

X-RAY STRUCTURAL STUDIES OF SOME METAL COMPLEXES
OF BIOLOGICAL INTEREST

A Thesis submitted for the Degree of
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by

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ABSTRACT

Chapter 1:A.

A brief guide to the crystallographic techniques used to determine the structures in this thesis, including diffractometer details.

Chapter 1:B.

Computing methods used, including both the X-ray package and local data processing programs. Program TWIDDLE, an on-line bond length and model program, WIZARD and PACKIT condensed data handlers, interactive ORTEP, and a text justifying program JUST.

Chapter 1:C

Nucleotide chemistry, formulation, and use of the parent bases as models for transition-metal nucleic acid interaction. Some crystal growth methods. Osmium tetroxide stains in microscopy.

Chapter 2.

Crystals of 9-methylhypoxanthine-dichloro-mercury(II) are monoclinic, space group P2₁/c, with $a=10.204$, $b=13.671$, $c=7.167$ Å, $\beta=98.24^\circ$. The structure consists of trigonal mercury co-ordinated by 2 Cl atoms and N(7). N(7)-Hg=2.305 Å, Hg-Cl are 2.402, 2.351 Å. Weak secondary Cl co-ordination is observed.

Chapter 3.

Crystals of hexaquomanganese(II)iodide.tetrakis (4,6-dimethylpyrimidine-2-one) are triclinic, P₁, with $a=12.022$, $b=7.661$, $c=10.235$ Å, $\alpha=93.68^\circ$, $\beta=105.92^\circ$, $\gamma=92.84^\circ$. The structure consists of octahedral hexaquomanganese ions, to which the DMP molecules are hydrogen bonded.

Chapter 4

Crystals of bis(1,3-Dimethyluracil)dichloro-copper(II) are triclinic, P₁, $a=12.029$, $b=8.449$, $c=3.883$ Å, $\alpha=93.66^\circ$, $\beta=93.69^\circ$, $\gamma=101.27^\circ$. The structure consists of square-planar co-ordinated Cu, with two trans Cl ligands, Cu-Cl 2.269, and two trans O(4) bound 1,3DMU ligands. This is the first observation of strong metal-uracil binding at neutral pH.

Chapter 5.

Crystals of Cobalt-5'Uridinemonophosphate.water are monoclinic, C2, $a=28.693$, $b=14.393$, $c=4.761$ Å, $\beta=90.96^\circ$. The structure consists of polymeric chains, made up of pairs of phosphate-oxygen-bridged cobalt ions. The polymer linkages are phosphate groups binding to 4 different cobalt ions. Each Co ion is octahedrally co-ordinated by 4 phosphate O atoms from 4 different phosphate groups, and to two water molecules. There is no uracil interaction with the metal.

Chapter 6

Crystals of Di-u-oxobis[(Cyclohexane-1,2-diolato)oxo (quinuclidine)osmium(vi)] are orthorhombic, Pbca, $a=23.394$, $b=10.303$, $c=11.743$ Å. The structure consists of a dimer of 6-co-ordinate Os, held together by a unique asymmetric Os-O bridge, with distances of 1.78 and 2.22 Å. Evidence for a 5-co-ordinate monomer with unique cis oxo ligands is presented.

Chapter 7.

Crystals of u-cyclooctane-1,2-diolato-5,6-diolato-bis (dioxodipyridine)osmium(vi))tetrahydrate are orthorhombic, P22₂, $a=8.363$, $b=14.546$, $c=14.441$ Å. The structure consists of two octahedrally co-ordinated Os atoms linked via ester bonds to opposite sides of the cyclooctane ring. Each osmium also has 2 trans oxo ligands and 2 cis pyridine ligands.

Appendix A.

Crystals of tris(diethylmalonato)iron(III) are monoclinic, C2/c, $a=18.176$, $b=11.918$, $c=13.811$ Å, $\beta=115.36^\circ$. The structure consists of three chelating diethylmalonate ligands, giving the iron close octahedral co-ordination. Mean Fe-O is 1.994 Å. This is the first malonic ester-metal complex.

Appendix B.

The crystal and molecular structures of catena-u-Formato-formatobis(pyridine)copper(II)monohydrate, and tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III), done as part of supervision of third-year projects.

In the beginning was the Word, and the Word
was with God, and the Word was God.

He was in the beginning with God.

All things came into being through Him, and
apart from Him nothing came into being that
has come into being.

In Him was life; and the life was the light
of men.

And the light shines in the darkness; and the
darkness did not overcome it.

To Him who gives me life, the Lord Jesus Christ.

Acknowledgements.

To my supervisor, Dr A.C. Skapski, for his patient monitoring of my progress, and for teaching me how to solve crystal structures.

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Preface.

This thesis is submitted in order to obtain a degree called 'Doctor of Philosophy'. It strikes me as strange, therefore, to find that most scientific research today has little connection with 'Philosophy', or even attempts to do much more than produce results. I must immediately say that this thesis is no exception !, it too contains original results. However, I would like to try to put them into a rather wider context.

This is because every 'thing' is not, in my understanding, a product of chance, but rather in some degree reflects the glory of the God who made it. Through my probing into a few relatively simple molecules, this opinion has been confirmed. Indeed, modern experimental science began in the 17th century because God-oriented men recognised that the creation was not just a machine set going ages ago, but in fact is continually upheld by His word moment by moment. Thus a study of creation ought to reveal a little of the character of Him who makes it.

Only a little, however. It is an oft-repeated error to spend more time studying the creation rather than following the Creator Himself. He has already revealed His personal character to us through Jesus Christ, in such a way as to make it possible for us to come to know Him in a personal way, rather as a son to a father. In a word, He loves us.

And there, I must end. If anything else strikes you from reading the thesis, may it be this wonderful truth that 'God so loves the world that He gave His only begotten Son, that whoever believes in Him should not perish, but have eternal life'. (John 3:16).

Chapter 1 A. Experimental

Introduction.

The use of X-RAY diffraction techniques for the elucidation of molecular structure has become widespread since the early observations of Von-Laue and Bragg (1). Many excellent treatises (2) have been published which clearly outline the theory and application of diffraction to crystalline materials; these require no further expansion here. This chapter serves to outline the experimental procedures used throughout the structural determinations contained in this thesis. A brief description of the preparation of suitable single crystals for three-dimensional structural analysis appears in chapter 1C. Thus, assuming the provision of such a crystal, the determination proceeds essentially by 4 stages which are: unit cell and space group determination, data collection, structure solution, and structure refinement. These steps are outlined below.

Unit cell and space group.

A crystal contains groups of atoms in particular arrangements, which repeat in a regular way in three dimensions. By considering each identical group of atoms as a point, a three-dimensional regular lattice may be described by the distance between each point, and the angle between the vectors along the lattice, conventionally referred to as a, b and c , with inter-vector angles α, β, γ . Although in general any lattice can be described as triclinic, usually the lattice can be simplified by allowing for symmetry elements relating the contents of part of the unit cell with itself. There are 7 crystal systems, i.e. unit-cell shapes, which with lattice centering give 14 Bravais lattices. Application of point-group and translational symmetry elements to the Bravais lattices give a unique set of space groups, totalling 230 in number.

A very useful way of treating X-ray diffraction phenomena is by assuming that diffraction maxima arise from a reflection off planes within the crystal, giving rise to the familiar Bragg equation:

$$n\lambda = 2.d.\sin\theta$$

where d is the interplanar spacing, λ the X-ray wavelength,

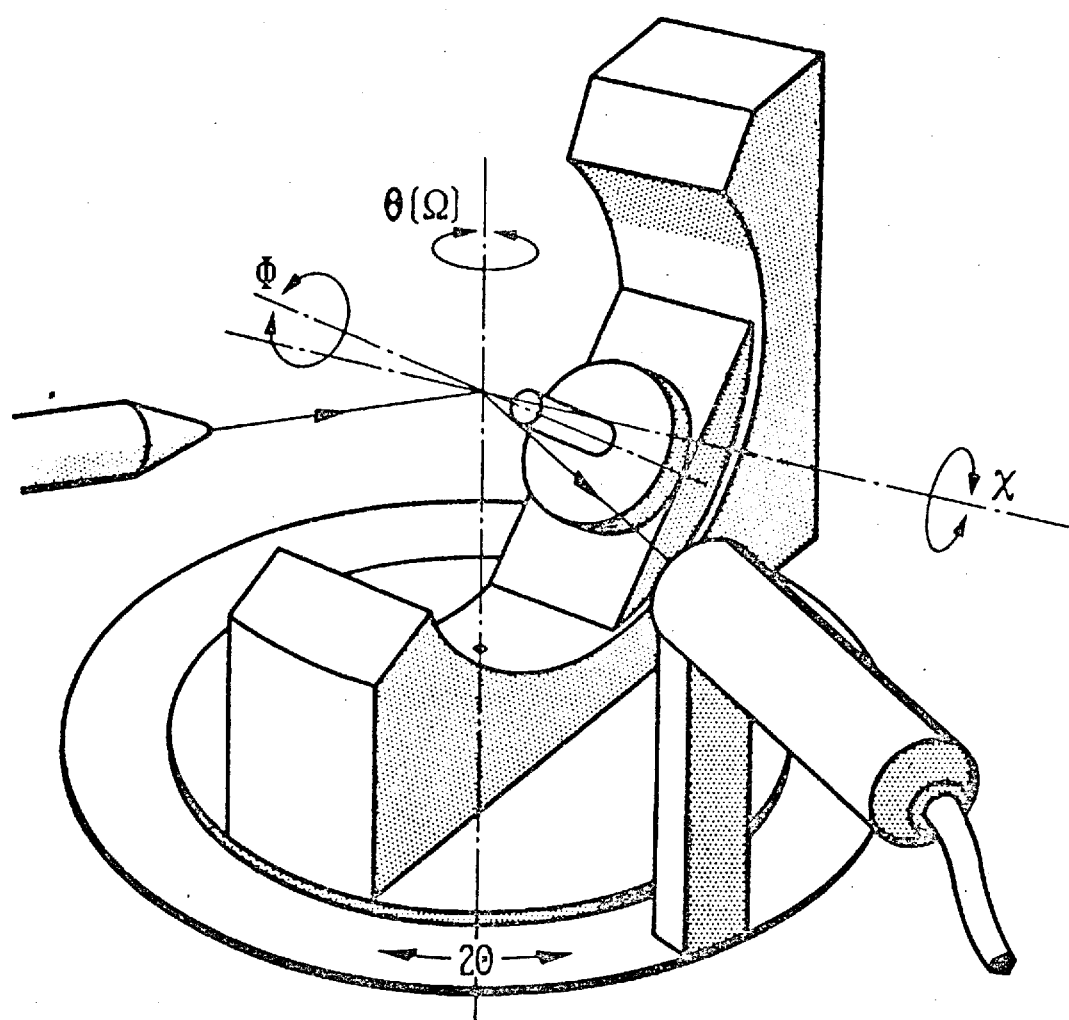


Figure 1. A schematic representation of the Siemens AED, a 4-circle diffractometer, showing the naming of the axes. The counter to crystal distance is variable, but for all the structures in this thesis it was fixed at 30cm. The collection collimator aperture is 2mm, with a length of 10cm.

θ the reflection angle, and n an integer (assumed 1 for most practical purposes).

Planes within a crystal are conveniently described by Miller indices. Another useful construction is the reciprocal lattice, defined as an array of points at the ends of lines (of length inversely proportional to the interplanar spacing) drawn perpendicular to the planes. The interpretation of X-ray photographs is straight-forward because the reciprocal lattice is directly related to the geometry of the photographic information. The unit cell can be determined from the reciprocal lattice.

Space group determination.

Normally oscillation and Weissenberg photographs yield sufficient information, but triclinic, and sometimes monoclinic, crystals require the use of a precession camera. For preliminary work, crystals are mounted on glass fibres with grease, and optically aligned so that edges are parallel to the centre axis of the camera. Oscillation and Weissenberg camera geometries require that the crystal rotates about a real lattice vector; precession geometry requires mounting about a reciprocal lattice vector.

Space group determination is necessarily indefinite in some cases, as only translational symmetry elements and lattice centering cause systematically absent reflections, but the choice can often be restricted by considering the known chemical properties of the crystal in question. For example optical activity precludes space groups having either mirror or inversion symmetry elements present.

Data collection.

The unit-cell and space group parameters determine the location of particular diffraction maxima in space. Measurement of the intensity of these reflections is termed data collection, and was done on a Siemens automatic off-line 4-circle diffractometer (see figure 1), at 10°C. The diffractometer was operated in ω -2 θ coupled mode, i.e. $\omega=2\theta$

The crystal under investigation is mounted with araldite on a quartz fibre which is fitted to a eucentric goniometer head, and aligned so that a real crystal axis is coincident with the ϕ axis of the diffractometer. Program LISTER cal-

culates setting angles for the circles from unit-cell parameters, allowing manual location of reflections and measurement of accurate θ -values, which in turn are refined by program CEDI to give accurate unit-cell dimensions. These allow generation of a 5-track paper tape which contains angle drive information for directing the diffractometer to the correct position for measuring the reflection.

Crystal alignment is carried out using horizontal half-shutters to set up a reciprocal-lattice plane in the ω - 2θ plane, thus defining a real axis perpendicular to this plane. Suitable reflections for alignment are at about 30° in θ . Adjustment of the goniometer arcs rapidly converges to give equal half-shutter counts for the hkl and $\bar{h}\bar{k}\bar{l}$ reflections, provided that the alignment reflections come from planes roughly parallel to the goniometer adjusting arcs. The height of the crystal in the X-ray beam can also be checked using the horizontal half-shutters until the open-shutter count is twice the half-shutter count. Final setting is done using coupled θ - ϕ scans to find the optimum ϕ value for a particular control reflection, and the ϕ position recording ring is set to the value required by the steering tape program for that reflection.

Diffractometer details.

Data collection uses a 5-value measuring procedure (3), which counts one side of peak, background, full peak, background, and other side of peak, the scan proceeding at 0.01° per step in θ . Background is measured for the time taken for a full peak scan (see fig. 2). The scan range is normally set to vary as a function of θ according to the shape of the diffraction maxima of a particular crystal. Values of 0.5° either side of the theoretical θ values are typical at θ ca 50.0° . The maximum time per step can be preset, for example values of 0.12, 0.24, and 0.6 secs give data collection rates of 1000, 600 and 300 reflections per day respectively. The counter circuits briefly check the intensity of the reflection before starting the scan, and adjust the step-time to give suitable counts (ca 10000) up to the preset maximum time. The very intense reflections are attenuated with nickel foil screens in the detector, which is a Na(Tl)I scintillation counter.

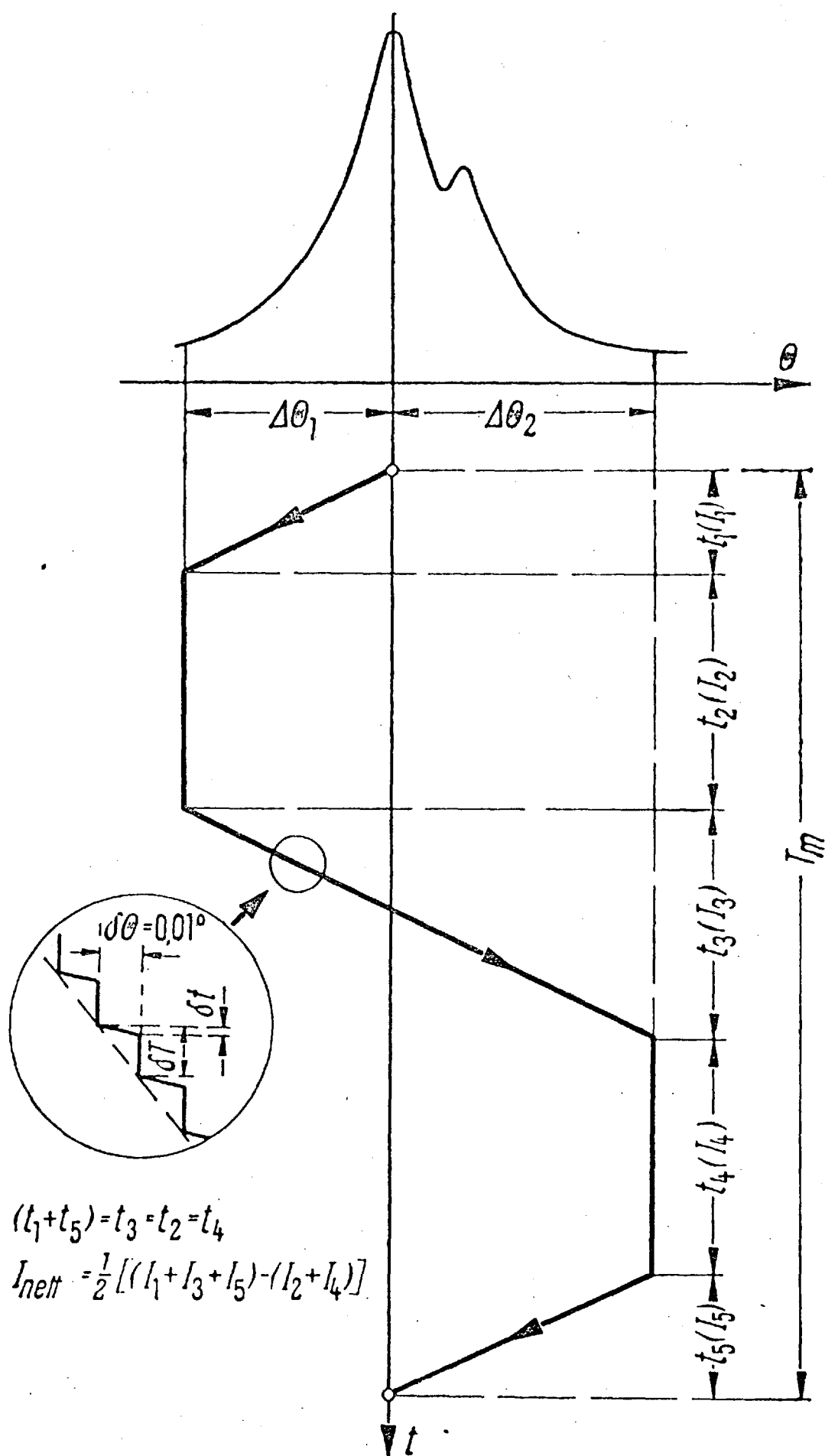


Figure 2. The 5-value reflection measuring procedure.

The X-rays are generated by a copper tube running at 40kv, 13 ma., and filtered with a nickel foil $\text{CuK}\beta$ filter. This passes $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) and longer wavelength radiation. The take-off angle is ca 3° , and beam collimators are available from 0.4 to 1.0 mm. in diameter, usually the example chosen is about 0.2 mm bigger than the crystal under study.

A reference reflection is measured every 50 reflections, and 4 control reflections every 300 reflections to monitor crystal misalignment and decomposition. Angle drive errors can be corrected to $\pm 0.2^\circ$, the machine embarks on a 0.01° step search to find the correct value. Larger errors can get through, but cause zero-check failure at reference check time. Longer wavelength radiation can be chopped out by pulse-height analysis of the counter output.

Data processing.

The counts for each part of the scan, together with scan times and attenuator information is punched onto an output paper tape along with the hkl of each reflection. This is used as input to program SODI, which scales the data to the reference reflection, and applies Lorentz and polarisation corrections, both of which are simple functions of the data collection geometry. The program checks on the relative sizes of half- and full-peak counts to ensure the intensity is roughly centred about the nominal θ value. Reflection intensity is computed from the following equation

$$I(\text{nett}) = 1/2[I(1)+I(3)+I(5)] - (I(2)+I(4))$$

and σI defined by $1/2 \sqrt{[I(1)+I(2)+I(3)+I(4)+I(5)]}$

A test given by $I < X \cdot \sigma I$ codes a reflection as

'unobserved', X is usually set to 2.58, which represents 99% probability.

Absorption correction.

