{\frac{1}{2}} \left| \begin{array}{cc} F_{000} & F_{h_2 k_2 l_2} \\ F_{h_2 k_2 l_2} & F_{000} \end{array} \right|^{\frac{1}{2}}}{F_{000}} \quad 2.30$$

The third of these is useful and may be understood by writing it in the form

$$|F_{\underline{h}} - \delta| \leq r \quad 2.31$$

where $\underline{h} = h_1 + h_2$, $\underline{k} = h_2$

and $\delta = F_{\underline{h}-\underline{k}} \cdot F_{\underline{k}} / F_{000}$

It may thus be seen that the structure factor $F_{\underline{h}}$ lies within a circle of radius r , centred at δ (Fig. 2.1). Further, if the magnitude of $F_{\underline{h}}$ is known, then $F_{\underline{h}}$ must lie somewhere on the arc PQ. Since the vector $\underline{k}$ may be varied arbitrarily, many relationships of the type 2.31 exist and these may be used to constrain $F_{\underline{h}}$ still further. It should be noted that the larger the magnitudes of $F_{\underline{h}}$ and $F_{\underline{k}}$, the smaller will be r and the uncertainty of the phase will be lower. Also as the complexity of the structure increases, so do F_{000} and r until eventually 2.31 imposes little restriction on $F_{\underline{h}}$.

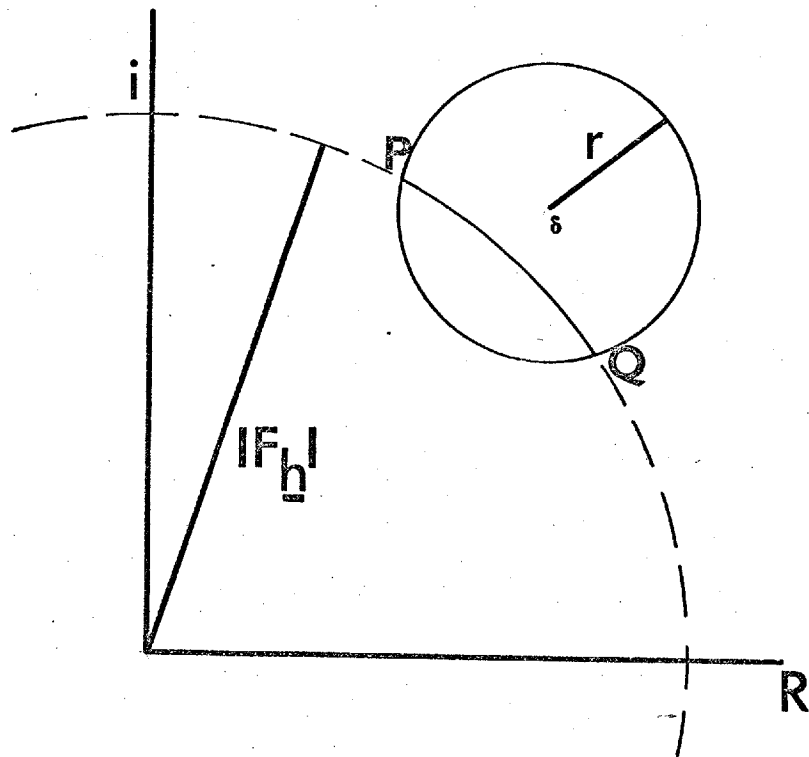


Figure 2.1

Unitary structure factors may be inserted in the determinants, and account taken of the symmetry relations among the U's. When this is done the Harker-Kasper inequalities are derivable.

2.2.2 Equalities among the Structure Factors

Sayre's Equation:⁴ A special equality relationship exists when the structure is composed of identical atoms which are fully resolved from one another. The electron density is given by

$$\rho(\underline{r}) = \frac{1}{V} \sum_{\underline{h}} F_{\underline{h}} \exp(-2\pi i \underline{r} \cdot \underline{h}) \quad 2.32$$

and its square is given by

$$\rho^2(\underline{r}) = \frac{1}{V} \sum_{\underline{h}} G_{\underline{h}} \exp(-2\pi i \underline{r} \cdot \underline{h}) \quad 2.33$$

where the $G_{\underline{h}}$ are the Fourier coefficients for the squared structure. Now from 2.32

$$\rho^2(\underline{r}) = \frac{1}{V^2} \sum_{\underline{h}'} \sum_{\underline{h}''} F_{\underline{h}'} F_{\underline{h}''} \exp(-2\pi i (\underline{h}' + \underline{h}'') \cdot \underline{r}) \quad 2.34$$

$$= \frac{1}{V^2} \sum_{\underline{h}} \left(\sum_{\underline{h}'} F_{\underline{h}'} F_{\underline{h}-\underline{h}'} \exp(-2\pi i \underline{h} \cdot \underline{r}) \right) \quad 2.35$$

putting $\underline{h} = \underline{h}' + \underline{h}''$

By comparison with 2.33

$$G_{\underline{h}} = \frac{1}{V} \sum_{\underline{h}'} F_{\underline{h}'} F_{\underline{h}-\underline{h}'} \quad 2.36$$

This is a general relationship connecting the Fourier coefficients of the square of a periodic function with those of the function itself. For a crystal comprising identical, resolved atoms, the structure and its square will be very similar except that the peaks in the latter are much sharper

than those of the former. If f is the scattering factor of the atom type and g that of the squared atom,

$$F_{\underline{h}} = \sum_{j=1}^N f \exp 2\pi i \underline{h} \cdot \underline{r}_j \quad 2.37$$

and

$$G_{\underline{h}} = \sum_{j=1}^N g \exp 2\pi i \underline{h} \cdot \underline{r}_j \quad 2.38$$

then

$$G_{\underline{h}} = F_{\underline{h}} g/f \quad 2.39$$

thus, substituting in 2.36

$$g/f F_{\underline{h}} = \frac{1}{V} \sum_{\underline{h}'} F_{\underline{h}'} F_{\underline{h}-\underline{h}'} \quad 2.40$$

This relationship does not appear particularly useful, since in order to find the phase of $F_{\underline{h}}$ the phases of all the other structure factors $F_{\underline{h}'}$, $F_{\underline{h}-\underline{h}'}$ need to be known! However, it has proved useful in finding likely sign relationships among the largest structure factors for centrosymmetric crystals. Also, when used in conjunction with a high-speed computer it becomes formidable⁵. The equation applies fairly well to structures containing unequal, though light atoms.

2.2.3 Probability Relationships

The Triple-Product Sign Relationship: If the structure factors involved are sufficiently large the Harker-Kasper inequality

$$\begin{aligned} (|U_{\underline{h}}| + |U_{\underline{h}'}|)^2 \leq & (1 + s(\underline{h})s(\underline{h}')s(\underline{h}+\underline{h}'))|U_{\underline{h}+\underline{h}'}| \\ & \times (1 + s(\underline{h})s(\underline{h}')s(\underline{h}-\underline{h}'))|U_{\underline{h}-\underline{h}'}| \end{aligned} \quad 2.41$$

may be used to show that, for a centrosymmetric crystal

$$s(\underline{h})s(\underline{h}')s(\underline{h}+\underline{h}') = +1 \quad 2.42$$

However, if the structure factors are not large enough to make the inequality determinative, there may still be a strong probability that the relationship is true. This is usually written

$$s(\underline{h})s(\underline{h}')s(\underline{h}+\underline{h}') \approx +1 \quad 2.43$$

Various estimates of the probability of 2.43 have been made, notably by Klug⁶ and Cochran and Woolfson⁷, who showed that, approximately

$$P_+(\underline{h}, \underline{h}') = \frac{1}{2} + \frac{1}{2} \tanh\left(\frac{\epsilon_3}{\epsilon_2^{3/2}} |U_{\underline{h}} U_{\underline{h}'} U_{\underline{h}+\underline{h}'}|\right) \quad 2.44$$

where

$$\epsilon_m = \sum_{j=1}^N n_j^m \quad 2.45$$

For a structure containing N equal atoms this becomes

$$P_+(\underline{h}, \underline{h}') = \frac{1}{2} + \frac{1}{2} \tanh(N |U_{\underline{h}} U_{\underline{h}'} U_{\underline{h}+\underline{h}'}|) \quad 2.46$$

Because of the complexity of structures now attempted inequalities alone are incapable of generating enough signs or phases for a correct solution, and probability methods have assumed paramount importance.

The Coincidence Method: For a centrosymmetric crystal or projection we have $s(\underline{h}) = s(-\underline{h})$ since $\cos \varphi = \cos -\varphi$ for all φ . Writing 2.43 in the form

$$s(\underline{h}+\underline{h}') \approx s(\underline{h})s(\underline{h}') \quad 2.47$$

$$s(\underline{h}-\underline{h}') \approx s(\underline{h})s(-\underline{h}') \approx s(\underline{h})s(\underline{h}') \quad 2.48$$

$$\text{i.e. } s(\underline{h}-\underline{h}') \approx s(\underline{h}+\underline{h}') \quad 2.49$$

Thus 2.49 may be used to relate pairs of structure factors that belong to the same parity group. The list of relations of

the type 2 49 is expanded considerably when allowance is made for space group symmetry.

Grant et al.⁸ have developed a systematic method of handling these relations. The largest U's are sorted into parity groups and allotted symbolic signs a_1, a_2, b_1, b_2 etc. The triple products are then tabulated in a two dimensional array - such that the product of the entry with its array coordinates defines the triple product relationship. Where two or more entries occupy the same array location - a coincidence - a relationship is shown to exist between the symbolic signs. In this way a large number of signs (absolute or symbolic) may be determined.

Phase Determining Formulae: Much work has been done recently, notably by Hauptman and Karle, on the development of useful formulae for the deduction of phases from structure factor magnitudes. These are normally expressed in terms of Normalised structure factors, defined as

$$E^2_{hkl} = \frac{U^2_{hkl}}{\bar{U}^2} \quad 2.50$$

It may be shown that⁹

$$\bar{U}^2 = \sum_{i=1}^N n_i^2 \quad 2.51$$

where the average is taken over all reflections within the sphere. Due to systematic absences, certain classes of reflections average to multiples of that predicted by 2.51

i.e

$$\bar{U}^2 = \epsilon \sum_{i=1}^N n_i^2 \quad 2.52$$

Values of ϵ are tabulated for different classes of reflections for all space groups in International Tables¹⁰, 2.50 then becomes

$$E_{hkl}^2 = \frac{U_{hkl}^2}{\epsilon \sum_{i=1}^n n_i^2} \quad 2.53$$

or,

$$E_{hkl}^2 = \frac{|F_{hkl}|^2}{N \epsilon \sum_{i=1}^n f_i^2} \quad 2.54$$

The formulae, applicable to space group $P\bar{1}$ become¹¹

$$\sum_1 = s(E_{2h}) \approx s(E_h^2 - 1) \quad 2.55$$

$$\sum_2 = s(E_h) \approx s \langle E_{h'} \cdot E_{h-h'} \rangle_{h'} \quad 2.56$$

$$\sum_3 = s(E_h) \approx s \langle E_{h'} (E_{1/2(h-h')}^2 - 1) \rangle_{h'} \quad 2.57$$

$$\sum_4 = s(E_{2h}) \approx s \langle (E_h^2 - 1)(E_{h-h'}^2 - 1) \rangle_{h'} \quad 2.58$$

$\sum_1$ and $\sum_4$ require only the magnitudes of the normalised structure factors and thus can be used at the outset to obtain signs of Invariant structure factors, provided the E 's are suitably large. $\sum_2$ and $\sum_3$ may be used to extend the set of known symbolic or invariant signs to more general reflections: this is the basis of the Symbolic Addition Method¹².

Non-Centrosymmetric Crystals

The methods outlined so far are of course applicable to centrosymmetric projections, but for a more general treatment we must reconsider Fig. 2.1. Recalling equation 2.31

$$|F_h - \delta| \leq r \quad 2.31$$

where $\delta = F_{h-k} F_k / F_{000}$

The larger the magnitudes of $F_{\underline{h}}$ and $F_{\underline{k}}$, the smaller will be r and thus $F_{\underline{h}}$ approaches the value δ . Thus we may write

$$F_{\underline{h}} \propto \left\langle \frac{F_{\underline{k}} F_{\underline{h}-\underline{k}}}{F_{\underline{k}}} \right\rangle_{\underline{k}} \quad 2.59$$

where the averaging is over the largest $F_{\underline{k}}$. Putting $F_{\underline{h}} = |F_{\underline{h}}| \exp i\varphi_{\underline{h}}$, we get

$$\varphi_{\underline{h}} \approx \left\langle \varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}} \right\rangle_{\underline{k}} \quad 2.60$$

This has obvious similarities with 2.56, and thus the Symbolic Addition procedure is equally applicable to non-centrosymmetric structures. However, it should be noted that the problems are far greater than for centrosymmetric crystals, since φ takes all values between 0 and 2π .

A further formula has been derived¹² for non-centrosymmetric crystals

$$\tan \varphi_{\underline{h}} \approx \frac{\left\langle |E_{\underline{k}} E_{\underline{h}-\underline{k}}| \sin(\varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}}) \right\rangle_{\underline{k}}}{\left\langle |E_{\underline{k}} E_{\underline{h}-\underline{k}}| \cos(\varphi_{\underline{k}} + \varphi_{\underline{h}-\underline{k}}) \right\rangle_{\underline{k}}} \quad 2.61$$

The so-called "Tangent Formula" may be used in conjunction with, or independently of the Symbolic Addition Procedure, and has been used in the solution of several complex structures.

An excellent review of the phase determining methods together with the necessary practical considerations has been given by I. and J. Karle.^{12,13}

2.3 Refinement of the Structural Parameters

The aim of the various methods of structural analysis, some of which have been discussed in this chapter, is to obtain a well resolved electron density map from which the positions

of all the atoms may be determined. Once this has been achieved, however, the problem remains of improving the accuracy of the positional and vibrational parameters, and estimating the error limits to which they are subject.

The Method of Least Squares: Consider a function of n variables

$$q_k = a_{k1}x_1 + a_{k2}x_2 \dots + a_{kn}x_n \quad 2.62$$

Now if q_k is measured experimentally it will be subject to a certain error, ϵ_k , i.e.

$$q_k + \epsilon_k = a_{k1}x_1 + a_{k2}x_2 \dots + a_{kn}x_n \quad 2.63$$

$$\epsilon_k = a_{k1}x_1 + a_{k2}x_2 \dots + a_{kn}x_n - q_k \quad 2.64$$

2.64 is termed an observational equation. If there are m such equations where $m > n$, subject to random, or Gaussian errors then the Theorem of Legendre (1806) states that the best solution for the variables x_i is that for which $\sum_{k=1}^m \epsilon_k^2$ is a minimum.

When the observational equations are linear in x_i the treatment is straightforward. The condition for a minimum may be expressed as

$$\frac{\delta}{\delta x_i} \cdot \sum_{k=1}^m \epsilon_k^2 = 0 \text{ for } i = 1, n \quad 2.65$$

When the expression for ϵ_k is squared and differentiated with respect to each variable in turn, n Normal Equations of the type

$$\sum_{k=1}^m \sum_{j=1}^n a_{ki} a_{kj} x_j = \sum_{k=1}^m a_{ki} q_k \quad 2.66$$

result. Thus the Normal Equation for x_i may be obtained by multiplying 2.62 throughout by the coefficient of x_i , and

summing over m . This may be expressed more neatly in matrix notation, thus

$$AX = Q \quad 2.67$$

where X and Q are column matrices, and A is a $n \times n$ matrix. A is also symmetric since

$$A_{ij} = A_{ji} = \sum_{k=1}^m a_{ki} a_{kj} \quad 2.68$$

Thus according to Legendre's Theorem the best values $(x_1 \dots x_n)$ are the solutions of 2.67 i.e.

$$A^{-1}AX = X = A^{-1}Q \quad 2.69$$

If we wish to include weights, allowing for the fact that some observations of q_k are more reliable than others, this may simply be done by including the particular observational equation w_k times, where w_k is the relative weight. More conveniently this may be done by multiplying 2.62 throughout by $(w_k)^{1/2}$. 2.66 then becomes

$$\sum_{k=1}^m \sum_{j=1}^n w_k a_{ki} a_{kj} x_j = \sum_{k=1}^m w_k a_{ki} q_k \quad 2.70$$

The standard deviations of the x_i are given by¹⁴

$$\sigma^2(x_i) = \frac{A_{ii}^{-1} \sum_{k=1}^m w_k \epsilon_k^2}{m-n} \quad 2.71$$

where A_{ii}^{-1} is the corresponding diagonal term of the inverse Normal Matrix. Thus in general, the better the data (i.e. smaller ϵ_k) and the larger the number of observations, the lower the standard deviations.

The crystallographic equation of condition is

$$\epsilon_{hkl} = |F_o| - s|F_c| \quad 2.72$$

assuming the F_o 's are subject to random errors, and $|F_c|$ is the

"true" value of the structure factor magnitude (i.e using the final atomic parameters). s is a scale factor to be adjusted - since the F'_0 's are on a relative scale. Comparison with 1.43 shows the observational equations to be non-linear in the variables x_i . The solution may be achieved by putting

$$s(|F_c|) \approx (s|F_c|)' + \sum_{i=1}^n \frac{\delta(s|F_c|)'}{\delta x_i} \delta x_i \quad 2.73$$

where the primed quantities are evaluated using estimated solutions x_i' . Substitution in 2.72 gives

$$\epsilon_{hkl} = |F_0| - (s|F_c|)' - \sum_{i=1}^n \frac{\delta(s|F_c|)'}{\delta x_i} \delta x_i \quad 2.74$$

2.74 is linear in the parameter changes δx_i and thus may be solved by the method given above. The Normal Equations are of the type

$$\begin{aligned} \sum_{h,k,l} \sum_{i=1}^n w_{hkl} \frac{\delta(s|F_c|)'}{\delta x_j} \frac{\delta(s|F_c|)'}{\delta x_i} \delta x_i \\ = \sum_{h,k,l} w_{hkl} \frac{\delta(s|F_c|)'}{\delta x_j} (|F_0| - s|F_c'|) \end{aligned} \quad 2.75$$

for $j = 1, n$

Thus the process becomes cyclic: equations of the type 2.75 are set up using approximate values for the parameters x_i , and solved for the shifts δx_i . The shifts are then added to the parameters and the process repeated until the shifts become arbitrarily small.

Note that only the parameters in the asymmetric unit must be considered as variables to be optimised. Parameters related through space group symmetry to those of the asymmetric unit are linearly dependent on the latter. Any attempt to vary

the linearly dependent parameters will give rise to a Normal Matrix having rows or columns identical and which is thus singular. No solution to the normal equations is then possible. When this restriction is observed (which physically amounts to preserving the space group symmetry as the parameters are varied) calculation of the derivatives in 2.75 is straightforward. There are four types of derivative to be considered

Scale Factors

$$\frac{\delta(s|F_c|)}{\delta s} = |F_c| \quad 2.76$$

Positional Parameters

$$|F_c| = \sum_{j=1}^N f_j T_j (\cos 2\pi(hx_j + ky_j + lz_j) \cos \varphi + \sin 2\pi(hx_j + ky_j + lz_j) \sin \varphi) \quad 2.77$$

$$= \sum_{j=1}^N T_j (a_j \cos \varphi + b_j \sin \varphi) \quad 2.78$$

where T_j is a temperature factor (Sect. 1.11) given by

$$\text{Isotropic: } T_j = \frac{\exp(-B \sin^2 \theta_{hkl})}{\lambda^2} \quad 2.79$$

$$\text{Anisotropic: } T_j = \exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)_j) \quad 2.80$$

2.78 may be factored into summations over the symmetry operations and the atoms in the asymmetric unit, thus

$$|F_c| = \sum_{i=1}^{N/ns} \sum_{j=1}^{ns} T_j (a_j \cos \varphi + b_j \sin \varphi) \quad 2.81$$

where ns is the number of symmetry operations.

The derivative is then given by

$$\frac{\delta |F_c|}{\delta x_i} = \sum_{j=1}^{ns} T_j \left(\frac{\delta a_j}{\delta x_i} \cos \varphi + \frac{\delta b_j}{\delta x_i} \sin \varphi \right) \quad 2.82$$

all terms in F_c vanishing except those for the particular atom and its symmetry equivalents. If the symmetry operations are considered to be applied to the Miller Indices we then get¹⁵

$$\begin{aligned} \frac{\delta (s|F_c|)}{\delta \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}} &= 2\pi s f_i \sum_{j=1}^{ns} -T_j \cos \varphi \cdot \begin{pmatrix} h_j \\ k_j \\ l_j \end{pmatrix} \sin(h_j x_i + k_j y_i + l_j z_i + t_j) \\ &+ T_j \sin \varphi \cdot \begin{pmatrix} h_j \\ k_j \\ l_j \end{pmatrix} \cos(h_j x_i + k_j y_i + l_j z_i + t_j) \quad 2.83 \end{aligned}$$

where t_j is a translational term.

Isotropic Thermal Parameters

$$\frac{\delta (s|F_c|)}{\delta B_i} = \left(- \frac{\sin^2 \theta}{\lambda^2} \right)_{hkl} s \sum_{j=1}^{ns} T_j (a_j \cos \varphi + b_j \sin \varphi) \quad 2.84$$

Anisotropic Thermal Parameters

$$\frac{\delta (s|F_c|)}{\delta \begin{pmatrix} \beta_{11} \\ \beta_{22} \\ \beta_{33} \\ \beta_{12} \\ \beta_{13} \\ \beta_{23} \end{pmatrix}_i} = \left(- \sum_{j=1}^{ns} \begin{pmatrix} h_j^2 \\ k_j^2 \\ l_j^2 \\ 2h_j k_j \\ 2h_j l_j \\ 2k_j l_j \end{pmatrix} s T_j (a_j \cos \varphi + b_j \sin \varphi) \right)_i \quad 2.85$$

Note that T_j becomes for the symmetry-related atoms

$$T_j = \exp - ((h^2)_j \beta_{11} + (k^2)_j \beta_{22} + (l^2)_j \beta_{33} + (2hk)_j \beta_{12} \\ + (2hl)_j \beta_{13} + (2kl)_j \beta_{23}) \quad 2.86$$

Where $(h^2)_j$ etc. are the transformed index products which account for the relationships between β 's of symmetry-related atoms. Levy¹⁶ has shown that, except for some atoms in special positions, $(h^2)_j = (h_j)^2$ etc. i.e. the transformed index products are given by the products of the transformed indices. An example of the modification of 2.85 for a structure containing special positions is given in Chapter 4.

Least squares refinement is one of the most time consuming operations in crystal structure analysis. For each reflection the matrix building step requires $NV(NV+1)/2$ multiplications, where NV is the number of variables. Since this process effectively determines the computing time (for **larger, lower** symmetry structures), the total time is approximately proportional to $NV(NV+1)/2 \times NO$ where NO is the number of independent reflections. Even with present day computers this type of calculation rapidly becomes impractical for larger structures, because of excessive storage requirements and time per cycle. For example on the CDC 6600 it is impractical to vary more than about 300 parameters simultaneously.

This problem may be overcome by using fixed atom contributions, in which successive parts of the structure are held fixed while the rest is refined, or by using the Block-Diagonal approximation. In this case the Normal Matrix is approximated as a sequence of (4×4) matrices (isotropic temperature factors) and (9×9) matrices (anisotropic) for each atom, centred on the leading diagonal. All other off-diagonal terms are ignored, and each of the individual matrices is treated as in the full matrix case. While this reduces drastically the computing time, in some respects it is quite

unsatisfactory. Neglect of the off-diagonal terms means that correlation is ignored between parameter shifts of different atoms. Yet more drastic approximations exist: (3x3) and (6x6) matrices may be set up for each atom, in which case correlation between thermal and positional parameter shifts of the same atom is ignored. Because of this incomplete treatment convergence is much slower than in the full matrix case, and the estimated standard deviations are often too small.

A more important objection to block-diagonal refinement is that it has no theoretical justification since the equations used no longer satisfy the condition for a minimum in $\sum \epsilon^2$. However, experience shows the ignored terms to be quite small in practice. The diagonal terms are the sums of squares and thus become progressively larger as the matrix is accumulated. The off-diagonal terms, however, are the sums of products which may be + or -, and thus tend to cancel in a random manner (in the absence of parameter correlations). However, in unfavourable cases, where large off-diagonal terms exist the full matrix and block diagonal methods may converge to different results.

Computation

Most of the calculations were carried out on the Imperial College IBM 7094, using the "X-ray '63" system. This is a comprehensive collection of crystallographic programs and is described in the University of Maryland technical report, TR64-6. At the Imperial College installation the system is stored in precompiled form on magnetic tape. The system is initiated with control cards, which cause the IBSYS monitor to be cleared from core and loading of the "Nucleus" routines of the X-ray '63 system. These are machine code (FAF) routines which perform the basic operations of input/output, tape handling, and also control the loading and execution of the crystallographic programs from

the system tape.

The individual crystal structure analysis programs are loaded and executed sequentially, at the user's request. No more than one such program is in core at a time, and essential crystallographic data is transmitted through a binary data file (on magnetic tape), which may be updated several times during a given job. The major programs, such as least-squares refinement, Fourier synthesis, have an elegant overlaid structure, which permits very efficient use of core space and maximisation of array capacities.

X-ray '63 is therefore an extremely versatile and convenient package, from the user's point of view. Its major disadvantages are its size, and relatively poor documentation, which combine to make updating of the system virtually impossible. The extensive use of magnetic tape is another serious disadvantage (six tape drives are required for a normal job): in the author's experience a high proportion of jobs submitted were found to fail because of the physical unreliability of magnetic tapes and tape drives.

Programs used were:-

- DATRDN - reduction of data, application of Lorentz and Polarisation corrections, and generation of primary data tapes.
- FOURR - Patterson, Fourier and difference Fourier syntheses.
- ORFLS - Busing-Martin-Levy full-matrix least-squares program.¹⁵ The conventional R factor is given by

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad 2.87$$

and is calculated on the basis of observed

reflections only. Unobserved reflections, or "less-thans" are included in the observational equations only if $|F_c| \geq |F_o|$. A separate R factor of less-thans is calculated, in which the numerator is accumulated only over those having $|F_c| \geq |F_o|$, and the denominator over the F_c magnitudes.

- BLOCKLS - A block-diagonal approximation of ORFLS. For a given atom, square, diagonal blocks are set up, equal, on a side to the number of variable parameters for that atom.
- BONDIA - Bondlengths, angles and their standard deviations; intermolecular distances.
- DATEFIX - Calculates normalised structure factor magnitudes and estimates scale and overall temperature factors.

Other 7094/ CDC 6600 programs used were:

- ORTEP - Crystal structure illustrations on the CalComp plotter. Written by C.K. Johnson (Publication ORNL-3794, 1965).
- ICABS - An absorption/extinction program, originally written by Coppens et al. (Acta Cryst., 18 1035 1965) for a CDC 1604, and ammended by P.G.H. Troughton.
- SOLO - Interlayer scaling of photographic data by the method of Rollett, Hamilton and Sparks (Acta Cryst., 18 129 1965) written by the author for an IBM 7094 or CDC 6600.

Atlas programs were used mainly in conjunction with the diffractometer: -

- SEKO - Generates setting angles and Five-values-measurement steering tape for the Siemens' automatic diffractometer, written by P.G.H. Troughton.
- SODI - Processes the Five-values-measurement diffractometer output tape, scales, $(LP)^{-1}$ corrects the data, and punches cards in X-ray '63 format. Written by P.G.H. Troughton.

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"Hence vain deluding joys,
The brood of folly without father bred,
How little you bested,
Or fill the fixed mind with all your toys."

.... Milton: Il penseroso.

Chapter 3. The Crystal Structure of 1:1 Cis-
trans(1,5) cyclodecadiene-silver nitrate.

Abstract

1:1 cis-trans(1,5)cyclodecadiene:AgNO₃, C₁₀H₁₆AgNO₃, is monoclinic, space group $P2_1/n$. The unitcell dimensions are $a = 10.455$, $b = 9.487$, $c = 11.344$ Å, $\beta = 95^\circ 52'$. The crystal structure has been determined from three-dimensional X-ray data, and positional and thermal parameters have been refined to a final R factor of 0.084 on 1297 observed reflections.

The crystal structure is of the polymeric type, with the silver ion complexed to one cis and one trans double bond of different olefin molecules, at Ag⁺-C=C (mid-point) distances of 2.37 and 2.35 Å respectively. The high reactivity of the trans double bond is accounted for by sp²-sp² torsional strain, and there are smaller amounts of sp³-sp³ and sp²-sp³ torsional strain present in the ring. The conformation of the olefin accounts for its cyclisation to a cis-decalin, but would produce the product in a chair-twist-boat form, which may flip to the stable chair-chair form. The conformation is similar to that of the ten-membered ring in Heliangine, except that the cis double bond is rotated by ca. 120° relative to the latter.

Introduction

The preparation and properties of Copper(I) and Silver(I) complexes of cyclodecadiene have been reported elsewhere¹. Our interest centred on the 1:1 silver nitrate adduct, as a possible means of studying the ring geometry in a reasonably undistorted form. In order to produce crystals suitable for an X-ray study the following procedure, similar to that employed by Brown² in the preparation of the adduct with Germacatriene,¹⁴ was followed.

Cyclodecadiene³ (1.7g) was dissolved in a saturated solution of silver nitrate in absolute ethanol (33ml. containing 1.1g. AgNO_3), and the solution left to stand for 24 hours under nitrogen in the dark. The crystals were filtered off, washed with petroleum ether, and redissolved in absolute ethanol (ca. 200 ml.). A slow stream of nitrogen was passed until the volume was reduced to ca. 100 ml. and the solution left to stand in the dark for 48 hours. A crop of transparent needles was obtained and dried in vacuo over CaCl_2 . A second crop was obtained on reducing the volume to ca. 20 ml. (yield 0.74g, 19% ; m.p. 142-4°d).

Analysis⁴

Found % Ag 35.26, C 39.71, N 4.87, O 15.71, H 5.55
 $\text{C}_{10}\text{H}_{16}\text{AgNO}_3$ requires Ag 35.25, C 39.23, N 4.58, O 15.68, H 5.27

Experimental

The crystals were transparent needles, elongated along b. A pronounced tendency to twinning was observed: two needles often growing "back to back" parallel to b. Weissenberg and Precession photographs exhibited Laue symmetry $2/\underline{m}$. The systematic absences were $\underline{h}0\underline{l}$, $\underline{h} + 1 \neq 2n$ and $0\underline{k}0$, $\underline{k} \neq 2n$, which define the space group uniquely as $\underline{P}2_1/\underline{n}$. The cell dimensions

were obtained from axial scans on a Siemen's four circle automatic diffractometer.

Crystal Data: $C_{10}H_{16}:AgNO_3$, $M = 306.1$, monoclinic $P2_1/n$,
 $a = 10.455 \pm 0.001$, $b = 9.487 \pm 0.004$, $c = 11.344 \pm 0.002$ Å,
 $\beta = 95^\circ 52' \pm 3'$, $V = 1119$ Å³, $D_m = 1.85 \pm 0.03$ (flotation),
 $D_c = 1.83$ g cm⁻³, $Z = 4$, $\mu = 152$ cm⁻¹ for CuK_{α} , $F_{000} = 592$.

The layers h, 0-6, l were photographed with Ni-filtered CuK_{α} radiation using the equi-inclination Weissenberg, multiple film technique. The crystals deteriorated rapidly when exposed to X-rays in air. However, deterioration was much slower when the crystals were sealed under nitrogen in Lindemann Tubes. Even then after ca. 150 hours the crystal became discoloured and a test exposure showed that the intensities of diffraction were reduced by about 50%, although no relative differences were apparent. The data were collected on three small crystals, exposing each crystal for a maximum of ca. 100 hours. The intensities of the diffraction spots were estimated by visual comparison with a calibrated wedge. 1645 independent data were recorded, of which 327 were judged to be unobserved and were assigned an intensity value of $1/2I_{min}$. No systematic spot-shape correction was applied, although for reciprocal lattice points lying near the equator of the upper-level photographs, the measured intensity was multiplied by the ratio of the length of the diffraction spot to that of the wedge spot.

The 0kl zone was collected on a Precession camera for the purpose of correlation. Three graded exposures were taken. The need to seal the crystals in Lindemann Tubes precluded the possibility of collecting Weissenberg data about a second axis. However, since the microdensitometer was found to be malfunctioning, visual estimation of the Precession intensity data had to be resorted to. This was rather unsatisfactory, since the spot shape was very dissimilar from that of the wedge,

and consequently such data were not included in the structural analysis, apart from preliminary layer scaling.

Structure Solution and Refinement

The data were corrected for Lorentz-Polarisation effects and placed on a uniform scale by hand correlation with the Okl precession data. A three-dimensional Patterson synthesis was computed, and from the Harker Sections ($1/2, 1/2-2y, 1/2$), ($1/2-2x, 1/2, 1/2-2z$) together with the ($2x, 2y, 2z$) Harker vector the silver coordinates were found to be

$$x = 0.159, \quad y = 0.143, \quad z = 0.794$$

A structure-factor calculation based on the silver ion position gave an R factor of 0.343. A three-dimensional Fourier map was computed, using the silver ion phases, and only those observed terms for which $|F_o| \geq 0.30|F_o|$. In this map the nitrate ion and the general arrangement of the olefin molecule were visible. Three cycles of ORFLS⁵ least squares on the silver and nitrate ions, including the layer scale factors as variables reduced R to 0.224. A difference Fourier with the same rejection test as before clearly showed the remaining atoms. A further three cycles of ORFLS gave an R value of 0.14, and a bond lengths and angles calculation showed sensible geometry at this stage. Correction of some misindexing and a further three cycles refinement reduced R to 0.125.

At this stage a difference Fourier showed considerable evidence of thermal anisotropy in the region of the silver ion. Its B factor was therefore converted into the corresponding anisotropic coefficients β_{ij} , and refinement was continued for another three cycles. R fell to 0.099. During this refinement the layer scale factors were held fixed to avoid correlation effects⁶ between the former and

the anisotropic thermal parameters. When fully anisotropic refinement was attempted the β_{ij} 's for some atoms became non-positive definite (i.e. failed to satisfy the criteria for an ellipsoid of thermal vibration). This was thought to be due to absorption errors. Absorption corrections were therefore calculated for the three crystals, using the Numerical Integration method⁷ with a sampling grid of 10x10x10. Since absorption would produce systematic errors in the layer scale factors, it was decided to return to the isotropic mode and refine their values. When this had been done refinement with the silver ion anisotropic gave an R factor of 0.092. However, the non-positive definite temperature factors still persisted when fully anisotropic refinement was attempted. Since the ratio of observations to variables was quite adequate (ca. 10:1) this was possibly indicative of systematic errors in the data, such as would be caused by crystal decay or scaling errors. However, it is interesting to note that the only two atoms thus affected were O1 and O3 of the nitrate group, and possibly this effect was due to some librational or rotational movements of the group as a whole. Similar effects have been observed in other silver nitrate complexes⁸.

Refinement was therefore continued with only the silver ion anisotropic. A difference Fourier showed all sixteen hydrogen atoms in sites close to those predicted by stereochemistry. They were included at their calculated positions, with B factors $0.5 \text{ \AA}^2$ greater than those of the corresponding carbon atoms. The hydrogen parameters were not refined. Fourteen strong reflections all having $|F_o| \ll |F_c|$ were omitted for suspected extinction. The silver formfactor was corrected for the effects of anomalous dispersion by vectorial addition of f_o with the real and imaginary components, $\delta f'$ and $\delta f''$.⁹

At this stage a bond lengths and angles calculation showed evidence of double bonding between atoms N and O1 of the nitrate group. The assignment of scattering factors was thus changed to O1, O2⁻, O3⁻. Refinement was terminated at a final R value of 0.084 when the maximum parameter shift was 0.01 times the corresponding standard deviation. Unit weights were used throughout: an analysis of discrepancies did not suggest a more appropriate weighting scheme, there being a random scatter of differences among ranges of F_o . Some runs were performed using weights inversely proportional to $\sin\theta$ - in an attempt to improve the standard deviations of the lighter atoms - but no significant improvement was obtained.

The final difference Fourier showed no spurious features, having a background level of ± 0.8 electron $\text{\AA}^{-3}$, rising to a maximum of 1.4 electron $\text{\AA}^{-3}$ in the region of the silver ion. 80 of the 327 "less-thans" calculated greater than $I_{\min}$, but none greater than twice $I_{\min}$. The final R factor of "less-thans" was 0.105. The final parameters in Tables 1 and 2, together with the hydrogen parameters in Table 3 were used to calculate the final structure factors listed in Table 4.

Discussion

Views of the structure are given in a and b axis projection in Figures 1 and 2 respectively.¹⁰ Figure 2 shows the structure to consist of ionic sheets, interconnected by layers of olefin molecules. Figure 1 illustrates the chain formation of the ionic moiety, and the continuous nature of the structure.

Both the cis and trans double bonds of the olefin molecule are involved in complex formation with silver ions as suggested by Jonassen et al.¹ on the basis of infrared

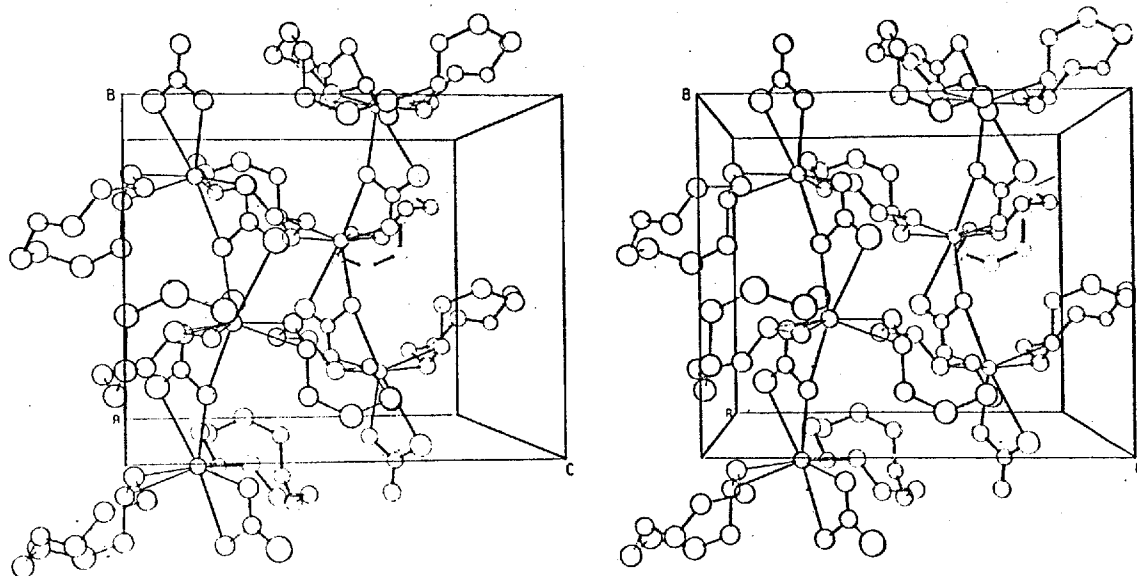


Figure 1

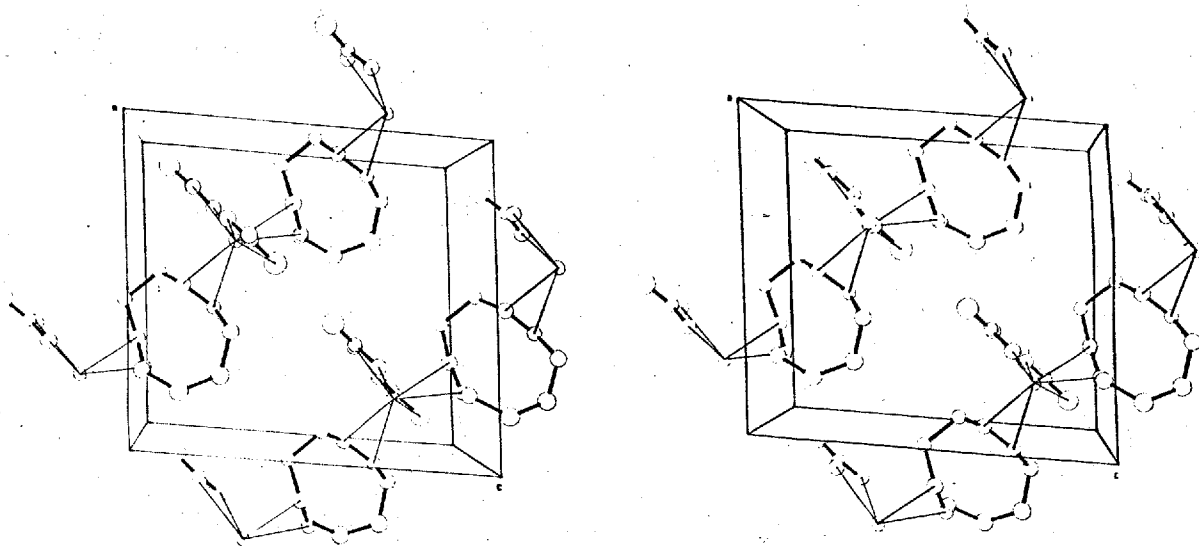


Figure 2

Stereoscopic unitcell projections

spectra. Of the two possible structures considered by these authors i. e. an intramolecular type of structure where both double bonds of the olefin are coordinated to the same silver ion, and a polymeric type where the double bonds are coordinated to separate silver ions, the latter is adopted. This is understandable in terms of the conformation of the cyclodecadiene ring. Selected bond lengths and angles, together with estimated standard deviations are given in tables 5 and 6. The standard deviations of the parameters were obtained from the diagonal terms of the inverse of the full least-squares matrix, and so their values should be realistic. The relatively high standard deviations of the light atom parameters reflect the preponderance of the heavy atom scattering matter (Z^2_h : $\sum Z^2_l \approx 3.5$).