The final treatment of raw data is through the application of an absorption correction, which allows for the absorption of incident and diffracted X-ray beam within the crystal. For spherical crystals this would be solely a function of θ , but most real crystals are anisotropic in shape, and thus the intensity of the diffraction varies

with crystal orientation. The absorption of X-rays follows the usual inverse exponential laws, but the problem is to determine the path length within the crystal of the incident and diffracted beams. The transmission factor, A , is given by the expression:

$$A(hkl) = \int (1/V) \exp[-\mu(r_i + r_d)] dv$$

where μ is the linear absorption coefficient; this is not usually solved analytically. Instead a numerical integration technique is used (4), which approximates the integral to the sum of a number of weighted terms. These are set up as a grid of points within the crystal having a weight dependent on their position and the shape of the crystal. The program ICABS, a modification of the algorithm of Coppens et.al.(5), performs the calculations. The final expression for intensity of the hkl reflection is:

$$F(\text{obs})^2 = K \cdot I(\text{obs}) \cdot [1/L \cdot p] \cdot [1/A]$$

Where K is a scale factor adjusted to put $I(\text{obs})$ onto an absolute scale. L =Lorentz factor, p =polarisation correction, A =transmission factor.

$$p = (1 + \cos^2 2\theta) / 2$$

$$L = 1 / (\sin 2\theta)$$

Structure solution.

The next stage is to find the phase of F , the structure factor. This can be done by several methods; the one used for this thesis is the heavy-atom method.

The structure factor may be expressed as follows:

$$F(hkl) = \sum_j f_j \exp 2\pi i (hx_j + ky_j + lz_j)$$

f_j is the scattering factor of the j 'th atom at position x_j, y_j, z_j (in fractions of a unit-cell translation along a, b and c respectively). f_j is a function of the number of electrons in atom j , and the diffraction angle θ . f decreases with increasing θ . In some cases, especially those atoms with X-ray absorption edges close to the λ value of the diffracting X-rays, other scattering occurs. This results in a phase change as well as a reduction in scatter; the effects are called anomalous dispersion and can be allowed for in the calculation. Scattering factors of heavy atoms were taken from Cromer and Waber (6), and those for hydrogen from Stewart, Davidson and Simpson (7).

The anomalous dispersion corrections were from Cromer and Libermann (8).

Scattering factors are also modified by the thermal motion of the atoms which causes a further reduction in f with increasing θ . The full anisotropic temperature factor is

$$\text{Exp}[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

Fourier synthesis.

The structure factor may be expressed as a simple function of electron density. Electron density, being a periodic function within a crystal, can be described by a Fourier synthesis. The latter is a series of solvable periodic equations summed to fit a real electron distribution. Thus we obtain

$$\rho(x,y,z) = 1/V \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

Substituting $F(hkl) = |F(hkl)| \exp(2\pi i \alpha')$

$$\rho(x,y,z) = 1/V \sum_{hkl} |F(hkl)| \cos 2\pi(hx + ky + lz - \alpha'_{hkl})$$

showing the problem of structure solution to be determining the phase angle α'_{hkl} . The heavy atom method computes a Patterson synthesis using F^2 as the coefficient, resulting in a map representing inter-atomic vectors. Since the peak size is proportional to the product of the scattering power of the atoms, heavy-atom vectors stand up against the background of light-atom-light-atom vectors. From a knowledge of the likely space group symmetry of the cell, the heavy atom co-ordinates can usually be determined. They are used to compute $F(\text{calc})$. The calculated phase is then combined with the modulus of the observed structure factor, to give an electron density map sufficiently close to the true electron density to locate further atom positions.

A common approach uses a difference Fourier synthesis, which uses $|F_{\text{obs}}| - |F_{\text{calc}}|$ as the coefficient, providing an electron density map that is zero for perfect model agreement, positive for unaccounted-for electron density and negative for errors in the model. Usually successive cycles of difference Fourier calculations are combined with some parameter refinement, and location of most non-hydrogen atoms is straightforward. Progress of the solution is monitored by the R factor:

$$R = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|} = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

which tends to 0 as $F(\text{calc})$ approaches $F(\text{obs})$.

Difference Fourier syntheses aid atom type identification, as does observation of the temperature factors of individual atoms. A relatively high temperature factor suggests too heavy an atom, as does a negative peak in the map.

Refinement.

The refinement of atomic coordinates and temperature factors proceeds via a least-squares procedure, well documented and programmed in X-RAY 72. The function minimized is

$$D = \sum_{hkl} W(hkl) \{ |F_o| - |kF_c| \}^2$$

The scale factor k is the inverse of the factor in the expression for $|F|$ on page 16, but must appear on the right side of the minimisation function with the other variables. w is generally unity for initial refinement, but during the later stages the scheme of Hughes (9) was applied, where $W=1$ for $F_c < F^*$, $W = (F^*/F_c)^2$ for $F_c > F^*$.

F^* is adjusted to give approximately constant $w \cdot |\Delta F|$. Throughout the structures in this thesis full-matrix refinement was used.

Problems which may arise at later stages of refinement often stem from disorder; several examples occur in this thesis. Although normally not too serious, the effect is an overall reduction in the accuracy of the structure determination, and often prevents location of hydrogen atoms from difference maps. (In such cases, hydrogen atom positions can sometimes be calculated by program HYDGNY).

References.

1. See International Tables For X-ray Crystallography, Vol.1, pp1-5, for a historical introduction.
2. G.H.Stout and L.H.Jensen 'X-Ray Structure Determination' -A practical guide.
C.W.Bunn Chemical Crystallography
M.J.Buerger 'X-ray Crystallography'
3. F.H.Allen, D.Rogers and P.G.H.Troughton Acta Cryst B27 (1971) 1325
4. W.R.Busing and H.A.Levy Acta Cryst 10 (1957) 180
5. P.Coppens, L.Leiserowitz and D.Rabinovich Acta Cryst. 18 (1965) 1035
6. D.T.Cromer and J.T.Waber Acta Cryst 18 (1965) 104
7. R.F.Stewart, E.R.Davidson and W.T.Simpson J.Chem.Phys. 42 (1965) 3175
8. D.T.Cromer and D.Libermann J.Chem.Phys 53 (1970) 1891
9. E.W.Hughes J.Amer.Chem.Soc. 63 (1941) 1737

Introduction.

Modern crystal structure refinement relies very heavily on sophisticated computer technology, which works very well in general terms, but often not so efficiently at local sites. Part of the work of this thesis has been the development of user-oriented software which simplifies use of the large computer packages available. These will be described in the context of a general overview of computing methods used.

Hardware.

The principal sites used were the University of London and Imperial College computer centres (ULCC and ICC). ULCC has CDC 7600, 6600 and 6400 machines, and ICC has a dual-main-frame CDC 6500 and Cyber 174 system. All CDC machines have 60-bit word memories. Both sites possess card punching facilities, ULCC has a microfilm machine, and ICC a Kingmatic flat-bed plotter. ICC's operating system, NOS, supports over 200 interactive terminals, including several Tektronix interactive graphics consoles. The graphic terminals are controlled by a CDC 1700 computer, which also handles paper tape I/O, and a fast link to the ULCC computers.

Software.

The principal crystallographic programs used were taken from the X-RAY 72 system (1), which is available from disc at ULCC. The following links of the system were most often required, and executed on the 7600.

DATORN Input of reflection intensities, atomic scattering factors, and unit-cell parameters, including space-group symmetry.

NORMSF Determines 'quasi-normalised structure factors', used for the Patterson synthesis as well as for direct phase determination. It also examines statistics of the reflections to estimate overall temperature factors.

LOADAT Input of atomic coordinates, temperature factors, and editing reflections.

CRYLSQ Least-squares refinement program.

FOURR Fourier syntheses from most coefficients.

FC Structure factor calculations for fixed atoms.

BONDLA Inter-atomic bond-length and angles, with standard deviations.

WTLSQ Applies weighting scheme

LSQPL Best-plane calculations.

WTANAL Examines weighting scheme.

The rest of the computing work was done at ICCG, the following programs used without modification:

LISTER Generates diffractometer setting angles

CEDI Does a least-squares best-fit calculation on θ values to give accurate unit-cell parameters. It is interactive, allowing free-format input and editing.

SEKO Produces a steering tape to direct the diffractometer to the correct position to start measuring the reflection intensity.

SODI Processes the output paper tape from the diffractometer, and applies lorentz and polarisation corrections. It scales the data to the reference reflection, and checks relative values of the half- and full- peak counts, to detect alignment errors.

ICABS Applies absorption correction. It is a very time-consuming process, often taking over 10 minutes on the 6500 or 174.

HYDGNV Calculates expected hydrogen atom co-ordinates for any type of parent atom bonding.

Data handlers.

SODI produces a card-image file containing one reflection per record. This is rather wasteful, especially if the data is off-lined as cards. Accordingly PACKIT and WIZARD were written to condense and process the reflection data. PACKIT produces a 6-reflection per card-image file, in integer form (i.e the output can be read manually and thus edited if required).

WIZARD unpacks the data again to its original format, and will pass unchanged any card other than condensed data. This enables condensed data to be treated as if it were single reflection-per-card format data. Listings of both programs are on page 22. The subsequently smaller disc files can be easily stored, and this led to the development of terminal job submission, rather than batch card

```

PROGRAM CONDENSE (OUTPUT,TAPE7,TAPE8,TAPE6=OUTPUT)
C THIS PROGRAM CONDENSES XRAY CARD IMAGES ON TAPE7 TO 6 REFLECTIONS
C PER CARD IMAGE ON TAPE8. BASED ON D.J.W.S ARCHIVE,AND B.A.C.S
C DATCOD, NOVEMBER 77.
C FILE VERSION NOVEMBER 8 1977 B.A.C.
C DIMENSION TITLE(16),ICK(6),ICK(6),ICL(6),IFOB(6),ISIG(6)
C SCAN FILE TO CHECK FOR BIG REFLECTIONS
SC = 1.
REWIND,7
14 READ(7,1000) (TITLE(J),J=1,16)
13 READ(.END.=11,7,1001) ANAME,JCDE,IK,IL,FSQ,SIGF
IF (FSQ/SC.GT.999990.0) GO TO 12
GO TO 13
12 SC = SC*5.0
WRITE(6,3001) SC
3001 FORMAT(1H0,20X,34H0H DEAR/ MY SCALE FACTOR WAS WRONG, /20X,
+ 15HFSQ DIVIDED BY ,F5.1)
WRITE(6,3002) IK,IL,FSQ
3002 FORMAT(1H0,19X,34H0H,314,12H REFLECTION ,8HHAS I = ,F10.2)
REWIND,7
GO TO 14
C READ FIRST CARD TO GET COMPOUND IDENTIFIER
11 REWIND,7
1000 FORMAT(16A5)
NCARD=0
N=1
IE=0
C....READ FIRST DATA CARD TO GET COMPOUND NAME
READ(7,1001) ANAME,JCDE,IK,IL,FSQ,SIGF
1001 FORMAT(7X,A6,1X,I1,314,F10.2,F10.4)
WRITE(6,2100) ANAME
WHAT = ANAME
2100 FORMAT(6HREMARK,4X,A6)
GO TO 2
1 N=0
C....INITIALISE THE OUTPUT ARRAYS
DO 3 I=1,6
ICK(I)=ICK(I)=ICL(I)=IFOB(I)=ISIG(I)=0
3 CONTINUE
4 N=N+1
C....READ THE REST OF THE DATA
6 READ(.END.=5,7,1001) ANAME,JCDE,IK,IL,FSQ,SIGF
IF (IK.EQ.0.AND.IL.EQ.0.AND.IL.EQ.0) GO TO 6
2 NCARD=NCARD+1
FSA=FSQ/SC
ICK(N)=IK+50
ICK(N)=IK + 50
ICL(N)=IL + 50
F = SORT(FSA)
IFOB(N) = F*100.
IF (JCDE.EQ.2) IFOB(N)=-IFOB(N)
SF=SIGF/SC
ISIG(N) = SF*10.0
IF (N.LT.6) GO TO 4
WRITE(6,2101) (ICK(J),ICK(J),ICL(J),IFOB(J),ISIG(J),J=1,6)
2101 FORMAT(6(3I2,I5,I2),2H )
GO TO 1
C....END OF THE DATA SEQUENCES
5 IF (N.EQ.1) GO TO 10
WRITE(6,2101) (ICK(J),ICK(J),ICL(J),IFOB(J),ISIG(J),J=1,6)
10 CALL DATE(THING)
WRITE(6,2000) THING
2000 FORMAT(1H0,19X,32HYOUR DATA HAS BEEN CONDENSED ON ,A10)
WRITE(6,2001) WHAT
2001 FORMAT(1H0, /20X,23HYOUR COMPOUND NAME IS ,A6)
WRITE(6,2002) (TITLE(M),M=1,16),NCARD
2002 FORMAT(1H0, /20X,16A5, /20X,6HIT HAS,14,12H REFLECTIONS)
STOP
END

```

```

PROGRAM WIZARD (INPUT,OUTPUT,TAPE10,TAPE7=INPUT,TAPE6=OUTPUT)
C....THIS PROGRAM DECODES 'CONDENSE' CARDS INTO XRAY FORMAT
C....ALL SINGING CUM DANCING VERSION WILL READ ANY CARD,BUT ONLY UNPACKS
C....CONDENSED DATA. A COMPOUND ID. CARD IN 10X,A6 FORMAT MUST BE THE
C....FIRST CARD OF THE DECK OF CARDS BEING READ. NO OTHER CONDITIONS.
C....PRESENT READ FORMAT ASSUMES 6 REFL. PER CARD,NOV.77 B.A.C.
C DIMENSION ICH(6),ICK(6),ICL(6),IFOB(6),ISIG(6)
C DIMENSION ARY(6)
NCARD = 0
NREF = 0
READ(7,1000) ANAME
1000 FORMAT(10X,A6)
12 READ(.END.=5,7,1100) ARY
1100 FORMAT(8A10)
DECODE(80,1101,ARY) AF
1101 FORMAT(70X,A1)
IF (AF.EQ.1H0) GO TO 2
WRITE(10,1100) ARY
GO TO 12
C SET COUNTERS
C READ THE CONDENSED DATA CARD
2 DECODE(80,1001,ARY) (ICK(J),ICK(J),ICL(J),IFOB(J),ISIG(J),J=1,6),AF
1001 FORMAT(6(3I2,I5,I2),A2)
C....UNPACKING THE CARD
N=0
3 N=N+1
JCDE=0
IF (IFOB(N).EQ.0) GO TO 4
IF (IFOB(N).GT.0) GO TO 10
JCDE = 2
IFOB(N) = -IFOB(N)
10 IK = ICK(N) - 50
IK = ICK(N) - 50
IL = ICL(N) - 50
FT = IFOB(N)
FSQ=FT*100.000
FSA=FT*F

```

submission.

The analysis of the atomic parameters can, in addition to the BONOLA link in X-RAY, be carried out interactively with program TWIDDLE. This program has two main streams of logic; the first is an interactive bond-length, angle and torsion angle routine capable of examining specific bonds, or contacts within a range, and sequential torsion angles. The calculation software was originally written by Dr D.J. Williams and has been modified to take free format input from the terminal. Updating, editing, and output in particular format for use by X-RAY or ORTEP, is possible.

The second scheme involves the generation and orientation of specific groups or molecules from a file containing external structural information. They are inserted in the cell as correct starting models for rigid-body refinement. The routines can also rotate a set of atoms about a given vector. The program invents new atom labels, or updates previous co-ordinates as required. The complete program is listed on pages 24 to 27, and a brief description of the program is now given.