The Silver Ion Coordination

The coordination polyhedron of the silver ion consists of a very irregular arrangement of eight atoms. The silver ion has close contacts with two oxygens, O1, O3_{III}, and two longer contacts with O2_{III} and O3. The group is completed by atoms C1_I, C2_I of one diene molecule and C5_{II} and C6_{II} of another molecule (table 2). The shortest Ag-O distance of 2.45 Å is not significantly shorter than the generally accepted value for the sum of the ionic radii (Ag⁺, O⁻), given as 2.46 Å¹¹. Thus the Ag-O interactions must be considered predominantly ionic. This is further suggested by the colourless nature of the crystals: compounds containing covalent Ag-O bonds generally having a cream colour¹². The four coordinating oxygens are closely coplanar, with the silver ion approximately 0.3 Å out of the plane.

The silver ion is complexed to one cis and one trans double bond of separate olefin molecules. The Ag⁺-C=C (mid-point) distances are 2.37 (cis) and 2.35 Å (trans). These values are fairly typical for a silver ion undergoing

relatively strong interactions with two olefinic bonds (a contraction of 0.07-0.10 Å occurs when the silver ion forms just one bond to the olefin^{8,13}). Although it is well established that both cis and trans olefinic bonds form linkages to silver, we believe this to be the first reported instance where a silver ion complexes both cis and trans double bonds. In the Humulene⁸ and Germacatriene¹⁴ adducts "preference" for the torsionally strained double bonds was found. In the former an endocyclic trans double bond has no interactions with silver, and in the latter an exocyclic trans double bond is similarly ignored: both double bonds are quite planar. No such effect pertains in the present study, since the cis bond is closely planar while the trans bond is very strained (Table 8), yet both enter into the coordination scheme. While it is to be expected that enhanced reactivity due to torsional strain is important in these cases, the geometric relation of the double bonds to each other, and their respective degrees of substitution are also important factors in determining the overall coordination scheme. In the present case both double bonds have their mean planes roughly perpendicular to the "plane" of the ring, and so are easily accessible for coordination in a polymeric fashion.

Though the silver-C=C (mid-point) distances are equal for both bonds within experimental error, the individual Ag⁺-C_{sp²} distances are significantly unequal (Table 7). This asymmetry has been noted in numerous other silver complexes¹⁵ and seems to be a requirement of the silver-olefin bond. The interaction is believed to arise from overlap of the filled π orbital of the double bond with a vacant silver orbital, and from overlap of a filled silver orbital with a vacant antibonding π^* orbital of the olefin. Paul et al.¹⁵ have suggested that the filled silver orbital can only overlap one

lobe of the π^* orbital, localised on a particular C_{sp^2} atom, thus giving rise to the observed asymmetry.

Maximum overlap of the π orbital would be expected when the line joining the mid-point of the double bond to the silver ion is normal to the plane of the double bond. The trans double bond satisfies this criterion quite well, the plane containing the silver and sp^2 carbon atoms making a dihedral angle of 87.6° with the mean plane of the double bond (Table 8). However, the cis double bond shows a corresponding dihedral angle of 102.6° , the silver ion being displaced towards the hydrogen atoms of the double bond. This may reflect an attempt of the silver ion to maximise the non-bonded contacts with C10 and C3. However, McKechnie and Paul¹⁶ have analysed the results for a number of compounds containing cis-bonds to silver, and have shown that a good correlation exists, in that the shorter the $Ag^+-C=C$ (mid-point) distance, the larger is the dihedral angle defined above. This suggests that as the strength of the $Ag^+-C=C$ interaction increases the π orbital of the olefin becomes twisted from its normal position (with its axis normal to the plane of the bond), consistent with a progressive shift towards sp^3 hybridisation. While the hydrogen parameters obtained from this study are not sufficiently reliable to warrant discussion of the deviations from planarity of the substituent groups attached to the double bond, the dihedral angle of 102.6° seems to correlate well with the data and interpretation given by McKechnie and Paul.

The four atoms of the nitrate group are, as expected, closely planar. The N-O bond lengths range from 1.17 - 1.33 Å. The short N-O1 distance of 1.17 is indicative of significant double-bond character, when compared with the value of 1.22 Å in the symmetrical nitrate group.¹⁷ However, O1 has a close

contact (2.45 Å) with the silver ion and this probably serves to weaken the N-O bond from pure double bond order by electrostatic interaction. The N-O³ distance of 1.33 Å is significantly longer than that of the symmetric nitrate ion. This is explicable in terms of the silver ion coordination, since O³ is coordinated to two silver ions at distances of 2.50 and 2.79 Å. O² is only coordinated weakly to silver, and has a "normal" bond length to nitrogen.

The silver and nitrate ions form approximately planar chains throughout the structure. If the nitrate ion is regarded as occupying only one coordination position then we may note that the vectors from silver to the two oxygen atoms and the two C=C mid-points define a distorted tetrahedron (Table 2). This amounts to disregarding the long contacts the silver ion makes with O²_{III} and O³, of 2.98 and 2.79 Å, and which are evidently weak interactions.

The Cyclodecadiene Ring

The conformation of the ring and its orientation with respect to the ionic layer is shown in Figure 3. The average C_{sp³}-C_{sp³} and C_{sp²}-C_{sp³} distances are 1.56 ± 0.022 and 1.49 ± 0.023 Å respectively, compared with accepted average values¹⁸ of 1.54 and 1.53 Å. The average C_{sp²}-C_{sp²} distance is 1.33 ± 0.021 Å, close to that of the uncomplexed double bond. Thus the silver - olefin bond has negligible effect on the C=C bond lengths, as has usually been observed for other adducts. The only individual bond length which differs significantly from its accepted value is that of C⁴ - C⁵ (1.45 Å) which is some 4-5 standard deviations shorter.

C - C_{sp³} - C angles range from 108.9 - 117.5°, with an average of 113.4°, rather higher than the tetrahedral angle. The comparable average in Germacratriene¹⁴ is 109.2°, where the presence of an extra C_{sp²} atom in the ring enables the

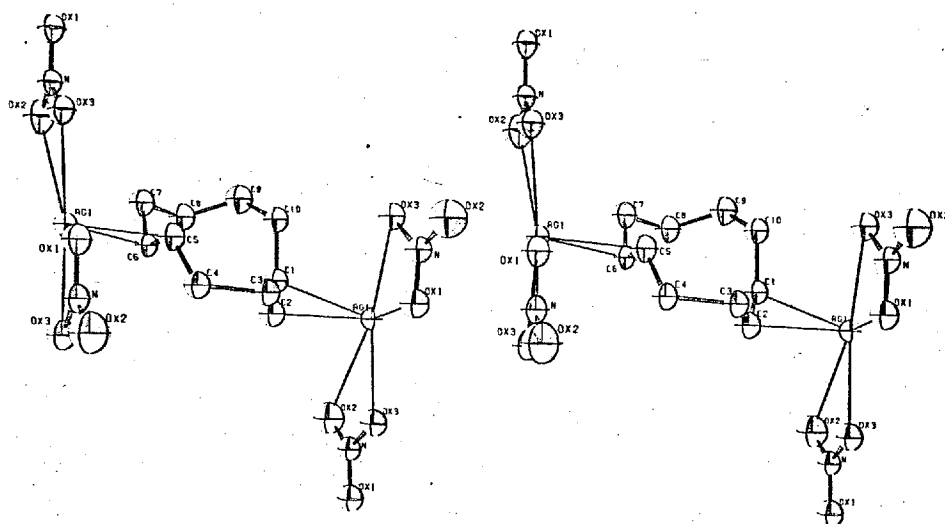


Figure 3

Stereoscopic illustration with thermal ellipsoids (for Ag^+ only, others isotropic) scaled to represent 50% probability.

average C - C_{sp}³ - C angle to become more nearly tetrahedral. Average values as high as 117° have been found in other medium rings.¹⁹⁻²² Hendrickson,²³ by comparison with the lower alkanes and cyclohexane, has suggested that the optimum CCC angle in the methylene group should be 112°, much closer to the average in the present study. The average C - C_{sp}² - C angle is 125.2°. Garbisch²⁶ quotes an unstrained value of 122° for a C=CH-C bond angle.

The ten-membered ring has a characteristically "opened out" appearance. Relative to the Dreiding model, C10 is moved outwards further than the model permits. This has the effect of alleviating the very unfavourable transannular interactions between one of the C10 hydrogens and atoms C5 and C6. The shortest non-bonded contact in the ring, other than for two atoms in a 1,3 relationship, is 3.07 Å, between C2 and C5.

The conformation is similar to that of the ten-membered ring in Heliangine,²⁴ which has a trans epoxide group in place of the trans double bond of cyclodecadiene. The conformations are related by a rotation of the cis double bond unit by ca. 120°. Heliangine cannot adopt the conformation of cyclodecadiene because of the requirements of the fused lactone ring adjacent to the cis double bond: this is illustrated schematically in Figure 5.

The geometries of the cis and trans double bonds are contrasted in Table 8, in terms of their least-squares planes. While the cis double bond is closely planar, substantial out-of-plane twisting exists at the trans double bond. An acute angle of 22° exists between the planes defined by C4 C5 C6 and C5 C6 C7. Thus appreciable sp²-sp² torsional strain is present, and this accounts in a qualitative manner for the greater observed reactivity²⁵ of the trans double bond.

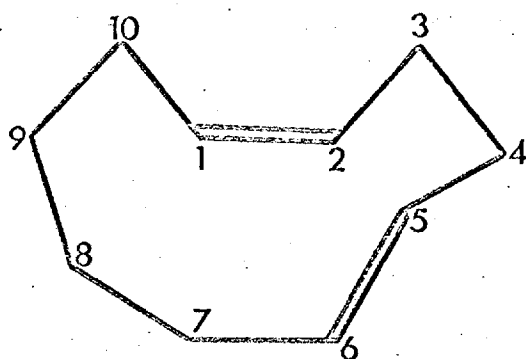
Similar degrees of sp^2-sp^2 torsional strain have been reported for Humulene⁸ and Germacatriene¹⁴ for endocyclic trans double bonds. Using a formula derived by Herzberg²⁷ for ethylene,

$$E_{\tau} = 8\tau^2 \text{ cal/mole}$$

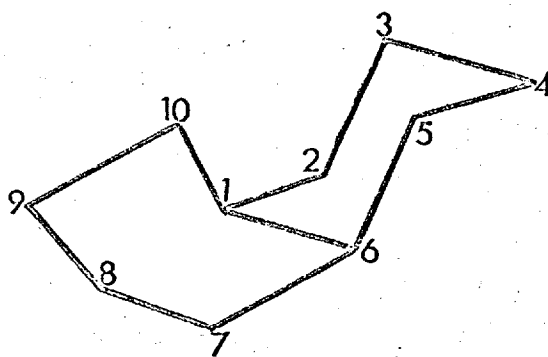
where τ is the dihedral angle defined above, it is possible to estimate the magnitude of this torsional strain to be ca. 3.9 Kcal mole⁻¹

Consideration of the dihedral angles listed in Table 10 shows that there are significant amounts of sp^3-sp^3 and sp^2-sp^3 single-bond torsional strain present. The C7 - C8 sp^3-sp^3 bond is approximately 25° from the favourable staggered conformation, and the C2 - C3 and C4 - C5 sp^2-sp^3 bonds differ by ca. 30° from their stabler conformations in which the double bond is eclipsed. Strain energy estimates by the methods of Hendrickson²³ and Garbisch *et al.*²⁸ indicate that the $E_{sp^2-sp^3}$ and $E_{sp^3-sp^3}$ torsional strain energies are ca. 1.5 and 1.3 Kcal mole⁻¹ respectively. The energy increase due to non-bonded interactions²³ has been ignored in these calculations, as has the strain energy due to valence-angle bending: while an analysis of the latter is quite straightforward, it is of doubtful value in view of the large standard deviations of the valence angles. The parameters used in the calculations are given in a following section.

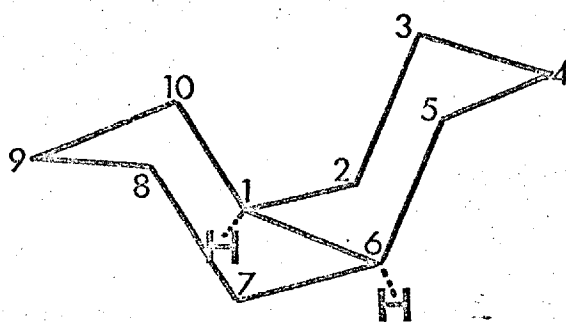
It is worthwhile considering the effects of the ionic layer on the conformation adopted by the cyclodecadiene molecule. Cyclodecadiene- Ionic layer contacts < 3.50 Å are given in Table 11. The closest approach of an oxygen atom to carbon is that between O3 and C4, 3.22 Å. Although this is shorter than the sum of Van der Waals radii, given as 3.40 Å for -CH₃ and O,²⁹ this distance is too large to represent



I



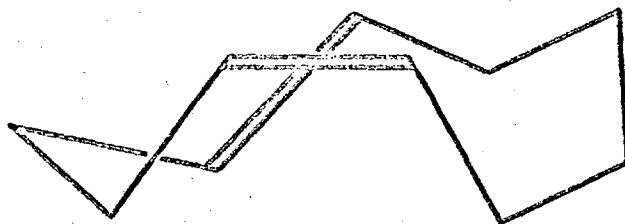
II



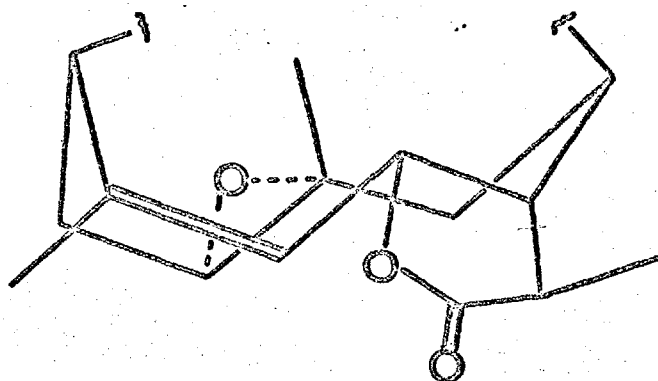
III

Figure 4

- I Cis-trans(1,5) cyclodecadiene
- II Cis-decalin in chair-twist-boat conformation
- III Cis-decalin in chair-chair conformation



i Cis-trans(1,5) cyclodecadiene



ii Heliangine

Figure 5

significant hydrogen bonding. Some of the distortion observed at the trans double bond is possibly due to non-bonded repulsions between silver and atoms C4, C7. These distances are rather shorter than the corresponding distances for the cis double bond (which shows no distortion), and in particular the $\text{Ag}^+ - \text{C4}$ distance of $3.17 \text{ \AA}$ is significantly shorter than the sum of ionic and Van der Waals radii, $11,29 \text{ \AA}$ $3.26 \text{ \AA}$

Stereochemistry of the Cyclisation Reactions

The conformation of cis-trans(1,5)cyclodecadiene accounts for its ready formation of substituted cis decalins in cyclisation reactions.²⁵ The conformational relationship of cyclodecadiene (I) to cis decalin (III) is shown in Figure 4. However, it is seen that if the conformation of I is adopted just prior to cyclisation, this gives a cyclisation product with one ring in a twist-boat conformation (II). The ring formed by C1, C6, C7, C8, C9, C10 (the ring not containing the bulky substituents in the reaction with bromine) may then flip to give the stable chair-chair conformation (III). The assumption that the conformation of I is preserved in solution seems reasonable in view of the evidence presented for Humulene⁸ and Germacratriene,¹⁴ where the conformations of the adducts are also closely similar to those of the cyclisation products.

Details of the Strain-Energy Estimates

The torsional potential functions^{23,28} used were of the form

$$\text{sp}^3 - \text{sp}^3: E_{\omega} = (K_{\omega}/2)(1 + \cos 3\omega)$$

$$\text{sp}^2 - \text{sp}^3: E_{\delta} = (K_{\delta}/2)(1 - \cos 3\delta)$$

where the angles ω and δ are defined in Table 10, and K is the appropriate rotational potential barrier. These formulae

apply best when the sp^3 atoms have identical substituents. Although this is not true in the present case, errors were minimised by using, where possible, K values appropriate to compounds having similar degrees of substitution.

Values used were

$$K_w = 2.8 \text{ Kcal mole}^{-1} \text{ (ethane}^{30}\text{)}$$

$$K_\delta = 2.0 \text{ Kcal mole}^{-1} \text{ (propene}^{31}\text{)}$$

$$K_\delta = 0.8 \text{ Kcal mole}^{-1} \text{ (cis butene}^{32}\text{)}$$

Acknowledgement

I should like to thank Dr. J.K. Sutherland for suggesting this problem and for helpful discussions, and Professors G. Wilke and J.G. Traynham for providing samples of cis-trans(1,5)cyclodecadiene.

Table 1

Final positional parameters as fractions of the unitcell edges, with standard deviations in parentheses.

Atom	<u>x</u>	<u>y</u>	<u>z</u>
Ag	0.16171(9)	0.14623(13)	0.79529(8)
N	0.3432(11)	0.3125(17)	0.6599(10)
O1	0.3323(9)	0.1897(15)	0.6669(8)
O2	0.4098(12)	0.3773(16)	0.5928(11)
O3	0.2776(9)	0.3937(12)	0.7277(8)
C1	0.2077(13)	0.2371(19)	0.0024(11)
C2	0.3040(13)	0.1544(20)	-0.0231(12)
C3	0.4328(13)	0.2076(18)	-0.0549(12)
C4	0.5373(13)	0.2206(19)	0.0535(12)
C5	0.5011(13)	0.3330(19)	0.1297(12)
C6	0.4328(12)	0.3159(17)	0.2206(11)
C7	0.3572(14)	0.4321(20)	0.2720(13)
C8	0.2093(14)	0.4047(20)	0.2384(14)
C9	0.1499(16)	0.4576(23)	0.1178(14)
C10	0.2050(13)	0.3948(19)	0.0059(12)

Table 2

Final thermal parameters of the non-hydrogen atoms.

Standard deviations in parentheses.

Atom	$\underline{\beta}_{11}$	$\underline{\beta}_{22}$	$\underline{\beta}_{33}$	$\underline{\beta}_{12}$	$\underline{\beta}_{13}$	$\underline{\beta}_{23}$
Ag	.00616(9)	.00674(22)	.00461(7)	-.00031(11)	-.00121(5)	.00008(10)

The anisotropic temperature factor is of the form:

$$\exp-(\underline{\beta}_{11}h^2 + \underline{\beta}_{22}k^2 + \underline{\beta}_{33}l^2 + 2\underline{\beta}_{12}hk + 2\underline{\beta}_{13}hl + 2\underline{\beta}_{23}kl)$$

Atom	$B(\overset{\circ}{A}^2)$
N	2.66(0.21)
O1	3.19(0.20)
O2	5.00(0.27)
O3	3.06(0.20)
C1	2.82(0.25)
C2	3.23(0.26)
C3	2.87(0.26)
C4	2.87(0.26)
C5	3.18(0.27)
C6	2.54(0.24)
C7	3.50(0.29)
C8	3.87(0.33)
C9	4.25(0.33)
C10	3.13(0.27)

Table 3

Hydrogen Positional and Thermal Parameters

Atom	x	y	z	$B(A^2)$
H1	0.1217	0.1856	0.0207	3.2
H2	0.2907	0.0438	-0.0203	3.7
H31	0.4186	0.3107	-0.0900	3.3
H32	0.4667	0.1442	-0.1183	3.3
H41	0.5439	0.1246	0.0992	3.5
H42	0.6278	0.2409	0.0234	3.5
H5	0.5279	0.4366	0.1092	3.7
H6	0.4331	0.2161	0.2605	3.1
H71	0.3807	0.5295	0.2385	3.8
H72	0.3757	0.4347	0.3649	3.8
H81	0.1590	0.4462	0.3041	4.3
H82	0.1970	0.2938	0.2373	4.3
H91	0.1633	0.5677	0.1181	4.6
H92	0.0505	0.4384	0.1128	4.6
H101	0.2991	0.4281	0.0042	3.5
H102	0.1494	0.4292	-0.0699	3.5

Table 4

Observed and Calculated Structure Factors (in electrons x 10)

for $C_{10}H_{16}:AgNO_3$

* indicates unobserved reflection

E indicates reflection omitted for suspected extinction

Tabulated as:

1. F_o , F_c for each group with constant h, k

0,0,L	-4 440 433	1 915 942	7 472 -512	12,1,L	-13 474 -512
-10 491 574	-2 271 -290	2 290 235	8 416 -639	-6 100 -100	-14 185 -240
-12 421 -414	0 437 -411	3 166 141	9 283 257	-5 124 144	4,2,L
-6 165 140	2 434 442	4 380 -364	10 260 250	-4 141 147	13 204 5
-6 326 -355	4 868 -927	5 491 -427	11 714 -79	-3 136 -147	12 444 -39
-4 911 204	6 568 516	6 529 -431		-2 130 -128	11 255 -235
-14 220 272	8 162 -136	7 414 378	7,1,L	-1 138 133	10 424 39
		8 591 555	-12 121 -121	1 534 -24	9 521 439
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4	354	322	7	546	-581	4, 3, 5			-7	92*	-2	-4	591	-567	6	92*	-99
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-1	63*	-61	10	381	340	7	96*	-101	8	164	-181	-10	363	-390	1	281	269
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6	434	-454	-5	199	-169	-8	96*	123	4	314	324	-1	290	-216	6	312	266
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-7	170	-164	H, 3, 3			2	516	-482	7	306	306	H, 4, 5			4, 4, 10		
-8	88	-84	12	150	128	1	231	245	8	128	148	11	45*	1	7	124	134
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6	100	127	8	367	363	-3	245	-207	12	251	-256	7	416	-424	3	85*	50
5	42*	-45	7	92*	-89	-4	512	-478	H, 4, 1			6	93*	28	2	97*	33
4	118	83	6	556	536	-5	229	221	12	178	-190	5	247	-207	1	366	305
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2	738	686	-7	261	-233	-1	106*	-32	8	409	377	-5	110*	-55	
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6	313	-272	4, 5, 5			-5	400	394	4	95*	27	-9	267	245	
7	103*	-35	10	67*	71	-6	99*	83	3	83*	89	4, 6, 7			
8	531	571	9	301	223	-7	92*	30	2	636	588	8	175	-219	
9	103*	98	8	99*	64	-8	80*	-46	1	499	-578	7	87*	-79	
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11	77*	4	6	154	-181	H, 5, 10			-1	405	395	5	423	-370	
H, 5, 1			4	102*	17	7	42*	-73	-2	363	-294	4	445	455	
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6	278	-215	-2	214	189	1	100*	-28	-8	152	-127	-2	415	419	
5	482	-492	-3	89*	-58	0	143	-153	-9	175	178	-3	326	329	
4	269	187	-4	94*	92	-1	102*	58	-10	306	286	-4	221	-226	
3	468	845	-5	742	676	-2	249	-257	-11	206	-228	-5	112*	-25	
2	373	-310	-6	106*	91	-3	100*	-7	H, 6, 3			-6	157	-167	
1	334	-342	-7	398	-381	-4	406	402	10	76*	-7	-7	318	-269	
-1	565	-725	-8	105*	-13	-5	95*	25	9	92*	157	-8	234	104	
-2	374	243	-9	98*	-16	-6	89*	-43	8	373	-356	-9	139*	122	
-3	901	836	-10	86*	100	-7	79*	-74	7	407	-385	4, 6, 8			
-4	78*	-9	-11	301	268	-8	221	-214	6	300	305	8	90*	-113	
H, 5, 2			4, 5, 6			-9	38*	14	5	150	146	7	72*	-0	
-5	124*	-120	10	183	197	H, 5, 11			4	90*	111	6	152	-150	
-6	193	167	9	76*	24	5	143	-110	3	590	611	5	344	297	
-7	551	-541	8	194	179	4	72*	76	2	525	-573	4	404	363	
-8	106*	-111	7	102*	-57	3	451	408	1	559	-501	3	227	-216	
-9	343	370	6	623	-655	2	85*	-93	0	434	417	2	108*	-40	
-10	94*	-46	5	156	139	1	341	-309	-1	101*	94	1	108*	-94	
H, 5, 3			4	372	379	0	91*	37	-2	382	328	0	326	-340	
11	70*	-2	3	145	156	-1	207	-209	-3	729	730	-1	344	372	
10	425	395	2	335	369	-2	92*	-13	-4	745	-708	-2	462	510	
9	100*	65	1	95*	-35	-3	434	404	-5	616	-584	-3	327	-274	
8	366	-364	0	790	-826	-4	97*	-15	-7	109*	76	-4	108*	-4	
7	115*	59	-1	165	199	-5	82*	-110	-8	151	178	-5	107*	-22	
6	311	-364	-2	322	251	-6	74*	-17	-9	367	327	-6	181	-201	
5	283	241	-3	288	-219	-7	220	-190	-10	184	-175	-7	266	237	
4	98*	535	-4	284	245	H, 5, 12			H, 6, 4			-8	207	202	
3	291	-215	-5	148	-127	3	178	-142	10	67*	84	-9	116*	-131	
2	584	-583	-6	563	-525	2	277	-273	9	213	-237	4, 6, 9			
1	250	-152	-7	109*	-24	1	73*	11	8	412	-408	7	53*	-17	
0	450	-453	-8	104*	70	0	228	-159	7	410	364	6	126*	165	
-1	127*	28	-9	94*	47	-1	77*	45	6	156	205	5	211	233	
-2	1198	1212	-10	198	180	-2	365	377	5	110*	-42	4	349	-317	
-3	436	-361	4, 5, 7			-3	74*	13	4	255	231	3	173	-157	
-4	471	-469	0	62*	17	-4	245	-194	3	308	-307	2	103*	11	
-5	180	124	8	80*	-104	-5	63*	46	2	591	-600	1	211	-217	
-6	480	-468	7	524	-494	-6	122*	-122	1	490	434	0	260	265	
-7	103*	53	6	103*	29	H, 5, 13			0	82*	-5	-1	151	194	
-8	498	536	5	550	526	0	51*	11	-1	265	229	-2	260	-255	
-9	103*	-4	4	152	-49	-1	313	323	-2	696	627	-3	105*	-34	
-10	94*	-3	3	212	170	-2	53*	-66	-3	573	-584	-4	103*	-7	
-11	76*	14	2	207	-202	-3	190	-259	-4	637	-635	-5	246	-241	
H, 5, 4			1	618	-740	-2	53*	-66	-5	302	293	-6	204	285	
11	283	307	0	224	201	-3	190	-259	-6	110*	-74	-7	232	221	
10	84*	4	-1	533	522	H, 6, 0			-7	155	115	-8	172	-219	
9	451	-408	-2	143	-115	1	349	440	-8	260	230	4, 6, 10			
8	104*	-104	-3	319	309	2	277	-273	-9	239	-253	6	179	204	
7	106*	-114	-4	106*	-48	3	178	-142	10	308	-281	5	251	-271	
6	104*	119	-5	540	-488	4	277	-273	9	412	-408	4	199	-202	
5	601	663	-6	109*	16	5	77*	45	8	410	364	3	80*	64	
4	221	-189	-7	265	231	6	365	377	7	156	205	2	93*	-21	
3	648	-651	-8	100*	45	7	74*	13	6	110*	-42	1	167	189	
2	104*	-57	-9	244	215	8	245	-194	5	255	231	0	270	275	
1	227	-200	-10	72*	-37	9	63*	46	4	308	-307	-1	209	-282	
0	590	482	4, 5, 8			10	122*	-122	3	283	-284	-2	242	-147	
-1	975	578	0	37*	-22	1	349	440	2	591	-600	-3	97*	18	
-2	164	-119	8	276	-297	2	277	-273	1	490	434	-4	133*	-141	
-3	609	-516	7	82*	-9	3	178	-142	0	82*	-5	-5	210	168	
-4	310	265	6	463	459	4	277	-273	-1	265	229	-6	245	164	
-5	445	-334	5	102*	62	5	77*	45	-2	696	627	-7	110*	-134	
-6	100*	-11	4	105*	78	6	365	377	-3	573	-584	-8	103*	-7	
-7	420	-441	3	106*	-68	7	74*	13	-4	637	-635	-9	246	-241	
-8	102*	-65	2	551	-618	8	245	-194	-5	302	293	-6	204	285	
-9	229	-213	1	211	228	9	63*	46	-6	110*	-74	-7	232	221	
-10	92*	11	0	413	423	10	122*	-122	-8	155	115	-8	172	-219	
-11	133*	-170	-1	104*	24	H, 6, 1			-9	260	230	4, 6, 11			
H, 5, 5			-2	210	175	11	234	-232	-10	308	-281	6	179	204	
11	51*	-10	10	85*	84	10	85*	84	H, 6, 5	5	251	-271	5	251	-271
10	397	-376	9	99*	-30	9	99*	-30	10	156	-164	4	199	-202	
9	93*	22	8	262	233	8	262	233	9	318	-313	3	80*	64	
8	251	179	7	473	517	7	473	517	8	373	364	2	93*	-21	
7	107*	0	6	552	-607	6	552	-607	7	426	388	1	167	189	
6	355	361	5	679	-724	5	679	-724	6	283	-284	0	270	275	
5	102*	-28	4	260	195	4	260	195	5	112*	28	-1	209	-282	
4	739	-715	3	113*	-95	3	113*	-95	4	268	-262	-2	242	-147	
3	89*	-84	2	343	338	2	343	338	3	447	-475	-3	97*	18	
2	83*	78	1	588	733	1	588	733	2	477	457	-4	133*	-141	
1	236	150	0	354	-412	0	354	-412	1	309	304	-5	210	168	
0	702	727	-1	436	-643	-1	436	-643	0	92*	-57	-6	245	164	
-1	227	-164	-2	186	152	-2	186	152	-1	278	235	-7	110*	-134	
-2	772	-763	-3	244	-184	-3	244	-184	-2	379	-348	-8	83*	-5	
H, 5, 6			-4	442	359	-4	442	359	-3	398	-354	-9	138*	95	
11	51*	-10													

Table 5

Intramolecular Bonded Distances (r) together with Estimated
Standard Deviations (σ) in Angstroms

Bond	r	σ	Bond	r	σ
C1 - C2	1.33	0.022	C8 - C9	1.53	0.023
C2 - C3	1.52	0.021	C9 - C10	1.56	0.023
C3 - C4	1.57	0.018	C10- C1	1.50	0.025
C4 - C5	1.45	0.023			
C5 - C6	1.32	0.020	N - O1	1.17	0.022
C6 - C7	1.51	0.023	N - O2	1.25	0.019
C7 - C8	1.58	0.021	N - O3	1.33	0.017

Table 6

Valence angles (θ°) with Estimated Standard Deviations (σ).

Angle	θ	σ	Angle	θ	σ
C1 - C2 - C3	124.5	(1.7)	C8 - C9 - C10	116.9	(1.5)
C2 - C3 - C4	113.9	(1.1)	C9 - C10- C1	114.4	(1.4)
C3 - C4 - C5	108.9	(1.2)	C10- C1 - C2	127.8	(1.4)
C4 - C5 - C6	124.7	(1.6)			
C5 - C6 - C7	123.9	(1.5)	O1 - N - O2	126.6	(1.4)
C6 - C7 - C8	109.0	(1.3)	O1 - N - O3	118.5	(1.2)
C7 - C8 - C9	117.5	(1.4)	O2 - N - O3	114.9	(1.5)

Table 7

Silver-ion Bonded Interactions (r), with E.S.D's (σ), in Å.

Atoms	r	σ	Atoms	r	σ
Ag - C1 _I	2.50	0.014	Ag - O1	2.45	0.010
Ag - C2 _I	2.41	0.013	Ag - O3	2.79	0.011
Ag - C5 _{II}	2.40	0.013	Ag - O2 _{III}	2.98	0.014
Ag - C6 _{II}	2.48	0.012	Ag - O3 _{III}	2.50	0.012
Ag - (C1=C2) _I mid-point			Ag - (C5=C6) _{II} mid-point		
	2.37	0.014		2.35	0.013

Angles within the Silver-ion Coordination Tetrahedron in °.
E.S.D's in parentheses.

Atoms	θ
(C1=C2) _I - Ag - (C5=C6) _{II}	140.3(0.49)
(C5=C6) _{II} - Ag - O1	106.0(0.40)
(C1=C2) _I - Ag - O1	105.2(0.41)
(C5=C6) _{II} - Ag - O3 _{III}	105.5(0.45)
(C1=C2) _I - Ag - O3 _{III}	101.7(0.44)
O1 - Ag - O3 _{III}	83.8(0.40)

Atoms with subscripts are related to those of the asymmetric unit by the following operations:

- I $\underline{x}$, $\underline{y}$, $1 + \underline{z}$
 II $\underline{x} - 1/2$, $1/2 - \underline{y}$, $1/2 + \underline{z}$
 III $1/2 - \underline{x}$, $\underline{y} - 1/2$, $3/2 - \underline{z}$

Table 8

Least-Squares Planes

Deviations of the atoms from the least-squares planes in Å.^o

Atom	d
C10	-0.0003
C1	0.0007
C2	-0.0007
C3	0.0003

The equation of the plane in Direct Space is

$$2.679\underline{x} - 0.1850\underline{y} + 10.608\underline{z} = 0.5387$$

C4	0.1209
C5	-0.1243
C6	-0.1105
C7	0.1139

The equation of the plane in Direct Space is

$$8.157\underline{x} + 0.6665\underline{y} + 6.109\underline{z} = 4.978$$

N	-0.0059
O1	0.0022
O2	0.0020
O3	0.0017

The equation of the plane in Direct Space is

$$7.343\underline{x} - 0.1804\underline{y} + 7.215\underline{z} = 7.220$$

Table 9

Non-bonded Distances within the Cyclodecadiene Molecule, Å.^o

C1	C4	3.44	C3	C10	3.11
C1	C5	3.38	C4	C7	3.83
C1	C6	3.32	C4	C10	3.84
C1	C7	3.77	C5	C8	3.47
C2	C5	3.07	C5	C9	3.85
C2	C6	3.33	C5	C10	3.32
C2	C9	3.73	C6	C9	3.35
C3	C6	3.29	C6	C10	3.31

Cyclodecadiene-Cyclodecadiene Contacts

C7	C1 _I	3.97	C2	C4 _{II}	3.96
C9	C6 _I	4.00	C9	C9 _{III}	3.99

Subscripted atoms are related to those of the asymmetric unit by the symmetry operations

I	$1/2 - \underline{x},$	$1/2 + \underline{y},$	$1/2 - \underline{z}$
II	$1 - \underline{x},$	$- \underline{y},$	$- \underline{z}$
III	$- \underline{x},$	$1 - \underline{y},$	$- \underline{z}$

Table 10

Dihedral Angles

The angle quoted is that required to rotate the projection of the bond between (Atom3 - Atom4) onto the bond between (Atom1 - Atom2). Clockwise rotations are denoted by positive angles.

Atoms	Angle	Type
C1 (C2 C3) C4	92.6	δ
C2 (C3 C4) C5	-68.2	ω
C3 (C4 C5) C6	92.2	δ
C4 (C5 C6) C7	-157.8	τ
C5 (C6 C7) C8	108.2	δ
C6 (C7 C8) C9	-84.8	ω
C7 (C8 C9) C10	61.1	ω
C8 (C9 C10) C1	52.3	ω
C9 (C10 C1) C2	-133.8	δ
C10(C1 C2) C3	-0.2	τ

Angles denoted by ω are sp^3-sp^3 torsion angles

δ are sp^2-sp^3 " "

τ are sp^2-sp^2 " "

Table 11

Cyclodecadiene-Ionic Layer non-bonded contacts $< 3.50 \text{ \AA}$.

Atoms	d	Atoms	d
Ag C3 _I	3.21	C3 O3 _{IV}	3.32
Ag C10 _I	3.35	C10 O3 _{IV}	3.32
O2 C7 _{II}	3.29	C4 Ag _V	3.18
O2 C2 _{III}	3.49	C7 Ag _V	3.25
O3 C2 _{III}	3.44	C4 N _V	3.32
C10 O1 _{III}	3.42	C5 O1 _V	3.45
C3 N _{IV}	3.42	C4 O1 _V	3.33
C3 O1 _{IV}	3.23	C4 O3 _V	3.22

Subscripted atoms are related to those of the asymmetric unit by the operations

I	$\underline{x}$,	$\underline{y}$,	$1 + \underline{z}$
II	$1 - \underline{x}$,	$1 - \underline{y}$,	$1 - \underline{z}$
III	$1/2 - \underline{x}$,	$1/2 + \underline{y}$,	$1/2 - \underline{z}$
IV	$\underline{x}$,	$\underline{y}$,	$\underline{z} - 1$
V	$1/2 + \underline{x}$,	$1/2 - \underline{y}$,	$\underline{z} - 1/2$

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"All generalizations are dangerous, even this one."

.....Alexandre Dumas fils.

CHAPTER 4. The Crystal Structures of Tetramethylammonium bis(isothiocyanato)- μ -tetrakis(acetato)dicopper(II), and Tetramethylammonium bis(isothiocyanato)- μ -tetrakis(formato)dicopper(II): a discussion of antiferromagnetism in copper(II) carboxylate dimers.