Entry into the program will put up prompts for data or keywords that can usually be answered without difficulty. Generally, a carriage return will either cause a warning message, or use of preset default values. Lists of numbers require two C/R to terminate the READ. Also, mixed keyword-numeric data lines are not allowed by free-format READs. Major keywords are ATOM, LIST, BOND, MODEL, STORE, VECTOR, STUCK, MODPOS, RESTART, END. Their purpose is generally self-evident, and consultation of the listing should allow a start to be made in using the program. The program requires on-line input/output on units 5 and 6, and optionally will use unit 7 to read data (at present in ORTEP format). A correct format file can be generated during the initial run through the STORE facility. This routine also allows for the correct generation of unit 4, for later use by MODPOS. Unit 3 is a simple atomic co-ordinate file for input to X-RAY. The program's internal co-ordinate system is orthogonal Angstrom, re-conversion into cell co-ordinates occurring via STORE.

```

PROGRAM TWIDLE (INPUT, OUTPUT, TAPE4, TAPE8, TAPE5=INPUT, TAPE6
+OUTPUT, TAPE3, TAPE7)
COMMON ATH(500), X(500), Y(500), Z(500), THAT(3,3), NN
COMMON ISYM, IEN, ORA(20,10), ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IRUN(25)
COMMON IR,NRUN,MEAS,SCALE,IENANT
COMMON TITLE(16), AX(20), AY(20), AZ(20), TIM(3,3), AP,BT,GM
C..... BOND LENGTH AND ANGLE PROGRAM OF D.J.W. IN INTERACTIVE FORM
C USE THE COMPILER NO. 3 B.A.C
C TWIDLE VERSION USER PROGRAM
C..... MODPOS ROUTINES OF B.A.C. AND SMOOTHER OPERATION MODS AUG78
1 NN = 1
1 CM = 0
NRUN = 0
IJIG = 1
SCALE = 1.0
WRITE(6,6000)
6000 FORMAT('SUPER TWIDLE .. COMMAND SUMMARY OBTAINED BY 'STUCK' ')
C... CHECK IF TAPE7 DATA IS AVAILABLE THIS IS IN ORTEP FORMAT
WRITE(6,6005)
6005 FORMAT('IS DATA AVAILABLE ON TAPE 7?')
READ(5,5110)AVC
5110 FORMAT(A2)
IF (AVC.EQ.2)GO TO 700
C... CHECK FOR LOCAL FILE DATA ON TAPE 7
CALL ORTEP
GO TO 701
C... INPUT OF DATA FROM TERMINAL
700 WRITE(6,6007)
6007 FORMAT('XTYPE TITLE')
READ(END=9,5,4000) (TITLE(IJ), IJ=1,16)
4000 FORMAT(16A5)
WRITE(6,6008)
6008 FORMAT('XTYPE CELL DIMENSIONS')
READ(END=9,5,5)A,B,C,AL,BE,GA
AP=AL
BT=BE
GM=GA
C..... STORES ANGLES AS DEGREES
CALL ORTGG
701 WRITE(6,6009)
6009 FORMAT('XTYPE ORTGG')
READ(END=800,5,5)AG,BG,CG
C... THIS SEQUENCE IS THE MAIN CONTROLLER OF THE PROGRAM
C... GENERALLY, CONTROL IS RETURNED TO THIS POINT
C... ONLY END WILL JUMP OUT OF THE LOOP
800 WRITE(6,6010)
6010 FORMAT('XTYPE IN REQUIRED COMMAND')
1 CM = CM + 1
IF (CM.EQ.10)WRITE(6,6085)
6085 FORMAT('XINGO :X////,XSORRY ABOUT THAT,X,XTYPE COMMAND')
READ(END=9,5,5000)ANAME
5000 FORMAT(A5)
IF (ANAME.EQ.5)GO TO 860
IF (ANAME.EQ.5)GO TO 710
IF (ANAME.EQ.5)GO TO 870
IF (ANAME.EQ.5)GO TO 880
IF (ANAME.EQ.5)GO TO 890
IF (ANAME.EQ.5)GO TO 900
IF (ANAME.EQ.5)GO TO 910
IF (ANAME.EQ.5)GO TO 920
IF (ANAME.EQ.5)GO TO 930
IF (ANAME.EQ.5)GO TO 940
IF (ANAME.EQ.5)GO TO 950
IF (ANAME.EQ.5)GO TO 960
IF (ANAME.EQ.5)GO TO 970
IF (ANAME.EQ.5)GO TO 980
IF (ANAME.EQ.5)GO TO 990
IF (ANAME.EQ.5)GO TO 1000
7000 FORMAT('UNRECOGNISED COMMAND, TRY AGAIN, STUCK WILL LIST COMMANDS')
GO TO 800
2 WRITE(6,7010)
7010 FORMAT('COMMAND FUNCTION')
WRITE(6,7011)
7011 FORMAT('ATOM COORD. ENTERING. KIND =1,2,3 FOR CELL,GRID,ANDS
+T3')
WRITE(6,7012)
7012 FORMAT('XINGO CALLS BONDLENGTH,ANGLE,AND DIHEDRAL SUBROUTINES')
WRITE(6,7013)
7013 FORMAT('STORE PUTS ORTEP READABLE DATA ON 7,MODPOS DATA ON 4,
+1,XRAY DATA ON3')
WRITE(6,7014)
7014 FORMAT('LIST GIVES A QUICK TABLE OF ATOM NAME AND NUMBER')
WRITE(6,7015)
7015 FORMAT('MODPOS CALLS GROUP ROTATION THETA,PHI,AND CHI ARE ALONGC,
+G X,Y ANDZ')
WRITE(6,7016)
7016 FORMAT('MODEL CALLS WIRE MODEL INITIALIZATION PACKAGE')
WRITE(6,7017)
7017 FORMAT('VECTOR CALLS GENERAL GROUP ROTATION PACKAGE')
WRITE(6,7018)
7018 FORMAT('END STOPS PROGRAM')
WRITE(6,7019)
7019 FORMAT('RESTART STARTS PROGRAM AGAIN')
WRITE(6,7019)
7019 FORMAT('YES,NO OBVIOUS REPLYS TO PROMPTS')
GO TO 800
C..... ATOM POSITION READING IN SECTION CALLED BY ATOM.....
720 NN = NN + 1
710 WRITE(6,6011)
N = NN
6011 FORMAT('ATOM NAME OR C/R')
READ(END=719,5,5100)ATHMNN
5100 FORMAT(A6)
IF (ATHMNN.EQ.5)GO TO 719
WRITE(6,6012)
6012 FORMAT('XIND, X, Y, Z')
READ(END=9,5,11P,XT,YT,ZT)
K = NN - 1
DO 715 JJ = 1,K
C THIS LITTLE ROUTINE ENABLES THE ATOM ARRAY TO BE UPDATED
IF (ATH(JJ).EQ.ATHMNN) NN = JJ
715 CONTINUE
IF (JP.EQ.1) GO TO 702
IF (JP.EQ.2) GO TO 703
X(NN) = XT
Y(NN) = YT
Z(NN) = ZT
GO TO 716
703 XT = XT/AG
YT = YT/AG
ZT = ZT/CG
C... THIS SERIES IS NOT TEALLY REQUIRED, BUT IM LEAVING IT IN
702 X(NN) = XT*THAT(1,1) + YT*THAT(2,1) + ZT*THAT(3,1)
Y(NN) = XT*THAT(2,1) + YT*THAT(2,2) + ZT*THAT(3,2)
Z(NN) = XT*THAT(3,1) + YT*THAT(3,2) + ZT*THAT(3,3)
716 IF (NN.LT.N) N = N - 1
NN = N
GO TO 720
719 WRITE(6,6015)
6015 FORMAT('DO YOU WANT A LIST')
READ(END=9,5,5005)AL
5005 FORMAT(A2)
IF (AL.EQ.2)GO TO 800
WRITE(6,399)
399 FORMAT('SEQUENCE NUMBER OF FIRST AND LAST LISTED ATOMS')
READ(END=5,5)NA,NB
GO TO 6
5 NA=1
NB=NN-1
C... LISTING OF ATOMIC ANGSTROM COORDS
6 WRITE(6,6013)
6013 FORMAT('NUMBER, NAME, X, Y, Z')
DO 250 NJ = NA,NB
WRITE(6,6014)NJ,ATH(NJ),X(NJ),Y(NJ),Z(NJ)
6014 FORMAT('X, Y, Z, X, Y, Z, X, Y, Z')
250 CONTINUE
GO TO 800
C BOND LENGTH AND ANGLE CONTROLLER.....
860 WRITE(6,6020)
6020 FORMAT('ENTER ATOM NUMBER SEQUENCES')
IR = 0
J=0
READ(END=3,5,5) (IRUN(I), I=1,25)
3 DO 103 II = 1,J
IF (IRUN(II).LE.0) GO TO 104
IR = IR + 1
103 CONTINUE
104 CALL DIHANG
GO TO 800
C..... MODEL INITIALIZES JIG SCALES AND FLAGS, THEN GOES TO BOND
800 WRITE(6,6021)
6021 FORMAT('ENTER MEAS,SCALE,IENANT')
READ(END=9,5,5)MEAS,SCALE,IENANT
IF (MEAS.EQ.1)WRITE(6,6022)SCALE
6022 FORMAT('SCALE ISX,F4.2,XIN,ANG,X')
IF (MEAS.EQ.2)WRITE(6,6023)SCALE
6023 FORMAT('SCALE ISX,F4.2,XIN,ANG,X')
IF (IENANT.EQ.1)WRITE(6,6024)
6024 FORMAT('IENANT IONOPH HAS BEEN REQUESTED')
IJIG = 2
GO TO 860
C EOF RECOVERY SECTION
9 WRITE(6,7020)
7020 FORMAT('XOTHER')
GO TO 800
C... DATA STORAGE ON TAPE 4 AND 7
870 CALL STORE
GO TO 800
C..... QUICK LIST OPTION LISTS ATOM NUMBER AND NAME
880 WRITE(6,70)
70 FORMAT('NO. NAME NO. NAME NO. NAME NO. NAME')
LTRAN=1
DO 71 KK=1,LT,5
J=KK
JB=KK+4
WRITE(6,72) (J,ATH(J),J=JA,JB)
72 FORMAT('J, X, Y, Z, X, Y, Z')
71 CONTINUE
GO TO 800
500 CALL MODPOS
GO TO 800
510 CALL VECTOR
GO TO 800
890 WRITE(6,6080)
6080 FORMAT('TRANSFORMATION MATRIX')
WRITE(6,6081) (THAT(I,J), J=1,3), I=1,3
6081 FORMAT('X, Y, Z')
WRITE(6,6181)
6181 FORMAT('INVERSE MATRIX')
WRITE(6,6182) (TIM(I,J), J=1,3), I=1,3
6182 FORMAT('X, Y, Z')
WRITE(6,6082)
6082 FORMAT('A, B, C, ALPHA, BETA, GAMMA')
WRITE(6,6083)A,B,C,AL,BE,GA,IJIG,IRUN(25)
6083 FORMAT('X, Y, Z, X, Y, Z, X, Y, Z')
WRITE(6,6084)
6084 FORMAT('XTO RESTART, TYPE TWIDLE CHEERIO')
STOP
END
SUBROUTINE ORTGG
C ROUTINE TO CONVERT TO ORTHOGONAL COORDINATES
C SETS UP TRANSFORMATION MATRIX THAT AND ITS INVERSE TIM
COMMON ATH(500), X(500), Y(500), Z(500), THAT(3,3), NN
COMMON ISYM, IEN, ORA(20,10), ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IRUN(25)
COMMON IR,NRUN,MEAS,SCALE,IENANT
COMMON TITLE(16), AX(20), AY(20), AZ(20), TIM(3,3), AP,BT,GM
DO 200 I=1,3
DO 200 J=1,3
200 THAT(I,J)=0.0
PI=3.1415926536
AL=AL*PI/180
BE=BE*PI/180
GA=GA*PI/180
ASB=ASIN(BE)
ACB=ACOS(BE)
BSA=BSIN(AL)
BCA=BCOS(AL)
COS=(COS(AL)*COS(BE)-COS(GA))/(SIN(AL)*SIN(BE))
SOS=SQRT(1-COS*COS)
C SETUP TRANSFORMATION MATRIX ** THAT **
THAT(1,1)=ASB*COS
THAT(2,1)=BSA
THAT(3,1)=ACB
THAT(2,2)=BCA
THAT(3,2)=C
C... SET UP INVERSE MATRIX
DO 210 I=1,3
DO 210 J=1,3
210 TIM(I,J)=0.0
TIM(1,1)=1./THAT(1,1)
TIM(2,1)=-THAT(2,1)/(THAT(1,1)*THAT(2,2))
TIM(2,2)=1./THAT(2,2)
TIM(3,1)=THAT(2,1)*THAT(3,2)-THAT(2,2)*THAT(3,1)
+/(THAT(1,1)*THAT(2,2)*THAT(3,3))
TIM(3,2)=-THAT(3,2)/(THAT(2,2)*THAT(3,3))
TIM(3,3)=1./THAT(3,3)
RETURN
END
SUBROUTINE DIHANG
C SUBROUTINE TO CALCULATE BOND LENGTHS, ANGLES AND DIHEDRAL ANGLES
COMMON ATH(500), X(500), Y(500), Z(500), THAT(3,3), NN
COMMON ISYM, IEN, ORA(20,10), ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IRUN(25)
COMMON IR,NRUN,MEAS,SCALE,IENANT
COMMON TITLE(16), AX(20), AY(20), AZ(20), TIM(3,3), AP,BT,GM
IR= NO OF ATOMS IN RUN
NRUN= NO OF RUN
IRUN= RUN ATOM
IF (IR.GT.0) GO TO 862
WRITE(6,6030)

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```

6030 FORMAT(40 ATOMS IN SEQUENCE)
RETURN
862 IF (IR.GT.1) GO TO 861
.. BOND LENGTH FROM FIRST ATOM TO ALL OTHERS
IS = IRUN(1)
WRITE(6,6033) ATM(IA)
5033 FORMAT(8BOND LENGTHS FROM *,A6)
WRITE(6,6034)
5034 FORMAT(ENTER MIN AND MAX BOND LENGTHS)
BMIN = 1.0
BMAX = 1.7
READ(END=8.5,*,BM,BX)
BMIN=BM
BMAX=BX
8 WRITE(6,6035)
5035 FORMAT(TARGET ATOM,NUMBER,BONLENGTH)
NL = NN - 1
DO 863 JJ = 1,NL
DO 863 JJ = 1,NL
IF (JJ.EQ.1A) GO TO 863
USUAL ORTHOGONAL EXPRESSION FOR BOND LENGTH
DX = X(JJ) - X(IA)
DY = Y(JJ) - Y(IA)
DZ = Z(JJ) - Z(IA)
RAB = SQRT(DX*DX + DY*DY + DZ*DZ)
IF (RAB.LT.BMIN OR RAB.GT.BMAX) GO TO 863
WRITE(6,6036) ATM(IJ),JJ,RAB
5036 FORMAT(4X,A6,4X,13,3X,F6.4)
863 CONTINUE
RETURN
861 NRUN = NRUN + 1
WRITE(6,6031) NRUN,IR
5031 FORMAT(NRUN NO, *,12,*, NO. OF ATOMS = *,12)
PI=3.1415926536
SET UP DIRECTION COSINES FOR FIRST 3 BONDS
ROT=0.0
IF (JIG.EQ.1) MEAS = 1
AJIG=0
IF (MEAS.EQ.1) AJIG=9.5
IF (MEAS.EQ.2) AJIG=25.0
K=IR-3
J=1
JF=IRUN(1)
JB=IRUN(2)
DELX1=X(1B)-X(1A)
DELY1=Y(1B)-Y(1A)
DELZ1=Z(1B)-Z(1A)
RAB = SQRT(DELX1*DELX1 + DELY1*DELY1 + DELZ1*DELZ1)
IF (IR.EQ.2) GO TO 864
IC = IRUN(3)
DELX2=X(1C)-X(1B)
DELY2=Y(1C)-Y(1B)
DELZ2=Z(1C)-Z(1B)
SECOND BOND AND ANGLE
RBC=SQRT(DELX2*DELX2+DELY2*DELY2+DELZ2*DELZ2)
DIRECTION COSINES DL,DM,DM
DL1=DELX1/RAB
DM1=DELY1/RAB
DN1=DELZ1/RAB
DL2=DELX2/RBC
DM2=DELY2/RBC
DN2=DELZ2/RBC
ANGLE BETWEEN FIRST 2 BONDS
R12=DL1*DL2+DM1*DM2+DN1*DN2
S12=SQRT(1-R12*R12)
ANG1=ACOS(R12)
ANG1=ANG1*180/PI
BEND1=ANG1
TANG1 = 180.0 - ANG1
IF (IR.EQ.3) GO TO 865
WRITE(6,6050)
5050 FORMAT(ATOM ATOM BOND ANGLE DIHE JIGSET BEND ROT,*)
THIRD BOND RCD
ID = IRUN(4)
401 DELX3=X(1D)-X(1C)
DELY3=Y(1D)-Y(1C)
DELZ3=Z(1D)-Z(1C)
RCD=SQRT(DELX3*DELX3+DELY3*DELY3+DELZ3*DELZ3)
DL3=DELX3/RCD
DM3=DELY3/RCD
DN3=DELZ3/RCD
R13=DL1*DL3+DM1*DM3+DN1*DN3
R23=DL2*DL3+DM2*DM3+DN2*DN3
S23=SQRT(1-R23*R23)
ANG2=ACOS(R23)
ANG2=ANG2*180/PI
BEND2=ANG2
TANG2 = 180.0 - ANG2
IF (IRUN(1),IRUN(1+3)) GO TO 402
CALCULATE DIHEDRAL ANGLE
DIHE=ACOS((R13-R12*R23)/(S12*S23))
CALCULATE SIGN OF ROTATION
DET=DL1*DM2*DN3+DM1*DN2*DL3+DN1*DL2*DM3-DN1*DM2*DL3-DM1*DL2*DN3-
+ DL1*DM2*DN3
JS=1
IF (DET.LT.0.0) JS=-1
DIHE=(180-DIHE*180/PI)*JS
IF (IEMANT.EQ.1) DIHE=-DIHE
GO TO 403
DIHE=0.0
402 CONTINUE
AJIG = AJIG + SCALE*RAB
BLIMIT=AJIG+SCALE*RBC
FORBIDDEN ROTATION SIGN REVERSAL SEQUENCE
IBE1=IS1(BEND1)
IDE=IS1(DIHE)
IF (IBE1.NE.IDE) GO TO 410
ROT=ROT-(180-DIHE)
IBE2=-IBE1
BEND2=IBE2*BEND2
GO TO 420
410 IBE2=IBE1
ROT=ROT+DIHE
BEND2=IBE2*BEND2
420 CONTINUE
IF (ROT.GT.180.0) ROT=-360-ROT
IF (ROT.LT.-180.0) ROT=360+ROT
PRINT FIRST LINE OF OUTPUT
WRITE(6,6051) ATM(IA),ATM(1B),RAB,TANG1,DIHE,AJIG,BEND1,ROT
6051 FORMAT(1A6,1X,A6,1X,F6.3,1X,F6.2,4F7.1)
IF (BLIMIT.GT.AJIG) AJIG=0
IF (I.GE.K) GO TO 450
RESET SEQUENCE
IA=IB
IB=IC
IC=ID
ID=IRUN(4+1)
DELX1=DELX2
DELY1=DELY2
DELZ1=DELZ2
DELX2=DELX3
DELX3=DELX4
DELX4=DELX5
DELX5=DELX6
DELX6=DELX7
DELX7=DELX8
DELX8=DELX9
DELX9=DELX10
DELX10=DELX11
DELX11=DELX12
DELX12=DELX13
DELX13=DELX14
DELX14=DELX15
DELX15=DELX16
DELX16=DELX17
DELX17=DELX18
DELX18=DELX19
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C.....THE NEXT SERIES OF STATEMENTS WRITES INSTRUCTION CARDS FOR ORTEP
C.....THE FORMAT SHOULD BE EASILY RECOGNIZABLE AS BASED ON ORTEP COMMANDS
652 WRITE(7,705)
705 FORMAT(6X,3H201)
WRITE(7,706)
706 FORMAT(6X,3H203,3H1.0)
WRITE(7,707)
707 FORMAT(6X,3H301,3X,3H18.,6X,3H12.,6X,3H30.,6X,2H.5)
WRITE(7,708)
708 FORMAT(6X,3H302,3H0.0)
JJE=NO
WRITE(7,709) JJ
709 FORMAT(6X,3H401,3X,6H155501,14,5H55501)
WRITE(7,725)
725 FORMAT(6X,3H501,3X,6H155501,3X,6H155501,3X,6H155501,3X,6H155501,
+3X,6H155501,17X,1H1)
WRITE(7,710)
710 FORMAT(5X,4H1101)
WRITE(7,711)
711 FORMAT(6X,3H604,30X,3H0.9)
WRITE(7,712)
712 FORMAT(6X,3H611,21X,2H.9)
WRITE(7,713)
713 FORMAT(6X,3H714)
WRITE(7,714)
714 FORMAT(2X,1H2,3X,3H612)
WRITE(7,715) NO,NO
715 FORMAT(6X,3H812,3H 1.13,3H 1.13,20H 3 1.1 1.7 .06)
WRITE(7,716)
716 FORMAT(5X,4H1102)
WRITE(7,717)
717 FORMAT(6X,3H202)
WRITE(7,718)
718 FORMAT(7X,2H-1)
854 WRITE(6,62)
62 FORMAT('TAPE7 CREATED READY FOR ORTEP')
ENDFILE7
RETURN
10 WRITE(6,604)
604 FORMAT('ENTER GROUP NAME')
9 READ(END=1,4,402) ANY
402 FORMAT(A10)
GO TO 9
11 READ(5,402) NGRP
C.....WRITE NEW GROUP DATA,....
WRITE(6,402) NGRP
WRITE(4,402) NGRP
DO 750 KK=1,NO
WRITE(4,400) ATN(KN),X(KN),Y(KN),Z(KN)
400 FORMAT(A6,3F8.4)
750 CONTINUE
WRITE(4,401)
401 FORMAT(3HEND1)
WRITE(6,63)
63 FORMAT('GROUP DATA WRITTEN TO TAPE 4')
RETURN
100 REWIND3
WRITE(6,610)
101 FORMAT('XRAY ATOMS ON TAPE3')
WRITE(6,105)
105 FORMAT('LIST AND LAST ATOMS TO BE STORED')
READ(END=110,5,1) IAF,IAL
GO TO 111
110 IAF=1
IAL=NO
111 WRITE(6,106)
106 FORMAT('STEP, FACTOR')
READ(5,1) TF
104 FORMAT(4HATOM,3X,A6,4F8.4)
DO 103 KK=IAF,IAL
CALL CELL(CX,CY,CZ,X(KK),Y(KK),Z(KK))
WRITE(3,104) ATN(KK),CX,CY,CZ,TF
103 CONTINUE
113 RETURN
END
SUBROUTINE BREAD
COMMON ATN(500),X(500),Y(500),Z(500),THAT(3,3),NN
COMMON ISYM,IEN,DRA(20,10),ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IJUN(25)
COMMON IR,NRUN,NEAS,SCALE,IENANT
COMMON TITLE(16),AX(20),AY(20),AZ(20),TIM(3,3),AP,BT,GM
IK=0
C.....ORTEP DECK READING .....
REWIND7
READ(7,7000) (TITLE(I),J=1,16)
7000 FORMAT(16A5)
IF (TITLE(1).EQ.5HATOM) GO TO 10
READ(7,7001) A,B,C,AL,BE,GA
7001 FORMAT(6F9.4)
GO TO 11
10 IK=1
WRITE(6,6000)
6000 FORMAT('CELL PARAMETERS')
READ(5,1) A,B,C,AL,BE,GA
11 AP=AL
BT=BE
GF=GA
CALL ORTGO
IF (IK.LT.1) GO TO 12
REWIND7
GO TO 13
C.....STORE SYMPOBS
12 DO 200 I=1,20
READ(7,7003) (INT, (DRA(I,J),J=1,8))
IF (INT.EQ.1) GO TO 201
7003 FORMAT(11A9,7A10)
200 CONTINUE
201 ISYM=1
13 CONTINUE
DO 1 N=1,500
READ(7,7004) ATN(N),CX,CY,CZ
7004 FORMAT(7X,A6,3F8.4)
CALL THOG(X(N),Y(N),Z(N),CX,CY,CZ)
READ(7,7005) IU
7005 FORMAT(71X,11)
IF (IU.NE.0) GO TO 2
1 CONTINUE
N=500
2 NN=NN+1
IF (IK.GT.0) RETURN
C.....STORE TRAILING INSTRUCTION CARDS
DO 203 I=1,50
READ(7,7006) (ORB(I,J),J=1,8)
7006 FORMAT(8A10)
IF (ORB(1,1).EQ.10H -1) GO TO 3
203 CONTINUE
3 IEN=I
RETURN
END
SUBROUTINE VECTOR
COMMON ATN(500),X(500),Y(500),Z(500),THAT(3,3),NN
COMMON ISYM,IEN,DRA(20,10),ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IJUN(25)
COMMON IR,NRUN,NEAS,SCALE,IENANT
COMMON TITLE(16),AX(20),AY(20),AZ(20),TIM(3,3),AP,BT,GM
DIMENSION T(3,3),R(3,3)
C.....THIS ROUTINE WILL ROTATE ANY GROUP OF ATOMS DEFINED FROM A SEQUENCE
C.....RUN ABOUT A VECTOR DEFINED BY TWO ATOMS WITH A PIVOT DEFINED BY
C.....ONE ATOM. ONLY ATOMS ALREADY IN THE MAIN ARRAY CAN BE USED. POSITION
C.....UPDATING IS AUTOMATIC, BUT NOT DISASTOROUS IF THE ROUTINE HAS BEEN
C.....CALLED FROM MODPOS.
C.....INPUT OF PERTINENT DATA
WRITE(6,600)
600 FORMAT('NO. OF FIRST AND LAST ATOMS')
READ(END=10,5,1) MA,MB
C.....THIS OF COURSE ASSUMES THE GROUP TO BE CORRECTLY SEQUENCED IIN THE LIST
WRITE(6,601)
601 FORMAT('ATOM NUMBERS WHICH DEFINE THE VECTOR')
READ(END=10,5,1) MA,MVB
C.....SET UP DIRECTION COSINES OF THE VECTOR
DX=X(MVA)-X(MVB)
DY=Y(MVA)-Y(MVB)
DZ=Z(MVA)-Z(MVB)
DE=SQRT(DX**2+DY**2+DZ**2)
D1=DX/DE
D2=DY/DE
D3=DZ/DE
C.....SELECT A PIVOT ATOM
WRITE(6,602)
602 FORMAT('PIVOT ATOM NUMBER')
READ(END=10,5,1) MP
C.....PRINT CURRENT DATA
1 WRITE(6,607) ATN(MVA),ATN(MVB),ATN(MP)
607 FORMAT('VECTOR FROM *A6,*X TO *A6,*X, PIVOT ATOM *A6')
C.....SHIFT GROUP TO ORIGIN WRT PIVOT
J=0
DO 200 I=MA,MB
J=J+1
T(1,J)=X(I)-X(MP)
T(2,J)=Y(I)-Y(MP)
T(3,J)=Z(I)-Z(MP)
200 CONTINUE
C.....SET UP THE ROTATION MATRIX R
WRITE(6,603)
603 FORMAT('ROTATION ALPHA IN DEGREES')
READ(END=10,5,1) AD
IO=0
C.....QUADRANT CHECKING SEQUENCE
32 IF (AD.LT.0.0) GO TO 31
IF (AD.LT.180.0) GO TO 30
IO=1
AD=AD-180.0
GO TO 30
40 AD=180.0
IO=0
GO TO 30
31 AD=360-AD
GO TO 32
30 CONTINUE
C.....CONVERT AD TO RADIAN AND DO TRIG CALC.
AR=AD*3.1415927/180.0
CR=COS(AR)
SR=1.0-CR
SA=SR*AR
C.....BUILD THE ROTATION MATRIX
R(1,1)=CR+0.1D1*3C
R(1,2)=0.1D1D2*3C + D3*SA
R(1,3)=0.1D1D3*3C - D2*SA
R(2,1)=0.1D1D2*3C - D3*SA
R(2,2)=CR + D2D2*3C
R(2,3)=D2D3*3C + D1*SA
R(3,1)=0.1D1D3*3C + D2*SA
R(3,2)=D2D3*3C - D1*SA
R(3,3)=CR + D3D3*3C
C.....PERFORM THE ROTATION: A MORE SOPHISTICATED FORTRAN COULD USE TWO
C.....DO LOOPS. THE INNER ONE OF THE FORM A=A+T(N,I)*R(N,K), N FROM 1 TO 3
DO 201 I=1,J
TX=T(1,I)
TY=T(2,I)
TZ=T(3,I)
DO 202 K=1,3
T(K,I)=TX*R(1,K) + TY*R(2,K) + TZ*R(3,K)
202 CONTINUE
201 CONTINUE
IF (IO.EQ.1) GO TO 40
C.....SHIFT GROUP COORDS BACK INTO REAL CELL
C.....AND UPDATE ATOM ARRAY
JJ=0
DO 203 I=MA,MB
JJ=JJ+1
X(I)=T(1,JJ)+X(MP)
Y(I)=T(2,JJ)+Y(MP)
Z(I)=T(3,JJ)+Z(MP)
203 CONTINUE
C.....LIST NEW COORDS
WRITE(6,604)
604 FORMAT('NAME X Y Z')
DO 204 N=MA,MB
WRITE(6,605) ATN(N),X(N),Y(N),Z(N)
605 FORMAT(A6,2X,3F8.4)
204 CONTINUE
C.....CONTINUATION OR DRBP
WRITE(6,606)
606 FORMAT('DO YOU WISH TO CONTINUE')
READ(END=10,5,500) CC
500 FORMAT(A2)
IF (CC.EQ.2HYES) GO TO 1
C.....E.O.F AND TERMINATION
10 WRITE(6,608)
608 FORMAT('END OF VECTOR ROUTINE')
RETURN
END
SUBROUTINE MODPOS
COMMON ATN(500),X(500),Y(500),Z(500),THAT(3,3),NN
COMMON ISYM,IEN,DRA(20,10),ORB(50,10)
COMMON A,B,C,AL,BE,GA,IJIG,IJUN(25)
COMMON IR,NRUN,NEAS,SCALE,IENANT
COMMON TITLE(16),AX(20),AY(20),AZ(20),TIM(3,3),AP,BT,GM
DIMENSION EA(50),MDX(50),MDY(50),MDZ(50)
REAL MDX,MDY,MDZ
C.....THIS IS THE CALCULATION SUBROUTINE
NJD=0
PI=3.1415927
IP=0

```

```

WRITE(6,6000)
6000 FORMAT('ENTER GROUP NAME')
READ(5,1000)NGP
1000 FORMAT(A10)
GO TO 11
12 WRITE(6,6001)
6001 FORMAT('ENTER PIVOT ATOM NAME')
READ(5,1001)PATH
1001 FORMAT(A6)
WRITE(6,6002)
6002 FORMAT('RING NUMBER,THETA,PHI,CHI')
C.....FIND THE PIVOT ATOM COORDS
CALL NCK(PATH,IP)
IF (IP.LT.0) GO TO 12
DELX=X(IP)
DELY=Y(IP)
DELZ=Z(IP)
40 READ,IRN,THETA,PHI,CHI
THETA=THETA*PI/180.
PHI=PHI*PI/180.
CHI=CHI*PI/180.
IF (LC.EQ.2HNE) GO TO 41
GO TO 2
C...GET THE GROUP COORDS OFF TAPE 4
11 REWIND4
1 READ(END=6,4,1000)MGP
IF (MGP.EQ.NGP) GO TO 8
GO TO 1
8 WRITE(6,1008)MGP
GO TO 12
2 MU = MU+1
1008 FORMAT('GROUP NAME IS ',A10)
READ(4,1006)EA(MU),MOOX(MU),MOOY(MU),MOOZ(MU)
1006 FORMAT(A2,4X,3F9,4)
IF (EA(MU).EQ.2HNE) GO TO 3
GO TO 2
3 M = MU-1
41 DO 400 N=1,M
CALL ANGLE(TET,THETA,MOOY(N),MOOZ(N),R)
YY=RYCOS(TET)
ZZ=R*SIN(TET)
CALL ANGLE(PHIT,PHI,ZZ,MOOX(N),S)
ZZ=SCOS(PHIT)
XX=SSIN(PHIT)
CALL ANGLE(CHIP,CHI,XX,YY,T)
XX=TCOS(CHIP)
YY=TSIN(CHIP)
AX(N) = XX + DELX
AY(N) = YY + DELY
AZ(N) = ZZ + DELZ
400 CONTINUE
REWIND8
DO 350 M=1,M
WRITE(6,8000)EA(M),IRN,M,AX(M),AY(M),AZ(M)
350 CONTINUE
WRITE(6,67)
67 FORMAT('SHALL I LIST GENERATED COORDINATES')
READ(5,1007)LA
1007 FORMAT(A2)
IF (LA.EQ.2HND) GO TO 4
DO 250 J=1,M
WRITE(6,8000)EA(J),IRN,J,AX(J),AY(J),AZ(J)
8000 FORMAT(A2,2I2,3F9,4)
250 CONTINUE
610 FORMAT('CONCURRENT ROTATION')
4 WRITE(6,610)
READ(5,1007)LC
IF (LC.EQ.2HND) GO TO 30
C.....RENTAPE8 AND SUBTRACT DELX/Y/Z TO GET NEW MODEL POSITION
REWIND8
DO 300 L=1,M
READ(6,1006)EA(L),PX,PY,PZ
MOOX(L)=PX-DELX
MOOY(L)=PY-DELY
MOOZ(L)=PZ-DELZ
300 CONTINUE
WRITE(6,6002)
GO TO 40
30 WRITE(6,6000)
6000 FORMAT('UPDATE ATOM ARRAY. ')
READ(5,1007)LB
IF (LB.EQ.2HND) RETURN
NA=0
REWIND8
DO 351 K=1,M
READ(6,8001)ART,AX(K),AY(K),AZ(K)
8001 FORMAT(A6,3F9,4)
NT=NN+K-1
II=NT
CALL NCK(ART,NT)
IF (NT.GT.0) GO TO 5
NA=NA+1
NT=II
5 ART(NT)=ART
X(NT)=AX(K)
Y(NT)=AY(K)
Z(NT)=AZ(K)
351 CONTINUE
NN=NA+NN
WRITE(6,6005)
6005 FORMAT('VECTOR. ')
READ(END=20,5,1007)VN
IF (VN.EQ.2HND) GO TO 20
CALL VECTOR
GO TO 4
20 RETURN
6 WRITE(6,607)NGP
607 FORMAT('NO GROUP CALLED ',A10,'ON TAPE 4')
RETURN
END
SUBROUTINE ANGLE(D,E,F,G,H)
PI=3.14159
IF (F.EQ.0.0.AND.G.EQ.0.0) GO TO 1
GO TO 2
1 D=H=0.0
RETURN
C...TEST FOR ZERO COORDS
2 H=SQRT(F**2+G**2)
IF (F.EQ.0.0) GO TO 50
Q=G/F
IF (G.LT.0.0) Q=-Q
P = ATAN(Q)
IF (F.LT.0.0.AND.G.LT.0.0) P=PI+P
IF (F.LT.0.0.AND.G.GT.0.0) P=PI-P
IF (F.GT.0.0.AND.G.LT.0.0) P=2*PI-P
IF (F.LT.0.0.AND.G.EQ.0.0) P=PI
D=H*P
GO TO 60
50 P=PI/2
IF (G.LT.0.0) P=PI+P
D=H*P
60 CONTINUE
RETURN
END
SUBROUTINE NCK(AR,IP)
COMMON ATN(500),X(500),Y(500),Z(500),THAT(3,3),NN
COMMON ISYM,IEH,ORA(20,10),ORB(50,10)
COMMON A(3),C(4),BE(6A),IJIG,IRUN(25)
COMMON IR,NRUN,MEAS,SCALE,IEANT
COMMON TITLE(16),AX(20),AY(20),AZ(20),TIM(3,3),AP,BT,GM
IP = -1
NN=NN+1
C.....IP REMAINS -VE IF NO ATOM MATCH FOUND
DO 10 I=1,ND
IF (AR.EQ.ATH(I)) IP=I
10 CONTINUE
RETURN
END

```

The plotting of molecular diagrams is the final stage of a structural determination, and often the most time-consuming, because here one has the ability to choose a view of the compound based on subjective judgements. The process has been greatly speeded up by overlaying the plotting program ORTEP, (2), so that it can be executed on-line. Two versions of the program were modified, the earlier and smaller ORTEP1 being further adapted to run interactively, and the larger ORTEP2 having hidden-line removal facilities can be run on-line.

The overlay scheme is outlined below, with core sizes given in octal words. The limit for on-line or interactive work at ICCG is 60000B.(about 24K).

```

OVERLAY(ORTEP,0,0)  Requires 54731B
Contains the main program, and smaller subroutines.
OVERLAY(ORTEP,1,0)  An extra 3430B
F800,BOND,LAP300
OVERLAY(ORTEP,2,0)  An extra 2570B
F700,LAP700
OVERLAY(ORTEP,3,0)  An extra 2436B
PRELIM,EIGEN
OVERLAY(ORTEP,4,0)  An extra 644B
F900
OVERLAY(ORTEP,5,0)  An extra 472B
F400
OVERLAY(ORTEP,5,1)  An extra 2476B
SEARC
OVERLAY(ORTEP,6,0)  An extra 520B
F200
OVERLAY(ORTEP,7,0)  An extra 331B
F600

```

The OVERLAY commands are standard FORTRAN features, and the set-up of the various subroutines should be straightforward. Overall saving of core is about 40%, compared to the unaltered version, at the expense of additional execution time because of reduced buffer sizes and extra disc I/O operations.

The earlier version of ORTEP has no hidden-line removal features, therefore overlaying the program in a similar way provides ample room to modify the main subroutine to enable genuine interactive control of the program. The

modifications are based on the 'saved sequence' instruction no.1103. The occurrence of the 1103 card triggers a change in the input READ unit number from file to the terminal, and a routine of key-word recognition sets up instructions directly by inserting values into the correct READ array locations. The following set of commands available are DRAW,SPIN,NAME,BOND,STEREO,PAGE,SHIFT,HELP and END. A listing of the HELP directory shows the general idea as to the operations available:

HELP DIRECTORY

DRAW Draws diagram at current scale and orientation.

The program initially draws the view set up on the input data file (unit 7).

SPIN Allows concurrent rotation about any plotter axis (Dummies a 502 instruction)

NAME Labels the atoms.All atoms labelled at given size

BOND,Labels bonds between two specified atoms, given by the ADDR of both atoms.

STEREO Plots a stereo pair of the screen contents

PAGE Changes the page size.

SHIFT Moves origin along the plotter x axis

HELP Displays this directory

COPY Puts a copy of the diagram on file for subsequent microfilm generation.

END Terminates the session, displaying accumulated rotation

The use of the program enables rapid generation of a view of the molecule in the desired orientation. The final diagram is plotted with ORTEP2 from the rotations found interactively. This is also an on-line operation, and a check of the diagram can be made visually before sending the file to be microfilmed.

The last program written was JUST, used to justify the text of this thesis. It is a simple justifier, assuming that the text is within a few characters of the desired right-hand margin. It was executed on the University of Cambridge IBM370/165 computer. It will only try to justify lines starting in columns 1 or 2, and adds blanks after words longer than 3 characters. Location of extra blanks depends on the number of blanks to be inserted. The program is listed below.

```

C.....7...TEXT JUSTIFIER
C.....MCRROOM VERSION 60 LINES PER PAGE
      DIMENSION AA(65),PP(59),LB(10)
      DATA SP/1H /
      NP=0
      DO 7 II=1,65
        AA(II)=SP
      7 CONTINUE
      WRITE(6,204)SP
      2 READ(5,100,END=9)(AA(N),N=1,65)
      100 FORMAT(65A1)
      3 NP=NP+1
C.....THIS IS THE LINE COUNTER FOR PAGINATION PURPOSES
      IF(NP.EQ.30) GO TO 82
C.....CHECK FOR LBANK INPUT LINE
      IF(AA(1).EQ.SP.AND.AA(2).EQ.SP)GO TO 50
C.....CHECK FOR CHARACTER IN COL. 59
      IF(AA(59).NE.SP) GO TO 50
C.....FIND END OF STRING
      N=59
      1 N=N-1
      IF(AA(N).NE.SP)GO TO 30
      GO TO 1
      30 NB=59-N
C.....NUMBER OF EXTRA LBANKS=NB
C.....CHECK FOR SHORT LINES
      IF(NB.GT.8)GO TO 50
C.....NOW FIND LBANKS AFTER 3CHAR. WORDS.
C.....INITIALIZE LB ARRAY
      DO 25 JK=1,10
        LB(JK)=0
      25 CONTINUE
      M=0
      DO 31 J=4,N
        IF(AA(J).EQ.SP) GO TO 32
        GO TO 31
      32 JJJ=J-3
        JONE=J-1
        JJ=J-2
        IF(AA(JJJ).NE.SP.AND.AA(JJ).NE.SP.AND.JONE.NE.SP)GO TO 33
        GO TO 31
      33 M=M+1
C.....PUT LOCATION OF MTH LBANK INTO LB.
      LB(M)=J
      31 CONTINUE
C.....CHECKS FOR FORMATING OF OUPJT TO AVOID GROUPS OF SPACES
C.....AT ONE END OF THE LINE
      MT=M
      MH=MT/2
      IF(NB.LT.MH)GO TO 73
      IF(NB.GE.MT)GO TO 76
      GO TO 77
      76 NB=MT
      GO TO 34
      77 NB1=NB+1
      DO 75 IM=NB1,MT
C.....SET LB TO 0 WHEN MTH IS MORE THAN NB
      LB(IM)=0
      75 CONTINUE
      GO TO 34
C.....NOW PAD LAST NB SPACES
      73 MK=MT-NB+1
      K=0
      DO 74 IK=MK,MT
        K=K+1
        LB(K)=LB(IK)
      74 CONTINUE
      34 CONTINUE
C.....ACTUAL JUSTIFYING
      NC=0
      M=1
      DO 63 KK=1,59
        PP(KK)=SP
      63 CONTINUE
C.....THIS ENSURES LBANKS ARE IN PP

```

```

DO 59 J=1,N
NC=NC+1
PP(NC)=AA(J)
IF(J.EQ.LB(M))GO TO 61
GO TO 59
61 NC=NC+1
PP(NC)=SP
M=M+1
59 CONTINUE
WRITE(6,201)(PP(N),N=1,59)
201 FORMAT(16X,59A1)
WRITE(6,204)SP
GO TO 2
C.....COPY WITH NO FURTHER ACTION
50 WRITE(6,200)(AA(N),N=1,65)
200 FORMAT(16X,65A1)
WRITE(6,204)SP
GO TO 2
C.....NEW PAGE ROUTINE
82 WRITE(6,204)SP
NP=0
WRITE(6,204)SP
204 FORMAT(A1)
GO TO 3
9 STOP
END

```

References.

1. J.H. Stewart, S.J. Kruger, H.L. Ammon, C. Dickinson and S.R. Hall (1972) The X-RAY system Tech. Rep. TR192 Computer Science centre, University of Maryland, College Park, Maryland
2. C.K. Johnson ORTEP programs for thermal ellipsoid plots. Oak Ridge National Laboratory, Tennessee.

Chapter 1C. Chemistry

Introduction to nucleic acid chemistry.

The role of metal ions in biochemical systems has long been established as being of essential significance, with almost all processes in living tissue requiring the presence of metals of one kind or another. In the area of nucleic acid biochemistry, metallo-enzymes are key molecules in the system of cell replication, and much work has been done to establish the way in which replication occurs. Generally the metals most widely found are alkali, or alkali earth group metals such as sodium or magnesium. Since these ions have relatively simple electronic configurations they do not lend themselves to study by spectroscopic methods. The use of transition metals as replacement probes for the investigation of the environment of metal sites is thus a common technique (1,2).