Abstract

The crystal structures of Tetramethylammonium bis(isothiocyanato)- μ -tetrakis(acetato)dicopper(II), and Tetramethylammonium bis(isothiocyanato)- μ -tetrakis(formato)dicopper(II) have been determined from diffractometer data. The crystals are isomorphous, in spacegroup $I4/mmm$. The unitcell-dimensions are: acetato complex, $\overset{0}{a} = 8.873$, $c = 18.087$, formato complex, $\overset{0}{a} = 8.917$, $c = 15.800$ Å. The structures were solved by standard methods, and positional and thermal parameters have been refined to the final R factors of 0.093 (acetato complex) and 0.037 (formato complex). The structures are dimeric, essentially similar to that of cupric acetate monohydrate, with the isothiocyanate groups replacing the axial water molecules. The copper atoms and isothiocyanate groups lie on crystallographic fourfold axes. In the formato complex the symmetry of the dimeric anion is strictly $4/mmm$ (D_{4h}). In the acetato complex the carboxylate groups are disordered about the $(\underline{x}, \underline{x}, \underline{z})$ diagonals, but the symmetry still conforms closely to D_{4h} . In the formato complex, which exhibits the greater spin coupling between the copper atoms (higher J value), the Cu...Cu distance is $2.710(\sigma = 0.002\text{Å})$, while in the acetato complex it is significantly smaller, viz. $2.647(\sigma = 0.003\text{Å})$. These results suggest that spin coupling arising from direct metal-metal bonding is not responsible for the observed antiferromagnetism.

Introduction

Preparation and properties of compounds of stoichiometry $(R_4N) Cu(CH_3CO_2)_2X$, ($X = NCS, NO_2$ or Br) were first reported by Goodgame and Marsham¹. The magnetic moments of these compounds were anomalously low at room temperature and quite similar to that of cupric acetate monohydrate². The temperature dependence of the susceptibility of the thio-cyanate complex was also found to correspond quite well with that of cupric acetate monohydrate. These observations prompted these authors to suggest a binuclear structure for the complexes, with the X^- ions replacing the water molecules in the cupric acetate monohydrate structure³. Infrared evidence indicated the thiocyanate ligands to be coordinated through nitrogen.

However, direct evidence of the dimeric structure was lacking since molecular weight determinations could not be made in solvents of low donor power, owing to poor solubility. The full structure determination of the compound of empirical formula $(Me_4N) Cu(CH_3CO_2)_2NCS$ was therefore undertaken. When crystals of the analogous formate complex later became available it was thought worthwhile to determine its structure also, in an attempt to correlate, experimentally, the extent of spin coupling with copper-copper distance in a pair of strictly analogous dimeric compounds. This would, it was hoped, then give new insight into the nature of the coupling mechanism. A preliminary account of this work has been published⁴.

The Crystal Structure of the $(Me_4N)_2-(Cu(CH_3CO_2)_2NCS)_2$ Complex.

Experimental

The crystals were green octahedra, truncated at top and bottom by square faces. They were strongly dichroic in plane-polarised light, and examination under crossed Nicols showed

them to be uniaxial, with the unique axis perpendicular to the square faces. Oscillation and Weissenberg photographs exhibited Laue symmetry $4/\text{mmm}$. The systematic absences were hkl , $h + k + l \neq 2n$, consistent with the spacegroups $I422$, $I4\text{mm}$, $I\bar{4}m2$ and $I4/\text{mmm}$. The structure has been solved in $I4/\text{mmm}$.

The unitcell-dimensions were determined from axial scans on a Siemens' four-circle automatic diffractometer, and intensity data were collected for a crystal of approximate dimensions $0.13 \times 0.16 \times 0.25 \text{ mm}^3$, mounted about the c axis. The θ - 2θ scan-technique was employed, using a "Five-value" measurement procedure (one side of peak, background, full peak, background on other side of peak, other side of peak). The diffractometer selects measuring times per-step (0.01° in θ) up to a preset maximum, and attenuators as necessary so as to achieve similar counting statistics for all but the weakest reflections.

Using nickel-filtered CuK_α radiation a total of 451 independent reflections was measured out to $\theta = 70^\circ$, within the octant $h, k, l \geq 0$, applying the condition in hkl , $k \geq h$, in addition to the body-centred condition. Of these 31 were judged to be unobserved, since the net count was less than 2.58 times its standard deviation (this corresponds to there being a less than 99% probability that the reflection is significantly different from background⁵); these reflections were assigned counts equal to 2.58σ . The data were placed on a uniform scale, using the 2, 0, 0 as reference reflection (measured every 20 reflections), and Lorentz and Polarisation corrections were applied.

Crystal Data

$(\text{Me}_4\text{N})_2(\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{NCS})_2$, $M = 627.6$, Tetragonal, $I4/\text{mmm}$
 $a = 8.873 \pm 0.001$, $c = 18.087 \pm 0.001 \text{ \AA}$, $U = 1424 \text{ \AA}^3$, $Z = 2$,
 $D_m = 1.45$ (spec. g. bottle), $D_c = 1.46 \text{ g.cm}^{-3}$, $\mu = 36 \text{ cm}^{-1}$ for CuK_α , $F_{000} = 652$.

Structure Solution and Refinement

Of the four possible spacegroups (plus one enantiomorph) only $I4/mmm$ is centrosymmetric. Assuming a dimeric structure similar to that of cupric acetate monohydrate,³ the molecule has a potential centre of symmetry mid-way between the copper atoms, and accordingly the spacegroup $I4/mmm$ was thought likely. In this spacegroup the Cu, N, C and S atoms must occupy fourfold positions (since the twofold positions would require $(4/mmm)$ site symmetry), and the $(0, 0, z)$ set was obviously compatible with a linear Cu...N-C-S arrangement. A three-dimensional Patterson synthesis confirmed these deductions, giving sequences of prominent peaks along $(0, 0, w)$ and $(\frac{1}{2}, \frac{1}{2}, w)$. The coordinates of the copper and sulphur atoms were found to be

Cu	0	0	0.070
S	0	0	0.345

This arrangement gave Cu...Cu and Cu...S distances of 2.53 and 5.0 Å, respectively, in good agreement with those expected for a dimeric structure with the N-C-S group coordinated through nitrogen. Three cycles of ORFELS⁶ least squares on these positions gave an R factor of 0.276, and a Fourier map clearly showed the remaining atoms. However, it was apparent at this stage that the bridging acetate groups were disordered. An ordered structure required the acetate oxygens to occupy 16-fold special positions of the type (x, x, z) or $(0, x, z)$, and the carbon atoms of the acetate group 8-fold positions of the type $(x, x, 0)$ or $(x, 0, 0)$. The positions were found to be

O	0.21	0.10	0.06
C2	0.26	0.14	0
C3	0.41	0.22	0

i.e. the acetate groups were substantially offset from the diagonal (x, x, z) mirror planes. In order to preserve the

spacegroup symmetry and stoichiometry of the complex, the acetate bridges were required to have two discrete orientations-related by mirroring in the ($\underline{x}$, $\underline{x}$, $\underline{z}$) plane- in a 1:1 ratio. The nitrogen atom of the tetramethylammonium ion was found to occupy the $(\frac{1}{2}, 0, \frac{1}{4})$ set of 4-fold positions, as expected. Although the site symmetry of these positions ($\underline{4m2}$) suggested that the methyl carbons should be ordered in 16-fold positions of the type $(0, \underline{x}, \underline{z})$, they were found to be systematically disordered in a manner similar to that of the acetate groups. The Fourier peaks for these methyl carbon atoms were also very diffuse, indicating large amplitudes of thermal vibration, or possibly some rotational movement of the group as a whole.

At this stage the spacegroup assignment was reconsidered, and in particular whether the requirement for the acetate bridges to lie on ($\underline{x}$, $\underline{x}$, $\underline{z}$) diagonals was simply a consequence of an incorrect choice of spacegroup. Consideration of the alternative spacegroups $\underline{I422}$, $\underline{I4mm}$ and $\underline{I4m2}$, however, showed that these would also require the acetate groups to lie on ($\underline{x}$, $\underline{0}$, $\underline{z}$) or ($\underline{x}$, $\underline{x}$, $\underline{z}$) in an ordered structure. Further the observed atomic positions were incompatible with these spacegroups: the large offset of the acetate oxygens and trigonal carbon atom from the ($\underline{x}$, $\underline{x}$, $\underline{z}$) diagonal would give rise to an impossibly distorted configuration of the acetate group in all spacegroups except $\underline{I4/mmm}$.

A further 5 cycles of ORFELS, including the disordered atoms with occupancies of one-half that required by the spacegroup, gave an $\underline{R}$ factor of 0.173. 5 cycles of fully anisotropic refinement reduced $\underline{R}$ to 0.12. The restrictions imposed by symmetry on the $\underline{\beta}_{ij}$ terms of atoms in special positions were determined by the method of Levy⁷: the requirement that $\underline{\beta}_{11} = \underline{\beta}_{22}$ for atoms lying on crystallographic $\underline{4}$ or $\underline{4}$ -fold axes necessitated re-programming of the appropriate ORFELS subroutines, as described by the authors.⁸

An absorption correction was applied, using the Gaussian Integration technique⁹, with ray-path lengths determined by the vector analysis method of Coppens et al. A sampling grid of 8 x 8 x 8 was selected from trial runs. A further 9 cycles of ORFLS then gave $R = 0.104$. From a difference Fourier the methyl hydrogens of the disordered acetate group were located. The hydrogens of the NMe_4 group were not visible, however, but were included as a hexagon of half-hydrogens. More refinement, with the hydrogens included as a fixed contribution, reduced R to 0.089, and an agreement analysis (DELSIG) showed that the average differences were approximately proportional to $|F_o|$. Accordingly, a weighting scheme, after Hughes¹², was applied. Each observation of $|F_o|$ was given a weight, $\sqrt{w}$, where

$$\sqrt{w} = \frac{F^*}{|F_o|} \quad \text{for} \quad |F_o| \geq F^* \quad 4.1$$

$$\sqrt{w} = 1 \quad \text{for} \quad |F_o| < F^* \quad 4.2$$

The function minimised was then $\sum w(|F_o| - |F_c|)^2$, and the weighted R factor was given by

$$R = \sqrt{\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}} \quad 4.3$$

A value of $F^* = 40$ was selected from the DELSIG analysis, as this gave approximately constant values of $w|F_o|^2$ over the well-populated ranges of $|F_o|$. After 9 cycles of ORFLS, refinement converged, with all parameter shifts vanishingly small, at a final weighted R factor of 0.093 on the 451 reflections. Although the weighted R factor was higher than the conventional, the parameter standard deviations were, on average, 15-20% lower. Unobserved reflections were

included in the refinement, but were omitted from all estimates of R .

The neutral copper and sulphur formfactors were those of Cromer and Waber.¹¹ The anomalous dispersion corrections were those of Cromer.⁵⁰ The dispersion-corrected copper and sulphur formfactors were obtained by vectorial addition of the real and imaginary components, as $((f_o + \delta f')^2 + \delta f''^2)^{1/2}$. The final difference Fourier showed no remarkable features, although the background level was rather high, viz. ± 0.5 , rising to a maximum of $1.2 \text{ e}\text{\AA}^{-3}$ in the vicinity of the copper atom.

The final positional and thermal parameters in Tables 1 and 2 were used to calculate the final structure factors listed in Table 3.

The Crystal Structure of the $(\text{Me}_4\text{N})_2(\text{Cu}(\text{HCO}_2)_2\text{NCS})_2$ Complex

Experimental

The crystals were similar to those of the acetato complex in colour and shape, except that the square faces were no longer well developed. Oscillation and Weissenberg photographs showed the crystals to be isomorphous with those of the acetato complex.

Crystal Data

$(\text{Me}_4\text{N})_2(\text{Cu}(\text{HCO}_2)_2\text{NCS})_2$, $M = 573.6$, Tetragonal, $I4/mmm$,
 $a = 8.917 \pm 0.001$, $c = 15.800 \pm 0.003 \text{ \AA}$, $U = 1256 \text{ \AA}^3$, $Z = 2$,
 $D_m = 1.52$ (floatation), $D_c = 1.53 \text{ g. cm}^{-3}$, $\mu = 43 \text{ cm}^{-1}$ for
 $\text{CuK}\alpha$, $F_{000} = 588$.

Structure Solution and Refinement

The relatively large change in the c cell-dimension relative to the acetate (ca. $2.3 \text{ \AA}$) was not thought to be indicative of any large scale structural change: replacement

of the $-\text{CH}_3$ group by hydrogen in the formate should permit a closer approach of the anions at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and give rise to a general contraction of the unitcell along c . Accordingly a copper position of

Cu O O 0.082

was inferred by comparison with the acetate. A structure-factor calculation based on this position gave an R factor of 0.50, and Fourier without a rejection test revealed the remaining atoms. It was immediately evident that the formate bridges were ordered along the (x, x, z) diagonals. The tetramethyl-ammonium groups were, however, systematically disordered as in the acetate structure.

Five cycles of ORFLS on these positions reduced R to 0.13. Five cycles of anisotropic refinement then gave $R = 0.070$. This refinement necessitated "patching" the ORFLS program to account for equalities among both positional and anisotropic thermal parameters⁷ for atoms in special positions, as described earlier. An absorption correction was applied, using an $8 \times 8 \times 8$ sampling grid, and five more cycles refinement reduced R to 0.052. A difference Fourier at this stage revealed the position of the hydrogen atom of the formate group. More refinement, including the positional parameter of the hydrogen atom as a variable, but fixing its B factor, reduced R to 0.050.

An agreement analysis (DELSIG) showed that the differences increased approximately linearly with structure-factor magnitudes, and accordingly the Hughes¹² weighting scheme was applied, as described earlier. A value of $F^* = 50$ was appropriate: this corresponded to giving weights of ca. 0.25 to the strongest reflections. Nine cycles of refinement gave an R factor of 0.047, and the standard deviations were some 20% lower than with unit weights.

Two strong reflections were omitted for suspected

extinction, and more refinement gave $R = 0.041$. The methyl hydrogens of the NMe_4 ions were not visible on a difference Fourier, and so they were included as a fixed contribution as a hexagon of "half-hydrogens". Nine cycles of ORFLS then gave $R = 0.040$. A further 3 strong reflections were removed for suspected extinction, and after nine more cycles of ORFLS, refinement converged at a final R factor of 0.037 on 380 reflections.

The final difference Fourier was very flat, having a background level of $\pm 0.2 \text{ eA}^{-3}$. The final positional and thermal parameters in Tables 4 and 5 were used to calculate the final structure factors listed in Table 6.

Discussion of the Structures

The main distances and angles in the dimeric anions are shown in Figure 1 (in each case two of the bridging groups have been omitted for clarity). Figures 2 and 3 are stereoscopic illustrations of the anions with thermal ellipsoids scaled to enclose 50% probability. These were produced with the program ORTEP, described by C.K. Johnson in the Oak Ridge Technical Report ORNL-3794 (1965).

In both structures the copper atoms and thiocyanate groups lie on crystallographic fourfold axes. In the formate the dimeric ion has strict $4/mmm$ (D_{4h}) symmetry. In the acetate, slight departures from D_{4h} symmetry occur, since the bridging groups do not lie on crystallographic mirror planes, and show small departures from planarity (Table 8). While high crystallographic symmetry has not been observed in other studies of copper acetate dimers^{3,13,14} the symmetry of the $-\text{Cu}(\text{CH}_3\text{CO}_2)_4\text{Cu}-$ unit has always been found to conform closely to D_{4h} .

The coordinating oxygens and nitrogen atom of the

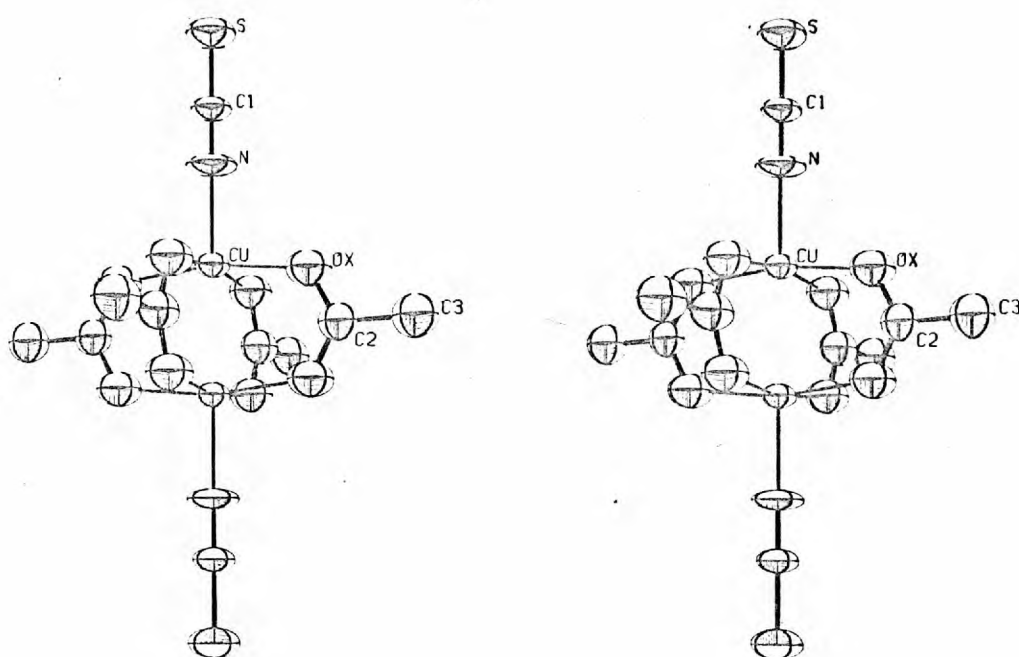


Figure 2 the $[\text{Cu}(\text{CH}_3\text{CO}_2)_2(\text{NCS})]^{2-}$ ion.

A stereoscopic drawing with thermal ellipsoids scaled to enclose 50% probability.

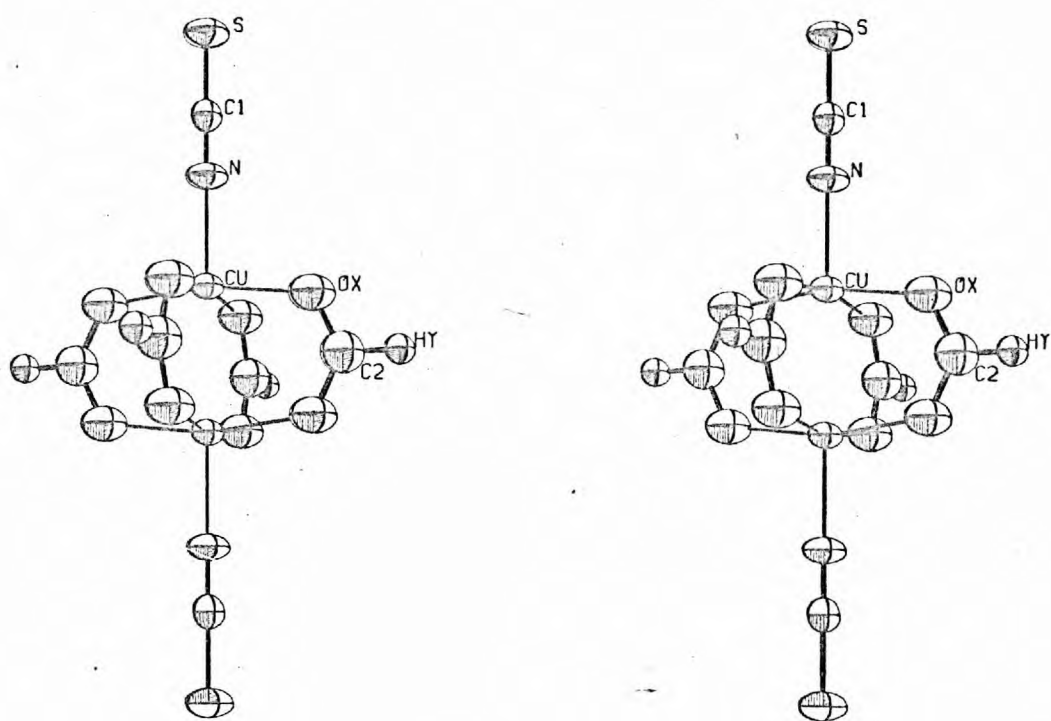


Figure 2 the $[\text{Cu}(\text{HCO}_2)_2(\text{NCS})_2]^{2-}$ ion.

A stereoscopic drawing with thermal ellipsoids scaled to enclose 50% probability.

thiocyanate group form a square-pyramidal arrangement about the metal atoms. The Cu-O distance of 1.984 ($\sigma = 0.002$) in the formate is normal, but the corresponding distance in the acetate, 2.030 ($\sigma = 0.012$) is rather longer than that found in comparable copper acetate dimers^{3,13,14}. The four coordinating oxygens are strictly planar in both structures, and in each case the copper atom is displaced above this plane, towards the nitrogen atom of the thiocyanate group. These displacements are: 0.26 (formate complex) and 0.20 Å (acetate complex). This is quite typical of square-pyramidally coordinated copper(II), both in binuclear and monomeric complexes: out-of-plane displacements of 0.27 Å have been reported in bis(6-amino-purine)copper(II),²⁴ where the adenine molecules bridge between copper atoms, and 0.21 Å in the pyridine adduct of bis(N-phenylsalicylaldiminato) copper(II)⁵².

In cases of square-pyramidal coordination of Cu(II), a lengthening of the fifth (axial) bond of the pyramid is generally observed.^{13,14,15,52} This is also the case in the present study, since the Cu-N distances of 2.080 ($\sigma = 0.015$), 2.104 ($\sigma = 0.007$) are significantly longer than normal (1.95-2.04 Å¹³). This effect is explicable qualitatively in terms of a Jahn-Teller effect if the unpaired electron in the $3d^9$ configuration of each copper atom resides in the $3d_{x^2-y^2}$ orbital for this type of coordination.

The NCS ion is in the isothiocyanic form (bonded through nitrogen), in accord with the general rule^{16,17} that elements in the first long period form isothiocyanate compounds while those of the second and third long periods form thiocyanate, M-SCN, or bridged, M-SCN-M compounds. The infrared spectrum of the acetate complex¹ has $\nu(C-S) = 784 \text{ cm}^{-1}$ cf. expected values of 690-720 cm^{-1} for thiocyanates and 780-860 cm^{-1} for isothiocyanates.^{16,18} The NCS ion and the Cu-N-C linkage are

strictly linear. The N-C and C-S distances in the formato complex, 1.143($\sigma = 0.011$), 1.634($\sigma = 0.008$), and in the acetato complex, 1.192($\sigma = 0.022$), 1.626($\sigma = 0.017$) are in good agreement with literature values.^{19,20} The C-N distances indicate predominant triple-bond character when compared with a C $\equiv$ N literature value of 1.15 Å.²² This would be expected from the observed linearity of the Cu-N-C linkage. Both linear and substantially "bent" isothiocyanate groups²¹ and M-N-C linkages¹⁹ have been reported. Hazell¹⁹ has shown that a good correlation exists between the C..N distance and the M-N-C angle: by plotting the data for a number of isothiocyanates and bridged structures, it was apparent that as the M-N-C angle approached 120° the C-N distance increased to that typical of a C=N interaction, 1.26 Å.²³ A similar correlation for the C-S distance was not so well-defined, however, this distance generally being shorter than that expected for a single bond as the M-N-C angle approached 180°. This is certainly the case in the present study, since the C-S distances are closer to that of a C=S interaction (1.56²²) rather than C-S⁻ (1.86²³). However this apparent anomaly might arise from an inappropriate choice for the C-S⁻ literature value: a rather shorter distance would be expected for a C-S⁻ bond adjacent to a triple bond. Data on the parent compound, thiocyanogen, should prove interesting in this respect, but is not available.

The copper-copper distance in the acetato complex is 2.647($\sigma = 0.003$), and in the formato, 2.710($\sigma = 0.002$). The difference, 0.063(21 σ) is highly significant, and the greater distance observed in the formato complex is surprising in view of the greater spin exchange observed for this compound from susceptibility measurements (Figure 5). This result, and its relevance to current theories of antiferromagnetism in binuclear complexes, is discussed in a following section.

The geometry of the acetate group is in good agreement with that observed in monopyridine copper acetate.^{13,14} The O-C-O angle of 127.6° ($\sigma = 1.9$) is not significantly different from Pauling's predicted value²³ of 125.3° for the RCOO^- ion. The acetate ion is planar, although the trigonal carbon atom is slightly above the plane of the other three (by $0.033 \text{ \AA}$): a similar effect has been observed in trimeric palladium acetate, Chapter 5. The acetate ion is essentially coplanar with the two bridged copper atoms (Table 8): thus in addition to possessing $\bar{4}/m$ crystallographic symmetry, the dimeric ions conform closely to $\bar{4}/mmm$ (D_{4h}).

The O-C-O angle in the formate ion, 126.8° ($\sigma = 0.3$) similarly shows no significant expansion from Pauling's value²³ (125.3°), even though the Cu...Cu separation is larger in this complex. However, rather smaller values have been reported in other formate-bridged structures, e.g. copper(II) formate tetrahydrate²⁶ (122°), anhydrous copper(II) formate¹⁵ (122°) and copper(II) formate dihydrate²⁵ (124°). In these compounds the formate groups bridge between copper atoms in anti-anti, or anti-syn relationships: the syn-syn structure found in the present study is novel for formate-bridged copper complexes.

The tetramethylammonium ions occupy special (fourfold) positions and attain apparent $\bar{4}m2$ (D_{2d}) crystallographic symmetry by statistical disorder: in fact the ions possess strict D_{2d} symmetry (ignoring the hydrogen atoms - which could not be located), but with only the $\bar{4}$ axis coincident with the crystallographic $\bar{4}$ axis. There are thus 1 independent C-N⁺ distance and 2 independent C-N⁺-C angles within the ion. In both structures significant departures from regular tetrahedral geometry are observed. In the acetate the C-N⁺-C angles are 112.9° (degeneracy 4) and 102.8° (degeneracy 2), and in the formate 107.2° (degeneracy 4) and 114.2° (degeneracy 2). However, in both structures the average C-N⁺-C angle is 109.5° , close to the

tetrahedral angle. The C-N⁺ distances are normal.

In the formate the S...S contact distance between adjacent dimeric units along c , $3.33 \overset{O}{\text{\AA}}$, is significantly shorter than twice the Van der Waals radius of sulphur, $3.70 \overset{O}{\text{\AA}}$,²³ and probably indicates a weak interaction between the sulphur atoms. In the acetato complex, because both the acetate groups and NMe₄ ions are disordered, there are two possible sets of contact distances between these groups. In the asymmetric unit given in Table 1, the shortest O(acetate)-C(NMe₄) contact distance is $3.36 \overset{O}{\text{\AA}}$. However, if the NMe₄ ions are reflected in $(\frac{1}{2}, 0, 0)$, according to the disorder, this distance becomes $3.03 \overset{O}{\text{\AA}}$, which is unreasonably short - the sum of Van der Waals radii for -CH₃ and O is $3.20 \overset{O}{\text{\AA}}$.²³ It seems probable, therefore, that the orientation of the NMe₄ ions is determined by that of the acetate groups (as in Figure 4), and there is no "independent" disordering of the NMe₄ ions. Otherwise all non-bonded contacts are normal.

Disorder Effects in (NMe₄)₂-(Cu(CH₃CO₂)₂NCS)₂

The NMe₄ ions in both complexes, and the acetate bridging groups in the acetato complex are subject to structural disorder of a type which appears to be quite common in crystal structure investigations. From a knowledge of the spacegroup and the number of formula weights per cell, it could be inferred that the acetate bridges should be ordered with their atoms on mirror planes of the type $(\underline{x}, 0, \underline{z})$ or $(\underline{x}, \underline{x}, \underline{z})$. Similarly the carbon atoms of the NMe₄ ions should lie on $(\underline{x}, 0, \underline{z})$ and $(\underline{x}, \frac{1}{2}, \underline{z})$ mirror planes. However, from Fourier maps it was apparent that these groups occupied two distinct orientations in the crystal (related as mirror images), and the Fourier simply showed a composite electron density. The orientations were too widely separated to be

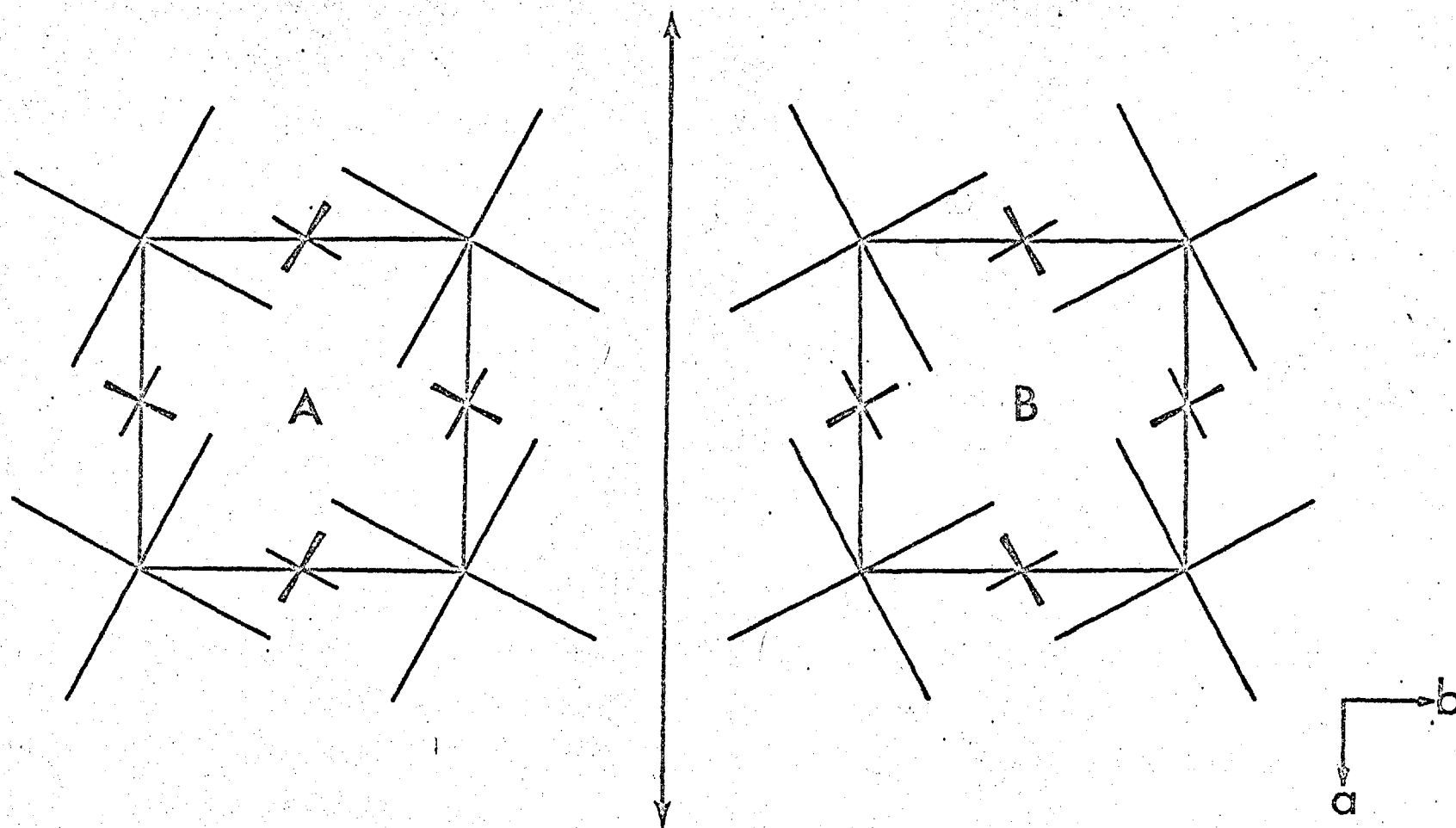


Figure 4 Illustrating the orientations of the acetate bridges and tetramethylammonium groups in $[\text{Me}_4\text{N}]_2 [\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{NCS}]_2$

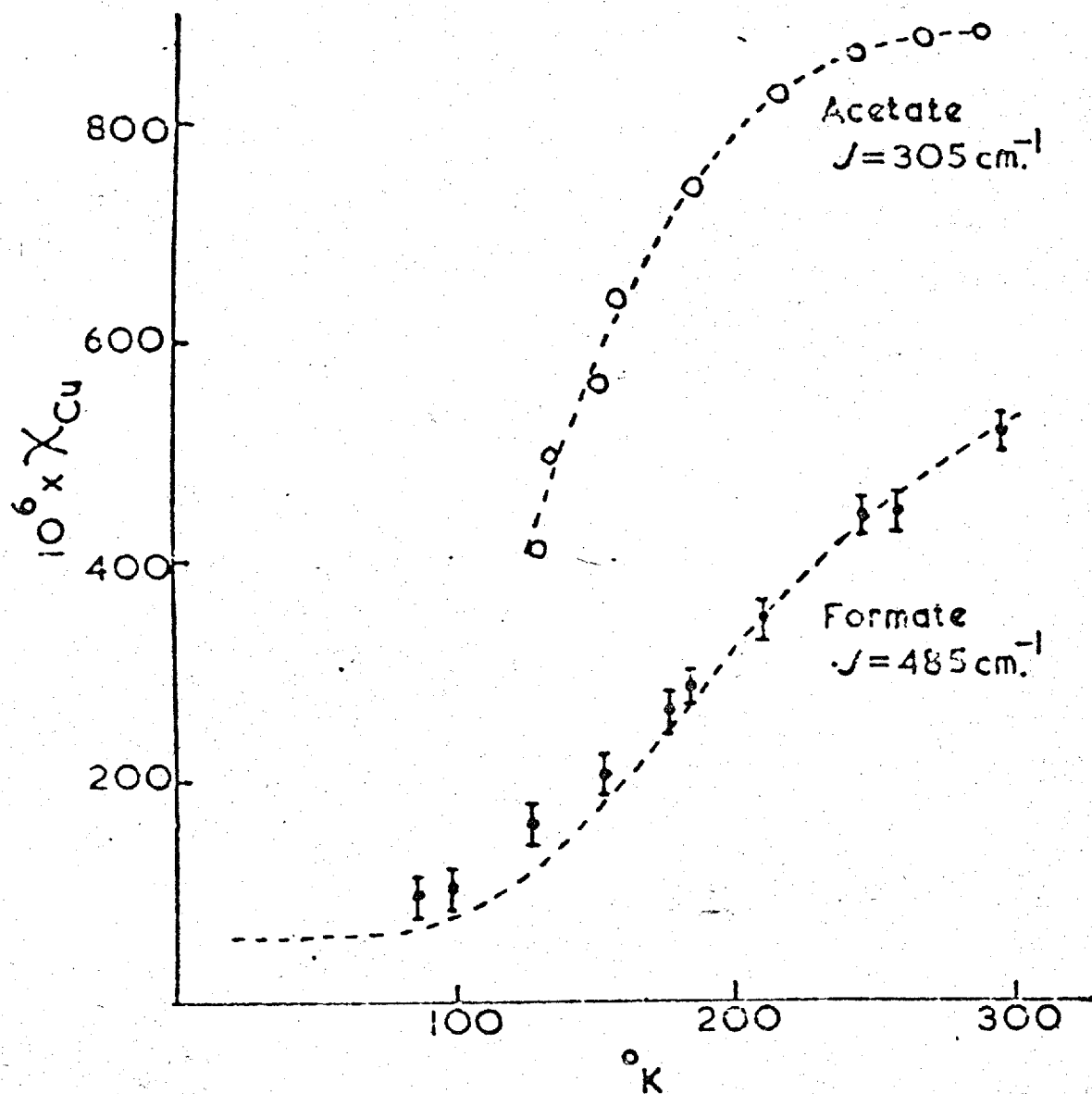


Figure 5 Temperature dependence of the magnetic susceptibilities of $[\text{Me}_4\text{N}]_2 [\text{Cu}(\text{RCO}_2)_2\text{NCS}]_2$ ($\text{R} = \text{H}$ or Me). Dotted lines represent calculated curves (using 4.6).

(Reproduced by permission of D.M.L. Goodgame and D.F. Marsham).

accounted for by thermal motion, and rotational motion was also unlikely as the maxima were quite sharp and well-defined: atoms placed on these sites refined with 'normal' temperature factors. Assuming, therefore a 'statically' disordered model, there were two possibilities to be considered, viz. Twinning and Disorder.

(i) Twinning

The composite electron density would arise if the crystal used for data collection was a twin. Although several crystals of this batch were examined, both under polarised light and X-rays, twinning was not suspected. However, if the reciprocal lattices of the twins coincide exactly, as they would in this case, then twinning would not have been discovered during these preliminary examinations.⁴⁷ $\frac{4}{mmm}$ Laue symmetry could be simulated if twins, of individual Laue symmetry $\frac{4}{m}$, were present in the crystal, related by a diad parallel to either a or b (Figure 4). Since there was no evidence of a doubling of the c translation or disorder streaks in any of the photographs, there was unlikely to be a regular sequence in the stacking of unitcells denoted by A and B, respectively, in the crystal. Thus the crystal should either consist of two discrete twins - in which case it is strange that no 'single' crystals (of Laue symmetry $\frac{4}{m}$) were encountered - or alternatively, contain domains, or mosaic blocks related by the twin operation (Polysynthetic Twinning).

Accordingly, some cycles of refinement were carried out using a 'Powder Least-Squares' program, originally written by Dr H. Villiger.⁴⁸ In this program the crystal was assumed to consist of twins of spacegroup $\frac{I4}{m}$, related by a diad parallel to a. Each independent reflection in $\frac{I4}{mmm}$ ($h, k, l \geq 0$; $k \geq h$) was considered to arise from the incoherent superposition of reflections $hkl, \bar{h}kl$ from either twin

(strictly hkl and $h\bar{k}\bar{l}$ become superimposed, but $|F_{hkl}| = |F_{h\bar{k}\bar{l}}|$ for a centrosymmetric crystal). The function minimised was then

$$\sum w_{hkl} (F_{hkl}^{O_2} - \frac{1}{2} (F_{hkl}^{C_2} + F_{h\bar{k}\bar{l}}^{C_2}))^2 \quad 4.4$$

where the weights, w_{hkl} are given by:²⁸

$$w_{hkl} = \frac{1}{4 F_O^2} \quad 4.5$$

However, this refinement did not produce any improvement: the R factor based on F was increased to 0.122, and the anisotropic temperature factors of the oxygen atom became non-positive definite. Thus the twinned model was thought to be unsatisfactory.

(ii) Disorder

In this case the ordered regions are assumed to be so small that the scattering of the twins is coherent. However, there should be some evidence from the X-ray photographs of a unitcell larger than that observed. Also the model used in the 'conventional' refinement, i.e. using atoms at half-weight, should give quite a good description of the structure, and rather better agreement in F_O and F_C than that observed.

Thus conflicting results make it difficult to reconcile the structure with either of these models. The net result of this effect is to produce bad agreement (generally $|F_O| \gg |F_C|$) for a few reflections to which the disordered atoms make a relatively large contribution. This results in poor accuracy and high standard deviations, particularly for the acetate-group parameters.

Antiferromagnetism in Copper(II) Carboxylate Dimers

The magnetic properties of cupric acetate monohydrate are anomalous, in that its magnetic moment is unusually low at

room temperature, and the susceptibility shows antiferromagnetic temperature dependence, passing through a maximum at ca. 255°K.³² This discovery has prompted a great deal of experimental and theoretical research in recent years, and now a very large number of antiferromagnetic compounds of Cu(II) is known.² These compounds are generally binuclear, containing carboxylate bridges,³ halogen bridges,² pyridine N-oxide bridges,²⁹ or other oxygen-bridged substances, such as acetylacetone.³⁰ Cupric acetate, because of its historical position as the first such compound, has been studied most extensively. However, the mechanism of the antiferromagnetic coupling remains an intriguing and largely unsolved problem. Interaction between copper ions in close proximity has been suggested⁵¹ to account for the E.S.R and absorption spectra of certain enzymes.

The most successful treatment has been that of Bleaney and Bowers²⁷ who concluded from Guha's susceptibility measurements,³¹ and their own paramagnetic resonance experiments that spin exchange occurred between discrete pairs of copper atoms in the crystal. The spins on adjacent copper atoms interacted to give a high energy (triplet) state with the spins parallel, and a lower (singlet) state with the spins paired. They derived the formula for the susceptibility

$$\chi = \frac{2g^2 N \beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3} \exp(J/kT)} + N\alpha \quad 4.6$$

where $N\alpha$ is the temperature-independent paramagnetism of two copper(II) ions, and J is the singlet-triplet energy level splitting: clearly the higher the J value, the lower the susceptibility. The antiferromagnetism then arises from thermal depopulation of the triplet state as the temperature is lowered. In order for 4.6 to fit the susceptibility data

of Guha³¹ it was necessary to use a J value of 315 cm^{-1} , whereas the paramagnetic resonance experiments led to $J = 259 \pm 50 \text{ cm}^{-1}$.

The origin of the spin coupling has been the subject of considerable dispute, and various theoretical treatments have been advanced. In view of the short copper-copper distance in cupric acetate monohydrate³, $2.64 \text{ \AA}$ cf. $2.55 \text{ \AA}$ in Cu metal, Figgis and Martin³² suggested formation of a weak δ bond from lateral overlap of half-filled $3d_{x^2-y^2}$ orbitals on adjacent copper atoms. This view was supported on the basis of the anisotropic g values observed in E.S.R spectra,³³ and by non-empirical Valence Bond³⁴ and Molecular Orbital calculations.³⁵

Hansen and Ballhausen³⁶ showed that the observed g values and main details of the electronic spectrum could be explained by considering the acetate dimer as two weakly linked chromophores, without invoking any direct metal-metal bonding.

In 1969 Jotham and Kettle³⁷ extended Bleaney and Bowers' treatment to include the effects of δ bonding between copper atoms. They derived a formula for the magnetic moment which gave better agreement than that obtained previously,³² and considered this good evidence for the existence of δ bonding. However, this work has been criticised⁴ since its results are insufficiently different from those of Bleaney and Bowers to permit discrimination between the two theories on experimental grounds.

Comparison with the much shorter Mo-Mo distance in $\text{Mo}(\text{OAc})_2$ ³⁸ ($2.11 \text{ \AA}$) has been used³⁹ as a basis for ruling out significant metal-metal bonding in the copper analogue, and recently the idea that spin exchange proceeds by a superexchange mechanism, involving carboxylate bridges, has

become increasingly favoured.⁴⁰

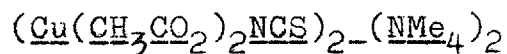
Relatively little work has been done on the effect of the copper-copper separation on the magnetic properties of these binuclear complexes. In the structure of Cu(II) succinate dihydrate,⁴¹ a copper-copper distance of 2.61 Å was reported. This is significantly shorter than that of cupric acetate,³ and also the magnetic moment is lower at room temperature.² This is in qualitative agreement with a direct exchange mechanism, since the $3d_{\sigma}$ overlap should increase with decreasing metal-metal separation. However, in the antiferromagnetic complexes, $(\text{Cu}(\text{ad})_2\text{H}_2\text{O})_2$,^{42,45} $(\text{Cu}(\text{adH})_2\text{Cl})_2^{2+}$ (⁴³) (adH = adenine), the copper-copper distances, 2.947, 3.066 Å respectively, are too large to permit significant direct exchange. It seems likely in these cases, therefore, that the spin exchange occurs via a superexchange mechanism, involving the bridging adenine molecules.

In view of this sparse and conflicting data, the structural studies of this chapter were undertaken to examine the correlation between copper-copper separation and spin exchange in a pair of strictly analogous dimers. The results are summarised below:



$$J = 485 \text{ cm}^{-1}$$

$$\text{Cu} \dots \text{Cu} = 2.710(2)$$



$$J = 305 \text{ cm}^{-1}$$

$$\text{Cu} \dots \text{Cu} = 2.647(3)$$

The J values were calculated by Goodgame et al.⁴ from the temperature dependences of the magnetic susceptibilities and experimental g values, using 4.6. The greater spin exchange observed for the formate corresponds well with the results for other dimeric Cu(II) formate complexes,⁴⁴ and the Cu...Cu separation of 2.647 Å is typical of dimeric Cu(II) acetate

complexes.^{3,13,14} Thus the formate-bridged complex has the higher J value (more spin exchange) and yet the Cu...Cu separation is significantly greater (by 0.063 Å, ca. 21σ). This suggests that the spin exchange arises primarily through the bridging ligands, and not as a result of metal-metal bonding in these complexes, since the 3d_g overlap of adjacent copper atoms is expected to decrease rapidly with increasing Cu...Cu separation.³²

Martin and Waterman⁴⁴ considered the higher J values observed for formate dimers as possibly arising from a contraction of the Cu...Cu distance, or alternatively, preserving a similar separation of ca. 2.64 Å, from the modification of the ligand field: in particular, the presence of the dative bonding ligands in the terminal positions (necessary to stabilise the formate-bridged structure⁴⁴) could enhance the 3d_g overlap by effectively "reducing" the positive charge on the copper atoms. Consideration of the present results shows that both these arguments are erroneous. Since the terminal NCS ligand is present in both complexes, no relative orbital expansion (leading to enhanced overlap) can be invoked in the formate. The formate ligands are unlikely to produce any such expansion effects, since the non-existence of a cupric formate monohydrate isostructural with cupric acetate monohydrate, has been attributed⁴⁴ to the low basicity of the formate ions resulting in a build up of localised positive charge on the copper atoms.

Thus the greater spin exchange in the formate complex cannot be accounted for in terms of direct overlap, and it seems likely, therefore, that metal-metal bonding plays only an insignificant role in determining the magnetic properties of these and related dimeric copper(II) carboxylates.

In the light of this result it is worthwhile

re-examining some of the arguments upon which the existence of metal-metal bonding in cupric acetate monohydrate was first advanced. Metal-metal bonding was first invoked since the Cu...Cu separation in cupric acetate monohydrate ($2.64 \text{ \AA}$ ³) was only slightly larger than that observed in copper metal ($2.55 \text{ \AA}$ ⁰). However, the value of this comparison is doubtful: since the metal structure is based on an array of positive ions with a delocalised "electron gas," a close approach of metal atoms is very unfavourable energetically. A more realistic distance is the Cu-Cu single-bond length, estimated from the hydride, 2.33 ,²³ or from the Cu_2 molecule, $2.22 \text{ \AA}$ ⁴⁶; when compared with these values, the distance of 2.64 in the dimeric acetate evidently rules out significant metal-metal bonding. Bleaney and Bowers²⁷ estimated that the Cu...Cu separation would have to be ca. $2.0 \text{ \AA}$ ⁰ in order to produce a J value as great as 300 cm^{-1} . Another key point in the argument was the diamagnetism of the isostructural chromous acetate.⁵⁴ The complete pairing of four d electrons from each metal atom suggested the formation of strong metal-metal bonds, yet the Cr-Cr distance was believed to be $2.64 \text{ \AA}$ ⁰,³² i.e. essentially the same as in copper acetate. However, the value assumed for the Cr-Cr distance was in considerable error, owing to the propagation of an error in the literature: the correct distance is now known to be $2.362 \text{ \AA}$ ⁰,⁴⁹ and this is not consistent with the idea of significant metal-metal bonding in the copper analogue.

It remains difficult to predict the relative importance of contributions to the spin exchange arising from the Coupled Chromophore model,³⁶ or from the Superexchange process.⁴⁰ However, it is clear from these experimental results that the spin exchange observed in copper(II) carboxylate dimers does not arise predominantly from metal-metal bonding, as has

hitherto been assumed.

Acknowledgement

I wish to thank Drs. D.M.L. Goodgame, D.F. Marsham and N.J. Hill for performing the magnetic and E.S.R. measurements, and for helpful discussions, and Dr. F.G.H. Troughton for help in collecting the diffractometer data.

Table 1Atomic Positions for $(\text{NMe}_4)_2 (\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{NCS})_2$

Atom	<u>x</u>	<u>y</u>	<u>z</u>
Cu	0	0	0.07317(12)
S	0	0	0.34402(30)
N1	0	0	0.1882(8)
Cl	0	0	0.2541(9)
C2	0.2546(24)	0.1383(23)	0
C3	0.4047(28)	0.2125(27)	0
O	0.2021(13)	0.1047(13)	0.0621(5)
N2	$\frac{1}{2}$	0	$\frac{1}{4}$
C4	0.4380(32)	0.1093(30)	0.2993(15)
H31	0.417	0.193	0.067
H32	0.410	0.290	-0.008
H33	0.500	0.157	-0.025

Numbers in parentheses here and in subsequent Tables are estimated standard deviations.

Table 2

Thermal parameters for non-hydrogen atoms of $(\text{NMe}_4)_2(\text{Cu}(\text{OAc})_2\text{NCS})_2$

The anisotropic temperature factor is given by:

$$\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0132(3)	0.0132	0.00157(8)	0	0	0
S	0.0263(8)	0.0263	0.00217(15)	0	0	0
N	0.0263(25)	0.0263	0.0009(4)	0	0	0
Cl	0.0163(18)	0.0163	0.0012(4)	0	0	0
C2	0.015(3)	0.0131(29)	0.0046(8)	0.0000(24)	0	0
C3	0.021(4)	0.014(3)	0.0056(10)	-0.002(3)	0	0
O	0.0198(18)	0.0210(18)	0.0031(3)	-0.0043(15)	0.0003(6)	0.0004(6)
N2	0.0145(16)	0.0145	0.0041(6)	0	0	0
C4	0.043(9)	0.028(4)	0.0102(14)	0.000(4)	0.001(2)	-0.009(2)

Table 3

Observed and Calculated Structure Factors (in electrons x 10)

for $(\text{NMe}_4)_2 (\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{NCS})_2$

* indicates unobserved reflection

Tabulated as:

1, $\overline{F}_O$, $\overline{F}_C$ for each group with constant h, k

0.0.1	7	156	-122	1.10.L	18	57	-70	15	140	140
2	563	773		1	99	95				
4	931	1.65		3	30	21				
6	403	-427		5	74	-52				
8	1071	-1702		7	132	-141				
10	417	-784								
12	722	721								
14	722	704								
16	438	428								
18	438	-24								
20	70	-40								
22	260	-259								
0.1.1	0	1124	1080	1.1.L	6	422	-388			
1	1136	1178		2	368	-400				
3	658	592		4	295	-286				
5	675	-681		6	422	-388				
7	1500	-1601		8	365	-403				
9	358	-451		10	277	-299				
11	237	722		12	581	574				
13	184	176		14	273	264				
15	627	590		16	64	92				
17	163	185		18	168	-172				
19	313	-215		20	96	-79				
21	141	-162								
0.2.1	0	1550	1873	1.2.L	11	274	283			
2	865	-649		13	142	145				
4	432	-403		15	429	387				
6	458	-464		17	100	81				
8	562	-598		19	252	-252				
10	344	-761		21	107	-126				
12	534	540								
14	275	532								
16	91	53								
18	210	-712								
20	105	-92								
0.3.1	0	1167	1144	1.3.L	6	440	-420			
1	93	-74		8	385	-364				
3	153	-139		10	306	-303				
5	272	-267		12	518	497				
7	744	-723		14	347	316				
9	176	70		16	207	176				
11	316	720		18	78	-74				
13	266	32		20	41*	-59				
15	274	288								
17	78	-12								
19	332	-713								
21	174	-27								
0.4.1	0	829	985	1.4.L	11	274	283			
2	57	23		13	142	145				
4	238	-727		15	429	387				
6	352	-737		17	100	81				
8	221	-741		19	252	-252				
10	256	-781		21	107	-126				
12	478	602								
14	154	220								
16	31*	79								
18	131	-141								
20	44*	-75								
0.5.1	0	927	924	1.5.L	6	440	-420			
1	512	530		8	385	-364				

Table 4Atomic Positions for $(\text{NMe}_4)_2 (\text{Cu}(\text{HCO}_2)_2 \text{NCS})_2$

Atom	<u>x</u>	<u>y</u>	<u>z</u>
Cu	0	0	0.08575(7)
S	0	0	0.39468(13)
N1	0	0	0.2189(4)
C1	0	0	0.2913(5)
C2	0.1996(6)	0.1996	0
H	0.287(7)	0.287	0
O	0.15603(27)	0.15603	0.06938(18)
N2	$\frac{1}{2}$	0	$\frac{1}{4}$
C4	0.6141(18)	0.0734(26)	0.2995(9)

Table 5

Thermal parameters for non-hydrogen atoms of $(\text{NMe}_4)_2(\text{Cu}(\text{HCO}_2)_2\text{NCS})_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.01068(13)	0.1068	0.00206(5)	0	0	0
S	0.0199(3)	0.0199	0.00217(8)	0	0	0
N1	0.0162(8)	0.0162	0.0019(3)	0	0	0
C1	0.0097(7)	0.0097	0.0032(4)	0	0	0
C2	0.0169(7)	0.0169	0.0042(3)	-0.0068(10)	0	0
O	0.0191(4)	0.0191	0.0035(1)	-0.0085(5)	-0.0005(1)	-0.0005
N2	0.0098(6)	0.0098	0.0043(3)	0	0	0
C4	0.039(3)	0.088(11)	0.0232(16)	-0.011(4)	-0.018(2)	-0.020(3)

Table 6

Observed and Calculated Structure Factors (in electrons x 10)
for $(\text{NMe}_4)_2 (\text{Cu}(\text{HCO}_2)_2 \text{NCS})_2$

* indicates unobserved reflection

E indicates reflection omitted for suspected extinction

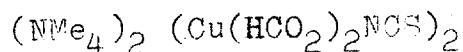
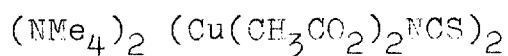
Tabulated as:

1, $\underline{F}_0$, $\underline{F}_c$ for each group with constant h, k

2	283	164	0.0.L	5	73	-72	8	30	-27	6	428	-431	1	170	164
4	164	78		7	60	-78	10	168	171	10	535	536	3	270	16
6	1532E	-1742		9	180	14				12	328	310	5	170	-100
8	482	-437						1.10.L		14	181	191	7	121	-110
10	715	616		0	242	227	1	77	74	16	168	-156	9	180	-17
12	646	651		2	170	11	3	170	21				11	170	16
14	220	241		4	48	-32	5	68	-76						
16	141	-131		6	111	-116	7	67	-62						
18	55	-41													
			0.1.L												
1	1068	1103		0	1319E	1505	0	1562E	2089	1	571	550			
3	477	474		2	1077	1153	2	330	329	3	94	90			
5	545	-531		4	914	-1025	4	358	-331	5	431	-422			
7	913	-909		6	1202	-1199	6	901	-939	7	506	-538			
9	323	-324		8	286	-308	8	52	38	9	221	-233			
11	344	313		10	731	729	10	590	594	11	107	103			
13	647	614		12	300	315	12	386	394	13	374	372			
15	155	163		14	101	100	14	47	19	15	67	70			
17	231	-211		16	309	-300	16	227	-217	17	154	-152			
19	270	-257		18	35	-40	18	55	-52						
			1.1.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.2.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.3.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.4.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.5.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.6.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.7.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.8.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			1.9.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						
10	516	512		11	235	230	11	280	278						
12	230	231		13	404	397	13	465	476						
14	179	-161		15	190	0	15	99	108						
16	345	-353		17	258	-254	17	175	-165						
18	105	-105													
			2.0.L												
0	1488E	1641		1	120	128	1	705	702						
2	766	-742		3	42	-49	3	332	337						
4	730	-707		5	189	-200	5	321	-318						
6	1066	-1102		7	478	-482	7	500	-507						
8	26	-17		9	104	-100	9	137	-145						

Table 7

Selected bond lengths



Atoms	dist	Atoms	dist
Cu...Cu _I	2.647(3)	Cu...Cu _I	2.710(2)
Cu-N1	2.080(15)	Cu-N1	2.104(7)
Cu-O	2.030(12)	Cu-O	1.984(2)
N1-C1	1.192(22)	N1-C1	1.143(11)
C1-S	1.626(17)	C1-S	1.634(9)
C2-O	1.252(13)	C2-O	1.226(3)
C2-C3	1.49(3)	C2-H	1.10(4)
N2-C4	1.43(3)	N2-C4	1.441(17)

Selected bond angles

Atoms	angle	Atoms	angle
Cu - O - C2	121.8(1.1)	Cu - O - C2	124.1(0.2)
Cu _I - Cu- O	84.3(0.3)	Cu _I - Cu- O	82.5(0.1)
O - C2- O _I	127.6(1.9)	O - C2- O _I	126.8(0.3)
O - C2- C3	116.1(1.0)	O - C2- H	116.6(0.2)
C4 - N2- C4 _{II}	112.9(1.5)	C4 - N2 - C4 _{III}	114.2(0.9)
C4 - N2- C4 _{III}	102.8(1.5)	C4 - N2 - C4 _{II}	107.2(1.0)

Subscripted atoms are related to those of the asymmetric unit by the operations:

$$\begin{array}{lll}
 \text{I} & \underline{x}, & \underline{y}, \quad -\underline{z} \\
 \text{II} & \frac{1}{2} + \underline{y}, & \frac{1}{2} - \underline{x}, \quad \frac{1}{2} - \underline{z} \\
 \text{III} & 1 - \underline{x}, & -\underline{y}, \quad \underline{z}
 \end{array}$$

Table 8Least-squares planes for $(\text{NMe}_4)_2 (\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{NCS})_2$ Distances of atoms from the least-squares plane, in $\overset{\circ}{\text{A}}$

Atom	dist
O	0.012
O _I	-0.012
C2	-0.033
C3	0.009

The equation of the plane in Direct Space is:

$$-4.157\underline{x} + 7.839\underline{y} + 0.00708 = 0$$

Cu	-0.001
O	0.013
C2	-0.033
C3	0.006
O _I	0.013
Cu _I	-0.001

The equation of the plane in Direct Space is:

$$-4.141\underline{x} + 7.848\underline{y} + 0.001068 = 0$$

Subscripted atoms are related to those of the asymmetric unit by:

$$\text{I} \quad \underline{x}, \quad \underline{y}, \quad -\underline{z}$$

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" 'Contrariwise,' continued Tweedledee, 'if it was so, it might be; and if it were so, it would be: but as it isn't, it ain't. Thats logic.' "

....Lewis Carroll: Through the Looking Glass.

Chapter 5. The Crystal Structure of
Trimeric diacetatopalladium(II).

Abstract

Diacetatopalladium(II), $(\text{Pd}(\text{CH}_3\text{CO}_2)_2)_3$, is monoclinic, with the unitcell dimensions $a = 15.799$, $b = 29.482$, $c = 8.287$, $\beta = 92^\circ 16'$, space group $\text{I}2_1/\text{n}$, $Z = 8$.

The structure was solved from 3325 independent, diffractometer-measured data, and was refined by block-diagonal least-squares methods to a final R factor of 0.036. The trimeric structure is confirmed; indeed there are two crystallographically independent but very similar trimers in the asymmetric unit. Both have approximate $\bar{6}m2$ symmetry, and have a novel type of structure, with only bridging acetates being used. The palladium atoms form an approximately equilateral triangle of side ca. $3.15\overset{\text{O}}{\text{\AA}}$, and double acetate bridges connect pairs of metal atoms - there being no direct metal-metal bonding. The coordination at the metal atoms is derived from square planar by displacing the metal atom ca. $0.24\overset{\text{O}}{\text{\AA}}$ from the plane of the oxygens towards the centroid of the triangle. This distortion, and the angular strain present in the $\text{Pd} - \text{O} - \text{C}$ linkages is thought to account for the instability of this compound.

Introduction

The title compound was first prepared by Wilkinson et al.¹, who suggested that the molecule was trimeric on the basis of ebullioscopic measurements in benzene at 37°C. Symmetrical, rather than monodentate coordination of the carboxylate groups was inferred from the infrared spectrum by comparison with the work of Nakamoto.¹⁷ In a series of α -amino acid complexes, bonded through one oxygen, the tendency was noted for a systematic lowering of the COO^- symmetric stretching frequency (ω_1), and a raising of the COO^- antisymmetric stretching frequency (ω_2) relative to that of the free ion. This was interpreted as a shift of the spectrum closer to that of the acid as the equivalence of the C - O bonds is destroyed. Thus in the title compound the ($\omega_2 - \omega_1$) separation of 173 cm^{-1} (cf. 164 cm^{-1} in sodium acetate) was regarded as indicative of symmetrical coordination - although no distinction between bridging and chelating groups could be made on this basis.

The full X-ray structural study of this compound was therefore undertaken in order to resolve this problem, and in view of the current interest in palladium compounds as industrial catalysts.^{18,19,20} A preliminary account of this work has been published.²²

Experimental

Diacetatopalladium(II) crystallises from a benzene/glacial acetic acid mixture as reddish-brown plates. Crystals were kindly supplied by Professor G. Wilkinson. Weissenberg and precession photographs exhibited Laue symmetry 2/m. The systematic absences were $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$, which define the spacegroup uniquely as $P2_1/n$. Cell parameters were derived from theta values in the range 40-70°

measured on a Siemen's automatic four circle diffractometer. Differential scans were performed for a total of 20 axial and $h0l$ reflections for a crystal in c axis mounting, and the unitcell parameters were obtained by least-squares refinement.

Intensity data were collected for a crystal of approximate dimensions $0.6 \times 0.3 \times 0.07$ mm³. The θ - 2θ scan technique was employed, using the five-point measurement procedure (cf. Chapter 4). Using nickel-filtered CuK_{α} radiation a total of 3325 independent reflections was measured, of which 97 were judged insignificant, since the net count was less than 2.58 standard deviations, and were assigned counts of 2.58σ . To economise on collecting time, data collection was stopped at $\theta = 45^\circ$; reflections out to 30° were collected with a maximum measuring time of 0.24 sec/step, and between 30° and 45° at 0.6 sec/step. The data were scaled, using the 0, 20, 0 as reference reflection (measured every 20 reflections), and Lorentz and Polarisation corrections were applied.

Crystal Data

$(\text{Pd}(\text{CH}_3\text{CO}_2)_2)_3 \cdot 1/2\text{H}_2\text{O}$, $M = 682.2$, monoclinic, $P2_1/n$, $a = 16.799 \pm 0.002$, $b = 29.482 \pm 0.004$, $c = 8.287 \pm 0.001$ Å, $\beta = 92^\circ 16' \pm 1'$, $V = 4101$ Å³, $D_m = 2.19$ (flotation), $D_c = 2.18$ g cm⁻³, $\mu = 222$ cm⁻¹ for CuK_{α} , $F_{000} = 2632$.

Structure Solution and Refinement

A Delauney² reduction showed the cell to be genuinely monoclinic. Thus there were six palladium atoms in the asymmetric unit, and the three-dimensional Patterson was correspondingly difficult to interpret. There was obvious overlap in the $(\frac{1}{2}, v, \frac{1}{2})$ Harker line, and also it was difficult to correlate this line with the $(u, \frac{1}{2}, w)$ Harker section, since the $(2x, 2v, 2z)$ vectors were swamped by the

large number of intervectors. A cluster of vectors at ca. 3 Å⁰ from the origin was apparent, however, and this was compatible with a trimeric structure in which all the Pd-Pd distances were approximately equal.

Since the crystal was centrosymmetric, and the space group known uniquely, it was decided to use the Symbolic Addition method³ to obtain phases of structure factors directly. The (LP)⁻¹ corrected data were placed on an absolute scale using the Datfix program⁴, and the normalised structure factors,

$$|E_{hkl}|^2 = \frac{|F_{hkl}|^2}{\epsilon \sum_{j=1}^N f_j^2(hkl)} \quad 5.1$$

were calculated. The zone weights⁵, ϵ , were unity except for the h0l and 0k0 zones, where ϵ was equal to 2. The Datfix program gave the following averages

Average values.....	$ E $	$ E ^2$	$ E ^2 - 1 $
	0.788	1.00	0.999
Theoretical	0.798	1.00	0.968
(Centrosymmetric)			

These values were surprisingly good in view of the fact that only ca. 35% of the data within the copper sphere had been collected.

The Symbolic Addition procedure attempts to build up a comprehensive set of signs (or phases in the non-centrosymmetric case) of structure factors, by systematic application of the $\sum_2$ relationship. Thus for a centrosymmetric crystal the sign ($s_{\underline{h}}$) of reflection h is related to the signs of other reflections by⁶

$$\sum_{\underline{k}} s_{\underline{h}} \approx \langle s_{\underline{h}-\underline{k}} \cdot s_{\underline{k}} \rangle_{\underline{k}} \quad 5.2$$

$\sum_{\underline{k}}$ may thus be used to extend the list of known signs from a "starting set" of signs known either numerically or algebraically.

Signs may be specified arbitrarily for some reflections (with certain restrictions) in order to define the origin of the unitcell. For a centrosymmetric crystal, referred to a centre of symmetry as origin, the structure factor expression becomes

$$F_{hkl} = 2 \sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j) \quad 5.3$$

For a primitive, centrosymmetric crystal there are eight independent centres of symmetry, of the type $(\frac{m}{2}, \frac{n}{2}, \frac{p}{2})$, in fractional coordinates, where $m, n, p = 0$ or 1 . For a shift of origin, 5.3 becomes

$$F_{hkl}^{mnp} = (-1)^{mh+nk+pl} F_{hkl} \quad 5.4$$

Therefore transferring the origin from one centre of symmetry to another merely permutes the signs of structure factors, but retains their magnitudes. From 5.4 it is apparent that the sign of a reflection transforms under a shift of origin according to the parity class of its hkl indices. Thus in order to obtain a correct set of signs from 5.2, the set must define a unique origin.

Signs must be allocated, therefore, to three reflections in order to determine the values of m, n and p , and hence define the origin. The first reflection so specified automatically fixes the signs of all reflections belonging to

the same parity class. Obviously a Structure Invariant, i.e. a reflection belonging to the even, even, even (ggg) parity class must not be specified in this way, since 5.4 shows that its sign is fixed invariantly for the eight alternative origins. A second reflection may then be allocated a sign, provided that it does not belong to the same parity class as the first. The third choice is still more restrictive, since it must have a different parity from the other two. Also it cannot have the same parity as the sum of the indices of the first two reflections: signs of structure factors in this parity class are already fixed, since the first two reflections combine, via 5.2 to fix a sign for one (and hence all) members of the class. Three reflections with these properties constitute a Linearly Independent (and hence origin determining) set.

In practice it is important to choose three reflections which enter into many $\sum_2$ relationships of high probability. The probability of correctness of a $\sum_2$ relationship is given approximately by⁷

$$P = \frac{1}{2} + \frac{1}{2} \tanh \frac{\sigma_3}{\sigma_2^{3/2}} (|E_n| \sum_{\underline{k}'} |E_{n-\underline{k}'}| |E_{\underline{k}'}|) \quad 5.5$$

$$\text{where } \sigma_n = \sum_{j=1}^N z_j^n \quad 5.6$$

In the initial stages of the phase determining procedure the summation over $\underline{k}'$ may contain only one term, and in this case it is necessary to accept only the relationships with the highest triple products.

Accordingly a " $\sum_2$ listing" was prepared, using only the 30 strongest reflections ($|E| > 2.80$), plus a few weaker reflections ($|E| > 2.40$) in parity groups which otherwise would not have been represented. Routines were used from Dr Drew's Tangent Refinement Program⁸, suitably modified by

the author. From the input, independent data set ($\pm h, k, l$), the program generated all equivalent reflections within the sphere, as follows

$$E_{h\bar{k}l} = (-1)^{h+k+l} E_{hkl} \quad 5.7$$

$$E_{\bar{h}k\bar{l}} = E_{hkl} \quad 5.8$$

The relationships of highest probability were

$\underline{h}$	$\underline{h-k'}$	$\underline{k'}$	α	Probability
1 8 5	4 25 2	-3 -17 3	39.9	1.000
	1 -12 5	0 20 0	41.2	1.000
	-1 22 3	2 -14 2	37.8	1.000
3 17 3	4 25 2	-1 -8 1	33.8	1.000
-3 17 5	1 -8 5	-4 25 0	32.2	1.000

where α is the triple product.

Thus by taking $s(1 \ 8 \ 5) = +$, $s(-3 \ -17 \ 3) = -$ as two of the origin determining set, this automatically gave one new sign, $s(4 \ 25 \ 2) = -$.

The choice of a third reflection to define the origin was rendered less satisfactory by a very uneven distribution of the stronger reflections among the eight parity groups. Thus in the four permitted parity groups, i.e. (ugg), (egu), (uug) and (guu), very few reflections entered into relationships of high probability. Virtually the only available choice was the $(-1 \ 5 \ 4)$ reflection, which had the following relationships

$\underline{h}$	$\underline{h-k'}$	$\underline{k'}$	α	Probability
-1 5 4	-3 19 2	2 -14 2	24.5	0.999
	1 -8 -1	-2 13 5	23.5	0.998
	-3 -17 5	2 22 -1	22.3	0.998

Thus $s(-1 \ 5 \ 4)$ was fixed as +, although this did not lead to the determination of any further signs. The number of generated signs was rather unsatisfactory at this stage, and so the listing was inspected for possible Σ_1 relationships. For space group $P2_1/n$ these relationships take the form

$$s(E_{2h,0,2l}) \approx s \sum_{k'} (-1)^{h+k'+1} (E_{hk',l}^2 - 1) \quad 5.9$$

and

$$s(E_{0,2k,0}) \approx s \sum_{h'l'} (-1)^{h'+k+1'} (E_{h',kl'}^2 - 1) \quad 5.10$$

From 5.10 it was found that $s(0 \ 20 \ 0) = +$ with a probability, given by?

$$P_{0,2k,0}^+ = \frac{1}{2} + \frac{1}{2} \tanh \frac{\sigma_3}{2\sigma_2} E_{0,2k,0} \sum_{h'l'} (-1)^{h'+k+1'} x(E_{h',kl'}^2 - 1) \quad 5.11$$

of 1.000. This was useful since the $(0 \ 20 \ 0)$ reflection entered into many Σ_2 relationships, and immediately established $s(1 \ -12 \ 5)$ as +.

The generation process stopped there, however, and so the $(-1 \ 8 \ 1)$ reflection was given a symbolic sign, denoted by a, and the sign determination was continued using the program. Using the "starting set" of known signs, the program searches through the Σ_2 list and establishes as many new signs as possible, using 5.2. The new signs are then added to the known set, and the process is repeated for another cycle. Convergence is usually obtained in 6-8 cycles. The program uses an acceptance criterion based on the triple-product sum of the Σ_2 relationships. Throughout this work a new sign was accepted only if the probability given by 5.5 was greater than 0.99.

After 6 cycles 10 signs were generated. The Σ_2 list was then reinspected, and the (0 10 4) reflection was assigned a symbol b: six more cycles gave 24 signs. The (-12 2 2) was then chosen as c, and 6 further cycles yielded 33 out of 37 signs. The starting set was thus

$\underline{h}$	$ \underline{E}_h $	s_h
1 8 5	3.77	+
-3 17 3	3.64	+
-1 5 4	3.00	+
-1 8 1	3.01	a
0 10 4	3.07	b
-12 2 2	3.62	c
0 20 0	3.19	+

At this stage no relationship between the values of a, b, c was apparent. The process was extended by including all the reflections having $|\underline{E}| \geq 2.50$. 6 cycles gave 42 of the possible 53 signs. Inclusion of all reflections with $|\underline{E}| \geq 2.0$ then gave 89 out of a total of 143 signs. In this case, however, the number of determined signs oscillated between 89 and 119 in the final cycles. This indicated that when the additional 30 signs were incorporated into the known set, they gave rise to "inconsistent" sign indications in the following cycle - and so became rejected. These inconsistencies usually suggest particular relationships between the symbols a, b, c.

Analysis of these inconsistencies gave good indications as to the correct values for a, b and c. There were 46 indications of probability > 0.95 , of the type $b = -$, and 11 of the type $a = b$ (including 8 of probability > 0.99). The indications for c were more indirect, of the types:-

c	=	-b	7 indications	F > 0.95
c	=	ab	8 "	F > 0.97
c	=	-a	7 "	F > 0.95

When compared with the direct indications i.e. $b = c = -$, these were all consistent with the result $c = +$.

An E-Map was then calculated, using the MODIFY and FOURR programs,⁴ based on the 89 uniquely determined signs, evaluated in terms of $a = b = -$, $c = +$. This map was almost featureless (the 89 terms constituted ca. 2% of the copper sphere) except for six peaks with heights of 8-13 (arbitrary) units. The background level of the map was ± 2 , and there were 7 spurious peaks of height 6-7 units. The six largest peaks, however, were seen to form two trimeric units - in good agreement with the origin region of the Patterson.

The tentative palladium coordinates were taken as

Pd1	0.200,	0.050,	0.250
Pd2	0.290,	-0.050,	0.233
Pd3	0.246,	0. ,	0.593
Pd4	0.660,	0.250,	0.270
Pd5	0.500,	0.280,	0.230
Pd6	0.540,	0.190,	0.400

Three cycles of ORFELS confirmed these positions, and gave an R value of 0.28. The largest positional parameter shift was ca. $0.2\overset{\circ}{\text{\AA}}$ - for the z coordinate of Pd5. A difference Fourier, rejecting those terms with $|F_c| \leq 0.70 |F_o|$, showed 4 complete acetate groups in bridging positions (the very high rejection ratio was used in case any of the palladium coordinates proved erroneous). Three more cycles of ORFELS on 22 atoms reduced R to 0.26, and a second difference Fourier, with a rejection ratio of 0.40, showed the remaining atoms. Three cycles of BLOKIS gave an R factor of 0.18.

Three further cycles of PICKLS with the palladium atoms anisotropic reduced R to 0.164. A difference Fourier at this stage still showed peaks of up to 6 electron $\overset{\circ}{\text{\AA}}^{-3}$ in the region of the metal atoms. An absorption correction was then

applied using the Numerical Integration technique of Busing and Levv,⁹ with ray-path lengths determined by the method of Coppens et al.¹⁰ A sampling grid of 6 x 12 x 32 was constructed within the crystal, relatively more grid points being allocated along the prominent b and c directions of the plate.

Three more cycles of BLOKLS gave an R value of 0.065, and the resulting difference Fourier showed a peak of approximately 2 eA^{-3} in a potentially hydrogen-bonding position between two trimers. A further 3 cycles of BLOKLS with this peak incorporated as an oxygen atom gave R = 0.062.

Fully anisotropic refinement gave eventually R = 0.046, and a difference Fourier enabled location of all 36 methyl hydrogen atoms. These were included as a fixed contribution - with temperature factors equal to those of the methyl carbons. More refinement gave R = 0.042.

Two of the strongest reflections, having $|F_o|$ considerably less than $|F_c|$, were omitted for suspected extinction. Two more reflections were removed because of errors in the diffractometer output tapes. Refinement was terminated at a final R factor of 0.036 on 3321 reflections, when the maximum parameter shift was 0.08 times the corresponding standard deviation. Unit weights were used throughout. In the final 3 cycles of refinement it was necessary to apply a damping factor of 0.3 to prevent the scale factor from oscillating.

The palladium formfactor used was that of Cromer and Waber.¹¹ Values of the anomalous dispersion corrections for palladium were obtained from International Tables;¹² the dispersion-corrected palladium formfactor was taken as $((f_o + \delta f')^2 + \delta f''^2)^{1/2}$. In the block-diagonal refinement 9 x 9 diagonal blocks were constructed for the anisotropic atoms. The parameter standard deviations were obtained from

the diagonal terms of the inverse 9×9 least-squares matrices, and are thus probably underestimated.

The final difference Fourier showed no spurious features and had a background level of $\pm 0.2 \text{ eA}^{-3}$. The final R factor of 'less thans' was 0.056 on 97 reflections. The final positional and thermal parameters in Tables 1 and 2, and the hydrogen parameters in Table 3 were used to calculate the final structure factors listed in Table 4.

Discussion

The asymmetric unit contains two trimers and a single water molecule. The two trimers are very similar structurally, and no chemically significant differences exist between them. One such trimer is shown in Figure 1 as an ORTEP¹³ stereodiagram. The palladium atoms form an approximately equilateral triangle of side $\approx 3.15 \text{ \AA}$, in which each metal atom is linked to the other two by double acetate bridges. The structure has a general similarity to that of $(\text{Pd}(\text{OAc})_2\text{ONCMe}_2)_3$, details of which appeared in the literature²¹ just prior to publication of our preliminary note. In this case acetoxime, coordinated through oxygen and nitrogen, replaces the second bridging acetate group.

The role of the water molecule is not clear. It has contacts of 3.07, 3.17 and $3.37 \text{ \AA}$ with acetate oxygen atoms, and comparison with twice the Van der Waals radius of oxygen, $2.80 \text{ \AA}$,²⁴ shows that these cannot represent hydrogen-bonded interactions unless the $\text{O} \dots \text{H}-\text{O}$ linkages are approximately linear. Unfortunately it was not possible to locate the hydrogen atoms of the water molecule. However, consideration of Table 8 shows that approximately tetrahedral angles are subtended at the water oxygen atom by O262, O132_I and O222, O132_I. It is possible therefore that the independent trimers

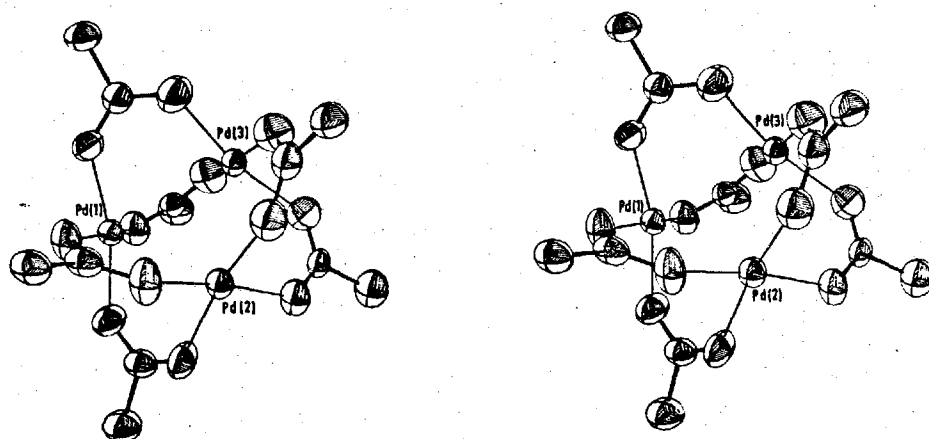


Figure 1. $[\text{Pd}(\text{OAc})_2]_3$

A stereoscopic drawing with thermal ellipsoids scaled to enclose 50% probability.

are linked in pairs by hydrogen bonds (through O132, and either O262 or O222). One of these modes (O132, O262) is illustrated in the packing diagram, Figure 3.