Almost all studies of nucleic acid/metal systems attempt to determine the precise location and binding of the metal. A review of the techniques available has recently appeared, and deals comprehensively with spectroscopic studies (3).

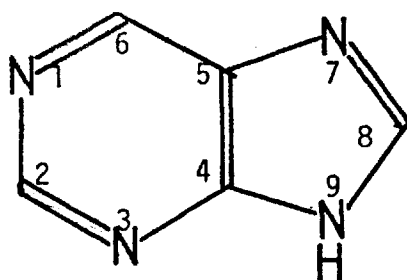
Of special interest is the use of X-ray crystallography to determine the precise nature of a metal-nucleic acid compound, and in recent years a great deal of work has been carried out on nucleic acid derivatives (4,5).

Generally the exact determination of a nucleic acid structure is not possible because of the large size of the molecule (MW ca. 0.5 million). This results in a very large unit cell. In fibre diffraction of nucleic acid strands the 11-fold repeat and the inter-base distance can be observed, consistent with the double-helix model for the structure. Individual base sequencing is not possible by crystallographic techniques. Therefore the single nucleotides, or their parent bases, are used in crystallographic studies as models of the macro molecule.

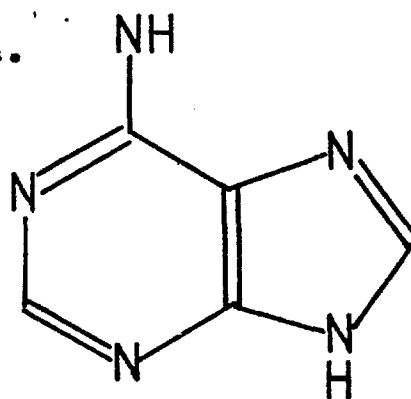
Constitution of a nucleotide.

A nucleotide consists of three moieties; an aromatic heterocyclic 'base', a sugar, and a phosphate. The bases can be of two types, the purine type (e.g. adenine) or the pyrimidine type (e.g. cytosine). See figure 1 for examples.

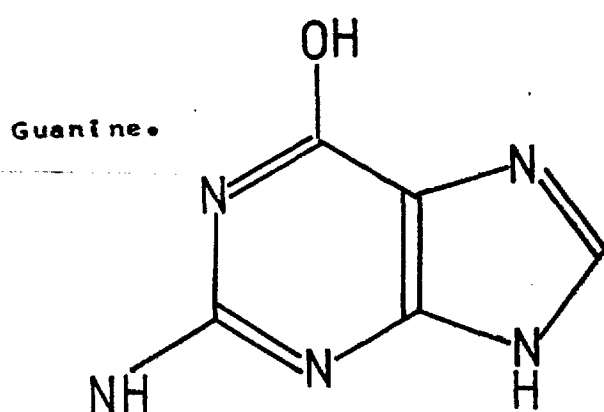
Figure 1. Some common nucleotide bases.



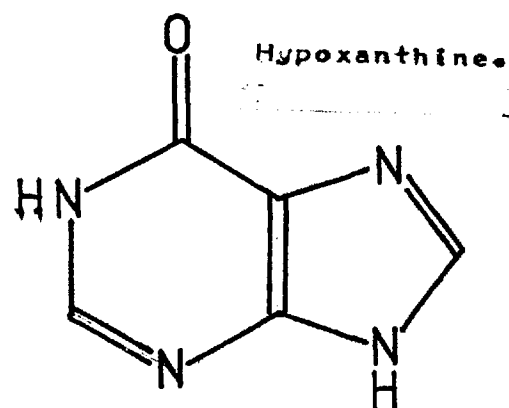
Purine.



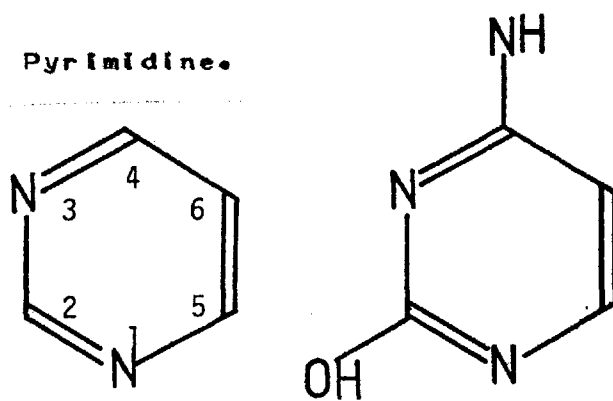
Adenine.



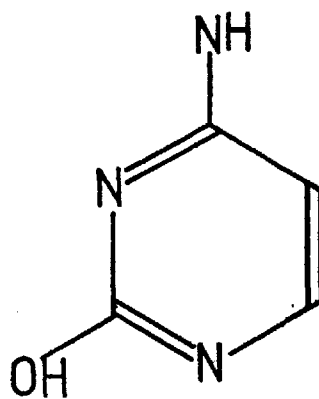
Guanine.



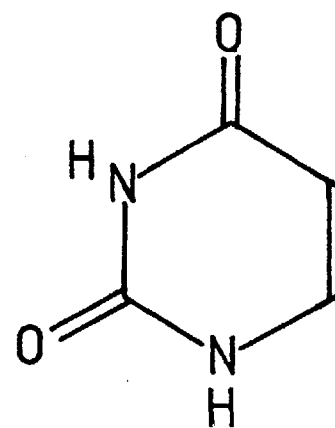
Hypoxanthine.



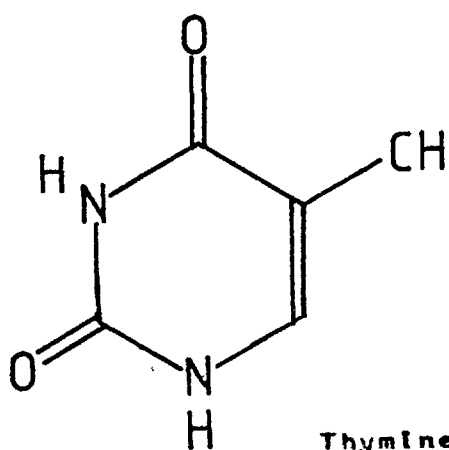
Pyrimidine.



Cytosine.



Uracil.



Thymine.

A nucleoside is formed by a (D)-ribose (or 2-deoxy-ribose) sugar binding to the base at N(9) in purines, and N(1) in pyrimidines. Most studies use the ribose sugar (because of availability). The names are abbreviated to letters, for example adenosine is the nucleoside formed between adenine and ribose, A. The deoxy form is represented by dA, dU etc. A nucleotide is a nucleoside with a phosphate group bonded to the sugar, either the 3' or the 5' position, and this is represented as 5'UMP (for 5'Uridine monophosphate, fig.2).

A nucleic acid is a polymer formed by 3'5' phosphate links between the sugars (Figure 3), RNA for ribose sugars, and DNA for deoxyribose sugars. The sequence of different bases along the chain is responsible for transmitting genetic information. DNA exists normally as a double-stranded fibre with the strands linked together by hydrogen bonds between the bases. The complementary base pairing system (6), restricts the hydrogen bonding to particular pairs of bases on opposite sides of the double strand. For example, G-C and A-T. This selectivity enables the copying of the sequence of bases to occur during replication, thus passing on genetic information.

The binding of a metal to a nucleotide is clearly capable of interfering with the hydrogen bonding, and it is known that certain transition metals have destructive effects on cell replication. Some platinum complexes in particular have been shown to have selective effects on certain kinds of cell, leading to possible antineoplastic use of such complexes. The mode of metal interaction thus has considerable importance in elucidating the nature of the anti-cancer drug effect.

Any comparative study of crystalline nucleic acid constituents with in vivo RNA or DNA must include careful reference to the effects of pH, solid state forces, and the relation between the structure of the model with the real nucleic acid. Most relevant work is carried out on nucleobases which have been substituted at N(9), or N(1), i.e. the location of the sugar moiety. None the less much interesting chemistry is associated with structures of the free bases, and a great deal of structural work has been done in this field.

Figure 2. Uridine 5'monophosphate

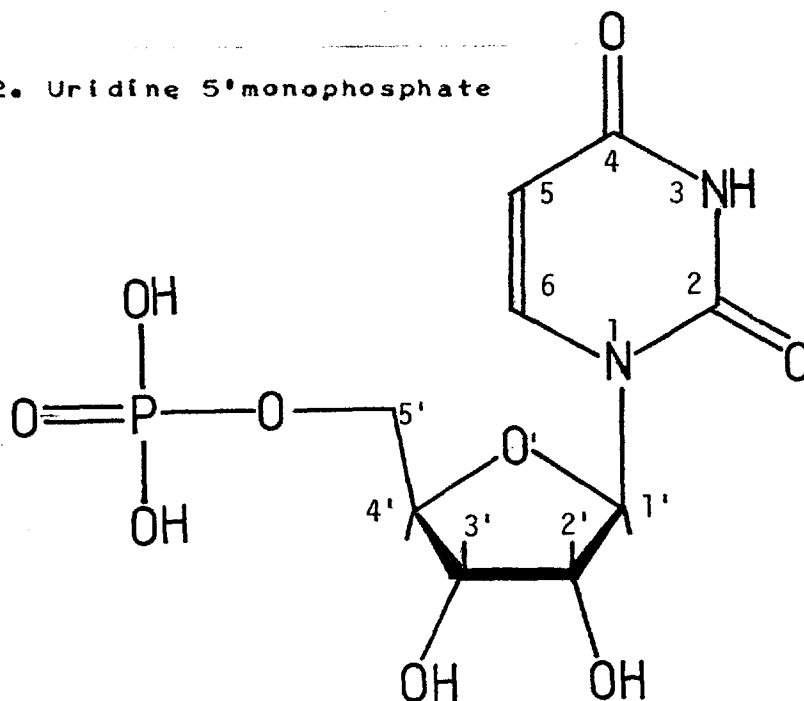
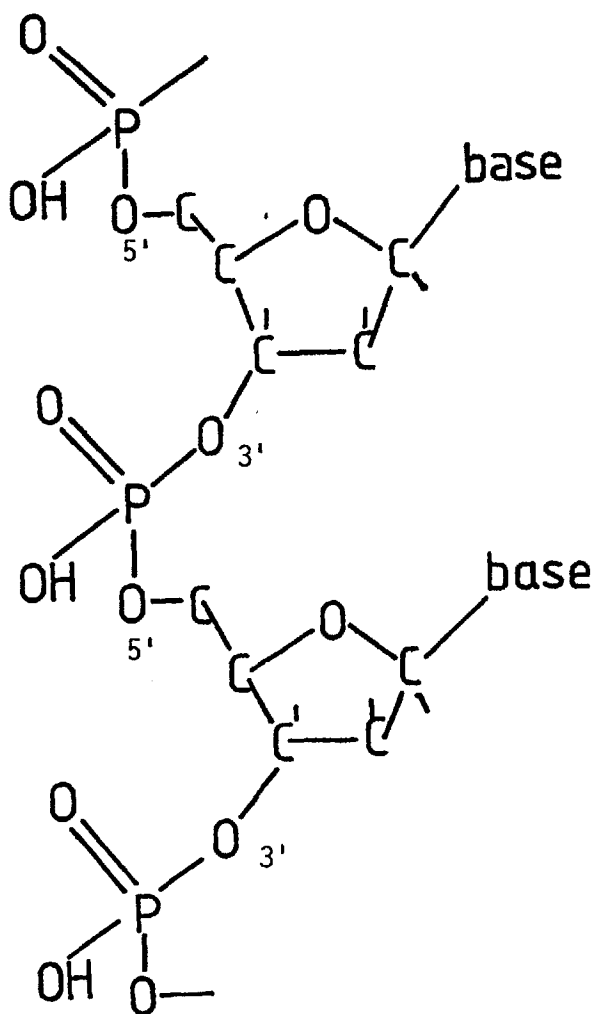


Figure 3. Section of a polynucleotide showing 3'-5' phosphate links.



Care must also be taken in drawing conclusions about the location of metal ions from studies on bases alone, as the nucleotides have the possibility of phosphate and sugar co-ordination. Even so, certain generalities can be made, so that for N(9) blocked purines, we expect N(7)-metal binding, and N(1) blocked cytosine gives N(3)-metal binding.

Purine-metal complexes tend to crystallize much more readily than the pyrimidine equivalents, and there is still a paucity of information on pyrimidine-metal complexes. Of special interest is uracil, and analogues, because uracil has no free nitrogen for co-ordination at neutral pH. The chemistry of metal ion interaction with uracil and thymine has been extensively studied (7,8,9), work which led to the isolation of many of the crystals examined in this thesis.

General structural features.

In examining the structures of nucleic acid bases and derivatives, certain general features will need to be taken into consideration. These include the tendency to form strong hydrogen bonds if at all possible, and also the tendency of the aromatic bases to stack above each other in a parallel fashion at about $3.5\text{\AA}$ separation (10,11). This base stacking usually occurs in such an orientation as to allow polar exocyclic substituents to overlap the delocalised π - system of the aromatic ring.

Empirical

Generally the methods used to prepare the compounds are based on the slow evaporation of solutions containing the starting constituents in suitable molar ratios. Recrystallisation is seldom useful. At a rough approximation most of the crystals studied were small, elongated prisms, often crystallising in a mass of very fine fibres.

Normally a sample of the crystalline batch is sent for analysis for C, H and N (Microanalytical Laboratory Imperial College). This is not always possible for limited batches of difficult growth. The selection of a crystal suitable for X-ray work is initially performed by examination using a polarising microscope. In general single crystals should give sharp extinction of polarised light, unless they belong to the cubic system. Usually the crystals have some regular morphology that allows orientation of the crystal

about a principal crystallographic axis. The crystals are mounted initially on glass fibre with grease, allowing re-mounting during preliminary work. Final mounting is on hand-drawn quartz fibres, using araldite as cement.

Osmium microscopic stains.

One of the uses of heavy metals in biochemical research is as dyes for electron and optical microscopy of tissue (12). Obviously if certain metals can be shown to bind to specific sites, a means of labelling a particular compound is made available. The fixation of double bonds by osmium tetroxide compounds is such an example.

Osmium tetroxide is commonly used to catalyse cis-hydroxylation of isolated double bonds, but it will form stable adducts in the absence of water. The presence of tertiary amines greatly speeds up the catalysis, yet in the absence of water stable compounds can be isolated. These adducts are of interest in determining the nature of the binding of osmium tetroxide to plant tissue containing double bonds such as in unsaturated alkaloids. The resultant adduct is either 5- or 6-co-ordinate depending on the ratio of alkene:osmium tetroxide:amine. The structures of some such compounds appear in chapters 6 and 7.

References

- 1 The Inorganic Chemistry of Biological processes (1972).
- 2 G.L.Eichorn Inorganic Biochemistry (1973).
- 3 L.G.Marzilli Prog.Inorg.Chem. 23 255-378
- 4 D.J.Hodgson Progr.Inorg.Chem. 23 211-254
- 5 G.A.Jeffery and M.Sundaralingam Adv.Carb.Chem.Biochem (1977) 34 345-76
- 6 J.D.Watson and F.H.C.Crick Nature 171 (1953) 737
- 7 McGoodgame and K.W.Johns J.C.S.Dalton (1977) 1680
- 8 K.W.Johns PhD Thesis University of London (1977)
- 9 I.Jeeves PhD Thesis University of London (1976)
- 10 C.E.Bugg, J.M.Thomas, M.Sundaralingam and S.T.Rao Biopolymers 10 (1971) 175-219
- 11 W.Saenger and D.Suck Eur.J.Biochem 32 (1973) 473
- 12 Some Biological Techniques in Electron Microscopy

Chapter 2.

The crystal and molecular structure of dichloro-(9-methylhypoxanthine)mercury(II).

Introduction.

9-methylhypoxanthine has several possible co-ordinating sites for metal atoms, and the possibility of chelation, using the N(7) and the exocyclic O(6) atom, especially to large atoms such as mercury, exists. Mercury can co-ordinate weakly to exocyclic oxygens as in dichlorobis(Uracil)mercury(II), and dichlorobis(dihydrouracil)mercury(II) (1), and also interacts slightly with the O(2) oxygen in the N(3) co-ordinated complex di-u-chlorobis[chloro(1-methylcytosine)]mercury(II) (2).

Good crystals of a mercury-hypoxanthine compound, formula $\text{Hg}(9\text{MeHYP})\text{Cl}_2$, were isolated, allowing a full structural investigation to be carried out (3). Infra-red spectroscopy at low frequencies showed bands in the region expected for terminal Hg-Cl bonds. These were at 275(w) and 325(s) in the i.r., and 276(s), 325(w) in the Raman spectra. There was no indication of bridging chlorine bonds. The structure could therefore have contained 4-co-ordinate mercury, linked through purine bridges with N(3) and N(7) bonds, or a chelate with O(6) and N(7), or three-co-ordinate mercury. 9-Methyladenine complexes are known to link to two metal atoms via N(1) and N(7) (4-6), but this would require the proton normally found on N(1) to move elsewhere in 9-methylhypoxanthine.

Experimental.

Crystals were grown from solutions of 1:1 acetone/water containing equimolar amounts of mercury(II)chloride and 9-Methylhypoxanthine.(7). Analysis results were found: C=17.15% H=1.35% N=12.79%. Calculated for $\text{C}_6\text{H}_6\text{N}_4\text{O}_5\text{HgCl}_2$ C=17.11% H=1.43% N=13.30%.

The crystals were of simple morphology, best described as clear elongated prisms. Preliminary oscillation and Weissenberg photographs showed them to be monoclinic, with systematic absences $h0l \quad l=2n+1$, $0k0 \quad k=2n+1$, consistent with space group $P2_1/c$ (no.14).

A crystal, 0.11 x 0.14 x 0.35 mm was mounted with its 'c'

axis parallel to the ϕ axis of the diffractometer, and 21 high-angle Cu K α reflections were measured accurately in θ . These, on least-squares analysis, gave $a=10.204(1)$, $b=13.671(1)$ and $c=7.167(1)$ Å, $\beta = 98.24(1)^\circ$, $U=989.5$ Å³. Other unit-cell data are $z=4$, $D_{\text{calc}}=2.83$ g cm⁻³, $MW=421.55$, $F(000)=768$, $\mu=346.3$ cm⁻¹.

1846 independent reflections were collected to $\theta=70^\circ$, at 1000 reflections per day, of which 104 were considered 'unobserved' as their nett count did not exceed 2.58 σ I. The 5,4,0 reflection was monitored every 50 reflections as a reference, and used to scale the data. Its nett count did not vary significantly during data collection (c.a. 2 days). The data were corrected for Lorentz and polarisation effects in the usual way. At a later stage the data were corrected for absorption using a 8 x 8 x 12 grid.

Solution and refinement of the structure.

A sharpened, origin-removed Patterson synthesis provided a straightforward determination of the mercury atom co-ordinates, and a Fourier synthesis gave $R=0.38$. Inclusion of the two chlorine atoms gave $R=0.19$. From a difference synthesis the light atoms were located, giving $R=0.088$. Least-squares full-matrix refinement with anisotropic temperature factors gave $R=0.077$, and use of absorption corrected data gave $R=0.067$. Application of anomalous dispersion corrections for Hg and Cl, removal of 7 reflections thought to be suffering from extinction, and inclusion of a weighting scheme with $F^*=40$ gave the final R of 0.059. Hydrogen atoms were added at the calculated positions, with thermal parameters of $U=0.04$ Å² and not refined. Table 2:1 lists the refined atom co-ordinates, Table 2:3 their thermal parameters and Table 2:2 the calculated hydrogen atom positions. Observed and calculated structure factor amplitudes are listed on pages 47 and 48.