The presence of water was not inferred from analysis or physical measurements. Since the temperature factor of the oxygen atom was anomalously high, $25 \text{ \AA}^2$, it was natural to consider whether a full water molecule was indicated, or whether the temperature factor was compensating for an artificially high occupancy factor. For example, an occupancy of 0.5 would bring the temperature factor more into line with those of the other atoms. Accordingly some cycles of full-matrix refinement were tried, inputting the oxygen with an occupancy (M) of 0.5, and a B factor of $12 \text{ \AA}^2$. Although there was high correlation between B and M , refinement converged with $M = 1.08$, $B = 25.5 \text{ \AA}^2$. As an additional check Hamilton's significance test²⁵ was applied as follows. Once convergence was obtained with M fixed at 1.0, M was reduced to 0.5 and the structure was again refined to convergence - in this case the maximum shift/standard deviation was 0.6 in the final cycle. Taking the refinement with $M = 1$ as "unconstrained" (R_0) Hamilton's R -factor ratio was

$$R = \frac{R_1}{R_0} = 1.005$$

Inspection of Hamilton's tables shows that the one-dimensional hypothesis (with 2825 degrees of freedom) may be rejected decisively at the 0.5% significance level,

$$R_{1,2825,0.005} = 1.001$$

Thus the model with $M = 1$ is a better description of the structure, with a confidence limit of 99.5%. The high B factor of the oxygen atom is therefore genuine, and is probably a consequence of weak bonding of the water molecule. While this latter result is quite emphatic, it should be remembered that

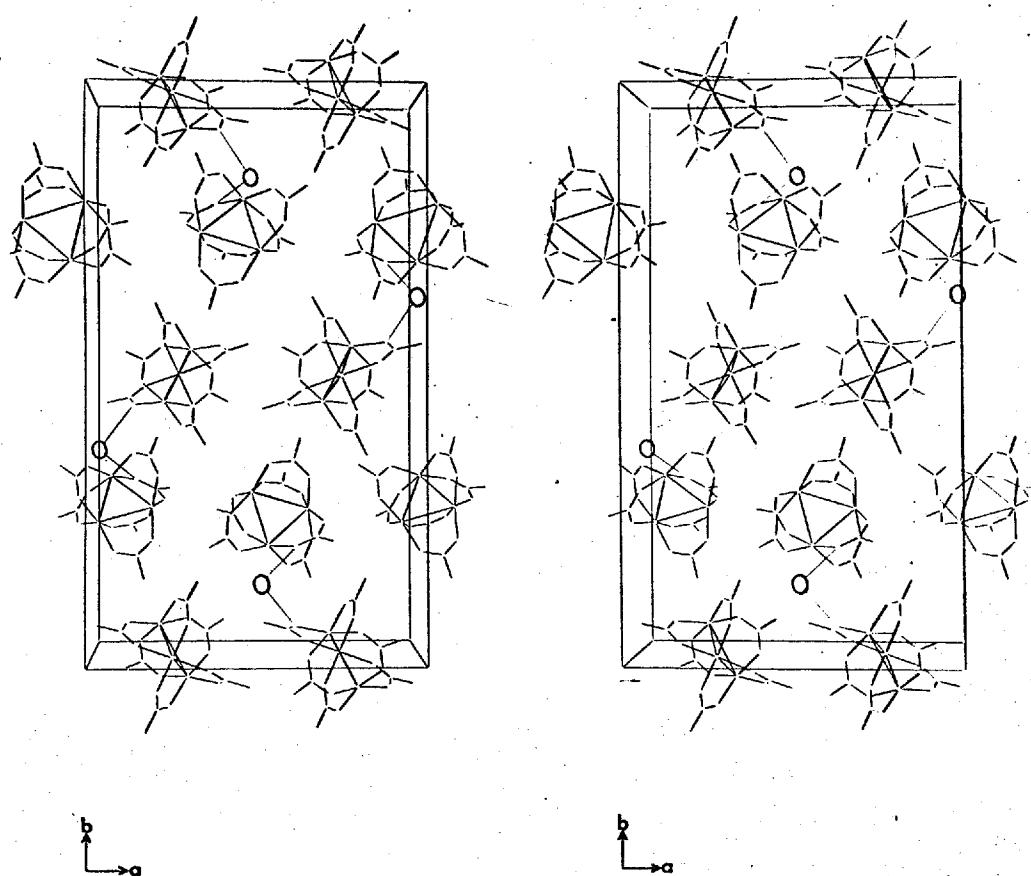


Figure 3 $(\text{Pd}(\text{CH}_3\text{CO}_2)_2)_3 \cdot 0.5\text{H}_2\text{O}$

Stereoscopic c axis projection

Solid lines between Pd atoms do not denote chemical bonds.

Hamilton's statistical treatment is only valid if there are (predominantly) random errors in the data: as has been observed this is unlikely to be true for diffractometer data.²⁶ However, it may be concluded with reasonable certainty that the stoichiometry is $2(\text{Pd}(\text{OAc})_2)_3 \cdot \text{H}_2\text{O}$.

The trimeric units have high potential symmetry - $\bar{3}m2$ (D_{3h}). This symmetry is illustrated in Figure 2, which also serves to label and compare the two trimers. None of this symmetry is required by the spacegroup, and in fact departures from strict D_{3h} symmetry, though small, are significant in terms of experimental error. The departures occur mainly within the triangle of palladium atoms. The Pd...Pd distances range from 3.105 to 3.204 Å (Table 5). Comparison with the estimated standard deviations ($\sigma_{\text{mean}} = 0.001$ Å) shows all six distances to be significantly unequal. There is a good general correlation between the two molecules, however, in that each has one "short", one "medium" and one "long" Pd...Pd distance. Comparison with the Pd-Pd bondlength of 2.58 Å in $(\text{PdAl}_2\text{Cl}_7(\text{C}_6\text{H}_6))_2$ ²³ shows there to be no metal-metal interaction in the trimeric units.

The Pd-O distances range from 1.973 to 2.016 - a scatter of 5σ . A χ^2 analysis¹⁴ of these values indicates that there is only a ca. 10% chance of the 24 independent bondlengths being equal within experimental error. These departures from strict D_{3h} symmetry probably reflect packing requirements, in which the lattice water molecules undoubtedly play some part.

The coordination at the metal atoms is very distorted square planar. The O-Pd-cisO angles range from 84.0 to 94.9° (Table 6). The distribution of these angles seems to be bimodal: acute angles are formed between cis oxygens of acetate groups bridging adjacent sides of the triangle of

metal atoms, while obtuse angles are formed between oxygens of groups bridging a given pair of metal atoms. The four coordinating oxygens define good planes (Table 2) which have an average dihedral angle of 89° with the planes of the metal atoms. In each case the palladium atom is displaced out of the plane of the oxygens, ca. $0.24 \text{ \AA}$ towards the centroid of the molecule. The O-Pd-transO angles range from 163.5 to 169.0° .

The driving force for this distortion is undoubtedly the need to preserve tolerable sp^2 angles at the coordinating oxygens and the trigonal carbon atom of the acetate group - since it is difficult for this group to bridge metal atoms some $3.15 \text{ \AA}$ apart. The Pd-O-C_{sp²} angles range from 127.9 to 133.3° (Table 6), indicating that considerable strain is present. The O-C-O carboxylate angles, in contrast, range from 124.5 to 128.5 , with a mean of 126.3° . This is close to the predicted value for the free acetate ion,²⁴ and to values observed in numerous other dimeric acetates²¹ where the metal-metal distances are typically much shorter (2.11 - $2.64 \text{ \AA}$). Thus it appears that the strain is primarily associated with the distortion of the square-planar coordination about the metal atoms, and the opening out of the Pd-O-C_{sp²} angles from 120° . The observed structure probably represents the best compromise between these conflicting geometric requirements.

This strain is in accord with the instability of the trimeric molecule. Thus at 80°C in benzene ebullioscopic measurements indicate a monomeric structure,¹ and the carboxylate groups may be readily replaced by a variety of mono-, bi- and tetradentate ligands to give monomers,¹ dimers¹ or trimers.²¹ The catalytic properties^{18,19,20} may arise from the ready formation of monomers. Although the palladium atoms are held in "accessible" positions on the extremities of the

molecule, there does not appear to be a preferred site for attack by reagents, and the dissociation is probably controlled by thermodynamic instability rather than kinetic factors.

Comparison with the structure recently determined by Pringle et al.²¹ of $(\text{Pd}(\text{OAc})\text{ONCMe}_2)_3$ provides several interesting features. In the latter molecule the structure is basically similar to that of palladium acetate, with a bridging acetoximate replacing an acetate group. In this case the coordination at the metal atoms is square planar within experimental error, yet the mean $\text{Pd}-\text{O}-\text{C}_{\text{sp}^2}$ (126.5), $\text{Pd}-\text{O}_{\text{sp}^3}-\text{N}$ (112.3) and $\text{Pd}-\text{N}_{\text{sp}^2}-\text{O}$ (116.1) angles are much closer to expected values, indicating that little strain is present. This is rather surprising, since in the acetoximate group the palladium atoms are bridged by two bonded atoms only 1.37 Å apart. This difference in structure arises from the fact that the planes of coordination are inclined at ca. 100° to the plane of the metal atoms. In palladium acetate the corresponding average dihedral angle is much closer to 90° (Table 2).

This tilting effect, which permits the close approach of the bonded N and O atoms of the bridging acetoximate group, might be expected to increase the non-bonded span of the acetate oxygens: Pringle et al.²¹ attributed their observed value of 129.0° for the O-C-O angle to this effect. However, Figure 4 shows that the acetoximate group could be incorporated into the palladium acetate structure, with relatively little change in the acetate oxygen positions: indeed a slight "inwards" displacement of the metal atoms should be possible (in palladium acetate the metal atoms are held apart by the need to minimise the deviations from square-planar geometry). This would then give a smaller Pd...Pd distance, and $\text{Pd}-\text{O}-\text{C}_{\text{sp}^2}$

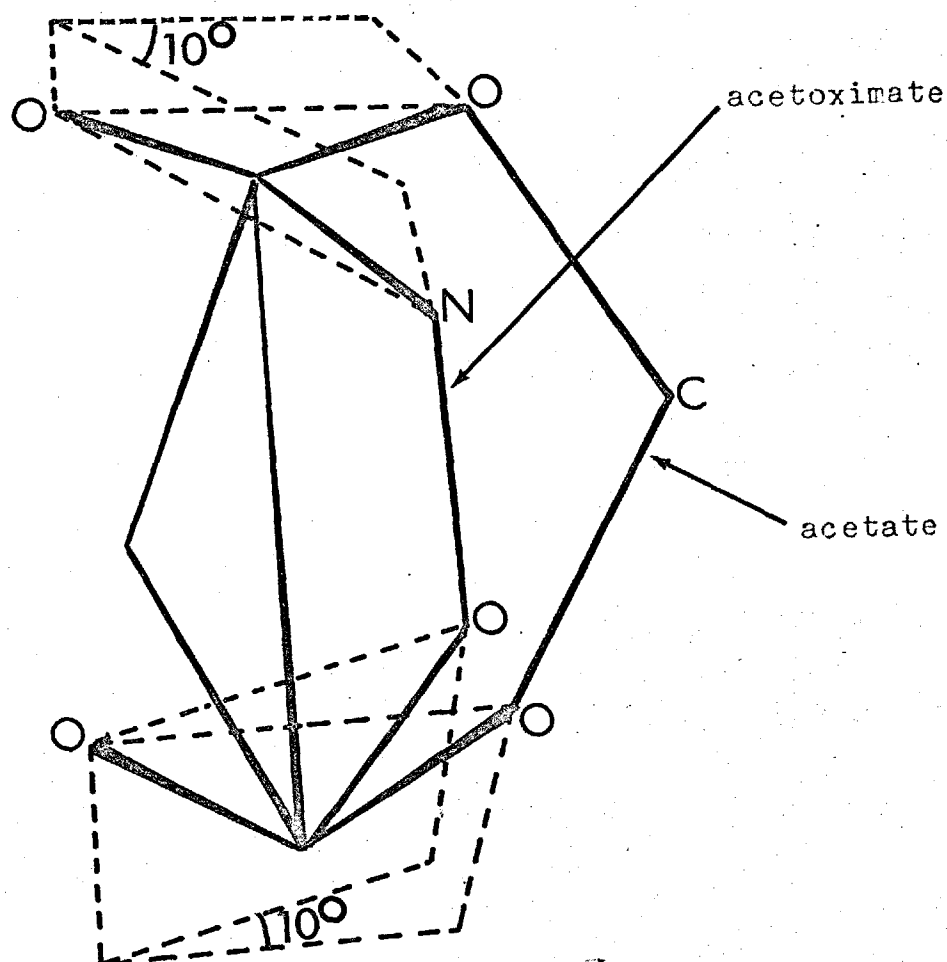


Figure 4 Illustrating the bridging in $[\text{Pd}(\text{OAc})_2]_3$ and $[\text{Pd}(\text{OAc})(\text{ONCMe}_2)]_3$ (schematic).

angles closer to 120° in the acetoximate-bridged structure, as in fact, is observed:-

	Pd...Pd _{mean}	Pd-O-C _{sp²}	O-C-O
(Pd(OAc) ₂) ₃	3.148(1)	130.4(0.8)	126.3(1.2)
(Pd(OAc)(ONCMe ₂)) ₃ ²¹	3.009(3)	126.5(1.0)	129.0(2.2)

Thus it would appear possible to incorporate the acetoximate bridging group without a concomitant "opening out" of the acetate group. Indeed expansion of the O-C-O angle in the acetate group seems unlikely by comparison with palladium acetate, where the strain is primarily associated with expansion of the more "flexible" Pd-O-C angles. In fact the expansion effect noted by Pringle et al.²¹ may not be genuine, since the observed value of 129.0° is within 2 standard deviations of Paulings²⁴ predicted value of 125.3° for the carboxylate-ion O-C-O angle.

The mean Pd-O bondlength of 1.993 is somewhat shorter than the mean Pd-O_{acetate} distance (2.05) found in (Pd(OAc)(ONCMe₂))₃²¹, but compares well with the Pd-O_{acetoxime} distance of 2.00 Å. This is possibly indicative of stronger attachment of the acetate groups in palladium acetate, although the relatively high standard deviations (0.02 Å) in the former study make it difficult to draw valid conclusions. Values of 1.965, 1.976 Å have been observed for palladium benzoyl acetate.¹⁵ A much larger Pd-O distance (2.11 Å) has been reported in bis(acetato) di-π-allyl-dipalladium(II).¹⁶

The acetate groups are closely planar, as expected, although in every case the central sp² carbon atom is above the plane of the other three. However, the magnitude of this departure is quite small, the maximum being that of C231, viz. 0.018 Å. The Pd-O-C-O-Pd linkages show larger deviations

from planarity, probably because of the **departures** from sp^2 hybridisation at the coordinating oxygens. Usually the palladium atoms lie alternately above and below the mean plane. Except for one such group, where Pd6 and O252 are respectively +0.078 and -0.113 Å from the mean plane, the groups are planar within ± 0.06 Å. The angles between the two Pd-O-C-O-Pd mean planes defining double acetate bridges range from 91.9 to 99.6°.

It is interesting to speculate on the structure of the analogous $(Pt(OAc)_2)_3$ compound. Its infrared spectrum¹ is anomalous since it gives an $(\omega_2 - \omega_1)$ separation of 133 cm^{-1} for the acetate group, in marked contrast to the value of 173 cm^{-1} in $(Pd(OAc)_2)_3$, and the free-ion value of 164 cm^{-1} . Thus the mode of coordination of the acetate groups is not clear. Metal-metal bonding has been suggested to account for the greater observed stability of the platinum trimer¹, and this is further suggested by the intense (almost black) colouration of the crystals. Metal-metal bonding could arise if the general $(Pd(OAc)_2)_3$ structure were retained, but with a more pronounced out-of-plane displacement of the metal atoms towards the centroid of the molecule. Trigonal prismatic coordination would then be achieved at the platinum atoms, with the formation of a 3-membered Pt-Pt-Pt ring (figure 5). This type of structure would also permit good sp^2 angles to be preserved within the carboxylate group, and also the Metal-O-C _{sp^2} angles should be much closer to 120° than in the palladium analogue.

An extended square-planar type of structure, similar to that originally assumed for $(Pd(OAc)_2)_3$ (Figure 6), must be considered extremely unlikely. In order to preserve square-planar coordination at the platinum atoms, the Pt-O-C _{sp^2} angles would have to be much nearer 180 than 120°, and then the metal-metal separation would be at least 3.5 Å. This is not in accord

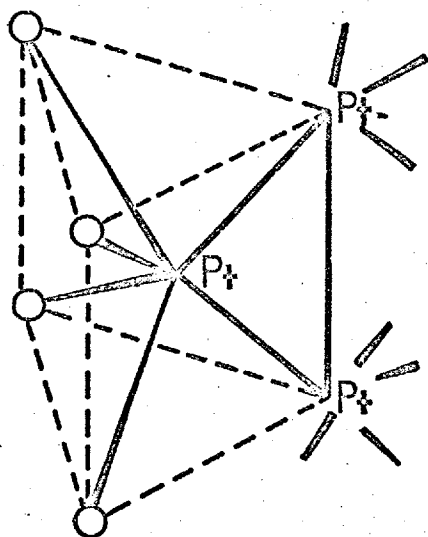


Figure 5

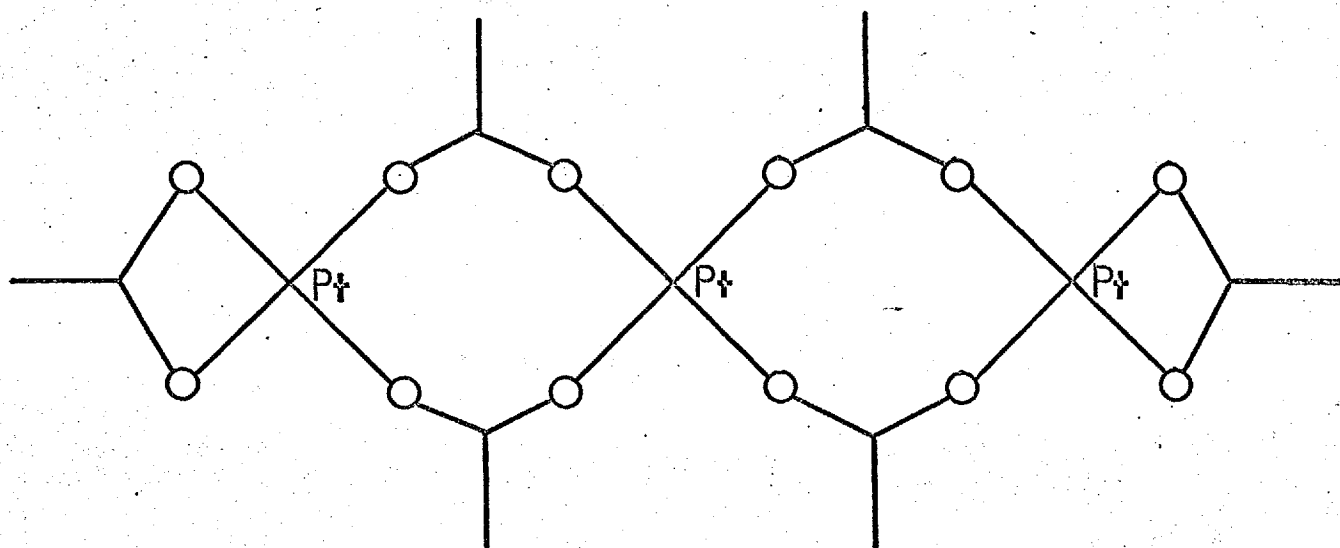


Figure 6

Possible structures for $(\text{Pt}(\text{OAc})_2)_3$

with the observed stability. Evidently the **structure** should be extremely interesting, but unfortunately attempts to prepare suitable single crystals have, as yet, been unsuccessful.

Conclusion

The structure solution provides a good demonstration of the power of the Symbolic Addition method for a centrosymmetric crystal, and its successful application to a multiple-heavy-atom problem. Of the 89 signs determined uniquely from $\sum_1$ and $\sum_2$ relationships, all were shown to be correct on subsequent structure solution.

The precision of the final parameters is good in view of the size of the structure ($F_{000} = 2632$), the artificially truncated data, and the overall preponderance of the palladium scattering power. Particularly surprising was the ready location of all 36 methyl hydrogen atoms, all in eminently sensible positions. This determination yields an accurate value of the Pd-O bondlength, viz. 1.993(9). In retrospect, it is unfortunate that more complete data were not collected, with a harder radiation such as MoK_{α} (so as to minimise residual absorption errors) so that a more detailed statistical comparison of the two independent molecules could have been attempted.

Table 1

Final Atomic Positions as fractions of the unitcell edges.

Standard deviations in parentheses.

Atom	<u>x</u>	<u>y</u>	<u>z</u>
Fd1	0.19949(6)	0.04552(3)	0.25569(11)
Pd2	0.28605(6)	-0.05016(3)	0.26590(11)
Pd3	0.24538(5)	0.00053(3)	0.58703(11)
Pd4	0.66379(5)	0.25379(3)	0.25486(10)
Pd5	0.48688(5)	0.28458(3)	0.23805(11)
Pd6	0.53667(5)	0.19027(3)	0.40540(10)
C111	0.3428(7)	0.0251(4)	0.0677(14)
C112	0.4029(9)	0.0437(4)	-0.0462(17)
O111	0.2870(5)	0.0507(3)	0.1025(11)
O112	0.3530(6)	-0.0143(3)	0.1182(11)
C121	0.1399(8)	-0.0321(5)	0.0595(14)
C122	0.0790(8)	-0.0515(5)	-0.0527(16)
O121	0.1316(5)	0.0074(3)	0.1076(11)
O122	0.1951(6)	-0.0578(3)	0.1049(12)
C131	0.4021(7)	-0.0433(4)	0.5361(16)
C132	0.4843(8)	-0.0540(5)	0.6075(17)
O131	0.3566(5)	-0.0222(3)	0.6276(10)
O132	0.3866(5)	-0.0563(3)	0.3970(11)
C141	0.1983(7)	-0.0943(4)	0.5244(17)
C142	0.1571(9)	-0.1373(5)	0.5763(20)
O141	0.2311(6)	-0.0969(3)	0.3927(13)
O142	0.1974(6)	-0.0606(3)	0.6137(11)
C151	0.0877(7)	0.0448(4)	0.5182(15)
C152	0.0090(8)	0.0585(5)	0.5771(17)
O151	0.1000(6)	0.0542(3)	0.3790(10)
O152	0.1342(5)	0.0246(3)	0.6125(10)
C161	0.2869(7)	0.0952(4)	0.5150(15)

Table 1 (Continued)

Atom	<u>x</u>	<u>y</u>	<u>z</u>
C162	0.3230(9)	0.1389(5)	0.5705(18)
O161	0.2539(6)	0.0953(3)	0.3801(10)
O162	0.2925(6)	0.0624(3)	0.6093(10)
C211	0.4091(7)	0.1972(4)	0.1589(14)
C212	0.3445(9)	0.1735(5)	0.0520(20)
O211	0.4153(5)	0.2393(3)	0.1317(10)
O212	0.4468(5)	0.1743(3)	0.2557(11)
C221	0.4286(7)	0.2535(4)	0.5533(15)
C222	0.3724(8)	0.2643(5)	0.6923(18)
O221	0.4283(5)	0.2821(3)	0.4437(10)
O222	0.4661(6)	0.2180(3)	0.5638(11)
C231	0.5894(8)	0.2955(4)	-0.0397(13)
C232	0.5999(8)	0.3148(5)	-0.2037(16)
O231	0.6485(5)	0.2784(3)	0.03113(9)
O232	0.5226(5)	0.3001(3)	0.0164(10)
C241	0.6167(7)	0.3446(4)	0.3649(14)
C242	0.6416(8)	0.3892(4)	0.4314(17)
O241	0.6680(5)	0.3158(3)	0.3501(11)
O242	0.5427(5)	0.3390(3)	0.3317(12)
C251	0.6516(7)	0.1568(4)	0.1743(15)
C252	0.6788(10)	0.1177(5)	0.0741(19)
O251	0.6805(5)	0.1946(3)	0.1462(10)
O252	0.6013(6)	0.1485(3)	0.2752(12)
C261	0.6854(7)	0.2118(4)	0.5811(14)
C262	0.7388(8)	0.2065(5)	0.7302(15)
O261	0.7113(5)	0.2341(3)	0.4670(9)
O262	0.6196(5)	0.1937(4)	0.5835(11)
O1	0.5135(18)	0.1369(13)	0.7993(36)

The numbering scheme is given in Figure 2

Table 2

Anisotropic Temperature Factors with standard deviations in parentheses. The anisotropic Temperature Factor is given by:-

$$\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd1	.00359(4)	.00070(1)	.0110(2)	.00024(2)	.00064(7)	-.00003(4)
Pd2	.00351(4)	.00072(1)	.0136(2)	.00020(2)	.00118(7)	-.00012(4)
Pd3	.00337(4)	.00067(1)	.0123(2)	-.00002(2)	.00071(7)	.00018(4)
Pd4	.00244(4)	.00067(1)	.0104(2)	.00004(2)	.00136(6)	.00002(3)
Pd5	.00240(4)	.00071(1)	.0130(2)	-.00006(2)	.00082(6)	-.00018(4)
Pd6	.00241(4)	.00074(1)	.0118(2)	-.00002(2)	.00177(6)	-.00026(4)
Cl11	.0035(6)	.0009(2)	.012(2)	-.0005(3)	.0013(9)	.0009(5)
Cl12	.0060(8)	.0009(2)	.022(3)	.0002(3)	.0042(12)	.0009(6)
Ol11	.0056(5)	.0012(1)	.020(2)	.0011(2)	.0056(8)	.0020(4)
Ol12	.0059(5)	.0012(1)	.021(2)	.0005(2)	.0055(8)	.0013(4)
Cl21	.0051(7)	.0011(2)	.011(2)	.0000(3)	.0020(10)	.0005(5)
Cl22	.0040(6)	.0016(2)	.017(3)	-.0003(3)	-.0005(10)	-.0017(6)
Ol21	.0053(5)	.0008(1)	.025(2)	.0001(2)	-.0052(8)	-.0004(4)
Ol22	.0046(5)	.0017(2)	.029(2)	.0009(2)	-.0047(8)	-.0040(5)
Cl31	.0037(6)	.0005(2)	.020(3)	-.0003(2)	-.0003(10)	.0015(5)
Cl32	.0032(6)	.0019(2)	.021(3)	-.0003(3)	-.0007(10)	.0014(7)
Ol31	.0036(4)	.0019(2)	.016(2)	.0010(2)	-.0031(7)	-.0010(4)
Ol32	.0030(4)	.0021(2)	.019(2)	.0012(2)	-.0013(7)	-.0009(4)
Cl41	.0024(5)	.0007(2)	.027(3)	.0001(2)	.0007(10)	.0023(6)
Cl42	.0043(7)	.0015(2)	.031(4)	-.0008(3)	.0026(13)	.0014(8)
Ol41	.0079(6)	.0008(1)	.031(2)	-.0006(2)	.0084(10)	.0002(4)
Ol42	.0078(6)	.0006(1)	.021(2)	-.0008(2)	.0044(8)	.0003(4)
Cl51	.0032(6)	.0007(2)	.017(2)	-.0002(2)	.0020(9)	-.0012(5)
Cl52	.0048(7)	.0011(2)	.022(3)	.0006(3)	.0033(12)	-.0007(6)
Ol51	.0052(5)	.0022(2)	.014(2)	.0017(3)	.0048(7)	.0018(4)
Ol52	.0030(4)	.0017(2)	.018(2)	.0009(2)	.0018(6)	.0005(4)

Table 2 (Continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C161	.0031(5)	.0007(2)	.016(2)	-.0006(2)	.0029(9)	-.0010(5)
C162	.0068(8)	.0011(2)	.022(3)	-.0009(3)	-.0014(13)	-.0002(6)
O161	.0082(6)	.0007(1)	.015(2)	-.0010(2)	-.0037(8)	-.0001(4)
O162	.0074(5)	.0007(1)	.017(2)	-.0011(2)	-.0012(8)	-.0000(4)
C211	.0029(5)	.0014(2)	.012(2)	-.0006(27)	.0003(9)	-.0017(5)
C212	.0046(7)	.0014(2)	.033(4)	-.0008(3)	-.0012(13)	-.0012(8)
O211	.0040(4)	.0008(1)	.020(2)	-.0008(2)	-.0035(7)	-.0003(4)
O212	.0047(4)	.0012(1)	.022(2)	-.0009(2)	-.0067(7)	.0010(4)
C221	.0037(6)	.0013(2)	.014(2)	-.0009(3)	.0028(9)	-.0016(6)
C222	.0042(7)	.0017(2)	.023(3)	.0000(3)	.0054(12)	-.0005(7)
O221	.0038(4)	.0015(1)	.019(2)	.0010(2)	.0058(7)	-.0001(4)
O222	.0062(5)	.0011(1)	.022(2)	.0008(2)	.0080(8)	.0003(4)
C231	.0053(7)	.0008(2)	.008(2)	-.0002(3)	.0017(9)	.0002(5)
C232	.0049(7)	.0017(2)	.014(3)	.0002(3)	.0019(11)	.0013(6)
O231	.0040(4)	.0018(2)	.010(1)	.0009(2)	.0019(6)	.0019(4)
O232	.0035(4)	.0024(2)	.013(2)	.0001(2)	.0012(6)	.0029(4)
C241	.0034(6)	.0008(2)	.012(2)	-.0002(2)	.0003(9)	.0005(5)
C242	.0038(6)	.0008(2)	.026(3)	.0000(3)	-.0021(11)	-.0022(6)
O241	.0030(4)	.0006(1)	.029(2)	-.0002(2)	.0011(7)	-.0019(4)
O242	.0040(4)	.0007(1)	.033(2)	-.0002(2)	-.0020(8)	-.0019(4)
C251	.0033(6)	.0008(2)	.016(2)	.0010(3)	.0009(9)	-.0009(5)
C252	.0085(9)	.0010(2)	.024(3)	.0009(4)	.0057(14)	-.0007(7)
O251	.0044(4)	.0009(1)	.019(2)	-.0001(2)	.0050(7)	-.0017(4)
O252	.0073(6)	.0006(1)	.030(2)	.0004(2)	.0105(9)	-.0007(4)
C261	.0038(6)	.0008(2)	.012(2)	.0005(3)	.0017(9)	-.0009(5)
C262	.0053(7)	.0014(2)	.011(2)	.0005(3)	-.0023(10)	-.0006(6)
O261	.0034(4)	.0018(1)	.012(2)	-.0009(2)	.0001(6)	.0017(4)
O262	.0034(4)	.0026(2)	.018(2)	-.0013(2)	-.0011(7)	.0028(5)
O1	.023(2)	.011(1)	.087(10)	-.0007(14)	.009(4)	.015(3)

Table 3

Hydrogen Parameters

Atom	<u>x</u>	<u>y</u>	<u>z</u>	$B(\overset{0}{\text{\AA}}^2)$
H111	0.420	0.075	-0.016	4.5
H112	0.410	0.020	-0.050	4.5
H113	0.374	0.067	-0.076	4.5
H121	0.022	-0.039	-0.066	5.1
H122	0.120	-0.025	-0.100	5.1
H123	0.084	-0.092	-0.046	5.1
H131	0.496	-0.030	0.680	4.9
H132	0.458	-0.070	0.700	4.9
H133	0.508	-0.062	0.526	4.9
H141	0.174	-0.134	0.646	5.0
H142	0.114	-0.144	0.500	5.0
H143	0.110	-0.128	0.633	5.0
H151	0.008	0.092	0.606	5.1
H152	0.080	0.035	0.683	5.1
H153	0.024	0.072	0.700	5.1
H161	0.304	0.153	0.516	4.4
H162	0.360	0.133	0.650	4.4
H163	0.306	0.135	0.650	4.4
H211	0.338	0.142	0.083	5.5
H212	0.320	0.177	0.100	5.5
H213	0.390	0.175	-0.033	5.5
H221	0.360	0.285	0.630	4.6
H222	0.426	0.285	0.716	4.6
H223	0.376	0.240	0.733	4.6
H231	0.564	0.332	-0.200	4.8
H232	0.580	0.290	-0.266	4.8
H233	0.650	0.315	-0.233	4.8

Table 3 (Continued)

Atom	<u>x</u>	<u>y</u>	<u>z</u>	$B(\overset{O}{\text{Å}}^2)$
H241	0.606	0.404	0.380	4.1
H242	0.700	0.383	0.453	4.1
H243	0.596	0.395	0.466	4.1
H251	0.720	0.118	0.100	5.8
H252	0.670	0.085	0.133	5.8
H253	0.660	0.125	0.	5.8
H261	0.764	0.230	0.750	4.5
H262	0.744	0.177	0.733	4.5
H263	0.704	0.215	0.816	4.5

Hydrogen atoms are labelled Hmnp, where m denotes the trimeric molecule, n is the number of the acetate group (Figure 2), and p is the atom number.

The hydrogen positions have standard deviations of ca. 0.20 Å, estimated from the accuracy with which the coordinates could be determined from a difference Fourier.

Table 4

Observed and Calculated Structure Factors (in electrons $\times 10$)
for $(\text{Fd}(\text{OAc})_2)_3$

* indicates unobserved reflection

E indicates reflection omitted for suspected extinction

Tabulated as:

k , F_o , F_c for each group with constant h , l .

1	764	10	1	1984	1979	17	348	438	6	489	4594	28	1078	-1093	3	645	887	8	789	887
2	36687	7211	1	3329	-379	17	770	89	7	219	313	29	938	485	1	1375	1847	9	849	-1459
3	111	-152	1	3484	-3484	18	1419	1594	8	750	759	30	432	-451	2	173	-137	10	822	812
4	8183	-13530	2	463	-976	19	737	948	9	1691	-1643	31	1084	1994	3	787	-798	11	407	451
5	1354	-1444	3	463	-976	20	778	107	10	177	179	32	1111	-1111	4	1936	-1936	12	874	874
6	761	-8124	4	739	-831	21	179	141	11	179	141	33	1311	-1311	5	437	6	554	-564	
7	1330	-603	5	1629	-1721	22	179	141	12	1188	1143	34	1286	-1286	6	444	-571	13	184	184
8	2151	1272	6	1124	-1272	23	179	141	13	179	141	35	1188	1143	7	444	-571	14	184	184
9	1440	1643	7	1124	-1272	24	179	141	14	179	141	36	1188	1143	8	444	-571	15	184	184
10	4078	8114	8	1124	-1272	25	179	141	15	179	141	37	1188	1143	9	444	-571	16	184	184
11	1665	1886	9	1124	-1272	26	179	141	16	179	141	38	1188	1143	10	444	-571	17	184	184
12	1504	1889	10	1124	-1272	27	179	141	17	179	141	39	1188	1143	11	444	-571	18	184	184
13	217	-374	11	1124	-1272	28	179	141	18	179	141	40	1188	1143	12	444	-571	19	184	184
14	84	-9	12	1124	-1272	29	179	141	19	179	141	41	1188	1143	13	444	-571	20	184	184
15	472	372	13	1124	-1272	30	179	141	20	179	141	42	1188	1143	14	444	-571	21	184	184
16	769	849	14	1124	-1272	31	179	141	21	179	141	43	1188	1143	15	444	-571	22	184	184
17	250	-827	15	1124	-1272	32	179	141	22	179	141	44	1188	1143	16	444	-571	23	184	184
18	145	344	16	1124	-1272	33	179	141	23	179	141	45	1188	1143	17	444	-571	24	184	184
19	382	344	17	1124	-1272	34	179	141	24	179	141	46	1188	1143	18	444	-571	25	184	184
20	1472	-1421	18	1124	-1272	35	179	141	25	179	141	47	1188	1143	19	444	-571	26	184	184
21	754	-702	19	1124	-1272	36	179	141	26	179	141	48	1188	1143	20	444	-571	27	184	184
22	2080	2683	20	1124	-1272	37	179	141	27	179	141	49	1188	1143	21	444	-571	28	184	184
23	1205	1214	21	1124	-1272	38	179	141	28	179	141	50	1188	1143	22	444	-571	29	184	184
24	2323	-2263	22	1124	-1272	39	179	141	29	179	141	51	1188	1143	23	444	-571	30	184	184
25	336	-321	23	1124	-1272	40	179	141	30	179	141	52	1188	1143	24	444	-571	31	184	184
26	1781	1615	24	1124	-1272	41	179	141	31	179	141	53	1188	1143	25	444	-571	32	184	184
27	1027	-993	25	1124	-1272	42	179	141	32	179	141	54	1188	1143	26	444	-571	33	184	184
28	844	-849	26	1124	-1272	43	179	141	33	179	141	55	1188	1143	27	444	-571	34	184	184
29	716	757	27	1124	-1272	44	179	141	34	179	141	56	1188	1143	28	444	-571	35	184	184
30	508	-478	28	1124	-1272	45	179	141	35	179	141	57	1188	1143	29	444	-571	36	184	184
31	149	-120	29	1124	-1272	46	179	141	36	179	141	58	1188	1143	30	444	-571	37	184	184
32	1579	1559	30	1124	-1272	47	179	141	37	179	141	59	1188	1143	31	444	-571	38	184	184
33	735	743	31	1124	-1272	48	179	141	38	179	141	60	1188	1143	32	444	-571	39	184	184
34	3395	-1397	32	1124	-1272	49	179	141	39	179	141	61	1188	1143	33	444	-571	40	184	184
35	339	272	33	1124	-1272	50	179	141	40	179	141	62	1188	1143	34	444	-571	41	184	184
36	1207	1194	34	1124	-1272	51	179	141	41	179	141	63	1188	1143	35	444	-571	42	184	184
37	436	-346	35	1124	-1272	52	179	141	42	179	141	64	1188	1143	36	444	-571	43	184	184
38	141	-154	36	1124	-1272	53	179	141	43	179	141	65	1188	1143	37	444	-571	44	184	184
39	378	-359	37	1124	-1272	54	179	141	44	179	141	66	1188	1143	38	444	-571	45	184	184
40	194	-192	38	1124	-1272	55	179	141	45	179	141	67	1188	1143	39	444	-571	46	184	184
41	2776	-2943	39	1124	-1272	56	179	141	46	179	141	68	1188	1143	40	444	-571	47	184	184
42	5457	-6125	40	1124	-1272	57	179	141	47	179	141	69	1188	1143	41	444	-571	48	184	184
43	399	131	41	1124	-1272	58	179	141	48	179	141	70	1188	1143	42	444	-571	49	184	184
44	1923	-1853	42	1124	-1272	59	179	141	49	179	141	71	1188	1143	43	444	-571	50	184	184
45	2626	-2679	43	1124	-1272	60	179	141	50	179	141	72	1188	1143	44	444	-571	51	184	184
46	1181	1189	44	1124	-1272	61	179	141	51	179	141	73	1188	1143	45	444	-571	52	184	184
47	2148	-2077	45	1124	-1272	62	179	141	52	179	141	74	1188	1143	46	444	-571	53	184	184
48	2248	-2194	46	1124	-1272	63	179	141	53	179	141	75	1188	1143	47	444	-571	54	184	184
49	1252	-1200	47	1124	-1272	64	179	141	54	179	141	76	1188	1143	48	444	-571	55	184	184
50	2626	2616	48	1124	-1272	65	179	141	55	179	141	77	1188	1143	49	444	-571	56	184	184
51	144	-724	49	1124	-1272	66	179	141	56	179	141	78	1188	1143	50	444	-571	57	184	184
52	1577	-1502	50	1124	-1272	67	179	141	57	179	141	79	1188	1143	51	444	-571	58	184	184
53	774	-710	51	1124	-1272	68	179	141	58	179	141	80	1188	1143	52	444	-571	59	184	184
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56	1835	-1882	54	1124	-1272	71	179	141	61	179	141	83	1188	1143	55	444	-571	62	184	184
57	570	-593	55	1124	-1272	72	179	141	62	179	141	84	1188	1143	56	444	-571	63	184	184
58	1550	-1526	56	1124	-1272	73	179	141	63	179	141	85	1188	1143	57	444	-571	64	184	184
59	1583	1569	57	1124	-1272	74	179	141	64	179	141	86	1188	1143	58	444	-571	65	184	184
60	207	-2817	58	1124	-1272	75	179	141	65	179	141	87	1188	1143	59	444	-571	66	184	184
61	1123	-1103	59	1124	-1272	76	179	141	66	179	141	88	1188	1143	60	444	-571	67	184	184
62	1031	-1011	60	1124	-1272	77	179	141	67	179	141	89	1188	1143	61	444	-571	68	184	184
63	314	-42	61	1124	-1272	78	179	141	68	179	141	90	1188	1143	62	444	-571	69	184	184
64	1488	-1501	62	1124	-1272	79	179	141	69	179	141	91	1188	1143	63	444	-571	70	184	184
65	502	-491	63	1124	-1272	80	179	141	70	179	141	92	1188	1143	64	444	-571	71	184	184
66	155	-123	64	1124	-1272	81	179	141	71	179	141	93	1188	1143	65	444	-571	72	184	184
67	263	-292	65	1124	-1272	82	179	141	72	179	141	94	1188	1143	66	444	-571	73	184	184
68	523	-484	66	1124	-1272	83	179	141	73	179	141	95	1188	1143	67	444	-571	74	184	184
69	435	-434	67	1124	-1272	84	179	141	74	179	141	96	1188	1143	68	444	-571	75	184	184
70	156	-63	68	1124	-1272	85	179	141	75	179	141	97	1188	1143	69	444	-571	76	184	184
71	709	-724	69	1124	-1272	86	179	141	76	179	141	98	1188	1143	70	444	-571	77	184	184
72	115	-30	70	1124	-1272	87	179	141	77	179	141	99	1188	1143	71	444	-571	78	184	184
73	922	907	71	1124	-1272	88	179	141	78	179	141	100	1188	1143	72					

1	419	430	3	247	232	21	411	411	12	743	-114	7,4,3	8	975	-1381	3	2987	2976	9	150	141
19	871	-156	4	1374	-1193	28	53	53	13	763	314	8	975	-1381	3	2987	2976	9	150	141	
12	1593	1533	6	1374	-1193	28	53	53	13	763	314	8	975	-1381	3	2987	2976	9	150	141	
14	601	609	4	1374	-1193	28	53	53	13	763	314	8	975	-1381	3	2987	2976	9	150	141	
13	1811	900	7	1270	1245	10	40	40	3	849	510	3	849	510	3	849	510	3	849	510	
17	739	-171	5	928	165	8	40	40	3	849	510	3	849	510	3	849	510	3	849	510	
17	2215	2210	8	903	-1484	8	40	40	3	849	510	3	849	510	3	849	510	3	849	510	
10	437	572	10	403	417	9	1368	-1374	1	381	374	8	975	-1381	3	2987	2976	9	150	141	
19	367	397	11	353	1220	1	272	-244	2	46	47	10	571	-691	14	170	-723	13	147	147	
10	486	-177	25	151	1484	6	2	2	4	4	47	10	571	-691	14	170	-723	13	147	147	
21	736	59	13	254	744	3	2924	2735	4	0	-33	13	164	-48	19	1591	-1342	13	1272	-1291	
22	114	-137	14	1259	1277	4	2643	-2413	5	120	-96	12	2328	2322	14	1	1	1	1	1	
23	957	-674	15	757	-771	5	2473	2711	0	259	-216	12	1215	1198	14	1	1	1	1	1	
24	895	-978	13	1218	1325	4	2473	2711	0	259	-216	12	1215	1198	14	1	1	1	1	1	
			17	954	801	7	1623	1354	0	189	373	5	1159	1170	18	1571	-2540	18	1571	-2540	
			10	344	-359	8	2456	-2474	0	217	-141	6	147	-751	21	543	-580	21	543	-580	
			19	565	-575	13	1315	-1315	-1	65	-15	7	147	-751	21	543	-580	21	543	-580	
			3	1018	1018	10	1114	1071	-1	65	-15	7	147	-751	21	543	-580	21	543	-580	
			13	253	-222	11	797	-814	-2	927	593	21	162	-193	21	162	-193	21	162	-193	
			22	146	83	12	746	-775													
			13	344	-348	13	613	-640													
			24	1475	-1430	14	443	-443													
			29	761	-822	15	2112	-2107													
			26	1163	1149	16	219	-166													
						17	188	-179													
						18	413	-423													
						19	639	-671													
						20	1038	-1038													
						21	309	294													
						22	867	945													
						23	1253	-1245													
						24	759	569													

10	793	683	4	442	442	7,4,4	8	8369	2698	10	150	144	1	130	-150	1	1598	-1537	1	7,4,4	
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			10	753	-651		14	117	-124	10	134	142	7	101	-79	7	101	-79	7	327	-341
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			19	1753	-1848		23	117	-124	10	134	142	16	101	-79	16	101	-79	16	327	-341
			20	1753	-1848		24	117	-124	10	134	142	17	101	-79	17	101	-79	17	327	-341
			21	1753	-1848		25	117	-124	10	134	142	18	101	-79	18	101	-79	18	327	-341
			22	1753	-1848		26	117	-124	10	134	142	19	101	-79	19	101	-79	19	327	-341
			23	1753	-1848		27	117	-124	10	134	142	20	101	-79	20	101	-79	20	327	-341
			24	1753	-1848		28	117	-124	10	134	142	21	101	-79	21	101	-79	21	327	-341
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			34	1753	-1848		38	117	-124	10	134	142	31	101	-79	31	101	-79	31	327	-341
			35	1753	-1848		39	117	-124	10	134	142	32	101	-79	32	101	-79	32	327	-341
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			80	1753	-1848		84	117	-124	10	134	142	77	101	-79	77	101	-79	77	327	-341
			81	1753	-1848		85	117	-124	10	134										

Table 5

Palladium-palladium non-bonded distances, Å. Standard
 deviations in parentheses

Pd1...Pd2	3.173(1)	Pd4...Pd5	3.105(1)
Pd1...Pd3	3.119(1)	Pd4...Pd6	3.136(1)
Pd2...Pd3	3.151(1)	Pd5...Pd6	3.204(1)

Selected bondlengths, Å. Standard deviations in parentheses

Pd1-O111	1.986(9)	Pd4-O231	1.998(8)
Pd1-O121	1.990(9)	Pd4-O241	1.990(8)
Pd1-O151	2.009(9)	Pd4-O251	1.988(8)
Pd1-O161	1.994(9)	Pd4-O261	1.988(8)
Pd2-O112	1.998(9)	Pd5-O211	1.980(8)
Pd2-O122	2.001(10)	Pd5-O221	2.003(9)
Pd2-O132	1.980(8)	Pd5-O232	2.007(9)
Pd2-O141	1.982(10)	Pd5-O242	2.000(8)
Pd3-O131	2.000(9)	Pd6-O212	1.973(9)
Pd3-O142	1.990(8)	Pd6-O222	1.979(9)
Pd3-O152	2.016(8)	Pd6-O252	1.989(9)
Pd3-O162	1.995(8)	Pd6-O262	1.992(9)
Average	1.995(9)	Average	1.993(9)

C-C	1.505(18) (mean of 12 values)
C-O	1.239(15) (mean of 24 values)

Table 6

Selected bond angles. Standard deviations in parentheses

O - Pd - CisO

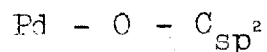
O111 Pd1 O121	94.0(0.4)	O231 Pd4 O241	92.1(0.4)
O111 Pd1 O161	86.5(0.4)	O231 Pd4 O251	85.0(0.3)
O121 Pd1 O151	85.2(0.4)	O241 Pd4 O261	84.9(0.4)
O151 Pd1 O161	91.0(0.4)	O251 Pd4 O261	94.9(0.3)
O112 Pd2 O122	94.9(0.4)	O211 Pd5 O221	92.5(0.4)
O112 Pd2 O132	84.0(0.4)	O211 Pd5 O232	86.8(0.4)
O122 Pd2 O141	85.2(0.4)	O221 Pd5 O242	86.5(0.4)
O132 Pd2 O141	92.9(0.4)	O232 Pd5 O242	91.2(0.4)
O131 Pd3 O142	93.3(0.4)	O212 Pd6 O222	93.0(0.4)
O131 Pd3 O162	85.8(0.4)	O212 Pd6 O252	86.1(0.4)
O142 Pd3 O152	85.7(0.4)	O222 Pd6 O262	84.7(0.4)
O152 Pd3 O162	91.9(0.4)	O252 Pd6 O262	93.0(0.4)

O - Pd - TransO

O111 Pd1 O151	165.3(0.4)	O231 Pd4 O261	163.5(0.3)
O121 Pd1 O161	167.0(0.4)	O241 Pd4 O251	169.0(0.3)
O112 Pd2 O141	167.9(0.4)	O211 Pd5 O242	168.8(0.3)
O122 Pd2 O132	165.4(0.4)	O221 Pd5 O232	164.1(0.4)
O131 Pd3 O152	164.3(0.3)	O212 Pd6 O262	166.8(0.4)
O142 Pd3 O162	168.3(0.4)	O222 Pd6 O252	165.9(0.4)
Average	166.4(0.4)	Average	166.4(0.4)

Table 6 (Continued)

Selected bond angles. Standard deviations in parentheses



Pd1 O111 C111	133.2(0.8)	Pd5 O211 C211	129.3(0.8)
Pd2 O112 C111	128.8(0.8)	Pd6 O212 C211	130.6(0.8)
Pd1 O121 C121	131.2(0.9)	Pd5 O221 C221	131.4(0.8)
Pd2 O122 C121	132.4(0.9)	Pd6 O222 C221	128.8(0.9)
Pd3 O131 C131	130.4(0.8)	Pd4 O231 C231	131.1(0.8)
Pd2 O132 C131	128.9(0.8)	Pd5 O232 C231	128.8(0.8)
Pd2 O141 C141	130.9(0.8)	Pd4 O241 C241	131.7(0.8)
Pd3 O142 C141	130.1(0.9)	Pd5 O242 C241	128.9(0.8)
Pd1 O151 C151	129.2(0.8)	Pd4 O251 C251	129.8(0.8)
Pd3 O152 C151	132.0(0.8)	Pd6 O252 C251	130.3(0.8)
Pd1 O161 C161	130.5(0.8)	Pd4 O261 C261	133.3(0.8)
Pd3 O162 C161	129.2(0.8)	Pd6 O262 C261	127.9(0.8)
Average	130.6(0.8)	Average	130.2(0.8)

Acetate group

O - C - O	126.3(1.2) (mean of 12 values)
O - C - C	116.9(1.1) (mean of 24 values)

Table 7

Least-squares planes

The least-squares plane is that through the four coordinating oxygen atoms. The distance of the palladium atom from the plane is given in each case.

	Atom	d, $\overset{\circ}{\text{A}}$
1	O111	-0.016
	O121	0.016
	O151	-0.017
	O161	0.016
	Pd1	0.24
2	O112	-0.022
	O122	0.022
	O132	0.023
	O141	-0.022
	Pd2	-0.23
3	O131	-0.035
	O142	0.035
	O152	-0.035
	O162	0.036
	Pd3	0.24
4	O231	-0.049
	O241	0.049
	O251	0.048
	O261	-0.048
	Pd4	0.24

Table 7 (Continued)

5	0232	-0.041
	0242	0.041
	0211	0.041
	0221	-0.041
	Pd5	0.24
6	0212	-0.008
	0222	0.008
	0252	0.008
	0262	-0.008
	Pd6	-0.24

Equations of the planes in direct space:-

1	$-6.115\underline{x} + 22.21\underline{y} - 4.416\underline{z} = -1.098$
2	$-6.459\underline{x} + 23.21\underline{y} + 4.118\underline{z} = -2.147$
3	$-0.4319\underline{x} + 0.6298\underline{y} + 8.284\underline{z} = 4.996$
4	$16.28\underline{x} + 4.801\underline{y} - 1.860\underline{z} = 11.79$
5	$-12.06\underline{x} + 19.14\underline{y} - 1.852\underline{z} = -0.6297$
6	$4.550\underline{x} + 24.97\underline{y} - 3.879\underline{z} = 5.384$

Acute angles between these planes and the triangle of metal atoms:-

1 - (Pd1 Pd2 Pd3)	89.0
2 - (Pd1 Pd2 Pd3)	88.8
3 - (Pd1 Pd2 Pd3)	89.6
4 - (Pd4 Pd5 Pd6)	89.4
5 - (Pd4 Pd5 Pd6)	89.5
6 - (Pd4 Pd5 Pd6)	88.8
Average	89.2

Table 8

Water-molecule environment

Atoms	Dist, $\overset{\circ}{\text{\AA}}$	Atoms	Angle, $^{\circ}$
O1...O262	3.07(3)	O262-O1-O222	50.8(0.8)
O1...O222	3.17(4)	O222-O1-O132 _I	110.7(0.9)
O1...O132 _I	3.37(3)	O262-O1-O132 _I	78.0(0.7)

The subscripted atom is related to that of the asymmetric unit by the operation:-

$$1-x, \quad -y, \quad -z$$

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"Forsan et haec olim meminisse iuvabit."
(Perhaps one day this too will be pleasant
to remember).

... Virgil: Aeneid, I. 203.

Chapter 6. The Crystal Structures of Propyl-
pentamminerhodium(III) Ferchlorate
and Hexafluoropropylpentammine-
rhodium(III) Ferchlorate: structural
trans influence in d^6 octahedral
complexes.

Abstract

The complexes, Propylpentamminerhodium(III) Perchlorate and Hexafluoropropylpentamminerhodium(III) Perchlorate, are isomorphous in spacegroup Pnma. The unitcell dimensions are $\underline{a} = 15.712$, $\underline{b} = 12.100$, $\underline{c} = 7.974 \overset{\circ}{\text{\AA}}$ (propyl complex), and $\underline{a} = 15.306$, $\underline{b} = 12.136$, $\underline{c} = 8.553 \overset{\circ}{\text{\AA}}$ (hexafluoropropyl complex). The structures were solved by standard methods from diffractometer-measured data, and refined by full-matrix methods to final R factors of : 0.053 (propyl) and 0.076 (hexafluoropropyl). The rhodium atom has normal octahedral environment with a σ -bonded alkyl, or fluoroalkyl group on one side, and an ammine group on the other side of a square plane containing four ammine groups and a central rhodium atom. The complex cations attain apparent m (C_s) symmetry by statistical disorder about the crystallographic mirror plane. A large trans-influence is exhibited by the propyl group, demonstrated by a relative lengthening of $0.183 \overset{\circ}{\text{\AA}}$ (23σ) in the trans Rh-N bond. A much smaller trans-influence is exhibited by the hexafluoropropyl group, $0.086 \overset{\circ}{\text{\AA}}$ (8σ), although both ligands possess strong trans-labilising effects in solution. This result emphasises an earlier distinction between a structural trans-influence, and a kinetic trans-effect in octahedral substitution reactions.

Introduction

The trans-effect, notably in square-planar platinum(II) complexes has been known for many years, and ligands have been classified according to their ability to influence the rate of substitution in the trans-position.¹ Current theories have rationalised substitution reactions in terms of two fundamental processes²:-

- (i) A thermodynamic effect (Trans-Influence), such as weakening of the trans-bond in the substrate.
- (ii) A kinetic effect (Trans-Effect) arising, say, from the ability of the ligand to stabilise the activated complex involved in a trans substitution mechanism.

In general, ligands with good σ -bonding, but no π -acceptor properties would be expected to possess trans-influence, whereas ligands with π -acceptor properties might operate through a kinetic trans-effect.

Data on trans labilising in octahedral complexes is less well-defined than for square-planar, but Wilkinson et al.³ have reported a strong such effect in the cation $(\text{Rh}(\text{NH}_3)_5\text{X})^{2+}$, where X = hydride, alkyl or fluoroalkyl. Accordingly, structural studies have been undertaken in this laboratory for complexes with X = ethyl,⁴ propyl, hexafluoropropyl, in order to establish whether a corresponding trans-influence exists in the crystal: in particular whether the π -acceptor properties of the $\text{C}_3\text{F}_6\text{H}$ ligand permit discussion of the substitution reactions of the $(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{F}_6\text{H})^{2+}$ cation in terms of a kinetic trans-effect. Also of interest was whether this "back-bonding" effect gives rise to a significant strengthening of the Rh-C(fluoroalkyl) linkage.

The Crystal Structure of Hexafluoropropylpentamminerhodium(III) Perchlorate

Experimental

The title compound crystallises from water as ill-defined colourless plates. Crystals were kindly supplied by Dr. K. Thomas. Weissenberg and precession photographs exhibited Laue symmetry mmm . The systematic absences were $0k1$, $k + 1 \neq 2n$, $hk0$, $h \neq 2n$. These absences were consistent with the spacegroups $Fnma$ (no. 62) and $Fn2_1a$ (no. 33).

Intensity data were collected on a Siemens' four-circle automatic diffractometer, for a crystal of approximate dimensions $0.5 \times 0.3 \times 0.1 \text{ mm}^3$, mounted about the b axis. Using nickel-filtered CuK_{α} radiation 1604 independent reflections were measured, out to 70° in θ , of which 56 were judged insignificant. The five-value measurement technique was employed, with a maximum measuring-time-per-step of 0.24 sec. The data were scaled, using the 006 reflection as reference (measured every 20 reflections), and Lorentz and Polarisation corrections were applied.

Crystal Data

$(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{F}_6\text{H})(\text{ClO}_4)_2$, $M = 538.$, Orthorhombic, $Fnma$,
 $a = 15.306 \pm 0.002$, $b = 12.136 \pm 0.002$, $c = 8.553 \pm 0.001 \text{ \AA}$,
 $U = 1589 \text{ \AA}^3$, $D_m = 2.21 \pm 0.04$ (floatation), $D_c = 2.25 \text{ g cm}^{-3}$,
 $Z = 4$, $\mu = 135 \text{ cm}^{-1}$ for CuK_{α} , $F_{000} = 1064$.

Structure Solution and Refinement

A three-dimensional, unsharpened Patterson gave Rh-Rh vectors equally compatible with either $Fn2_1a$ or $Fnma$. However, since there was only one peak attributable to Rh-Cl vectors (the non-centrosymmetric spacegroup $Fn2_1a$ required two independent perchlorate ions), the centrosymmetric spacegroup

Pnma was assumed. The rhodium coordinates were then given by:

Rh 0.610, $\frac{1}{4}$, 0.333

with a probable chlorine position:

Cl 0.380, 0.50, 0.166

Three cycles of ORFLS⁹ least-squares on the rhodium position only, gave an R factor of 0.40. A difference Fourier at this stage, with a rejection ratio of 0.40 confirmed the above chlorine position, and clearly showed the octahedral environment of the rhodium atom. Three more cycles of ORFLS on these positions reduced R to 0.26, and a difference Fourier, with a rejection ratio of 0.20, showed the perchlorate oxygen atoms as diffuse peaks, and also indicated that the fluoropropyl group was disordered across the (x, $\frac{1}{4}$, z) mirror plane.

It proved extremely difficult to locate the atoms of the fluoropropyl group, since the peaks were very diffuse, and consequently there was overlap between peaks from one atom and the mirror image of a neighbouring atom. Three more cycles of ORFLS, including the perchlorate oxygens and four atoms of the disordered fluoropropyl group (the latter were weighted as carbon atoms, with multiplicities of 0.5), gave R = 0.22.

An absorption correction was applied at this stage in an attempt to improve the resolution of the fluoroalkyl group: μ was quite high (135 cm.^{-1}) and the crystal very anisotropic in shape. The Gaussian Integration method⁵ was used, with ray-path lengths determined by the method of Coppens et al.⁶ From some trial runs the optimum grid size was chosen as $16 \times 6 \times 24$: this corresponded to allocating more grid points along the prominent directions of the plate. A further 3 cycles of ORFLS reduced R to 0.17. The difference Fourier map was now much cleaner, and the terminal $-\text{CF}_3$ group of the fluoroalkyl residue was visible. Five cycles of ORFLS, with the rhodium atom anisotropic, then gave R = 0.154. A difference Fourier,

with a rejection ratio of 0.40, enabled location of three more atoms, C2, F12, F2 (Figure 1), of the fluoropropyl group. More refinement gave $R = 0.13$, and a difference Fourier showed the remaining fluorine atom, F11. The structure was thus formulated as $(\text{Rh}(\text{NH}_3)_5\text{CF}_2\text{CFH.CF}_3)^{2+}$ which was consistent with the method of preparation³ (from hydridopentamminerhodium(III) sulphate and $\text{CF}_2=\text{CF.CF}_3$).

Initially the terminal carbon atoms of the fluoropropyl group, C 1 and C 3, were placed on the $(\underline{x}, \frac{1}{4}, \underline{z})$ mirror plane, and only the fluorines and the methylene carbon were thought to be disordered. However, once more atoms of the group were added, the $\underline{B}$ -factor of C 1 rose steadily, and the C 1-C 2 distance became unreasonably short ($1.2 \overset{\circ}{\text{\AA}}$). Consequently the Fourier peak for this atom was reinspected, and it was seen to be distinctly "elongated" in a direction perpendicular to the mirror plane. Thus C 1 was offset ca. $0.2 \overset{\circ}{\text{\AA}}$ from the mirror plane, and allowed to refine isotropically with a trial $\underline{B}$ -factor of $7.5 \overset{\circ}{\text{\AA}}^2$. The $\underline{B}$ -factor fell to ca. $5.0 \overset{\circ}{\text{\AA}}^2$ and the C 1-C 2 distance was now more realistic.

Three cycles of ORFELS with only rhodium anisotropic gave $R = 0.121$. Five cycles of fully anisotropic refinement then gave a constant R of 0.082. The anisotropic temperature factor coefficients required to be fixed at zero during the anisotropic refinement were determined by the method of Levy.⁴ A difference Fourier at this stage enabled location of the hydrogen atom of the $\text{C}_3\text{F}_6\text{H}$ group, and those of the four crystallographically independent ammine ligands.

After 6 more cycles of ORFELS, with the hydrogens included as a fixed contribution, refinement was terminated, with all positional-parameter shifts less than 0.11 times the corresponding standard deviation, at a final R factor of 0.076 on 1603 reflections. The 0 5 5 reflection was omitted from

least-squares refinement, as it was suspected to overlap with the 0 4 4 from contaminating iron radiation. Unobserved reflections were included in the analysis throughout, but were omitted from Fourier summations and estimates of R : 12 of the 56 unobserveds calculated marginally greater than the threshold. Unit weights were used throughout. The scattering factors for Rh^{3+} and Cl^- were those tabulated by Cromer and Waber⁷. The dispersion corrections were those of Cromer⁸; the dispersion-corrected rhodium and chlorine formfactors were taken as $((f_0 + \delta f')^2 + \delta f''^2)^{1/2}$.

The final difference Fourier showed no unusual features, having a background level of ± 0.5 , rising to a maximum of 1.5 eA^{-3} near the rhodium atom.

In view of the disorder exhibited by the rest of the fluoropropyl group, it seemed unlikely that the terminal carbon, C 3 should reside on the $(\underline{x}, \frac{1}{4}, \underline{z})$ mirror plane, as had, in fact, been observed from the Fourier maps, and assumed in the refinement. Accordingly this atom was offset slightly from the mirror plane (in a manner similar to that of C 1), and allowed to refine isotropically. A slight decrease in R was obtained, relative to a previous refinement with C 3 isotropic. However, when anisotropic refinement was attempted an extremely strong correlation (correlation coefficients > 0.7) was observed between the $\underline{y}$ and β_{22} parameters for this atom. This (presumably) prevented convergence of the refinement: C 3 persistently collapsed onto the mirror plane, but when this occurred an extremely large shift in $\underline{y}$ resulted in the following cycle. This behaviour could be avoided by fixing β_{22} , and refining $\underline{y}$, and vice versa, but this procedure was obviously unsatisfactory. In view of these correlation effects it was thought that the structural model with C 3 confined to the mirror plane was more satisfactory.

Some refinement in the non-centrosymmetric spacegroup, $Pn2_1a$, was attempted. However, no improvement in agreement or bondlengths was obtained, and the standard deviations were considerably larger, owing to the increased number of parameters. Thus the parameters obtained from the centrosymmetric refinement are to be regarded as final ones. The positional and thermal parameters in Tables 1 and 2 together with the hydrogen parameters in Table 3, were used to calculate the final structure factors listed in Table 4.

The Crystal Structure of Propylpentamminerhodium(III) Perchlorate

Experimental

Preliminary examination revealed the crystals to be isomorphous with those of the hexafluoropropyl complex. Intensity data were collected on the diffractometer for a crystal of approximate dimensions $0.6 \times 0.25 \times 0.10 \text{ mm}^3$, mounted about the c axis. Using nickel-filtered CuK_α radiation, 1517 independent reflections were measured, to $\theta = 70^\circ$, of which 101 were judged insignificant. The data were scaled, using the 0 8 0 reflection as reference, measured every 20 reflections, and Lorentz and Polarisation corrections were applied. The structure solution then proceeded concurrently with that of the hexafluoropropyl complex.

Crystal Data

$(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{H}_7)(\text{ClO}_4)_2$, $M = 430.$, Orthorhombic, $Pnma$ (no. 62).
 $a = 15.712 \pm 0.001$, $b = 12.100 \pm 0.001$, $c = 7.974 \pm 0.001 \text{ \AA}$,
 $U = 1516 \text{ \AA}^3$, $D_m = 1.88 \pm 0.03$, $D_c = 1.88 \text{ g cm}^{-3}$, $Z = 4$, $\mu =$
 125 cm^{-1} for CuK_α , $F_{000} = 872$.

Structure Solution and Refinement

In view of the obvious similarities with the hexafluoropropyl complex, it was decided to assume similar positions for the rhodium and chlorine atoms, i.e.

Rh	0.6150,	$\frac{1}{4}$,	0.3392,	$\underline{B} = 3.5 \overset{O_2}{\text{\AA}}$
Cl	0.3615	0.4984,	0.1587,	$\underline{B} = 6.4 \overset{O_2}{\text{\AA}}$

Six cycles of ORFLS gave an $\underline{R}$ factor of 0.22, and a difference Fourier with a rejection ratio of 0.60 enabled location of all atoms except for the methylene carbon of the propyl group. The other carbon atoms were placed on the $(\underline{x}, \frac{1}{4}, \underline{z})$ mirror plane, although the peak corresponding to C 1 was relatively weak, and "smeared out" across the mirror plane. Five cycles of ORFLS on these positions then gave $\underline{R} = 0.14$. A small, diffuse peak in the difference Fourier (height $1.5 \overset{O}{\text{eA}}^{-3}$) was tentatively assigned as C 2, in a disordered position, offset from the mirror plane. An absorption correction was applied at this stage, using the Gaussian Integration Technique⁵ described earlier, with an optimised sampling grid of 6 x 14 x 32. Three more cycles of ORFLS gave $\underline{R} = 0.091$. There was still some electron density in the region of C 2, however, and also its $\underline{B}$ factor was very high ($14.5 \overset{O}{\text{\AA}}^2$), and the C 1-C 2 distance was unreasonably short ($1.1 \overset{O}{\text{\AA}}$). Accordingly, C 2 was removed and a difference Fourier ($\underline{R} = 0.096$) was computed. This showed an annulus of electron density corresponding to C 2, indicating that the propyl group was rotationally disordered about the C 1...C 3 axis. This ring was approximated by placing "one-sixth" carbon atoms at intervals of 60° around the ring, with two on the mirror plane (multiplicity = 0.08) and two each side of the mirror plane (multiplicity = 0.17).

Five cycles of ORFLS with anisotropic temperature factors for all but the atoms of the propyl group gave $\underline{R} = 0.058$. Prior to this refinement, C 1 was offset from the

mirror plane, in view of its high B factor and some residual difference-Fourier peaks. Refinement with C 1 and C 3 anisotropic then gave $R = 0.056$. Attempts to refine C 3 anisotropically, but offset from the mirror plane, were unsuccessful, as in the case of the hexafluoropropyl complex: in this case the y and z_{22} parameters were found to be linearly dependent (correlation coefficients > 0.99). Attempts to refine the C 2 fragments anisotropically also failed, since the temperature factors became non-positive-definite, and the standard deviations of their positional parameters were increased.

A difference Fourier enabled location of the hydrogens of two of the ammine ligands. The other hydrogens could not be located, but were included as fractional atoms in reasonable orientations. After 9 cycles of refinement, applying a damping factor of 0.5, refinement was judged complete at a final R factor of 0.053 on 1513 reflections, when all parameter shifts were less than 0.09 times the corresponding standard deviation. Unit weights were used throughout. The reflections, 6 0 0 (anomalously high background count), 2 0 0 (mispunch on diffractometer output tape), 5 0 5 and 10 5 0 (suspected overlap with accompanying iron radiation maxima), were omitted from the least-squares refinement. The final difference Fourier showed no untoward features, having a background level of $\pm 0.3 \text{ eA}^{-3}$. The final positional and thermal parameters in Tables 5 and 6 were used to calculate the final structure factors listed in Table 7.

Discussion of the Structures

In both structures the rhodium atom has the expected octahedral coordination, with a σ -bonded alkyl or fluoroalkyl group on one side, and an ammine group on the other side of

a square plane containing four ammine groups and the central rhodium atom. The complex cations lie on crystallographic mirror planes, and attain apparent $\underline{m}$ ($\underline{C}_s$) symmetry by statistical disorder about this mirror plane. The $(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{F}_6\text{H})^{2+}$ complex ion is shown as an ORTEP¹⁰ stereodigram in Figure 1, and the coordination octahedra for both structures are given in Figure 2.

In the propylpentamminerhodium(III) cation, the independent Rh-N distances in the square plane (Table 8) are all within 1.5 standard deviations of a mean value of 2.075 ($\sigma = 0.008$): the sum of covalent radii is 2.06 Å.¹¹ The Rh-N bond trans to the propyl group, 2.258 ($\sigma = 0.008$) shows a relative trans lengthening of 0.183(23 σ), in good agreement with that observed by Skapski and Troughton,⁴ 0.181 Å(23 σ), in the ethylpentamminerhodium(III) cation.

In the hexafluoropropyl complex the Rh-N distances in the square plane are all within one standard deviation of a mean value of 2.084 Å ($\sigma = 0.011$). The trans Rh-N distance of 2.170 ($\sigma = 0.011$) shows a relative trans lengthening, in this case, of 0.086 Å(8 σ). In $\text{K}_3((\text{CN})_5\text{CoC}_2\text{F}_4\text{H})^{12}$ a very small trans-influence was observed for the tetrafluoroethyl group, 0.03 Å(2 σ). This result is consistent with that of the present study, and shows that the σ -bonded fluoroalkyl group has a much smaller trans-influence than does the corresponding alkyl group.

However, in studies on the $(\text{Rh}(\text{III})(\text{NH}_3)_5\text{R})^{2+}$ cations, Wilkinson et al.³ have shown that both the ethyl and tetrafluoroethyl ligands are strongly trans directing in substitution reactions, with comparable degrees of activity. Thus it appears that the trans-labilisation observed for σ -bonded alkyl groups may be explained largely in terms of a trans bond weakening mechanism, i.e. a "Structural" trans-

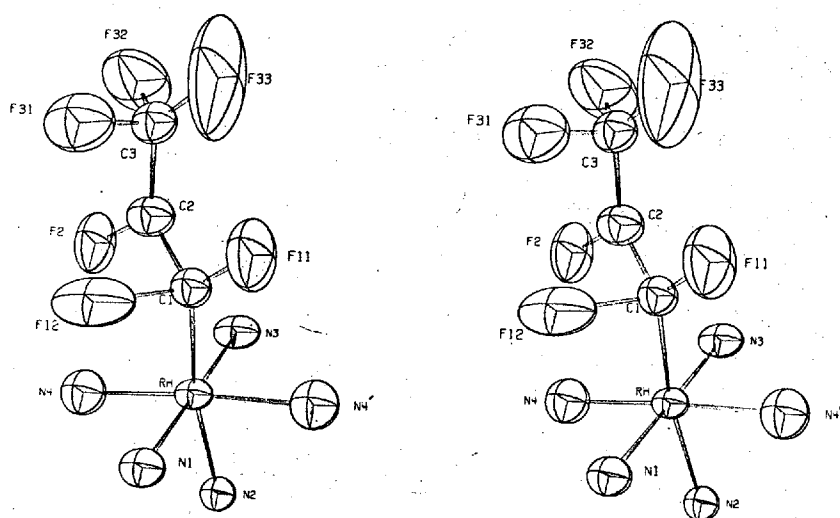


Figure 1 The $[\text{Rh}(\text{NH}_3)_5\text{C}_3\text{F}_6\text{H}]^{2+}$ ion
 A stereoscopic drawing with thermal ellipsoids scaled to
 enclose 35% probability.

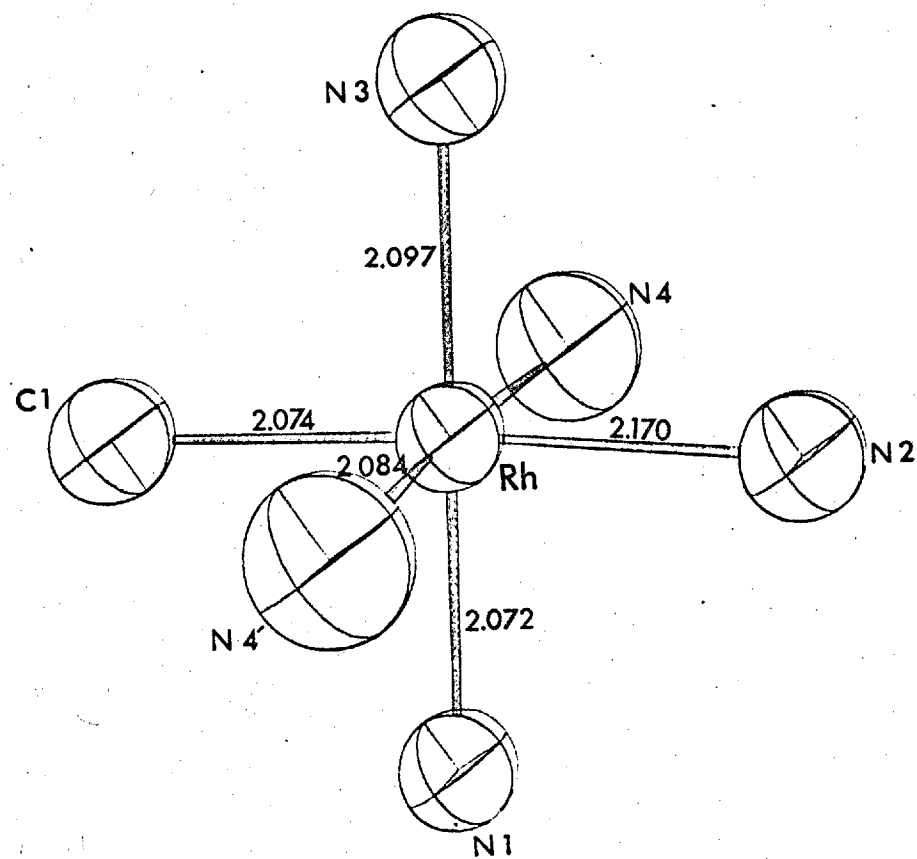
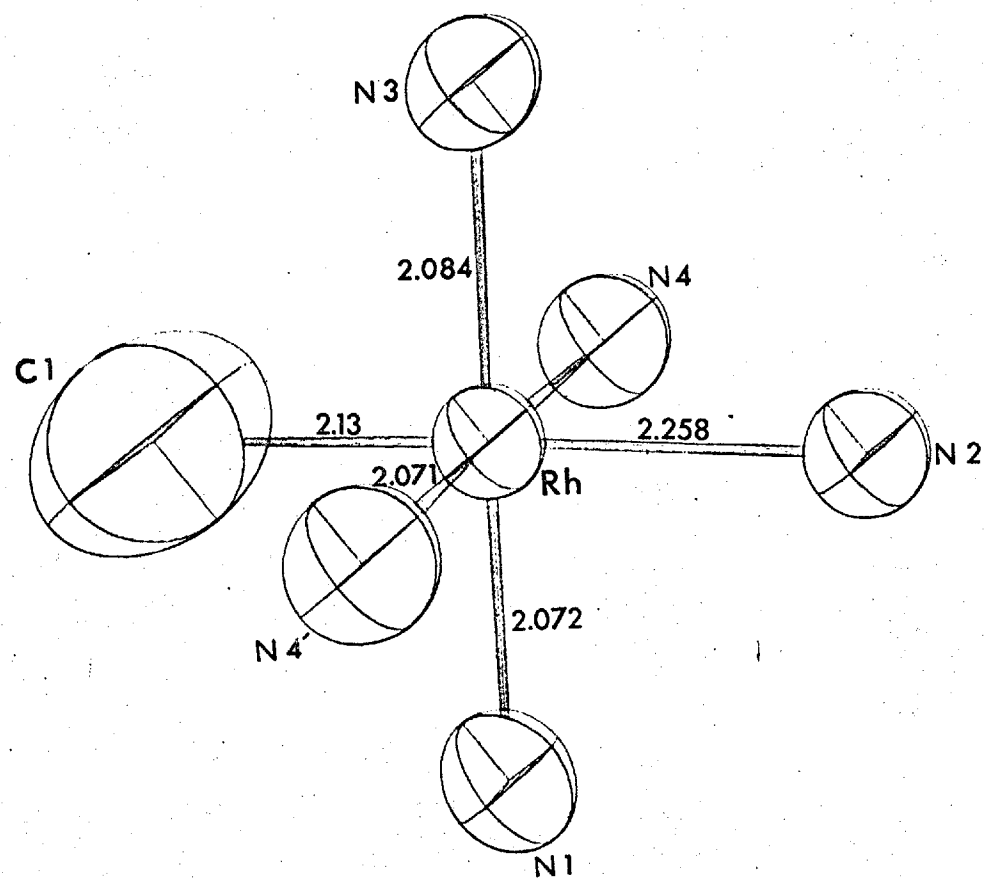


Figure 2

influence. However, other factors, presumably of a kinetic nature, must evidently be invoked to account for the high trans-labilising effect of σ -bonded fluoroalkyl ligands. A possible such factor is a preferential stabilisation of the activated-complex-intermediate involved in trans substitution, arising from the π -acceptor ($d_{\pi} - \sigma^*$) properties of the fluoroalkyl group.¹² This presupposes an S_N2 displacement mechanism, although a "pure" S_N2 mechanism is extremely unlikely in octahedral complexes;¹ more likely is an intermediate type of mechanism, in which both the entering and leaving groups are very weakly coordinated. A similar " π -stabilisation" effect has been postulated in square-planar substitution reactions of Pt(II) complexes, although in this system there is much more evidence for the reactions proceeding via S_N2 mechanisms.¹ The pronounced trans bond weakening observed in the ethylpentammine- and propylpentamminerhodium(III) cations strongly favours the S_N1 mechanism in these cases.