The final difference Fourier map has no significant positive features, but does show some negative regions in the vicinity of the mercury atom, due most probably to absorption errors. The crystal had a broken top, but continued trial-and-error absorption correction runs were not thought worthwhile in view of the straightforward nature of the structure.

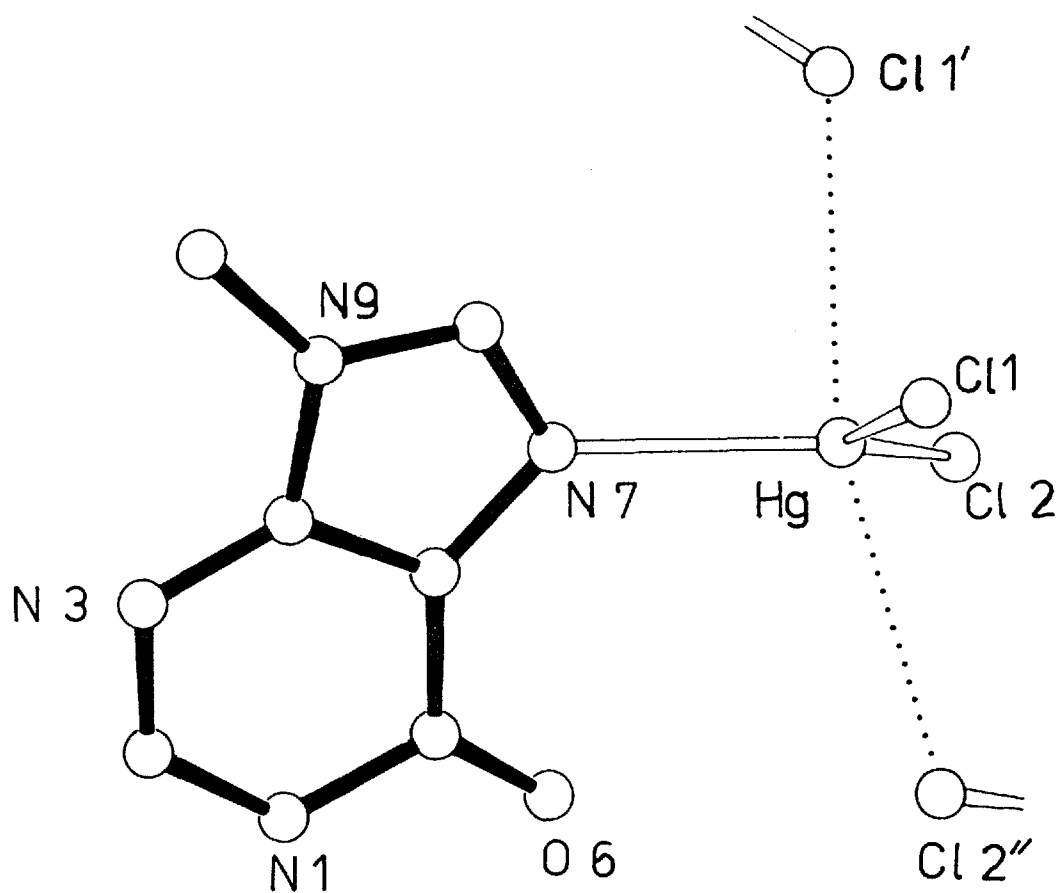


Figure 2:1 The molecule of 9-Methylhypoxanthine dichloro mercury(II), showing the secondary co-ordination.

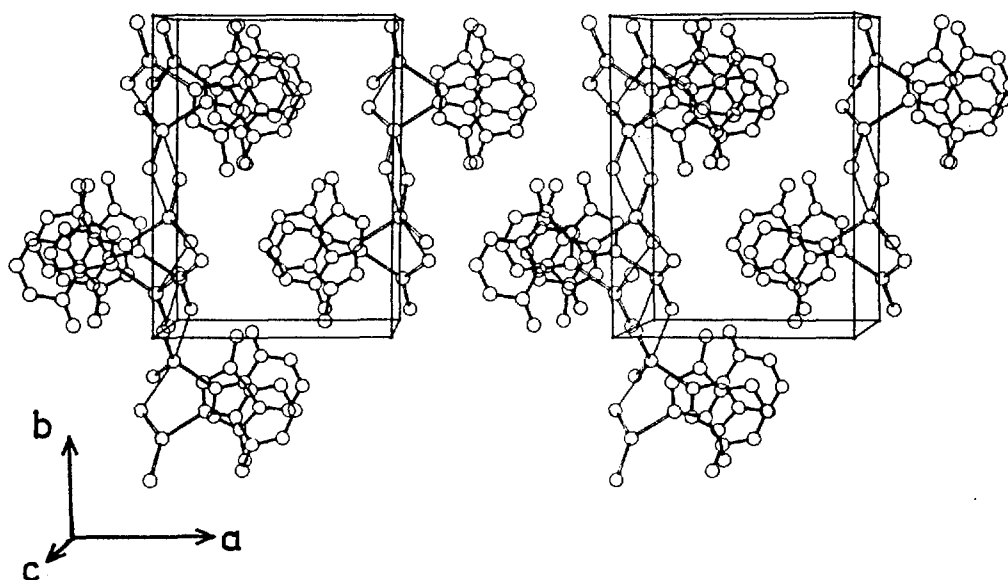


Figure 2:2 A stereoscopic view of the contents of the unit cell.

Description and discussion of structure.

The molecular structure is shown in figure 2:1, from which it can be seen that the mercury is trigonal planar, binding to N(7) and to two chlorine atoms. The Hg-Cl bond lengths are 2.402(3) Å and 2.351(3) Å, normal for strong trigonal Hg-Cl bonds (8,9). However, the N(7)-Hg bond is slightly long at 2.305(8) compared with 2.16 Å found in the guanosine-Hg compound (Catena-(u-chloro)-chloro(guanosine)mercury(II)) (10), which has sp^1 hybridisation. This longer bond length may reflect a slightly different hybridisation of the mercury. The short Hg-Cl bond in the guanosine complex is 2.339(7) Å, which is significantly shorter than the sp^2 Hg-Cl bonds in the title complex. Bond lengths and angles are given in Table 2:4. From this the asymmetrical nature of the trigonal co-ordination, compared with ideal sp^2 inter-ligand angles of ca. 120° , can be seen. The inter-ligand angles are N(7)-Hg-Cl(1) 101.5(2), N(7)-Hg-Cl(2) 118.0(2), Cl(1)-Hg-Cl(2) 140.5(1). These four atoms, however, lie almost exactly in the same plane (see Table 2:5 for least-squares planes calculations). The reason for the wide Cl(1)-Hg-Cl(2) angle is not immediately apparent; a view of the packing of the molecules (Figure 2:2) shows that O(6) of a purine on a symmetry related molecule seems to come in between the two bonding chlorine atoms. The close approach distance is 3.49 Å for Cl(2)....O(6), Cl(1)....O(6) being more than 4 Å. The sum of the Van-de-Waals radii is only 3.2 Å however, so there should not be severe steric strain. An alternative approach to explain the co-ordination about the mercury is to assume that it is a highly distorted linear Cl-Hg-Cl sp system, the distortion being caused by the addition of a fairly weak Hg-N(7) bond. The asymmetrical nature of the resultant co-ordination sphere is more than likely caused by the size of the purine ring restricting geometry. Figure 2:3 depicts a space-filling diagram of the molecule.

Bond lengths and angles within the 9-methylhypoxanthine moiety are unexceptional, and may be compared with those found in tetra-aquabis-(9-methylhypoxanthine)-copper(II) sulphate (11) and also those of inosine (12), and hypoxanthine hydrochloride (13). A least-squares plane through the purine ring indicates that it is satisfactorily planar.

Figure 2:4 Thermal ellipsoid plots, with the ellipsoids scaled to include 50% probability.

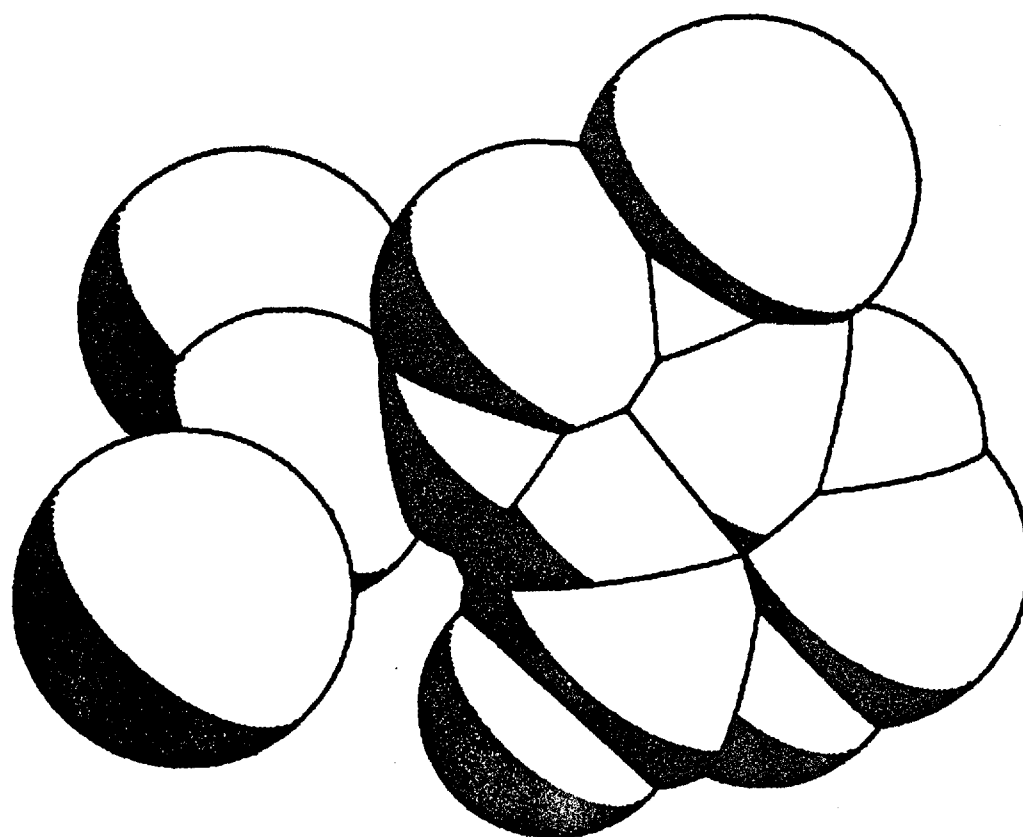
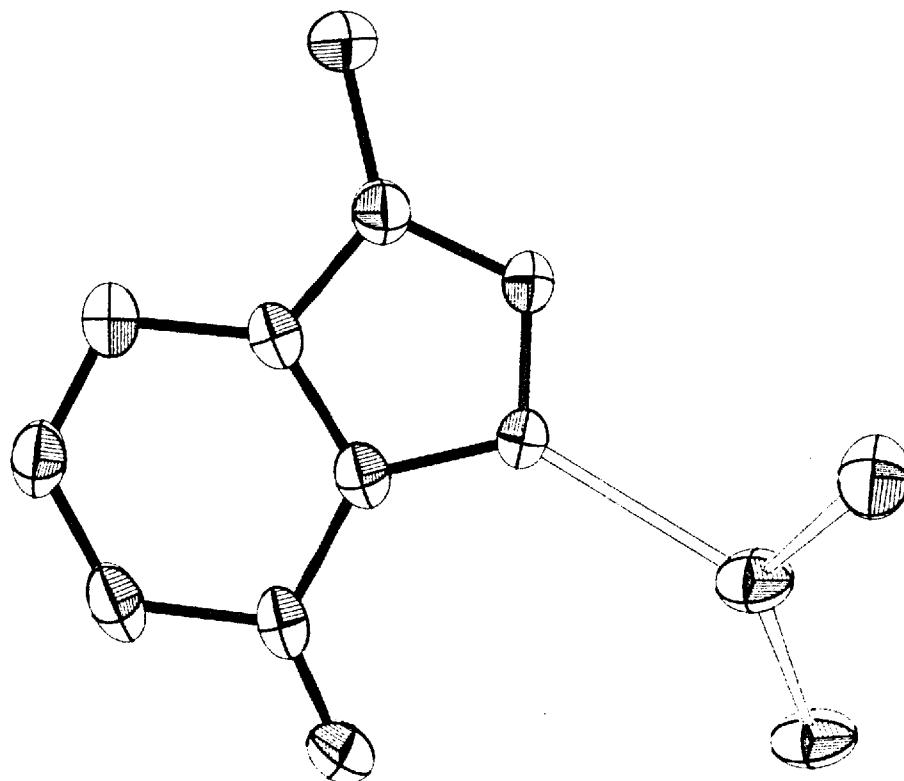


Figure 2:3 The molecule, drawn as a space filling diagram, using Van-de-Waals radii.

with exocyclic atom deviations of -0.09 and -0.03 Å for O(6) and the methyl group. These values are less than the equivalent value for O(6) and C(1') in inosine, which are -0.16 and -0.15 Å respectively.

A view of the molecule showing thermal ellipsoids is given in figure 2:4, from which it may be noted that many of the ellipsoids have principal axes in similar directions. This probably reflects the absorption error. The purine base plane makes an angle of 60° with the mercury co-ordination plane, and O(6) does not approach the mercury atom, being over 3.84 Å away. O(6) does form a strong hydrogen bond to a neighbouring purine base at N(1) of 2.85 Å.

Secondary co-ordination of trigonal mercury is almost always observed, for example $(\text{CH}_3)_3\text{S}^+(\text{HgI}_3)^-$ (14), and the series $[\text{CH}_3]_4\text{N}^+ \text{HgX}_3^-$ ($\text{X}=\text{Cl}, \text{Br}, \text{or I}$) (8,9). This normally consists of occupying the two 'axial' positions of the mercury atom at about 2.9 Å, with halogen atoms. The title complex is no exception to this observation, and has symmetry related chlorine atoms at $2.979(3)$ Å [Cl(1)] and $2.925(3)$ Å [Cl(2)]. They are shown in Figure 2:1, with dotted lines representing the interactions. Inclusion of these atoms would lead to the description of the co-ordination as being midway between square-planar and trigonal bipyramidal.

The crystal packing diagram (Figure 2:2) shows that this secondary co-ordination leads to a two-dimensional net in the bc plane, and explains the easy cleavage of the crystals in this plane. Other intramolecular forces are also involved within the net in the form of purine base-base stacking. A view perpendicular to two such stacked bases is shown in figure 2:5. The pattern of the overlap is typical for purine bases (15), the interplanar distance being 3.47 Å which compares with 3.50 Å in inosine (13). The O(6)...N(1)* hydrogen bond is the only specific source of attraction between the bc planes, and at 2.85 Å is typical of strong hydrogen bonding.

* $-x-1, -y, -z$

Table 2:1 Fractional atomic co-ordinates with estimated standard deviations in parentheses (Non H-atoms)

Atom	x	y	z
H ₂	0.01373(5)	0.13945(3)	-0.00350(6)
Cl(1)	0.1359(2)	0.2098(2)	0.2756(4)
Cl(2)	0.0383(3)	0.0239(2)	-0.2390(4)
N(1)	-0.5092(9)	0.1376(7)	0.0270(14)
C(2)	-0.5630(10)	0.2270(9)	0.0437(11)
N(3)	-0.5010(8)	0.3101(3)	0.0389(10)
C(4)	-0.3729(9)	0.2974(3)	0.0084(14)
C(5)	-0.3079(9)	0.2104(3)	-0.0095(14)
C(6)	-0.3793(10)	0.1204(3)	-0.0072(16)
O(6)	-0.3395(8)	0.0376(6)	-0.0315(13)
N(7)	-0.1789(7)	0.2298(6)	-0.0342(11)
C(8)	-0.1697(9)	0.3259(8)	-0.0315(15)
N(9)	-0.2841(9)	0.3711(6)	-0.0069(13)
C(10)	-0.3092(12)	0.4749(9)	0.0026(21)

Table 2:2 Calculated hydrogen atom positions. The number refers to the parent atom

Atom	x	y	z
H(1)	-0.575	0.090	0.050
H(10)	-0.417	0.480	-0.021
H(11)	-0.272	0.503	0.129
H(12)	-0.269	0.511	-0.097
H(2)	-0.658	0.230	0.064
H(8)	-0.079	0.367	-0.050

Table 2:3 Anisotropic temperature parameters of the non-hydrogen atoms, $\text{\AA}^2$, with estimated standard deviations in parentheses. Hg $\times 10^4$, others $\times 10^3$

Atom	U11	U22	U33	U12	U13	U23
Hg	468(4)	291(4)	332(4)	15(2)	85(2)	-71(2)
Cl(1)	33(1)	44(1)	36(1)	1(1)	4(1)	-11(1)
Cl(2)	67(2)	29(1)	38(1)	5(1)	20(1)	-4(1)
N(1)	24(4)	43(7)	43(6)	-9(4)	7(4)	6(4)
C(2)	22(4)	43(6)	38(5)	5(4)	8(4)	6(5)
N(3)	24(4)	39(5)	44(5)	1(3)	10(4)	0(4)
C(4)	21(4)	32(5)	29(5)	-4(4)	4(4)	0(4)
C(5)	22(4)	34(5)	27(5)	-2(4)	3(4)	4(4)
C(6)	20(4)	40(6)	37(6)	-5(4)	6(4)	0(4)
O(6)	36(4)	30(4)	66(6)	-9(3)	12(4)	-5(4)
N(7)	20(3)	27(4)	29(4)	2(3)	5(3)	-0(3)
C(8)	22(4)	29(5)	37(5)	1(4)	9(4)	1(4)
N(9)	26(4)	31(4)	35(5)	-1(3)	8(3)	-4(3)
C(10)	41(6)	25(5)	68(3)	-0(5)	19(6)	-2(6)

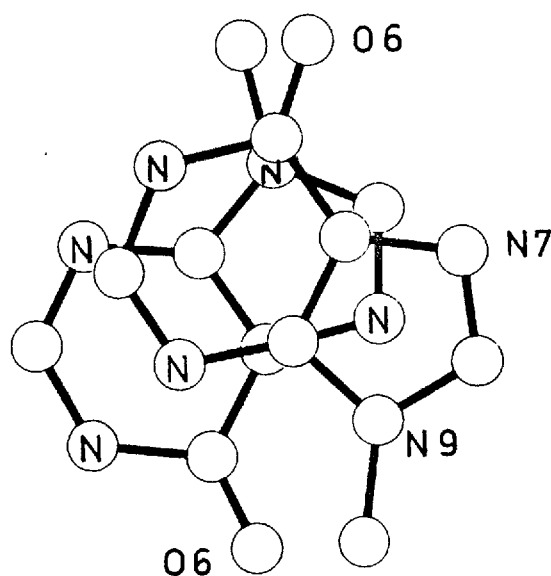


Figure 2:5 A View perpendicular to the purine bases, showing the overlap of symmetry related bases.

Table 2:4 Interatomic bond lengths ($\text{\AA}$) and angles ($^\circ$), with estimated standard deviations in parentheses.