The greater trans-influence exhibited by the propyl group (relative to the hexafluoropropyl group) can probably be explained in terms of its superior σ -bonding capacity. This effectively permits a larger transfer of electron density into the vacant $4d_{z^2}$ orbital of the rhodium and thus gives rise to a greater shielding of the dative-bonding lone-pair of the trans ammine group.

The Rh-C(fluoroalkyl) distance of 2.074 ($\sigma = 0.018$) is in good agreement with the value of 2.08 Å ($\sigma = 0.03$) observed in π -C₅H₅-Rh(III)(CO)(C₂F₅)I.¹³ These values are surprisingly similar to the Rh-C(alkyl) distances of 2.050 ($\sigma = 0.016$)⁴ and 2.08 Å observed in other octahedral complexes of Rh(III): the Rh-C(fluoroalkyl) distance is expected to be shorter on account of $d_{\pi} - \sigma^*$ back-donation from filled metal orbitals to vacant C-F antibonding orbitals.¹⁹ A direct comparison of the

structures of π -C₅H₅-Mo(CO)₃Et¹⁵ and π -C₅H₅-Mo(CO)₃C₃F₇¹⁶ shows a shortening of 0.12 Å. In view of these conflicting results, and the relatively poor precision of most of the determinations of the Rh-C bondlength, more structural data is needed before a definite deduction can be made as to the Rh-C (fluoroalkyl) bond order.

The Rh-C(propyl) distance of 2.13 Å ($\sigma = 0.03$) is rather longer than comparable values. This is thought not to be a genuine effect, but arises because of the rotational disorder of the methylene carbon atom of the propyl group. There was a pronounced tendency for C 1 to be "pulled" into the ring of electron density corresponding to C 2: removal of the C 2 fragments gave a Rh-C 2 distance of 2.25 Å on least-squares refinement, and subsequent addition of the fragments resulted in a progressive contraction of the Rh- C 1 distance.

The fluoropropyl group is formulated as -CF₂CFH.CF₃, and has an approximately staggered conformation (Figure 1), but otherwise shows large departures from expected geometry. The C 1-C 2 and C 2-C 3 distances are 1.44 ($\sigma = 0.03$) and 1.61 ($\sigma = 0.02$) cf. a C-C single-bond distance of 1.54 Å.¹⁷ The C-F distances range from 1.20 to 1.63 ($\sigma = 0.03$) cf. a literature value of 1.33 Å,¹⁷ and the F-C-F and F-C-C angles range from 84 to 129° (Table 2). It is thought that these anomalies are associated with the disorder. It was assumed that the -C₃F₆H group occupied statistically disordered orientations either side of the mirror plane, but otherwise adopted a rigid conformation. This is unlikely in practice, and the thermal ellipsoids of the fluorine atoms show distinct evidence of degrees of rotation about the C-C bonds (Figure 1). It seems probable therefore, that some degree of conformational disorder is present, but unfortunately it cannot be resolved from the Fourier maps. In addition, the proximity of some

disordered atoms to the $(x, \frac{1}{4}, z)$ mirror plane gave rise to strong correlation effects in least-squares refinement, as described earlier. This may give rise to "uncertainties" in the positions of such atoms.

The Rh-C 1-C 2 angle in the fluoropropyl complex, 118.2° ($\sigma = 1.4$) compares well with results for other metal-perfluoralkyl linkages, $116-123^\circ$.^{12,13,16} This has been cited as evidence for some $d_{\pi} - \sigma^*$ double-bond character in the metal-fluoroalkyl bond, although similar angles, 120.9° ($\sigma = 1.1$),⁴ 120.9° ¹⁵ have been observed in metal-alkyl analogues, where back bonding is far less likely. All N-Rh-cisN and N-Rh-transN angles are very close to 90° and 180° , respectively, in both structures. However, the $N4_I$ -Rh-C 1 and $N4$ -Rh-C 1 angles are distorted ca. 10° from their ideal values of 90° (Table 2). The C 1-Rh-trans-N angles are 172° ($\sigma = 2.7$) and 169.0° ($\sigma = 0.5$) in the propyl and fluoropropyl complexes, respectively. Similar degrees of distortion were observed in the ethylpentamminerhodium(III) cation.⁴

As expected the $(ClO_4)^-$ ions play no part in the coordination of the metal atoms. In the propyl complex the Cl-O distances range from 1.332 to 1.410 ($\sigma = 0.011$), and in the fluoropropyl complex, 1.28 to 1.43 ($\sigma = 0.02$): a value of $1.42 \overset{0}{\text{\AA}}$ was found in the structure of perchloric acid monohydrate.¹⁸ The O-Cl-O angles range from $102.7 - 119.3^\circ$ ($\sigma = 0.8$) (propyl complex) and $98.1 - 121.2^\circ$ ($\sigma = 1.1$) (fluoropropyl complex): in both structures the mean O-Cl-O angle is 109.1° , close to the tetrahedral angle. The temperature factors of the oxygen atoms indicate very large amplitudes of vibration, or possibly some orientational disorder.

The non-bonded contact F 2...F 12 in the fluoropropyl group, $2.33 \overset{0}{\text{\AA}}$, is rather short: the shortest F...F (1,4) interaction observed in the staggered $-C_3F_7$ group was $2.61 \overset{0}{\text{\AA}}$.¹⁶

This may reflect a larger departure from staggered geometry for the $-\text{C}_3\text{F}_6\text{H}$ group, although the C-F and F...F distances in the present study are likely to be in error¹⁶ since librational corrections have been neglected. There are some N...F distances ($2.64 - 2.82\overset{\circ}{\text{A}}$) slightly shorter than the sum of Van der Waals radii ($2.85\overset{\circ}{\text{A}}$ ¹¹). However, the hydrogen positions do not suggest hydrogen bonding. Otherwise all non-bonded contacts are normal (Table 10).

Table 1

Positional parameters for Hexafluoropropylpentamminerhodium(III) Perchlorate. Numbers in parentheses here and in subsequent tables are estimated standard deviations.

Atom	<u>x</u>	<u>y</u>	<u>z</u>
Rh	0.61387(6)	$\frac{1}{4}$	0.33014(11)
Cl	0.35948(17)	0.51390(23)	0.14772(29)
N 1	0.5324(7)	$\frac{1}{4}$	0.1367(13)
N 2	0.7287(7)	$\frac{1}{4}$	0.1814(12)
N 3	0.6974(7)	$\frac{1}{4}$	0.5245(13)
N 4	0.6151(6)	0.4217(8)	0.3222(12)
O 1	0.3120(13)	0.4408(22)	0.0749(27)
O 2	0.3466(12)	0.6022(17)	0.0689(23)
O 3	0.4484(7)	0.4908(13)	0.1504(16)
O 4	0.3097(7)	0.5199(11)	0.2889(11)
C 1	0.5054(12)	0.2173(13)	0.4678(20)
C 2	0.4901(14)	0.2864(18)	0.6012(23)
C 3	0.4062(9)	$\frac{1}{4}$	0.7030(18)
F11	0.4612(16)	0.1193(14)	0.4927(28)
F12	0.4353(7)	0.2987(18)	0.3818(16)
F2	0.5191(11)	0.3832(12)	0.5751(26)
F31	0.3432(12)	0.3000(17)	0.6340(21)
F32	0.4233(19)	0.3027(19)	0.8181(22)
F33	0.3739(27)	0.1560(20)	0.744(6)

The numbering scheme is given in Figure 1

Table 2

Anisotropic thermal parameters for non-hydrogen atoms of Hexafluoropropylpentamminerhodium(III) Perchlorate. The anisotropic temperature factor is given by:

$$\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$$

Rh	.00329(4)	.00832(8)	.01088(14)	0	.00017(6)	0
Cl	.00616(13)	.00983(21)	.0160(4)	-.0010(1)	.0004(2)	.0002(2)
N 1	.0038(5)	.0104(10)	.0149(17)	0	.0011(7)	0
N 2	.0048(5)	.0077(8)	.0149(17)	0	-.0015(8)	0
N 3	.0038(5)	.0152(14)	.0153(18)	0	-.0001(8)	0
N 4	.0077(6)	.0118(9)	.0254(19)	.0015(6)	-.0012(9)	-.007(1)
O 1	.0276(20)	.069(5)	.104(8)	-.033(3)	.036(3)	-.072(5)
O 2	.0201(15)	.046(3)	.087(6)	.017(2)	.017(2)	.054(4)
O 3	.0092(7)	.0308(20)	.053(3)	.008(1)	.006(1)	.008(2)
O 4	.0122(7)	.0256(16)	.0241(18)	.004(1)	.002(1)	.001(1)
C 1	.0056(9)	.0074(18)	.014(3)	-.0018(8)	.007(1)	-.005(2)
C 2	.0058(10)	.012(3)	.016(3)	-.001(1)	.003(1)	-.006(2)
C 3	.0040(6)	.0097(13)	.016(2)	0	.0007(10)	0
F11	.0158(19)	.0083(13)	.043(5)	-.004(1)	-.007(2)	.000(2)
F12	.0039(5)	.037(5)	.023(2)	.006(1)	.0020(9)	.009(3)
F 2	.0097(11)	.0067(10)	.044(5)	-.0021(9)	.004(2)	-.005(2)
F31	.0072(8)	.021(3)	.028(3)	.003(1)	.003(1)	-.006(2)
F32	.020(2)	.021(3)	.021(3)	-.005(2)	.001(2)	-.009(2)
F33	.024(4)	.0073(16)	.157(23)	-.000(2)	.046(8)	-.005(5)

Table 3

Hydrogen parameters
for Hexafluoropropylpentamminerhodium(III) Perchlorate

Atom	<u>x</u>	<u>y</u>	<u>z</u>	$\overset{\circ}{B}(\text{\AA}^2)$
H 11	0.472	$\frac{1}{4}$	0.113	4.8
H 12	0.580	0.305	0.067	4.8
H 21	0.786	$\frac{1}{4}$	0.200	4.2
H 22	0.720	0.288	0.133	4.2
H 31	0.746	$\frac{1}{4}$	0.533	6.7
H 32	0.670	0.325	0.600	6.7
H 41	0.554	0.433	0.300	5.5
H 42	0.654	0.443	0.243	5.5
H 43	0.620	0.413	0.377	5.5
H 2	0.554	0.275	0.683	4.5

Hydrogen atoms are labelled H mn where m is the number of the ammine nitrogen, and n is the atom number. H 2 is bonded to C 2. The positions were estimated from difference Fourier, with probable accuracies of ca. 0.2 Å.

Table 4

Observed and Calculated Structure Factors (in electrons x 10)
for Hexafluoropropylpentamminerhodium(III) Perchlorate.

* indicates unobserved reflection

Tabulated as:

1, $\underline{F}_O$, $\underline{F}_C$ for each group with constant h, k.

1.0.L	2	408	427	0	404	-1019	0	1385	1377	2	67	90	
2	1420	-1369	3	124	-96	1	2609	-991	3	76	-90		
4	1306	-1471	4	447	-433	2	117	89	6	87	-134		
6	1426	1302	5	324	279	3	159	193	7	116	89		
8	190	-246	6	114	113	4	147	114	8	414	-180		
10	165	-171	7	242	220	5	1240	-1280	9	131	126		
0.1.L	8	225	243	6	88	-93	19	212	217	10	2295	-2539	
1	1191	-1041	9	219	-225	7	-640	649	1	1171	-1081		
3	133	36	10	172	-191	8	26	-11	2	1667	1028		
5	73	863	1.4.L	2	294	-259	9	54	35	3	176	137	
7	534	-396	3	691	-730	13	24	49	4	1194	1097		
9	46	39	4	402	-407	0	444	418	5	1462	1352		
0.2.L	4	606	636	1	44	-35	1	287	-223	6	692	554	
0	888	-804	5	394	381	2	217	-152	3	1400	1352		
2	458	306	6	164	168	3	316	199	4	539	-487		
4	372	324	7	77	-84	4	247	-197	5	610	-619		
6	513	-566	8	310	-304	5	47	39	6	132	-143		
8	328	347	9	106	-160	6	308	305	7	172	151		
10	23	-19	10	129	140	7	44	21	8	353	344		
0.3.L	1	434	-399	8	243	-216	9	67	83	19	136	-154	
3	1279	1163	2	696	-685	10	59	609	1	1123	1144		
5	128	123	3	465	368	0	444	418	2	185	13		
7	196	-707	4	591	580	1	331	-106	3	640	-847		
9	519	453	5	274	-229	2	419	-343	4	455	-446		
0.4.L	7	27	-1	6	91	-47	3	319	-304	5	171	117	
0	2794	2093	8	79	-24	4	229	36	6	429	460		
2	1236	-1296	9	201	-204	5	359	-353	7	206	200		
4	440	-762	1	147	152	6	307	292	8	226	-256		
6	1086	1040	1.6.L	7	382	-390	7	29	15	10	207	-223	
8	213	-180	1	717	-728	8	28	-13	1	366	301		
10	133	-163	2	301	217	9	161	108	2	208	-159		
0.5.L	3	151	-57	3	987	-981	10	26	-11	3	790	-764	
1	1360	-1324	4	344	-288	0	1821	-1878	4	494	477		
3	151	-57	5	425	-409	1	220	-220	5	461	424		
5	415	-458	6	201	199	2	785	792	6	86	37		
7	92	164	7	212	-194	3	86	-87	7	193	169		
0.6.L	9	1279	1163	8	53	36	4	264	247	8	50	-69	
0	850	-820	9	147	152	5	99	92	9	298	-299		
2	191	179	1.7.L	1	442	375	6	717	-736	10	119	128	
4	131	68	2	296	254	7	61	-70	1	593	-505		
6	457	-420	3	558	-515	8	229	214	2	1241	-1236		
8	273	302	4	393	-279	9	45	-49	3	354	251		
0.7.L	1	1235	1160	5	129	124	0	244	-200	4	613	600	
3	122	-141	6	132	92	1	1390	1436	5	265	-281		
5	111	-896	7	223	241	2	94	99	6	140	-121		
7	411	375	8	147	135	3	153	-92	7	65	35		
9	25	4	9	145	-159	4	68	78	8	260	-283		
0.8.L	1	1333	1307	5	279	259	5	940	-917	9	86	58	
0	353	-326	6	112	92	6	60	-85	1	447	-411		
2	429	-419	7	49	-29	7	453	444	2	639	617		
4	516	509	8	146	-164	8	32	-15	3	428	-357		
6	125	-169	9	70	-63	9	42	17	4	345	-351		
0.9.L	1	127	-239	1.8.L	1	220	240	0	669	746	5	119	-146
3	125	45	2	517	-455	2	517	-455	1	99	-85		
5	151	167	3	126	-129	3	385	364	2	359	-287		
7	222	-247	4	385	364	4	279	259	3	48	23		
0.10.L	0	291	-321	5	279	259	5	112	92	4	220	-215	
2	327	326	6	112	92	6	49	-29	5	160	164		
4	90	32	7	49	-29	7	146	-164	6	49	-29		
6	205	-219	8	146	-164	8	146	-164	7	125	-117		
0.11.L	1	505	504	9	70	-63	9	70	-63	8	198	204	
3	103	73	1.9.L	1	361	-326	1	361	-326	9	229	244	
5	336	-337	2	361	-326	2	361	-326	1	327	343		
7	161	166	3	361	-326	3	361	-326	2	574	524		
0.12.L	0	425	361	4	273	252	4	273	252	3	769	-772	
2	281	-276	5	148	-114	5	148	-114	4	951	-945		
4	171	-159	6	51	46	6	51	46	5	175	204		
6	196	227	7	34	5	7	34	5	6	230	235		
0.13.L	8	124	-130	8	124	-130	8	124	-130	7	276	291	
1	116	-126	1.10.L	1	159	169	0	159	169	8	154	148	
3	53	19	2	174	-123	1	174	-123	9	132	-170		
5	96	110	3	62	80	2	62	80	1	415	334		
0.14.L	0	116	-164	4	404	402	3	404	402	2	278	-348	
2	64	72	5	176	-160	4	176	-160	3	724	713		
1.0.L	1	723	691	6	166	67	5	166	67	4	189	148	
3	213	-2010	7	72	-57	6	72	-57	5	202	185		
5	251	-203	1.11.L	1	178	188	0	178	188	6	86	-63	
7	745	756	2	171	149	1	171	149	7	143	149		
9	487	514	3	283	-264	2	283	-264	8	63	-48		
10	359	320	4	117	-124	3	117	-124	9	190	-216		
0.15.L	0	425	361	5	99	63	4	99	63	1	117	55	
2	281	-276	6	63	52	5	63	52	2	657	-612		
4	171	-159	7	77	64	6	77	64	3	106	62		
6	196	227	8	112	92	7	112	92	4	331	469		
0.16.L	1	116	-126	9	70	-9	8	70	-9	5	175	-174	
3	53	19	1.12.L	1	211	-202	0	211	-202	6	59	-37	
5	96	110	2	190	-191	1	190	-191	7	27	3		
0.17.L	0	116	-164	3	144	154	2	144	154	8	175	-180	
2	64	72	4	144	154	3	144	154	9	130	-105		
1.0.L	1	723	691	5	98	106	4	98	106	1	434	405	
3	213	-2010	6	29	5	5	29	5	2	274	308		
5	251	-203	7	46	-19	6	46	-19	3	296	-268		
7	745	756	8	143	134	7	143	134	4	142	-130		
9	487	514	9	42	-49	8	42	-49	5	128	-138		
10	359	320	1.14.L	1	76	-74	0	76	-74	6	56	-42	
0.18.L	0	425	361	2	92	52	1	92	52	7	56	-42	
2	281	-276	3	76	110	2	76	110	8	119	126		
4	171	-159	4	143	134	3	143	134	9	130	-105		
6	196	227	5	42	-49	4	42	-49	1	434	405		
0.19.L	1	116	-126	6	29	5	5	29	5	2	274	308	
3	53	19	7	46	-19	6	46	-19	3	296	-268		
5	96	110	8	143	134	7	143	134	4	142	-130		
0.20.L	0	425	361	9	42	-49	8	42	-49	5	128	-138	
2	281	-276	1.15.L	1	76	-74	0	76	-74	6	56	-42	
4	171	-159	2	92	52	1	92	52	7	56	-42		
6	196	227	3	76	110	2	76	110	8	119	126		
0.21.L	1	116	-126	4	143	134	3	143	134	9	130	-105	
3	53	19	5	42	-49	4	42	-49	1	434	405		
5	96	110	6	29	5	5	29	5	2	274	308		
0.22.L	0	425	361	7	46	-19	6	46	-19	3	296	-268	
2	281	-276	8	143	134	7	143	134	4	142	-130		
4	171	-159	9	42	-49	8	42	-49	5	128	-138		
6	196	227	1.16.L	1	76	-74	0	76	-74	6	56	-42	
8	185	-178	2	92	52	1	92	52	7	56	-42		
10	157	174	3	76	110	2	76	110	8	119	126		
0.23.L	1	116	-126	4	143	134	3	143	134	9	130	-105	
3	53	19	5	42	-49	4	42	-49	1	434	405		
5	96	110	6	29	5	5	29	5	2	274	308		
0.24.L	0	425	361	7	46	-19	6	46	-19	3	296	-268	
2	281	-276	8	143	134	7	143	134	4	142	-130		
4	171	-159	9	42	-49	8	42	-49	5	128	-138		
6	196	227	1.17.L	1	76	-74	0	76	-74	6	56	-42	
8	185	-178	2	92	52	1	92	52	7	56	-42		
10	157	174	3	76	110	2	76	110	8	119	126		
0.25.L	1	116	-126	4	143	134	3	143	134	9	130	-105	
3	53	19	5	42	-49	4	42	-49	1	434	405		
5	96	110	6	29	5	5	29	5	2	274	308		
0.26.L	0	425	361	7	46	-19	6	46	-19	3	296	-268	
2	281	-276	8	143	134	7	143	134	4	142	-130		
4	171	-159	9	42	-49	8	42						

4.11.L	5.11.L	6.10.L	7.10.L	8.10.L
0 81 67	1 146 -164	0 308 248	1 73 -39	0 172 -179
4.12.L	2 193 -211	1 336 -368	2 270 -246	1 121 -116
0 390 -397	3 276 378	2 321 413	3 229 218	2 179 167
1 107 -100	4 208 328	3 107 193	4 148 221	3 77 71
2 143 124	5 92 -43	4 58 -74	5 48 -23	4 56 44
3 10 -13	6 98 -38	5 187 198	6 90 -24	5 56 59
4 129 119	5.12.L	6.11.L	7.11.L	8.11.L
5 48 48	1 183 -188	0 176 -169	1 134 -126	0 195 -221
4.13.L	2 187 159	1 149 -18	2 33 -4	1 195 -221
0 36 -5	3 183 218	2 128 124	3 227 236	2 291 -268
1 64 69	4 108 -119	3 49 88	4 32 -39	3 92 80
2 26 4	5 85 -108	4 72 40	5 104 -117	4 54 29
3 37 -28	6.12.L	7.12.L	8.12.L	9.12.L
4 22 3	1 89 167	0 136 -140	1 37 -21	0 111 216
4.14.L	2 160 167	1 147 121	2 190 202	1 131 139
0 39 87	3 84 -33	2 47 97	3 154 -184	2 121 -131
1 27 30	4 109 -136	3 69 -46	4 154 -184	3 24 -29
2 46 -89	5.14.L	6.14.L	7.14.L	8.14.L
5.0.L	1 74 74	0 28 11	1 74 84	0 42 40
1 222 -144	2 32 -48	1 70 85	2 90 -117	1 62 -92
2 2042 2082	8.0.L	6.13.L	8.0.L	2 36 -29
3 1146 1135	0 345 332	0 172 244	0 983 1015	3 554 581
4 159 -853	1 1215 1243	1 88 103	1 1002 1037	4 310 -423
5 457 -409	2 682 587	2 80 -89	2 576 -619	5 317 -521
6 349 -301	3 292 -269	3 24 17	3 31 34	6 610 613
7 178 -166	4 36 -64	6.14.L	4 310 -423	7 161 157
8 359 344	5 161 -159	0 67 67	5 317 -521	8 163 -150
9 287 304	6 217 -219	7.0.L	6 610 613	9 223 -222
10 66 -87	7 428 412	1 30 49	7 168 -178	9.0.L
5.1.L	8 195 199	2 1042 1047	8 33 -26	0 42 40
1 422 393	9 115 -139	3 61 34	9 33 -26	1 62 -92
2 1658 1629	6.1.L	4 838 -901	8.1.L	2 36 -29
3 594 -481	0 867 970	5 203 170	0 486 556	3 554 581
4 873 -879	1 726 770	6 134 135	1 655 -693	4 310 -423
5 163 201	2 486 -443	7 148 -139	2 169 -191	5 317 -521
6 40 -24	3 281 309	8 268 298	3 152 151	6 610 613
7 89 89	4 464 -466	9 84 -80	4 151 -146	7 161 157
8 135 311	5 158 -168	7.1.L	5 400 350	8 163 -150
9 112 -126	6 561 511	1 614 614	6 289 291	9 223 -222
10 186 -218	7 135 133	2 98 -193	7 453 -464	9.1.L
5.2.L	8 227 -233	3 1014 -1043	8 135 -136	0 42 40
1 426 264	9 25 -25	4 218 186	9 34 25	1 62 -92
2 595 -331	6.2.L	5 265 269	8.2.L	2 36 -29
3 1505 -1515	0 1802 1109	6 169 -190	0 647 -649	3 554 581
4 451 419	1 866 -826	7 237 244	1 94 -72	4 310 -423
5 417 444	2 625 -614	8 145 -146	2 423 427	5 317 -521
6 126 -131	3 98 -169	9 263 -277	3 339 366	6 610 613
7 181 158	4 223 -270	7.2.L	4 48 38	7 161 157
8 45 -24	5 746 763	1 383 -421	5 72 -48	8 163 -150
9 287 -265	6 434 398	2 811 -823	6 285 -292	9 223 -222
5.3.L	7 434 -443	3 774 766	7 223 -206	9.2.L
1 456 -466	8 127 -139	4 548 553	8 230 237	0 42 40
2 806 -779	9 67 -55	5 127 -128	9 117 136	1 62 -92
3 574 558	6.3.L	6 44 -31	8.3.L	2 36 -29
4 639 641	0 223 -274	7 223 -214	0 606 -665	3 554 581
5 95 57	1 249 -197	8 265 -265	1 658 696	4 310 -423
6 86 57	2 534 532	9 155 148	2 151 177	5 317 -521
7 162 -136	3 45 -13	7.3.L	3 44 78	6 610 613
8 287 -292	4 293 248	1 365 -382	4 174 202	7 161 157
9 137 139	5 258 248	2 811 -823	5 369 -370	8 163 -150
5.4.L	6 297 -335	3 774 766	6 293 -267	9 223 -222
1 415 -437	7 95 -106	4 548 553	7 376 371	9.4.L
2 656 647	8 208 258	5 127 -128	8 125 129	0 42 40
3 756 726	9 40 39	6 44 -31	9 21 -4	1 62 -92
4 637 -625	6.4.L	7 223 -214	8.4.L	2 36 -29
5 349 -345	0 260 -320	8 265 -265	0 565 794	3 554 581
6 184 -170	1 475 433	9 155 148	1 588 626	4 310 -423
7 106 -84	2 225 156	7.4.L	2 350 -367	5 317 -521
8 266 289	3 232 -247	1 365 -382	3 180 -150	6 610 613
9 229 237	4 93 19	2 811 -823	4 416 -412	7 161 157
5.5.L	5 184 -121	3 774 766	5 441 -421	8 163 -150
1 182 181	6 121 -104	4 548 553	6 467 474	9 223 -222
2 845 861	7 343 341	5 127 -128	7 254 251	9.5.L
3 927 -447	8 133 153	6 44 -31	8 136 -131	0 42 40
4 666 -649	9 86 -111	7 223 -214	9 31 -23	1 62 -92
5 201 154	6.5.L	8 265 -265	8.5.L	2 36 -29
6 55 38	0 853 929	9 155 148	0 219 192	3 554 581
7 30 -19	1 498 536	7.5.L	1 610 -637	4 310 -423
8 286 266	2 574 -563	1 365 -382	2 350 -367	5 317 -521
9 92 -66	3 85 -63	2 811 -823	3 180 -150	6 610 613
5.6.L	4 365 -389	3 774 766	4 416 -412	7 161 157
1 454 497	5 299 -338	4 548 553	5 441 -421	8 163 -150
2 157 -136	6 461 459	5 127 -128	6 467 474	9 223 -222
3 1166 -1143	7 195 198	6 44 -31	7 254 251	9.6.L
4 147 142	8 173 -189	7 223 -214	8 136 -131	0 42 40
5 393 351	9 22 -1	8 265 -265	9 31 -23	1 62 -92
6 155 -151	6.6.L	9 155 148	8.6.L	2 36 -29
7 144 131	0 416 444	7.6.L	0 512 -487	3 554 581
8 51 -44	1 647 -734	1 365 -382	1 212 -206	4 310 -423
9 221 -222	2 429 -436	2 811 -823	2 212 -206	5 317 -521
5.7.L	3 168 -89	3 774 766	3 151 154	6 610 613
1 427 -375	4 258 -242	4 548 553	4 100 98	7 161 157
2 581 -555	5 546 534	5 127 -128	5 37 20	8 163 -150
3 584 541	6 285 288	6 44 -31	6 243 -254	9 223 -222
4 379 409	7 359 -358	7 223 -214	7 171 -170	9.7.L
5 171 -162	8 82 -77	8 265 -265	8 165 184	0 42 40
6 56 14	6.7.L	9 155 148	8.7.L	1 62 -92
7 199 -194	0 354 -382	7.7.L	0 470 -442	2 36 -29
8 204 -212	1 105 -96	1 365 -382	1 526 561	3 554 581
5.8.L	2 288 275	2 811 -823	2 179 186	4 310 -423
1 155 -127	3 86 55	3 774 766	3 75 96	5 317 -521
2 488 449	4 99 56	4 548 553	4 153 117	6 610 613
3 445 470	5 38 54	5 127 -128	5 340 -343	7 161 157
4 216 -247	6 272 -272	6 44 -31	6 265 -277	8 163 -150
5 234 -234	7 143 -136	7 223 -214	7 227 245	9 223 -222
6 84 -68	8 148 148	8 265 -265	8 68 74	9.8.L
7 91 -77	6.8.L	9 155 148	8.8.L	0 42 40
8 123 143	0 354 -382	7.8.L	0 518 547	1 62 -92
5.9.L	1 105 -96	1 365 -382	1 387 384	2 36 -29
1 51 31	2 288 275	2 811 -823	2 225 -219	3 554 581
2 353 379	3 86 55	3 774 766	3 78 49	4 310 -423
3 38 -38	4 99 56	4 548 553	4 267 -275	5 317 -521
4 298 -261	5 38 54	5 127 -128	5 316 34	6 610 613
5 139 151	6 272 -272	6 44 -31	6 265 -277	7 161 157
6 49 28	7 143 -136	7 223 -214	7 227 245	8 163 -150
7 37 -16	8 148 148	8 265 -265	8 68 74	9 223 -222
5.10.L	6.9.L	9 155 148	8.9.L	9.9.L
1 894 279	0 430 404	7.9.L	0 518 547	0 42 40
2 61 -48	1 258 246	1 365 -382	1 387 384	1 62 -92
3 355 -352	2 177 -162	2 811 -823	2 225 -219	2 36 -29
4 86 111	3 41 -6	3 774 766	3 78 49	3 554 581
5 179 179	4 217 -273	4 548 553	4 267 -275	4 310 -423
6 44 -153	5 181 -191	5 127 -128	5 316 34	5 317 -521
7 68 67	6 270 263	6 44 -31	6 265 -277	6 610 613
	7 104 103	7 223 -214	7 111 -117	7 161 157

9.11.1	4	518	945	12.4.1	1	409	-409	13.9.1	1	46	-38	15.8.1	1	46	-49
2	184	221	78	2	300	-300	2	151	135	2	41	-37	2	41	-37
3	102	-102	103	3	209	209	3	72	54	3	23	-19	3	23	-19
4	159	-171	-167	4	103	103	4	159	-172	4	159	-172	4	159	-172
9.12.1	1	84	83	5	103	103	5	103	103	5	103	103	5	103	103
2	68	-59	-536	6	103	103	6	103	103	6	103	103	6	103	103
3	138	-179	34	7	103	103	7	103	103	7	103	103	7	103	103
10.0.1	0	171	209	8	103	103	8	103	103	8	103	103	8	103	103
1	635	-640	34	9	103	103	9	103	103	9	103	103	9	103	103
2	114	-152	649	10	103	103	10	103	103	10	103	103	10	103	103
3	77	48	53	11	103	103	11	103	103	11	103	103	11	103	103
4	250	269	298	12	103	103	12	103	103	12	103	103	12	103	103
5	267	310	298	13	103	103	13	103	103	13	103	103	13	103	103
6	177	159	298	14	103	103	14	103	103	14	103	103	14	103	103
7	231	-269	298	15	103	103	15	103	103	15	103	103	15	103	103
8	181	-190	298	16	103	103	16	103	103	16	103	103	16	103	103
10.1.1	0	1009	-1027	17	103	103	17	103	103	17	103	103	17	103	103
1	422	-423	29	18	103	103	18	103	103	18	103	103	18	103	103
2	376	402	119	19	103	103	19	103	103	19	103	103	19	103	103
3	61	29	194	20	103	103	20	103	103	20	103	103	20	103	103
4	382	394	194	21	103	103	21	103	103	21	103	103	21	103	103
5	311	306	194	22	103	103	22	103	103	22	103	103	22	103	103
6	446	-422	194	23	103	103	23	103	103	23	103	103	23	103	103
7	245	-242	194	24	103	103	24	103	103	24	103	103	24	103	103
8	108	128	194	25	103	103	25	103	103	25	103	103	25	103	103
10.2.1	0	840	-897	26	103	103	26	103	103	26	103	103	26	103	103
1	666	748	29	27	103	103	27	103	103	27	103	103	27	103	103
2	245	237	119	28	103	103	28	103	103	28	103	103	28	103	103
3	120	89	194	29	103	103	29	103	103	29	103	103	29	103	103
4	271	269	194	30	103	103	30	103	103	30	103	103	30	103	103
5	480	-429	194	31	103	103	31	103	103	31	103	103	31	103	103
6	404	-405	194	32	103	103	32	103	103	32	103	103	32	103	103
7	241	261	194	33	103	103	33	103	103	33	103	103	33	103	103
8	185	91	194	34	103	103	34	103	103	34	103	103	34	103	103
10.3.1	0	130	641	35	103	103	35	103	103	35	103	103	35	103	103
1	225	264	119	36	103	103	36	103	103	36	103	103	36	103	103
2	815	-332	194	37	103	103	37	103	103	37	103	103	37	103	103
3	68	-87	194	38	103	103	38	103	103	38	103	103	38	103	103
4	210	-152	194	39	103	103	39	103	103	39	103	103	39	103	103
5	183	-179	194	40	103	103	40	103	103	40	103	103	40	103	103
6	323	350	194	41	103	103	41	103	103	41	103	103	41	103	103
7	161	164	194	42	103	103	42	103	103	42	103	103	42	103	103
8	110	-119	194	43	103	103	43	103	103	43	103	103	43	103	103
10.4.1	0	315	314	44	103	103	44	103	103	44	103	103	44	103	103
1	406	-415	194	45	103	103	45	103	103	45	103	103	45	103	103
2	66	-77	194	46	103	103	46	103	103	46	103	103	46	103	103
3	32	-31	194	47	103	103	47	103	103	47	103	103	47	103	103
4	133	129	194	48	103	103	48	103	103	48	103	103	48	103	103
5	211	221	194	49	103	103	49	103	103	49	103	103	49	103	103
6	130	129	194	50	103	103	50	103	103	50	103	103	50	103	103
7	197	-221	194	51	103	103	51	103	103	51	103	103	51	103	103
8	127	-141	194	52	103	103	52	103	103	52	103	103	52	103	103
10.5.1	0	699	-712	53	103	103	53	103	103	53	103	103	53	103	103
1	379	-360	194	54	103	103	54	103	103	54	103	103	54	103	103
2	554	364	194	55	103	103	55	103	103	55	103	103	55	103	103
3	56	-32	194	56	103	103	56	103	103	56	103	103	56	103	103
4	224	241	194	57	103	103	57	103	103	57	103	103	57	103	103
5	241	273	194	58	103	103	58	103	103	58	103	103	58	103	103
6	336	-436	194	59	103	103	59	103	103	59	103	103	59	103	103
7	179	-193	194	60	103	103	60	103	103	60	103	103	60	103	103
8	107	110	194	61	103	103	61	103	103	61	103	103	61	103	103
10.6.1	0	667	-689	62	103	103	62	103	103	62	103	103	62	103	103
1	561	555	194	63	103	103	63	103	103	63	103	103	63	103	103
2	219	205	194	64	103	103	64	103	103	64	103	103	64	103	103
3	90	89	194	65	103	103	65	103	103	65	103	103	65	103	103
4	270	251	194	66	103	103	66	103	103	66	103	103	66	103	103
5	378	-377	194	67	103	103	67	103	103	67	103	103	67	103	103
6	266	-279	194	68	103	103	68	103	103	68	103	103	68	103	103
7	219	217	194	69	103	103	69	103	103	69	103	103	69	103	103
10.7.1	0	390	422	70	103	103	70	103	103	70	103	103	70	103	103
1	137	158	194	71	103	103	71	103	103	71	103	103	71	103	103
2	217	-220	194	72	103	103	72	103	103	72	103	103	72	103	103
3	78	-59	194	73	103	103	73	103	103	73	103	103	73	103	103
4	136	-132	194	74	103	103	74	103	103	74	103	103	74	103	103
5	93	-85	194	75	103	103	75	103	103	75	103	103	75	103	103
6	179	221	194	76	103	103	76	103	103	76	103	103	76	103	103
7	107	113	194	77	103	103	77	103	103	77	103	103	77	103	103
10.8.1	0	174	163	78	103	103	78	103	103	78	103	103	78	103	103
1	174	-166	194	79	103	103	79	103	103	79	103	103	79	103	103
2	119	-106	194	80	103	103	80	103	103	80	103	103	80	103	103
3	72	62	194	81	103	103	81	103	103	81	103	103	81	103	103
4	40	5	194	82	103	103	82	103	103	82	103	103	82	103	103
5	138	164	194	83	103	103	83	103	103	83	103	103	83	103	103
6	116	108	194	84	103	103	84	103	103	84	103	103	84	103	103
10.9.1	0	328	-341	85	103	103	85	103	103	85	103	103	85	103	103
1	216	-214	194	86	103	103	86	103	103	86	103	103	86	103	103
2	143	150	194	87	103	103	87	103	103	87	103	103	87	103	103
3	29	-29	194	88	103	103	88	103	103	88	103	103	88	103	103
4	131	139	194	89	103	103	89	103	103	89	103	103	89	103	103
5	104	172	194	90	103	103	90	103	103	90	103	103	90	103	103
6	160	-174	194	91	103	103	91	103	103	91	103	103	91	103	103
10.10.1	0	222	-239	92	103	103	92	103	103	92	103	103	92	103	103
1	275	268	194	93	103	103	93	103	103	93	103	103	93	103	103
2	113	113	194	94	103	103	94	103	103	94	103	103	94	103	103
3	84	-2	194	95	103	103	95	103	103	95	103	103	95	103	103
4	78	60	194	96	103	103	96	103	103	96	103	103	96	103	103
5	151	-166	194	97	103	103	97	103	1						

Table 5

Atomic parameters for Propylpentamminerhodium(III) Perchlorate

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$
Rh	0.61493(4)	$\frac{1}{4}$	0.33902(9)
Cl	0.36225(11)	0.49921(15)	0.15859(23)
N 1	0.5316(6)	$\frac{1}{4}$	0.1376(12)
N 2	0.7265(5)	$\frac{1}{4}$	0.1604(10)
N 3	0.7000(6)	$\frac{1}{4}$	0.5396(11)
N 4	0.6161(4)	0.4212(5)	0.3356(8)
O 1	0.3416(7)	0.4045(8)	0.0704(13)
O 2	0.3494(10)	0.5977(9)	0.0877(15)
O 3	0.4396(7)	0.4937(11)	0.2262(24)
O 4	0.3065(7)	0.5017(9)	0.2971(11)
C 1	0.5102(16)	0.226(8)	0.505(4)
C 3	0.3952(10)	$\frac{1}{4}$	0.6907(21)

Atomic parameters for the disordered Methylene Group

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}(\overset{\circ}{\text{A}}^2)$
C 21	0.434(8)	$\frac{1}{4}$	0.458(16)	8.5(3.0)
C 22	0.499(5)	$\frac{1}{4}$	0.637(9)	5.0(1.4)
C 23	0.477(4)	0.305(4)	0.591(7)	5.3(1.0)
C 24	0.448(2)	0.282(3)	0.522(5)	2.5(0.6)

Estimated Hydrogen Parameters

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}(\overset{\circ}{\text{A}}^2)$
H 21	0.740	0.175	0.117	4.4
H 22	0.780	$\frac{1}{4}$	0.167	4.4
H 41	0.660	0.450	0.280	5.4
H 42	0.570	0.463	0.317	5.4
H 43	0.610	0.438	0.417	5.4

The hydrogen atoms are labelled H $\underline{mn}$ where $\underline{m}$ is the number of the ammine nitrogen, and $\underline{n}$ is the atom number. These positions were observed from a difference Fourier, with a probable accuracy of ± 0.2 Å.

Table 6

Anisotropic thermal parameters for Propylpentamminerhodium(III) Perchlorate.

Atom	$\underline{B}_{11}$	$\underline{B}_{22}$	$\underline{B}_{33}$	$\underline{B}_{12}$	$\underline{B}_{13}$	$\underline{B}_{23}$
Rh	.00336(3)	.00636(5)	.01426(12)	0	.00112(5)	0
Cl	.00490(8)	.00783(13)	.0177(3)	-.00024(8)	-.0005(1)	.0001(2)
N 1	.0046(4)	.0087(7)	.024(2)	0	-.0017(8)	0
N 2	.0037(3)	.0070(6)	.0184(15)	0	.0018(6)	0
N 3	.0062(5)	.0089(7)	.016(2)	0	-.0009(7)	0
N 4	.0062(3)	.0080(5)	.0215(12)	.0010(3)	-.0000(5)	-.0021(7)
O 1	.0170(8)	.0259(13)	.063(3)	-.0088(9)	.006(1)	-.028(2)
O 2	.0284(14)	.0224(13)	.072(4)	.003(1)	-.009(2)	.028(2)
O 3	.0111(6)	.0295(16)	.177(8)	.006(1)	-.029(2)	-.017(3)
O 4	.0181(8)	.0293(14)	.042(2)	-.009(1)	.014(1)	-.013(2)
C 1	.011(2)	.044(12)	.048(6)	.011(5)	.017(3)	.006(9)
C 3	.0073(9)	.032(3)	.031(4)	0	.007(2)	0

Table 7

Observed and Calculated Structure Factors (in electrons x 10)
for Propylpentamminerhodium(III) Perchlorate.

* indicates unobserved reflection

Tabulated as:

$\underline{l}$, $\underline{F}_O$, $\underline{F}_C$ for each group with constant h , k .

0.0.L	7	148	174	7.3.L	7	244	-274	2	131	-144		
2	1735	-1244	104	1	1100	1044	1	144	134	124		
4	1277	-1307	139	1	22	-7	0	108	271	4	114	221
4	1234	1172	1.4.L	3	276	-228	1	3.9.L	4	194	244	
4	129	-147	1	3	174	171	1	1020	1044	7	141	211
0.1.L	1	434	467	4	444	-501	3	110	114	4	11	24
2	541	-544	5	704	-5	3	110	114	4	11	24	
3	357	-243	6	504	512	3	110	114	4	11	24	
4	687	741	7	44	54	3	110	114	4	11	24	
5	144	131	8	72	-44	3	110	114	4	11	24	
6	114	104	9	72	-44	3	110	114	4	11	24	
7	324	-343	0	144	154	3	110	114	4	11	24	
8	44	-44	1	144	154	3	110	114	4	11	24	
9	104	-94	2	144	154	3	110	114	4	11	24	
0.2.L	1	164	-44	3	144	154	3	110	114	4	11	24
2	374	-444	4	144	154	3	110	114	4	11	24	
4	407	357	5	144	154	3	110	114	4	11	24	
4	314	-337	6	144	154	3	110	114	4	11	24	
4	34	34	7	144	154	3	110	114	4	11	24	
0.3.L	1	410	844	8	144	154	3	110	114	4	11	24
3	104	74	9	144	154	3	110	114	4	11	24	
4	114	-793	0	144	154	3	110	114	4	11	24	
7	237	234	1	144	154	3	110	114	4	11	24	
9	41	74	2	144	154	3	110	114	4	11	24	
0.4.L	1	630	-598	3	144	154	3	110	114	4	11	24
2	394	358	4	144	154	3	110	114	4	11	24	
3	944	1044	5	144	154	3	110	114	4	11	24	
4	192	-118	6	144	154	3	110	114	4	11	24	
5	221	-274	7	144	154	3	110	114	4	11	24	
6	234	15	8	144	154	3	110	114	4	11	24	
7	324	-307	9	144	154	3	110	114	4	11	24	
8	54	44	0	144	154	3	110	114	4	11	24	
0.5.L	1	346	342	1	144	154	3	110	114	4	11	24
2	473	491	2	144	154	3	110	114	4	11	24	
3	381	-366	3	144	154	3	110	114	4	11	24	
4	366	-364	4	144	154	3	110	114	4	11	24	
5	106	101	5	144	154	3	110	114	4	11	24	
6	97	-71	6	144	154	3	110	114	4	11	24	
7	148	132	7	144	154	3	110	114	4	11	24	
8	179	173	8	144	154	3	110	114	4	11	24	
0.6.L	1	74	75	9	144	154	3	110	114	4	11	24
2	590	-603	0	144	154	3	110	114	4	11	24	
4	105	-98	1	144	154	3	110	114	4	11	24	
4	411	427	2	144	154	3	110	114	4	11	24	
5	123	118	3	144	154	3	110	114	4	11	24	
6	184	143	4	144	154	3	110	114	4	11	24	
7	56	55	5	144	154	3	110	114	4	11	24	
8	194	-189	6	144	154	3	110	114	4	11	24	
0.7.L	1	205	-203	7	144	154	3	110	114	4	11	24
2	247	-293	8	144	154	3	110	114	4	11	24	
3	223	233	9	144	154	3	110	114	4	11	24	
4	233	229	0	144	154	3	110	114	4	11	24	
5	58	-60	1	144	154	3	110	114	4	11	24	
6	46	28	2	144	154	3	110	114	4	11	24	
7	100	-93	3	144	154	3	110	114	4	11	24	
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3	72	-80	5	144	154	3	110	114	4	11	24	
5	424	411	6	144	154	3	110	114	4	11	24	
7	157	-153	7	144	154	3	110	114	4	11	24	
0.10.L	1	113	-111	8	144	154	3	110	114	4	11	24
2	174	-171	9	144	154	3	110	114	4	11	24	
3	139	142	0	144	154	3	110	114	4	11	24	
4	121	123	1	144	154	3	110	114	4	11	24	
0.11.L	1	105	-116	2	144	154	3	110	114	4	11	24
2	27	24	3	144	154	3	110	114	4	11	24	
3	186	199	4	144	154	3	110	114	4	11	24	
2.0.L	1	125	-33	5	144	154	3	110	114	4	11	24
2	264	49	6	144	154	3	110	114	4	11	24	
3	323	328	7	144	154	3	110	114	4	11	24	
4	74	-51	8	144	154	3	110	114	4	11	24	
5	628	580	9	144	154	3	110	114	4	11	24	
6	304	36	0	144	154	3	110	114	4	11	24	
7	188	-207	1	144	154	3	110	114	4	11	24	
8	314	17	2	144	154	3	110	114	4	11	24	
9	30	-29	3	144	154	3	110	114	4	11	24	
2.1.L	1	105	-116	4	144	154	3	110	114	4	11	24
2	27	24	5	144	154	3	110	114	4	11	24	
3	186	199	6	144	154	3	110	114	4	11	24	
2.2.L	1	125	-33	7	144	154	3	110	114	4	11	24
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3	323	328	9	144	154	3	110	114	4	11	24	
4	74	-51	0	144	154	3	110	114	4	11	24	
5	628	580	1	144	154	3	110	114	4	11	24	
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7	188	-207	3	144	154	3	110	114	4	11	24	
8	314	17	4	144	154	3	110	114	4	11	24	
9	30	-29	5	144	154	3	110	114	4	11	24	
2.3.L	1	105	-116	6	144	154	3	110	114	4	11	24
2	27	24	7	144	154	3	110	114	4	11	24	
3	186	199	8	144	154	3	110	114	4	11	24	
2.4.L	1	125	-33	9	144	154	3	110	114	4	11	24
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3	323	328	1	144	154	3	110	114	4	11	24	
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7	188	-207	5	144	154	3	110	114	4	11	24	
8	314	17	6	144	154	3	110	114	4	11	24	
9	30	-29	7	144	154	3	110	114	4	11	24	
2.5.L	1	105	-116	8	144	154	3	110	114	4	11	24
2	27	24	9	144	154	3	110	114	4	11	24	
3	186	199	0	144	154	3	110	114	4	11	24	
2.6.L	1	125	-33	1	144	154	3	110	114	4	11	24
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3	323	328	3	144	154	3	110	114	4	11	24	
4	74	-51	4	144	154	3	110	114	4	11	24	
5	628	580	5	144	154	3	110	114	4	11	24	
6	304	36	6	144	154	3	110	114	4	11	24	
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9	30	-29	9	144	154	3	110	114	4	11	24	
2.7.L	1	105	-116	0	144	154	3	110	114	4	11	24
2	27	24	1	144	154	3	110	114	4	11	24	
3	186	199	2	144	154	3	110	114	4	11	24	
2.8.L	1	125	-33	3	144	154	3	110	114	4	11	24
2	264	49	4	144	154	3	110	114	4	11	24	
3	323	328	5	144	154	3	110	114	4	11	24	
4	74	-51	6	144	154	3	110	114	4	11	24	
5	628	580	7	144	154	3	110	114	4	11	24	
6	304	36	8	144	154	3	110	114	4	11	24	
7	188	-207	9	144	154	3	110	114	4	11	24	
8	314	17	0	144	154	3	110	114	4	11	24	
9	30	-29	1	144	154	3	110	114	4	11	24	
2.9.L	1	105	-116	2	144	154	3	110	114	4	11	24
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3	186	199	4	144	154	3	110	114	4	11	24	
3.0.L	1	125	-33	5	144	154	3	110	114	4	11	24
2	264	49	6	144	154	3	110	114	4	11	24	
3	323	328	7	144	154	3	110	114	4	11	24	
4	74	-51	8	144	154	3	110	114	4	11	24	
5	628	580	9	144	154	3	110	114	4	11	24	
6	304	36	0	144	154	3	110	114	4	11	24	
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5	208	-213	6	7.0.1	1270	9	404	404	3	211	274	
6	101	-96	1	233	-322	10	404	404	4	21	274	
7	418	223	2	1222	1270	11	404	404	5	41	274	
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24			19	122	1270	28	404	404	22	41	274	
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39			34	122	1270	43	404	404	37	41	274	
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67			62	122	1270	71	404	404	65	41	274	
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70			65	122	1270	74	404	404	68	41	274	
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77			72	122	1270	81	404	404	75	41	274	
78			73	122	1270	82	404	404	76	41	274	
79			74	122	1270	83	404	404	77	41	274	
80			75	122	1270	84	404	404	78	41	274	
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101			96	122	1270	105	404	404	99	41	274	
102			97	122	1270	106	404	404	100	41	274	
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106			101	122	1270	110	404	404	104	41	274	
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108			103	122	1270	112	404	404	106	41	274	
109			104	122	1270	113	404	404	107	41	274	
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112			107	122	1270	116	404	404	110	41	274	
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126			121	122	1270	130	404	404	124	41	274	
127			122	122	1270	131	404	404	125	41	274	
128			123	122	1270	132	404	404	126	41	274	
129			124	122	1270	133	404	404	127	41	274	
130			125	122	1270	134	404	404	128	41	274	
131			126	122	1270	135	404	404	129	41	274	
132			127	122	1270	136	404	404	130	41	274	
133			128	122	1270	137	404	404	131	41	274	
134			129	122	1270	138	404	404	132	41	274	
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137	</											

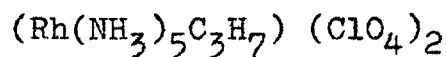
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Table 8
Selected bondlengths

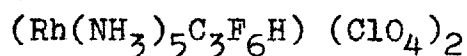
(Rh(NH ₃) ₅ C ₃ F ₆ H) (ClO ₄) ₂		(Rh(NH ₃) ₅ C ₃ H ₇) (ClO ₄) ₂	
Atoms	dist	Atoms	dist
Rh - N 1	2.072(11)	Rh - N 1	2.072(9)
Rh - N 2	2.170(11)	Rh - N 2	2.258(8)
Rh - N 3	2.097(11)	Rh - N 3	2.084(9)
Rh - N 4	2.084(10)	Rh - N 4	2.071(6)
Rh - C 1	2.074(18)	Rh - C 1	2.13(3)
Cl - O 1	1.31(2)	Cl - O 1	1.384(11)
Cl - O 2	1.28(2)	Cl - O 2	1.334(11)
Cl - O 3	1.390(11)	Cl - O 3	1.332(12)
Cl - O 4	1.430(10)	Cl - O 4	1.410(10)
C 1- C 2	1.44(3)	C 1- C 2 _{mean}	1.22(10)
C 2- C 2	1.61(2)	C 2- C 3 _{mean}	1.74(8)
C 1..C 3	2.55(2)	C 1..C 3	2.36(3)
C 1- F11	1.39(3)		
C 1- F12	1.63(2)		
C 2- F 2	1.28(3)		
C 3- F31	1.28(2)		
C 3- F32	1.20(2)		
C 3- F33	1.29(3)		
C - C _{mean}	1.53(3)		
C - F _{mean}	1.35(3)		

Table 9

Selected bond angles



Atoms	angle	Atoms	angle
N 1- Rh - N 2	90.1(0.3)	N 4- Rh - N 4 _I	178.2(0.3)
N 1- Rh - N 3	179.3(0.4)	N 4- Rh - C 1	98.7(2.7)
N 1- Rh - N 4	89.7(0.2)	C 1- Rh - N 4 _I	83.0(2.7)
N 1- Rh - C 1	89.6(0.8)	O 1- Cl - O 2	119.3(0.7)
N 2- Rh - N 3	89.2(0.3)	O 1- Cl - O 3	112.2(0.8)
N 2- Rh - N 4	89.1(0.2)	O 1- Cl - O 4	105.7(0.6)
N 2- Rh - C 1	172.1(2.7)	O 2- Cl - O 3	110.8(0.9)
N 3- Rh - N 4	90.3(0.2)	O 2- Cl - O 4	102.7(0.7)
N 3- Rh - C 1	91.1(0.8)	O 3- Cl - O 4	104.6(0.9)



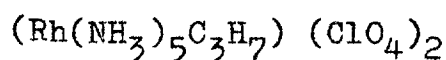
N 1- Rh - N 2	91.1(0.4)	O 2- Cl - O 4	108.7(1.0)
N 1- Rh - N 3	179.5(0.4)	O 3- Cl - O 4	121.2(0.7)
N 1- Rh - N 4	88.8(0.3)	Rh - C 1- C 2	118.1(1.3)
N 1- Rh - C 1	88.4(0.6)	Rh - C 1- F11	130.0(1.4)
N 2- Rh - N 3	88.3(0.4)	Rh - C 1- F12	98.9(1.0)
N 2- Rh - N 4	88.5(0.3)	C 2- C 1- F11	107.4(1.7)
N 2- Rh - C 1	169.0(0.5)	C 2- C 1- F12	84.1(1.3)
N 3- Rh - N 4	91.2(0.3)	F11- C 1- F12	105.5(1.6)
N 3- Rh - C 1	92.2(0.6)	C 1- C 2- C 3	113.5(1.6)
N 4- Rh - N 4 _I	176.1(0.4)	C 1- C 2- F 2	110.0(1.8)
N 4- Rh - C 1	102.5(0.5)	C 3- C 2- F 2	128.5(1.8)
C 1- Rh - N 4 _I	80.5(0.5)	C 2- C 3- F31	102.7(1.4)
O 1- Cl - O 2	103.4(1.4)	C 2- C 3- F32	97.0(1.6)
O 1- Cl - O 3	114.6(1.2)	C 2- C 3- F33	133.9(2.1)
O 1- Cl - O 4	98.1(1.1)	F31- C 3- F32	106.8(1.6)
O 2- Cl - O 3	109.2(1.0)	F31- C 3- F33	104.9(2.3)

Table 9 (Continued)

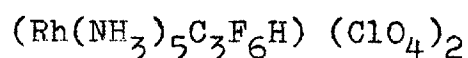
Atoms	angle	Atoms	angle
F32- C3- F33	109.2(2.7)	F32-F31 -F33	60.5(1.5)
F31-F32- F33	60.8(1.6)	F - C - F _{mean}	106.6(2.0)
F31-F33- F32	58.7(1.1)	C - C - F _{mean}	109.1(1.7)

Table 10

Selected non-bonded contacts



Atoms	dist	Atoms	dist
N 4...O 3	3.04	N 3...C 3 _V	3.75
N 1...O 3	3.36	C 3...O 1 _V	3.66
N 3...O 1 _{III}	3.04	C 1...O 3 _I	3.64
N 2...O 1 _{III}	3.37		



F11...F31	3.09	F 2...Rh	3.02
F11...F33	2.57	F12...N 1	2.64
F11...F2	3.40	F 2...N 4	2.66
F12...F31	2.58	N 4...F33 _{II}	2.90
F12...F 2	2.33	N 4...F11 _I	2.82
F 2...F31	2.92	O 3...N 4	3.06
F 2...F32	2.73	N 3...O 1 _{III}	3.03
F12...Rh	2.83	F 2...O 3 _{IV}	2.85

Roman subscripted atoms are related to those of the asymmetric unit by the operations:

$$\text{I} \quad x, \frac{1}{2}-y, z$$

$$\text{II} \quad 1-x, \frac{1}{2}+y, 1-z$$

$$\text{III} \quad \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$$

$$\text{IV} \quad 1-x, 1-y, 1-z$$

$$\text{V} \quad \frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$$

Table 11

Least-squares Planes

Distances of the atoms from the least-squares planes, in Å.

$$(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{F}_6\text{H})(\text{ClO}_4)_2$$

Rh	0.026
N 1	0.017
N 3	0.016
N 4	-0.029
N 4 _I	-0.029

Equation of the plane in direct space:

$$12.181\underline{x} - 5.179\underline{z} - 5.792 = 0$$

$$(\text{Rh}(\text{NH}_3)_5\text{C}_3\text{H}_7)(\text{ClO}_4)_2$$

Rh	0.018
N 1	0.005
N 3	0.005
N 4	-0.014
N 4 _I	-0.014

Equation of the plane in direct space:

$$12.120\underline{x} - 5.074\underline{z} - 5.751 = 0$$

Roman subscripted atoms are related to those of the asymmetric unit by the operation

$$\underline{x}, \quad \frac{1}{2} - \underline{y}, \quad \underline{z}$$

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"Es bildet ein Talent sich in der Stille,
Sich ein Charakter in dem Strom der Welt."
(Genius is formed in quiet, character in
the stream of human life).

... Goethe: Tasso, I. ii.

APPENDIX

Publications

The Insignificance of Metal–Metal Bonding in the Antiferromagnetism of Copper(II) Carboxylate Dimers

By D. M. L. GOODGAME,* N. J. HILL, D. F. MARSHAM, A. C. SKAPSKI,* M. L. SMART, and P. G. H. TROUGHTON
(*Department of Chemistry, Imperial College of Science and Technology, London, S.W.7*)

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The Insignificance of Metal-Metal Bonding in the Antiferromagnetism of Copper(II) Carboxylate Dimers

By D. M. L. GOODGAME,* N. J. HILL, D. F. MARSHAM, A. C. SKAPSKI,* M. L. SMART, and P. G. H. TROUGHTON
(Department of Chemistry, Imperial College of Science and Technology, London, S.W.7)

Summary Magnetic and structural studies on a pair of analogous copper(II) acetate and formate dimers suggest that metal-metal bonding is not important in explaining their antiferromagnetism.

THE antiferromagnetism of copper(II) acetate monohydrate has stimulated much experimental and theoretical work on this, and related compounds, in recent years. Bleaney and Bowers showed¹ that the antiferromagnetism could be explained by spin coupling of the form $-JS_1S_2$. However the coupling mechanism has been the subject of controversy, and various theoretical treatments have been advanced. Figgis and Martin suggested² a direct metal-metal, δ , bond between the two copper atoms, which are only 2.64 Å apart,³ but emphasized² that this would be weak (in line with subsequent orbital-overlap calculations⁴). Hansen and Ballhausen⁵ accounted for the observed g -values and electronic spectrum with a coupled chromophore model, without invoking any direct metal-metal bonding. Comparison with the very short Mo-Mo separation (2.11 Å) in $\text{Mo}(\text{OAc})_2$ ⁶ has been used⁷ as a basis for ruling out significant metal-metal bonding in the copper analogue, and the idea that the spin coupling proceeds predominantly by super exchange *via* the carboxylate bridges has become increasingly favoured.⁸

of their magnetic susceptibilities are summarized in Figure 1. Using the Bleaney and Bowers formula,¹ the J values, calculated from the experimental susceptibilities, the g -values determined from e.s.r. spectra, and with $N_A = 60 \times 10^{-6}$ c.g.s.u. are: acetate 305 cm.⁻¹, formate 485 cm.⁻¹. The greater spin exchange observed for the formate correlates well with the results for other dimeric copper(II) formate complexes.⁹

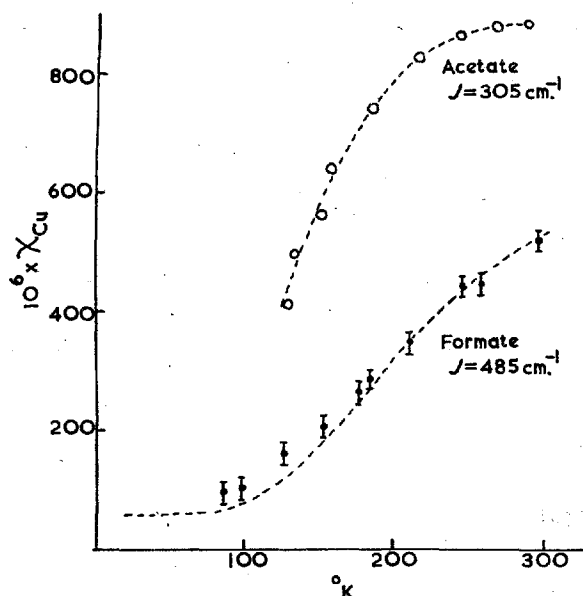


FIGURE 1. Temperature dependence of the magnetic susceptibilities of $(\text{Me}_4\text{N})_2[\text{Cu}(\text{RCO}_2)_2(\text{NCS})]_2$, ($\text{R} = \text{H}$ or Me). Dotted lines represent the calculated curves.

Direct experimental evidence to correlate the extent of spin exchange with copper-copper distance in strictly analogous compounds has been lacking hitherto. We have isolated the crystalline compounds $(\text{Me}_4\text{N})_2[\text{Cu}(\text{RCO}_2)_2(\text{NCS})]_2$ where $\text{R} = \text{H}$ or Me . The temperature variations

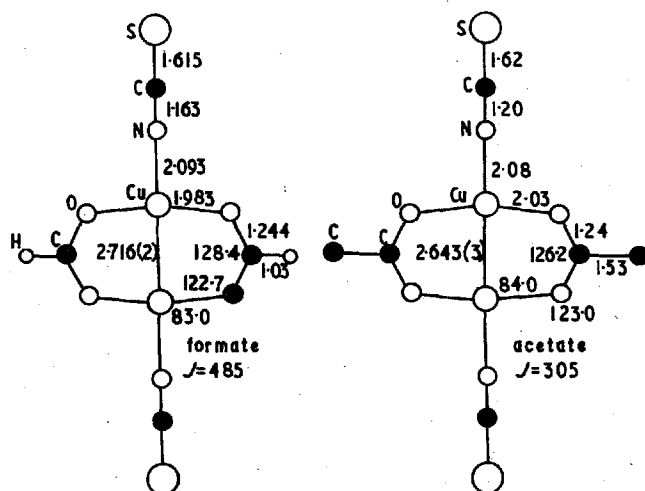


FIGURE 2. Standard deviations for the formate are: Cu-Cu, 0.002; Cu-O, 0.004; C-O, 0.008; Cu-N, 0.009; C-N, 0.014; C-S, 0.011 Å; Cu-Cu-O, 0.1; Cu-O-C, 0.3; O-C-O, 0.5°, and for the acetate: Cu-Cu, 0.003; Cu-O, 0.01; C-O, 0.02; C-C, 0.04; Cu-N, 0.02; C-N, 0.03; C-S, 0.02 Å; Cu-Cu-O, 0.3; Cu-O-C, 1.3; O-C-O, 1.3°.

The compounds formed green tetragonal crystals with the following unit-cell dimensions: $(\text{Me}_4\text{N})_2[\text{Cu}(\text{HCO}_2)_2(\text{NCS})]_2$, $a = 8.917$, $c = 15.800$ Å, $U = 1256.3$ Å³, $Z = 2$; $(\text{Me}_4\text{N})_2[\text{Cu}(\text{MeCO}_2)_2(\text{NCS})]_2$, $a = 8.873$, $c = 18.087$ Å, $U = 1424.0$ Å³, $Z = 2$. The space group for both is $I4/mmm$.

Three-dimensional X-ray data were collected on a Siemens four-circle automatic diffractometer using $\text{Cu-K}\alpha$ radiation. The structures were solved by standard methods and least-squares refinement of the formate has reached $R = 0.049$ for 381 reflections. For the acetate the refinement has been complicated by disorder among the acetate groups, and R is currently 0.099 for 421 reflections.

Figure 2 shows the main distances and angles of the two dimeric anions (in each case two of the bridging groups have been omitted for clarity). In both cases the copper atoms and the thiocyanate ligands lie on fourfold axes. In the acetate the $\text{Cu} \cdots \text{Cu}$ separation of 2.643 Å ($\sigma = 0.003$ Å) is typical of dimeric cupric acetate complexes.^{3,10} In the formate the $\text{Cu} \cdots \text{Cu}$ separation is 2.716 Å ($\sigma = 0.002$ Å). Despite this, however, the path length *via* the bridging ligands is shorter in the formate, with a concomitant readjustment of the relevant angles. There are no significant differences between the thiocyanate ligands in the two anions.

The formate-bridged complex therefore has a higher J value, more spin exchange, and yet the $\text{Cu} \cdots \text{Cu}$ separation is very significantly greater.

The above results suggest that any contribution to the spin exchange from a direct metal-metal bond is insignificant, as such an interaction would be expected to decrease rapidly with increasing copper-copper separation. It therefore seems probable that the carboxylate bridges play a major role in the spin-exchange process. This might be by a superexchange mechanism, as mentioned above, but, unfortunately, it is difficult to predict the magnitude or the effects of the structural differences on this process.

On the other hand it may be noted that all the models invoking a direct copper-copper bond (which are reviewed briefly in ref. 11), depend among other things on an energy difference between a pair of molecular orbitals of symmetry b_{1g} and b_{2u} , but this difference is not, as hitherto assumed, necessarily dependent on the existence of direct metal-metal bonding. These are antibonding orbitals involving $d_{x^2-y^2}$ orbitals and suitable molecular orbitals of the carboxylate ligands. The ligand orbitals involved in the b_{1g} and b_{2u} molecular orbitals of a copper(II) carboxylate are not the same; they belong to the irreducible representations A_1 and B_1 , respectively of C_{2v} , the point group of a carboxylate ion (neglecting the alkyl group). There is, therefore, no reason to believe that the copper-oxygen or oxygen-carbon bonding energies of b_{1g} and b_{2u} are identical. We may expect that there will therefore be

an energy difference between these states, even in the absence of a direct copper-copper interaction. Furthermore the splitting might conceivably increase with the copper-copper separation.

Such molecular orbital models have been criticized as being too simple.^{2,5} Interelectronic repulsion must be taken into account, in which case wave functions related to those of the "coupled chromophore" model are obtained. There will then be a singlet-triplet splitting due to electrostatic configuration interaction, and the effects of covalency will appear as a perturbation on the coupled chromophore states making an addition to the singlet-triplet splitting. Incidentally, this model is incompatible with a "six-level" theory for magnetic susceptibility such as was suggested by Jotham and Kettle.¹¹ The temperature dependencies of the susceptibilities predicted by their theory are insufficiently different from those predicted by the "four-level" theory for it to be possible to discriminate decisively between the theories on experimental grounds.

Whatever the relative importance of the contributions arising from the coupled chromophore model, or from the superexchange process, we conclude from our experimental evidence that direct metal-metal bonding plays only an insignificant role in determining the magnetic properties of these compounds.

We thank Professor D. Rogers for his interest in this work.

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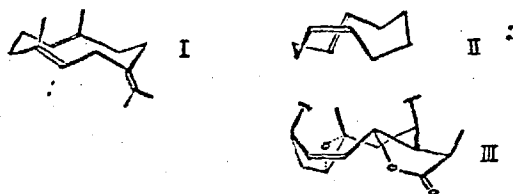
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In the two structures most of the corresponding bond lengths and bond angles are nearly identical. However, the angle C(4)-C(7)-N in the *anti*-form (132°) differs much from that in the *syn*-form (121°). This can be explained by the *anti*- and *syn*-arrangement of the two oximes. In the *anti*-form most of the strain between the oxygen atom and the hydrogen atom H(5) is compensated by the expansion of the C(4)-C(7)-N angle to 132° and by the rather large twist of the side chain around the bond C(4)-C(7). The angle between the side chain plane and the benzene ring plane are found to be 20° and 10° in the *anti*- and *syn*-form respectively.

It is also interesting to compare the molecular geometry of *anti*-*p*-chlorobenzaldoxime with that of the corresponding *p*-methylated oxime (III) (see the above and the below quoted papers), and with that of *anti*-2,6-dimethyl-4-chloro-*p*-methylbenzaldoxime (IV) (Gram Jensen and Jerslev, Acta Crystallogr. B 25, Part 4, 5, 6 or 7 (in press), 1969). In the latter paper the two *p*-methylated *anti*-oximes are compared. In all the four structures most of the corresponding bond lengths and bond angles agree quite well. The majority of the deviations can be ascribed to the different steric strains in the molecules and to the different bonding systems which may be expected for unmethylated oximes compared to *p*-methylated oximes.

In the *p*-chlorobenzaldoximes the molecules are linked together by inter-molecular O-H...N bonds. The *anti*-form (I) has a chain association, whereas the *syn*-form (II) is associated to dimers, as already established by Jerslev (Dissertation, Copenhagen, 1950). In the reinvestigation of I the refinement has been carried out by the full matrix least squares method to an R value of 0.06 [weighted R 0.07, $\nu = (F^2)^{-1}$]. All the hydrogen atoms were revealed from a difference-synthesis.



place of the *trans* double bond and a fused lactone ring.. One would expect heliangine, therefore, to behave differently in cyclisation reactions.

The *cis*-double bond is closely planar, but the *trans* double bond has an sp^2-sp^2 torsional strain of 22° , which is consistent with the observed greater reactivity of this double bond^(2,3)

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XIII-62. A CRYSTALLOGRAPHIC COMPARISON OF THE CONFORMATIONS OF CIS-CIS and CIS-TRANS 1:5 CYCLODECAADIENE RINGS.

By D. Rogers and M.L. Smart, Chemical Crystallography Laboratory, Imperial College, London, S.W.7.

An earlier study⁽¹⁾ has shown that germacratratriene(I), which contains a *trans-trans* 1:5 cyclodecadiene ring, cyclises to a *trans*-decalin derivative, and that its AgNO₃ adduct has a conformation that readily explains such a cyclisation. *Cis-trans* 1:5 cyclodecadiene, however, cyclises to *cis*-decalin derivatives.⁽²⁾ An X-ray study of the AgNO₃ adduct of *cis-trans* 1:5 cyclodecadiene (C₁₀H₁₆.AgNO₃) has been done to determine the ring conformation and to account for these different cyclisation products.

The crystals are monoclinic, $P2_1/n$, $a = 10.455$, $b = 9.487$, $c = 11.344$, $\beta = 95^\circ 52'$, $Z = 4$. Photographic data were collected from three encapsulated crystals. R is now 0.088 and still refining.

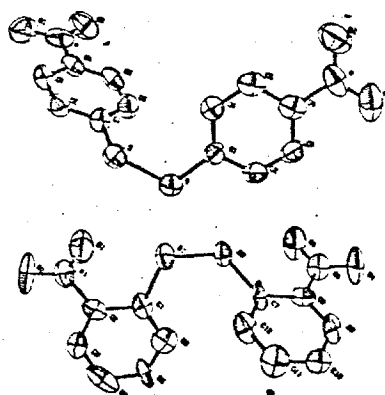
The crystal structure bears a marked similarity to that of germacratratriene AgNO₃, i.e. sheets of Ag and NO₃ ions alternating with sheets of olefin molecules. Each olefin bridges the gap between the ionic layers, and its two double bonds each coordinate to one Ag ion in adjacent layers, and each Ag ion coordinates to one *cis* and one *trans* double bond in different molecules, thus forming an infinite 3D network. The coordinations around the Ag and NO₃ ions are generally similar to those in the germacratratriene complex.

The conformation of the olefin(II) readily accounts for the cyclisation to *cis*-decalin, and, as in all previous studies of medium-sized polyolefin rings, the planes of the double bonds are almost perpendicular to the "plane" of the ring. The nearest analogue that has been studied by X-rays is heliangine(III)⁽³⁾, containing an epoxide ring in

XIII-63. THE CRYSTAL STRUCTURES OF ORTHO AND PARA-DINITRO-PHENYL DISULFIDES*. By John S. Ricci, Jr. and Ivan Bernal, State University of New York, Stony Brook, New York and Brookhaven National Laboratory, Upton, L. I., New York.

The crystal and molecular structures of the title compounds were determined from equi-inclination, integrated, Weissenberg data. Of particular interest to us were the effects of the nitro group substituents on the C-S and S-S bonding parameters.

Both isomers are monoclinic, the ortho crystallizing in $P2_1/c$ and the para in $C2/c$. The final R(F) factors are 6.2% and 7.6%, respectively, for the ortho and para structures. The average value of the C-S bond length for the ortho isomer is 1.796(8) Å and for the para isomer it is 1.820(28) Å respectively. The dihedral angles between the nitro groups and their phenyl rings



are: for the ortho isomer, $18.6(5)^\circ$ and $7.0(5)^\circ$ while the single independent value of this quantity for the para isomer is $8.2(5)^\circ$. In the ortho isomer there are short O...S contacts of 2.588(7) Å and 2.636(8) Å.

*Research supported in part by U. S. Atomic Energy Commission.

The Crystal Structure of Trimeric Palladium(II) Acetate

By A. C. SKAPSKI* and M. L. SMART

(Chemical Crystallography Laboratory, Imperial College of Science and Technology, London, S.W.7)

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The Crystal Structure of Trimeric Palladium(II) Acetate

By A. C. SKAPSKI* and M. L. SMART

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Summary Palladium(II) acetate has a trimeric structure, of approximate symmetry D_{3h} , in which each of the palladium atoms is joined to the other two by double acetate bridges.

THE title compound was first prepared by Wilkinson and his co-workers,¹ who suggested that it was trimeric, but could not distinguish between chelated and bridging acetate groups from the i.r. spectra. The compound is involved in numerous oxidation reactions with olefins, and has been used widely in industry, notably in the production of vinyl acetate from ethylene.²

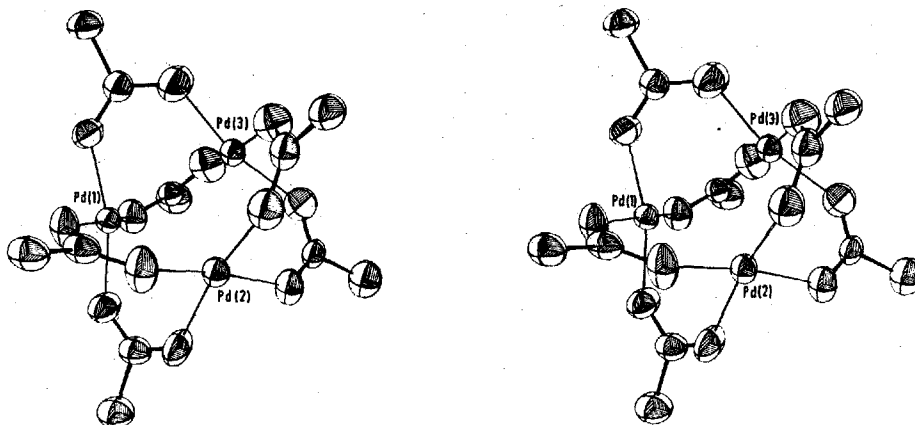
We have now determined the crystal structure of palladium(II) acetate and confirm that the molecules are trimeric, with only bridging acetate groups being used.

Diacetatopalladium(II) forms red-brown plates which are monoclinic, with unit-cell dimensions $a = 16.799$, $b = 29.482$, $c = 8.287$ Å, $\beta = 92^\circ 16'$, $U = 4101$ Å³, space group $P2_1/n$ (No. 14). The asymmetric unit ($Z = 4$) contains two trimers and a single water molecule, i.e. $2[\text{Pd}_3(\text{ac})_6] \cdot \text{H}_2\text{O}$ (ac = acetate); $D_m = 2.19$, $D_c = 2.18$ g cm⁻³. A second, violet, form of the compound has recently been reported.³

Three-dimensional X-ray data were collected on a Siemens four-circle automatic diffractometer. Using Cu-K α

radiation a total of 3325 independent reflections were measured (to $\theta = 45^\circ$) of which 97 were judged to be unobserved. The positions of the six independent palladium atoms were determined by the symbolic addition

square-planar co-ordination and reasonable angles at the co-ordinating oxygens. The Pd-Pd distances range between 3.105 and 3.203 Å. These differences are significant and probably reflect slight distortions caused by packing



FIGURE

procedure,⁴ and thereafter standard Fourier methods were used to locate the light atoms. Least-squares refinement has now reached $R = 0.036$.

The refinement has shown the two independent trimers to be almost identical, there being no chemically significant differences between them. The structure of one such trimer is shown in the Figure. The molecules consist of a nearly equilateral triangle of palladium atoms (*ca.* 3.15 Å apart) which are joined together by double acetate bridges such that the co-ordination at the metal atoms is approximately square-planar. A certain amount of strain is involved in such a structure, and this seems a likely explanation for the relatively low stability of the trimeric molecule.¹ To relieve some of this strain the metal atoms are pushed out of the 'plane' of the oxygens *ca.* 0.25 Å towards the centre of the triangle. This allows tolerable angles to be achieved at the acetate bridges. The main distortion here is at the Pd-O-C angles (see Table), the more rigid O-C-O groups are opened out less. The Pd-O distances are normal. Although the palladium atoms are pushed towards each other, no metal-metal bonding is involved, the position of the metal atoms being a compromise between

requirements. The symmetry of the trimers is very nearly $\bar{6}m2$ (D_{3h}), yet the packing of the molecules is such that none of this potential symmetry is utilised.

TABLE

	Range	σ	No. of independent values	Average
Pd-O	1.973—2.014 Å	0.009 Å	24	1.992 Å
Pd-Pd (non bonded)	3.105—3.203 Å	0.001 Å		
Pd-O-C	127.8—133.2°	0.8°	24	130.3°
O-C-O	124.8—128.7°	1.1°	12	126.4°
O-Pd-trans-O	163.5—168.9°	0.4°	12	166.4°

The role of the water molecule is not clear. Although it lies between two independent trimers in a potentially hydrogen-bonding position, its nearest approach to an acetate oxygen atom is 3.08 Å.

We thank Professor G. Wilkinson for providing the crystals.

(Received, April 14th, 1970; Com. 531.)

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"Nunc est bibendum, nunc pede libero

Pulsanda tellus."

(Now is the time for drinking, now the time to
beat the earth with unfettered foot).

Horace: Odes.