($'$) = $-x, -y, -z$, ($''$) = $x, 1/2-y, z-1/2$

Hg-Cl(1)	2.402(3)	Hg-Cl(2)	2.351(3)
Hg-N(7)	2.305(8)	Hg-Cl(2)'	2.925(3)
Hg-Cl(1)''	2.979(3)		
Cl(1)-Hg-Cl(2)	140.5(1)	Cl(1)-Hg-N(7)	101.5(2)
Cl(2)-Hg-N(7)	117.9(2)		
N(1)-C(2)	1.353(15)	C(2)-N(3)	1.302(15)
N(3)-C(4)	1.366(13)	C(4)-C(5)	1.378(15)
C(5)-C(6)	1.431(15)	C(6)-N(1)	1.402(14)
C(6)-O(6)	1.224(14)	C(5)-N(7)	1.379(12)
N(7)-C(8)	1.318(13)	C(8)-N(9)	1.354(13)
N(9)-C(4)	1.370(13)	N(9)-C(10)	1.445(15)
C(6)-N(1)-C(2)	125.0(10)	N(1)-C(2)-N(3)	125.4(10)
C(2)-N(3)-C(4)	111.9(10)	N(3)-C(4)-C(5)	127.5(10)
N(3)-C(4)-N(9)	125.3(10)	C(5)-C(4)-N(9)	107.1(9)
C(4)-C(5)-C(6)	119.2(9)	C(4)-C(5)-N(7)	109.1(9)
C(6)-C(5)-N(7)	131.6(9)	C(5)-C(6)-N(1)	110.7(9)
C(5)-C(6)-O(6)	127.8(10)	N(1)-C(6)-O(6)	121.5(10)
C(5)-N(7)-Hg	134.5(7)	C(6)-N(7)-Hg	118.4(6)
C(5)-N(7)-C(8)	104.9(8)	N(7)-C(8)-N(9)	113.3(9)
C(8)-N(9)-C(4)	105.5(8)	C(8)-N(9)-C(10)	128.0(9)
C(4)-N(9)-C(10)	126.5(9)		

Table 2:5 Least-squares planes, and deviations therefrom. Estimated standard deviations in parentheses.

Equation of plane. $4.878x + 9.444y - 4.339z - 1.436 = 0$

Defining the plane:

Hg -0.037(1) Cl(1) 0.013(3) Cl(2) 0.014(3) N(7) 0.010(3)

Equation of plane. $1.449x - 0.522y + 0.870z + 0.632 = 0$

Defining the plane:

N(1) 0.010(10) C(2) -0.000(11) N(3) 0.013(9)

C(4) -0.005(10) C(5) 0.012(10) C(6) -0.029(11)

N(7) 0.019(8) C(8) 0.001(10) N(9) -0.020(9)

Not defining the plane:

O(6) -0.095(9) C(10) -0.045(10) Hg 0.555(1)

$10|F_0| \quad 10|F_2|$

1	1070	1080	1090	1100	1110	1120	1130	1140	1150	1160	1170	1180	1190	1200	1210	1220	1230	1240	1250	1260	1270	1280	1290	1300	1310	1320	1330	1340	1350	1360	1370	1380	1390	1400	1410	1420	1430	1440	1450	1460	1470	1480	1490	1500	1510	1520	1530	1540	1550	1560	1570	1580	1590	1600	1610	1620	1630	1640	1650	1660	1670	1680	1690	1700	1710	1720	1730	1740	1750	1760	1770	1780	1790	1800	1810	1820	1830	1840	1850	1860	1870	1880	1890	1900	1910	1920	1930	1940	1950	1960	1970	1980	1990	2000	2010	2020	2030	2040	2050	2060	2070	2080	2090	2100	2110	2120	2130	2140	2150	2160	2170	2180	2190	2200	2210	2220	2230	2240	2250	2260	2270	2280	2290	2300	2310	2320	2330	2340	2350	2360	2370	2380	2390	2400	2410	2420	2430	2440	2450	2460	2470	2480	2490	2500	2510	2520	2530	2540	2550	2560	2570	2580	2590	2600	2610	2620	2630	2640	2650	2660	2670	2680	2690	2700	2710	2720	2730	2740	2750	2760	2770	2780	2790	2800	2810	2820	2830	2840	2850	2860	2870	2880	2890	2900	2910	2920	2930	2940	2950	2960	2970	2980	2990	3000	3010	3020	3030	3040	3050	3060	3070	3080	3090	3100	3110	3120	3130	3140	3150	3160	3170	3180	3190	3200	3210	3220	3230	3240	3250	3260	3270	3280	3290	3300	3310	3320	3330	3340	3350	3360	3370	3380	3390	3400	3410	3420	3430	3440	3450	3460	3470	3480	3490	3500	3510	3520	3530	3540	3550	3560	3570	3580	3590	3600	3610	3620	3630	3640	3650	3660	3670	3680	3690	3700	3710	3720	3730	3740	3750	3760	3770	3780	3790	3800	3810	3820	3830	3840	3850	3860	3870	3880	3890	3900	3910	3920	3930	3940	3950	3960	3970	3980	3990	4000	4010	4020	4030	4040	4050	4060	4070	4080	4090	4100	4110	4120	4130	4140	4150	4160	4170	4180	4190	4200	4210	4220	4230	4240	4250	4260	4270	4280	4290	4300	4310	4320	4330	4340	4350	4360	4370	4380	4390	4400	4410	4420	4430	4440	4450	4460	4470	4480	4490	4500	4510	4520	4530	4540	4550	4560	4570	4580	4590	4600	4610	4620	4630	4640	4650	4660	4670	4680	4690	4700	4710	4720	4730	4740	4750	4760	4770	4780	4790	4800	4810	4820	4830	4840	4850	4860	4870	4880	4890	4900	4910	4920	4930	4940	4950	4960	4970	4980	4990	5000	5010	5020	5030	5040	5050	5060	5070	5080	5090	5100	5110	5120	5130	5140	5150	5160	5170	5180	5190	5200	5210	5220	5230	5240	5250	5260	5270	5280	5290	5300	5310	5320	5330	5340	5350	5360	5370	5380	5390	5400	5410	5420	5430	5440	5450	5460	5470	5480	5490	5500	5510	5520	5530	5540	5550	5560	5570	5580	5590	5600	5610	5620	5630	5640	5650	5660	5670	5680	5690	5700	5710	5720	5730	5740	5750	5760	5770	5780	5790	5800	5810	5820	5830	5840	5850	5860	5870	5880	5890	5900	5910	5920	5930	5940	5950	5960	5970	5980	5990	6000	6010	6020	6030	6040	6050	6060	6070	6080	6090	6100	6110	6120	6130	6140	6150	6160	6170	6180	6190	6200	6210	6220	6230	6240	6250	6260	6270	6280	6290	6300	6310	6320	6330	6340	6350	6360	6370	6380	6390	6400	6410	6420	6430	6440	6450	6460	6470	6480	6490	6500	6510	6520	6530	6540	6550	6560	6570	6580	6590	6600	6610	6620	6630	6640	6650	6660	6670	6680	6690	6700	6710	6720	6730	6740	6750	6760	6770	6780	6790	6800	6810	6820	6830	6840	6850	6860	6870	6880	6890	6900	6910	6920	6930	6940	6950	6960	6970	6980	6990	7000	7010	7020	7030	7040	7050	7060	7070	7080	7090	7100	7110	7120	7130	7140	7150	7160	7170	7180	7190	7200	7210	7220	7230	7240	7250	7260	7270	7280	7290	7300	7310	7320	7330	7340	7350	7360	7370	7380	7390	7400	7410	7420	7430	7440	7450	7460	7470	7480	7490	7500	7510	7520	7530	7540	7550	7560	7570	7580	7590	7600	7610	7620	7630	7640	7650	7660	7670	7680	7690	7700	7710	7720	7730	7740	7750	7760	7770	7780	7790	7800	7810	7820	7830	7840	7850	7860	7870	7880	7890	7900	7910	7920	7930	7940	7950	7960	7970	7980	7990	8000	8010	8020	8030	8040	8050	8060	8070	8080	8090	8100	8110	8120	8130	8140	8150	8160	8170	8180	8190	8200	8210	8220	8230	8240	8250	8260	8270	8280	8290	8300	8310	8320	8330	8340	8350	8360	8370	8380	8390	8400	8410	8420	8430	8440	8450	8460	8470	8480	8490	8500	8510	8520	8530	8540	8550	8560	8570	8580	8590	8600	8610	8620	8630	8640	8650	8660	8670	8680	8690	8700	8710	8720	8730	8740	8750	8760	8770	8780	8790	8800	8810	8820	8830	8840	8850	8860	8870	8880	8890	8900	8910	8920	8930	8940	8950	8960	8970	8980	8990	9000	9010	9020	9030	9040	9050	9060	9070	9080	9090	9100	9110	9120	9130	9140	9150	9160	9170	9180	9190	9200	9210	9220	9230	9240	9250	9260	9270	9280	9290	9300	9310	9320	9330	9340	9350	9360	9370	9380	9390	9400	9410	9420	9430	9440	9450	9460	9470	9480	9490	9500	9510	9520	9530	9540	9550	9560	9570	9580	9590	9600	9610	9620	9630	9640	9650	9660	9670	9680	9690	9700	9710	9720	9730	9740	9750	9760	9770	9780	9790	9800	9810	9820	9830	9840	9850	9860	9870	9880	9890	9900	9910	9920	9930	9940	9950	9960	9970	9980	9990	10000	10010	10020	10030	10040	10050	10060	10070	10080	10090	10100	10110	10120	10130	10140	10150	10160	10170	10180	10190	10200	10210	10220	10230	10240	10250	10260	10270	10280	10290	10300	10310	10320	10330	10340	10350	10360	10370	10380	10390	10400	10410	10420	10430	10440	10450	10460	10470	10480	10490	10500	10510	10520	10530	10540	10550	10560	10570	10580	10590	10600	10610	10620	10630	10640	10650	10660	10670	10680	10690	10700	10710	10720	10730	10740	10750	10760	10770	10780	10790	10800	10810	10820	10830	10840	10850	10860	10870	10880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4	411	450	0	327	314	4	410	402	3	112	112	9	87
5	126	126	1	81	81	5	146	134	4	358	377	0	80
6	368	371	1	327	300	6	375	364	5	87	87	1	81
7	107	100	1	140	140	7	107	100	6	338	330	2	80
8	200	208	2	271	276	8	200	208	7	99	84	3	87
9	368	371	1	327	300	9	368	371	8	101	87	4	156
10	107	100	1	140	140	10	107	100	9	134	134	5	156
11	200	208	2	271	276	11	200	208	10	114	104	6	187
12	368	371	1	327	300	12	368	371	11	101	101	7	156
13	107	100	1	140	140	13	107	100	12	134	134	8	187
14	200	208	2	271	276	14	200	208	13	114	104	9	156
15	368	371	1	327	300	15	368	371	14	101	101	10	187
16	107	100	1	140	140	16	107	100	15	134	134	11	156
17	200	208	2	271	276	17	200	208	16	114	104	12	187
18	368	371	1	327	300	18	368	371	17	101	101	13	156
19	107	100	1	140	140	19	107	100	18	134	134	14	187
20	200	208	2	271	276	20	200	208	19	114	104	15	156
21	368	371	1	327	300	21	368	371	20	101	101	16	187
22	107	100	1	140	140	22	107	100	21	134	134	17	156
23	200	208	2	271	276	23	200	208	22	114	104	18	187
24	368	371	1	327	300	24	368	371	23	101	101	19	156
25	107	100	1	140	140	25	107	100	24	134	134	20	187
26	200	208	2	271	276	26	200	208	25	114	104	21	156
27	368	371	1	327	300	27	368	371	26	101	101	22	187
28	107	100	1	140	140	28	107	100	27	134	134	23	156
29	200	208	2	271	276	29	200	208	28	114	104	24	187
30	368	371	1	327	300	30	368	371	29	101	101	25	156
31	107	100	1	140	140	31	107	100	30	134	134	26	187
32	200	208	2	271	276	32	200	208	31	114	104	27	156
33	368	371	1	327	300	33	368	371	32	101	101	28	187
34	107	100	1	140	140	34	107	100	33	134	134	29	156
35	200	208	2	271	276	35	200	208	34	114	104	30	187
36	368	371	1	327	300	36	368	371	35	101	101	31	156
37	107	100	1	140	140	37	107	100	36	134	134	32	187
38	200	208	2	271	276	38	200	208	37	114	104	33	156
39	368	371	1	327	300	39	368	371	38	101	101	34	187
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41	200	208	2	271	276	41	200	208	40	114	104	36	187
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47	200	208	2	271	276	47	200	208	46	114	104	42	187
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53	200	208	2	271	276	53	200	208	52	114	104	48	187
54	368	371	1	327	300	54	368	371	53	101	101	49	156
55	107	100	1	140	140	55	107	100	54	134	134	50	187
56	200	208	2	271	276	56	200	208	55	114	104	51	156
57	368	371	1	327	300	57	368	371	56	101	101	52	187
58	107	100	1	140	140	58	107	100	57	134	134	53	156
59	200	208	2	271	276	59	200	208	58	114	104	54	187
60	368	371	1	327	300	60	368	371	59	101	101	55	156
61	107	100	1	140	140	61	107	100	60	134	134	56	187
62	200	208	2	271	276	62	200	208	61	114	104	57	156
63	368	371	1	327	300	63	368	371	62	101	101	58	187
64	107	100	1	140	140	64	107	100	63	134	134	59	156
65	200	208	2	271	276	65	200	208	64	114	104	60	187
66	368	371	1	327	300	66	368	371	65	101	101	61	156
67	107	100	1	140	140	67	107	100	66	134	134	62	187
68	200	208	2	271	276	68	200	208	67	114	104	63	156
69	368	371	1	327	300	69	368	371	68	101	101	64	187
70	107	100	1	140	140	70	107	100	69	134	134	65	156
71	200	208	2	271	276	71	200	208	70	114	104	66	187
72	368	371	1	327	300	72	368	371	71	101	101	67	156
73	107	100	1	140	140	73	107	100	72	134	134	68	187
74	200	208	2	271	276	74	200	208	73	114	104	69	156
75	368	371	1	327	300	75	368	371	74	101	101	70	187
76	107	100	1	140	140	76	107	100	75	134	134	71	156
77	200	208	2	271	276	77	200	208	76	114	104	72	187
78	368	371	1	327	300	78	368	371	77	101	101	73	156
79	107	100	1	140	140	79	107	100	78	134	134	74	187
80	200	208	2	271	276	80	200	208	79	114	104	75	156
81	368	371	1	327	300	81	368	371	80	101	101	76	187
82	107	100	1	140	140	82	107	100	81	134	134	77	156
83	200	208	2	271	276	83	200	208	82	114	104	78	187
84	368	371	1	327	300	84	368	371	83	101	101	79	156
85	107	100	1	140	140	85	107	100	84	134	134	80	187
86	200	208	2	271	276	86	200	208	85	114	104	81	156
87	368	371	1	327	300	87	368	371	86	101	101	82	187
88	107	100	1	140	140	88	107	100	87	134	134	83	156
89	200	208	2	271	276	89	200	208	88	114	104	84	187
90	368	371	1	327	300	90	368	371	89	101	101	85	156
91	107	100	1	140	140	91	107	100	90	134	134	86	187
92	200	208	2	271	276	92	200	208	91	114	104	87	156
93	368	371	1	327	300	93	368	371	92	101	101	88	187
94	107	100	1	140	140	94	107	100	93	134	134	89	156
95	200	208	2	271	276	95	200	208	94	114	104	90	187
96	368	371	1	327	300	96	368	371	95	101	101	91	156
97	107	100	1	140	140	97	107	100	96	134	134	92	187
98	200	208	2	271	276	98	200	208	97	114	104	93	156
99	368	371	1	327	300	99	368	371	98	101	101	94	187
100	107	100	1	140	140	100	107	100	99	134	134	95	156

References.

1. J. A. Carrabine and M. Sundaralingam. *Biochem* 10 (1971) 292
2. M. Authier-Martin and A. L. Beauchamp. *Can. J. Chem.* 55 (1977) 1213.
3. N. Barba-Behrens, R. A. Cartwright, D. M. L. Goodgame and A. C. Skapski. *Inorg. Chim Acta* 31 (1978) L471
4. P. De Meester, D. M. L. Goodgame, A. C. Skapski and Z. Warnke. *Biochim. Biophys. Acta* 324 (1973) 301
5. M. J. McCall and M. R. Taylor. *Acta Cryst.* B32 (1977) 1637
6. N. Barba-Behrens, D. M. L. Goodgame and Z. Warnke. *Inorg. Chim Acta* 31 (1978) 257
7. N. Barba-Behrens. Personal communication.
8. E. Fata, R. Nitsche, H. Roetschi and S. Zingg. *Phys. Rev.* 125 (1962) 514
9. J. G. White. *Acta Cryst* 16 (1963) 397
10. M. Authier-Martin, J. Hubert, R. Rivest and A. L. Beauchamp. *Acta Cryst.* B34 (1978) 273
11. E. Sletten and R. Kaale. *Acta Cryst* B33 (1977) 158-160
12. A. P. I. Nuns and P. Tollin. *Acta Cryst* B26 (1970) 1101
13. J. Sletten and L. H. Jensen. *Acta Cryst.* B25 (1969) 1608
14. R. H. Fenn. *Acta Cryst.* 20 (1966) 20
15. C. E. Rugg, J. M. Thomas, M. Sundaralingam and S. T. Rao. *Biopolymers* 10 (1971) 175-219

Chapter 3.

The crystal and molecular structure of Hexaquo-
manganese(II).iodide Tetrakis(4,6-dimethylpyrimidine-2-one).

Introduction.

The interaction of pyrimidine bases with metals has been the subject of investigation within this department (1,2), and crystal structures of several metal-pyrimidine complexes have been determined (3,4). Preparative work with 4,6 dimethyl pyrimidin-2-one (4,6-DMP) and manganese led to the isolation of small yellow crystals of stoichiometry 4,6-DMP :Mn varying between 3:1 and 4:1. Their e.p.r. spectra could not be explained on the basis of simple molecular models. The methyl groups probably prevent N-Mn co-ordination, and thus the compound was thought to contain O(2)-Mn bonds, and so a structural investigation using X-ray diffraction was initiated.

Experimental.

Powder diffraction photographs of the first batches of the material confirmed its crystallinity, and so experimental work on growing crystals suitable for single-crystal X-ray studies was implemented. The crystals were prepared from solutions of 4,6-DMP and MnI_2 in propan-1-ol. (The manganese iodide was prepared by mixing dried $MnCl_2$ and sodium iodide in propan-1-ol, this resulted in the precipitation of salt leaving a solution of manganese iodide). Ratios of 1:4 4,6-DMP to MnI_2 were used. Large yellow prismatic crystals appeared on standing the solution for 2 or 3 days.

Preliminary Weissenberg and precession photographs showed the crystals to be triclinic, space group $P1$ or $P\bar{1}$. A crystal of size 0.16 x 0.12 x 0.46 mm was mounted with its 'c' axis parallel to the diffractometer ϕ axis, and 36 high-angle reflections were measured. By least-squares fitting these gave unit-cell parameters of $a=12.022(1)$, $b=7.661(5)$, $c=10.235(1)$ Å, $\alpha=93.63(1)^\circ$, $\beta=105.92(1)^\circ$, $\gamma=92.84(1)^\circ$, $U=902.43$ Å³. Other pertinent data are $F(000)$ 455 $D(calc)=1.68$ gm/cm³, $\mu=183.8$ cm⁻¹, $M=913.36$ (for C₂₄ H₄₄ I₂ Mn N₈ O₁₀). A grid of 10 x 10 x 10 was used for the absorption correction of the data at a later stage.

3449 independent reflections were measured on the diffract-

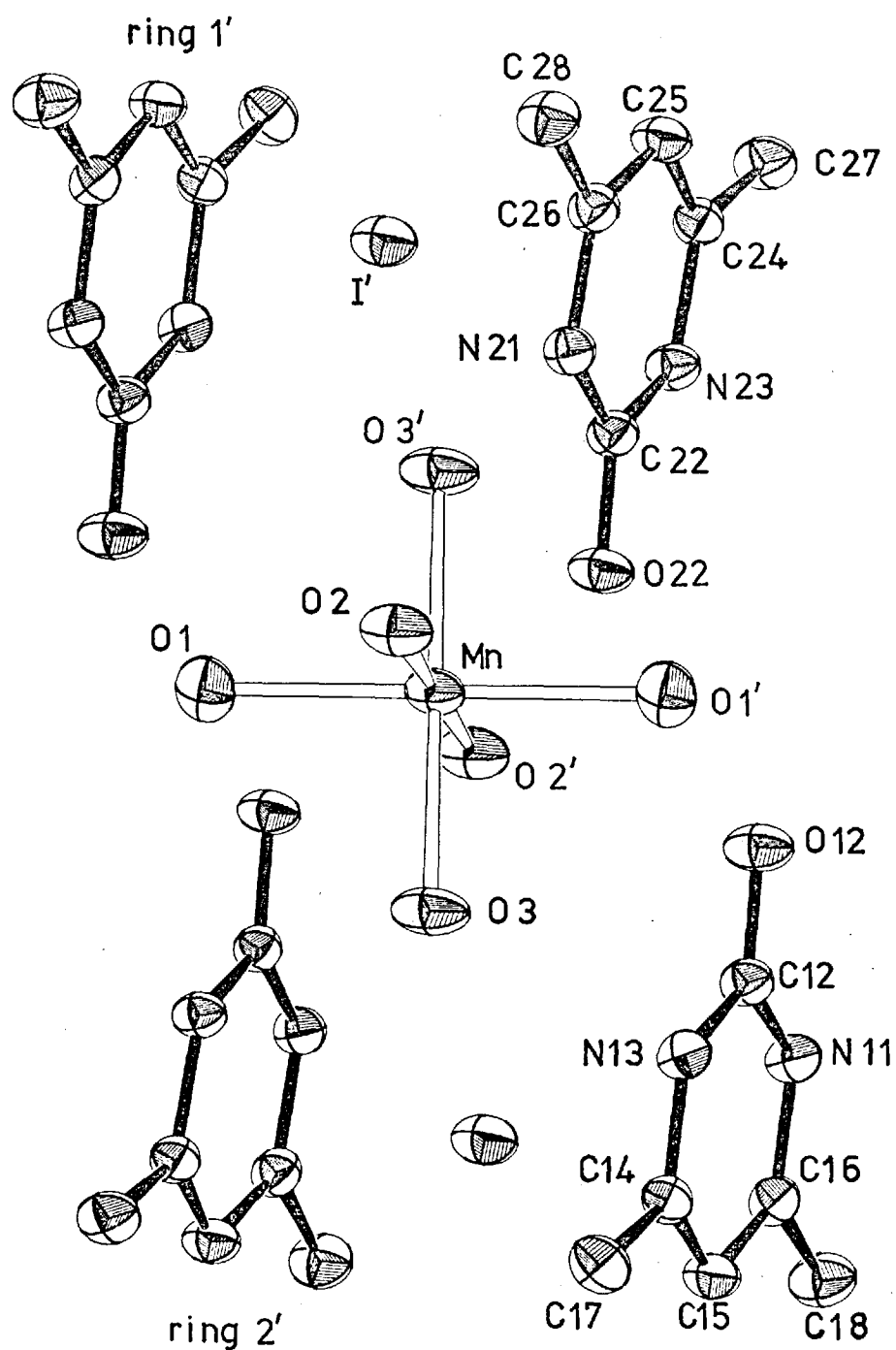


Figure 3:1 The components of the chemically unique contents of the unit cell. The manganese atom lies on a centre of symmetry. Thermal ellipsoids are scaled to include 50% probability.

ctometer, collecting at a rate of ca. 1000 reflections per day. The 3,3,0 reflection was monitored as a reference every 50 reflections, and its count did not alter significantly during the period of data collection. 182 reflections were treated as unobserved, their nett count being less than 2.58 σ . Lorentz and polarisation corrections were applied, and the data scaled by the reference.

Solution and refinement of the structure.

A sharpened, origin-removed Patterson synthesis showed 3 large peaks, the largest of which was assigned as an iodine-iodine vector. At this stage refinement was in P1, and a Fourier synthesis with one iodine gave $R=0.49$. From the difference map two further peaks consistent with the Patterson were assigned as iodine and manganese, the manganese being fixed at the origin for convenience. This reduced R to 0.29, and the rest of the structure could be easily located. The space group was changed to $P\bar{1}$, and isotropic refinement of all the atoms gave $R=0.11$ using data limited to 40° in θ . Use of all the data ($\theta=70^\circ$) gave $R=0.15$, and anisotropic refinement of manganese and iodine reduced R to 0.097. Application of an absorption correction reduced R to 0.056, and full-matrix least-squares refinement of all the atoms anisotropically reduced R to 0.040. From a difference Fourier all the hydrogen atoms could be located, and were contributed as fixed-atom parameters. Anomalous dispersion corrections for Mn and I, removal of the 1,-2,1 reflection for extinction effects, and application of the usual weighting scheme with $F^*=45$ gave the final R of 0.034. Table 3:1 lists the non-hydrogen atomic co-ordinates, Table 3:2 lists the anisotropic thermal parameters, and Table 3:3 the hydrogen atom positions. The observed and the calculated structure factor amplitudes can be found on pages 61 to 62.

Description and discussion of the structure.

The crystal structure consists of three different components and they are shown in Figure 3:1. The manganese is surrounded by six water molecules in closely octahedral co-ordination, and the 4,6-DMP molecules are not co-ordinating, but associate through hydrogen bonds to the water

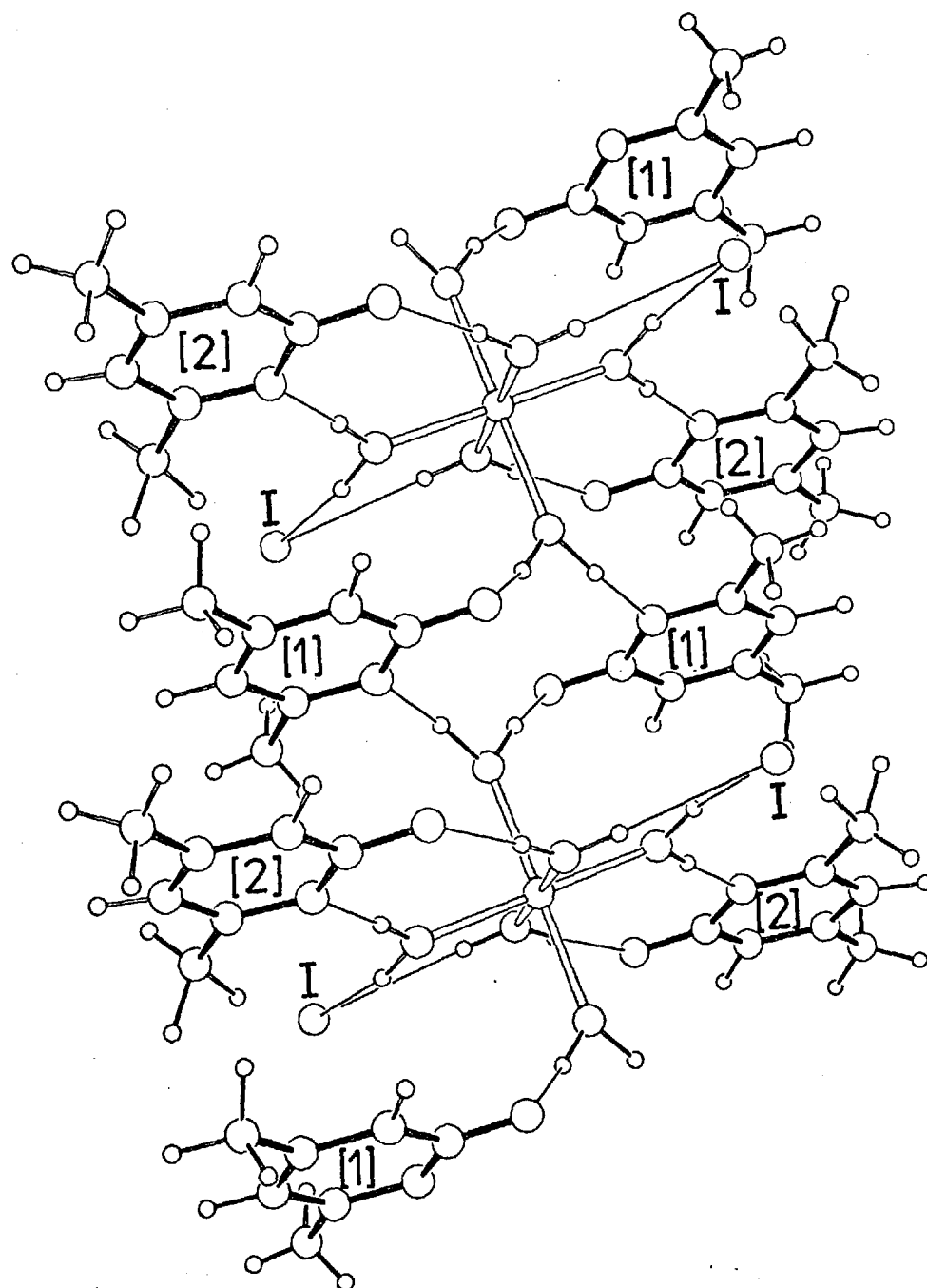


Figure 3:2 The hydrogen bonding network.

co-ordination sphere. The iodine ions are also hydrogen bonded to the hexaquomanganese cation.

The octahedral geometry about the manganese is distorted very slightly, with two shorter equatorial and one longer axial bond lengths of 2.166(4), 2.160(4) and 2.214(3) Å, whilst the unique angles are 90.1(1), 92.8(2), and 95.0(1)°. Table 3:4 lists all the bond-lengths and angles in the structure. The manganese co-ordination is similar to that in Tutton's salt (5), manganese ammonium sulphate hexahydrate, but with a reversal of the relative lengths of the equatorial and axial bonds, which are 2.193(6), 2.200(6), and 2.150(6) Å.

The angular distortion is sufficient to show very clearly on the e.p.r spectrum of the compound. It consists of a peak at $g=2$, which is expected for a high-spin d^5 electron configuration, and also two broad shoulders which are normally attributed to marked off-axis distortions. The reason for the distortion is not clear, because high-spin d^5 systems should not show Jahn-Teller distortions (6). No other obvious structural features indicate a reason, and thus the distortion must be tentatively attributed to favourable hydrogen bonding schemes, and base overlap.

Both independent 4,6-DMP molecules are linked via hydrogen bonds to water molecules co-ordinated to the manganese ion. Internal bond-lengths and angles are similar between the rings, and closely similar to those found in the free molecule (7) apart from the carbonyl bonds, which are 1.248(5) and 1.265(5) Å. These are significantly longer than those found for pyrimidine carbonyl bonds (ca. 1.22 Å) (8), and they probably reflect the involvement of carbonyl oxygen electron density with strong hydrogen bonds.

Least-squares planes through the pyrimidine moieties are shown in Table 3:5, from which it can be seen that they are essentially planar.

The hydrogen bonding network is shown in Figure 3:2, and tabulated in Table 3:6. Both carbonyl oxygens are bonded to two atoms; O(12) to N(23) and O(1), O(22) to N(13) and O(2). The hydrogen atoms are on the water molecules, which confirms that the C=O linkage is in the keto rather than the enol form. The protonation of N(n3) is further confirmed by the internal angles of 122.3° and 123.0°, compared

with the unprotonated values of 118.8° and 118.6° for N(n1) (see Singh's paper (9)). The angles at the water molecules to their hydrogen atoms are also in Table 3:6. Although they are consistent with the difference of the equatorial and axial bonds, they do not help in explaining the origin of the difference.

The bases overlap at a perpendicular distance of $3.32 \text{ \AA}$, and make an angle of 1.2° with each other. The orientation is similar to that found in cytosine, with the carbonyls overlapping the aromatic ring (10), and is depicted in Figure 3:3. Figure 3:4 shows a view of the unit-cell, indicating the mode of packing of the molecules, which is clearly influenced by hydrogen bonding and good base stacking.

The lack of direct manganese-pyrimidine co-ordination precludes much discussion as to the significance of the structure in biological terms. Re-examination of the original spectroscopic data showed clear differences to that of the batch of crystals actually used for structure determination. Attempts at the growth of dehydrated examples which ought to have metal-base binding, has so far been unable to produce crystals suitable for X-ray structure determination. However, the unit-cell and space group has been determined as triclinic, $P1$ or $P\bar{1}$, $a=10.00$, $b=9.86$, $c=10.65 \text{ \AA}$, $\alpha=61.0^\circ$, $\beta=115.0^\circ$, $\gamma=120.0^\circ$, $V=775 \text{ \AA}^3$. The experimental work consisted of drying all the starting compounds in a vacuum desiccator, and using distilled solvents over sodium or molecular sieves. The biggest problem is allowing solvent evaporation to occur in a dehydrated environment, which seems best overcome by using a large desiccator with phosphorous pentoxide as the drying agent.

The stoichiometry of the dry compound is 4:1 4,6-DMP:Mn, with no water present (confirmed by i.r. spectra). This must lead to a very crowded environment about the manganese and thus probably accounts for the instability of the resultant compound.

Figure 3:4 A stereoscopic view of the contents of the unit cell

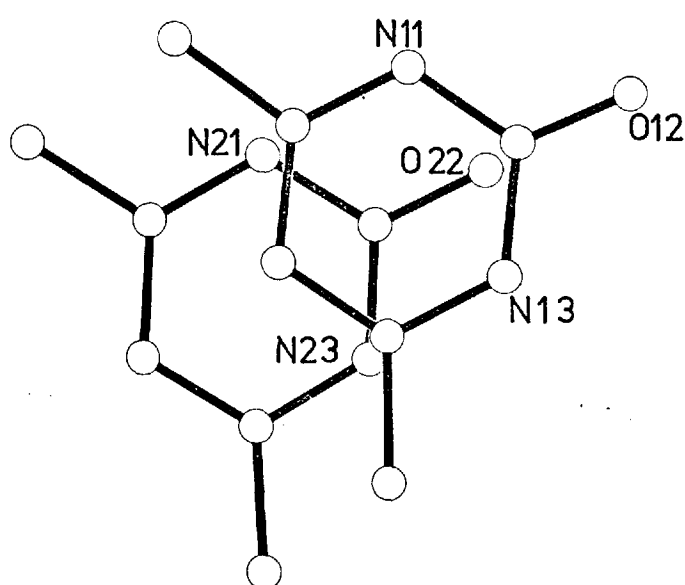
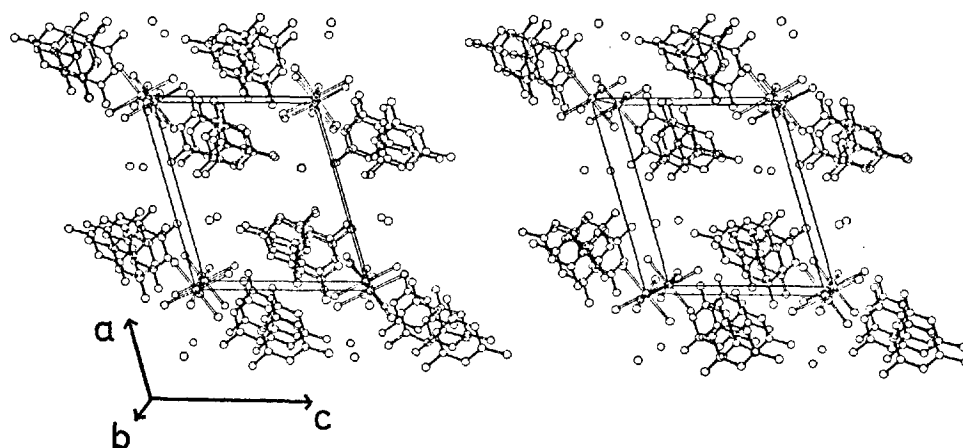


Figure 3:3 A view perpendicular to the pyrimidine bases showing how they overlap.

Table 3:1 Atomic coordinates of the non-hydrogen atoms
with standard deviations in parentheses.

Atom	x	y	z
Mn	0	0	0
I	0.3643(1)	0.2695(1)	0.2011(1)
O(1)	0.0613(3)	-0.2585(4)	0.0364(3)
O(2)	0.0870(3)	0.0917(5)	0.2152(3)
O(3)	0.1442(3)	0.0812(5)	-0.0750(4)
N(11)	0.1483(3)	0.5475(5)	-0.1502(4)
C(12)	0.0775(4)	0.4504(5)	-0.2598(4)
O(12)	-0.0253(3)	0.4050(4)	-0.2666(3)
N(13)	0.1200(3)	0.3997(5)	-0.3674(3)
C(14)	0.2302(4)	0.4419(6)	-0.3673(4)
C(15)	0.3017(4)	0.5363(6)	-0.2578(5)
C(16)	0.2572(4)	0.5870(5)	-0.1488(4)
C(17)	0.2636(4)	0.3809(7)	-0.4934(5)
C(18)	0.3334(4)	0.6876(7)	-0.0239(5)
N(21)	-0.2082(3)	0.0393(5)	0.3056(4)
C(22)	-0.1326(4)	0.1341(5)	0.4127(4)
O(22)	-0.0300(2)	0.1797(4)	0.4125(3)
N(23)	-0.1685(3)	0.1844(5)	0.5252(3)
C(24)	-0.2786(4)	0.1519(5)	0.5316(4)
C(25)	-0.3556(4)	0.0640(6)	0.4218(5)
C(26)	-0.3164(4)	0.0063(5)	0.3101(4)
C(27)	-0.3065(4)	0.2159(6)	0.6598(5)
C(28)	-0.3991(4)	-0.0953(7)	0.1905(5)

Table 3:2 Anisotropic thermal parameters $\times 10^3$ (Mn, I $\times 10^4$), $\text{\AA}^2$
with estimated standard deviations in parentheses.

ATOM	U11	U22	U33	U12	U13	U23
Mn	365(5)	513(6)	344(5)	-39(4)	168(4)	-93(4)
I	413(2)	621(2)	509(2)	-51(1)	186(1)	-66(1)
O(1)	73(2)	57(2)	48(2)	11(2)	35(2)	4(2)
O(2)	45(2)	73(2)	40(2)	-10(2)	18(1)	16(2)
O(3)	45(2)	84(2)	52(2)	-17(2)	23(2)	-23(2)
N(11)	41(2)	42(2)	36(2)	-5(1)	15(1)	-5(1)
C(12)	39(2)	40(2)	37(2)	-2(2)	16(2)	-2(2)
O(12)	41(2)	67(2)	44(2)	-13(1)	20(1)	-13(1)
N(13)	43(2)	40(2)	35(2)	-4(1)	16(1)	-5(1)
C(14)	42(2)	39(2)	45(2)	4(2)	24(2)	3(2)
C(15)	34(2)	48(2)	46(2)	-2(2)	15(2)	0(2)
C(16)	41(2)	35(2)	39(2)	-2(2)	13(2)	1(2)
C(17)	57(3)	57(3)	48(3)	7(2)	30(2)	-3(2)
C(18)	47(3)	59(3)	49(3)	-10(2)	11(2)	-6(2)
N(21)	38(2)	40(2)	38(2)	-2(1)	14(1)	-4(1)
C(22)	38(2)	36(2)	37(2)	0(2)	17(2)	0(2)
O(22)	35(1)	59(2)	45(2)	-6(1)	19(1)	-10(1)
N(23)	37(2)	42(2)	35(2)	-4(1)	15(1)	-3(1)
C(24)	39(2)	37(2)	42(2)	1(2)	20(2)	1(2)
C(25)	35(2)	50(3)	47(2)	-3(2)	19(2)	-2(2)
C(26)	39(2)	36(2)	40(2)	-2(2)	13(2)	-1(2)
C(27)	52(3)	56(3)	44(3)	-3(2)	27(2)	-5(2)
C(28)	46(3)	55(3)	46(3)	-7(2)	10(2)	-12(2)

Table 3:3 Unrefined hydrogen atom positions.

Parent	Atom	x	y	z
O(1)	H(10)	0.107	-0.350	-0.012
	H(20)	0.033	-0.340	0.084
O(2)	H(30)	0.050	0.125	0.280
	H(40)	0.160	0.135	0.220
O(3)	H(50)	0.167	0.035	-0.156
	H(60)	0.210	0.160	-0.012
N(13)	H(13)	0.077	0.315	-0.440
C(15)	H(15)	0.390	0.565	-0.252
C(17)	H(171)	0.350	0.410	-0.496
	H(172)	0.213	0.445	-0.568
	H(173)	0.247	0.250	-0.520
C(18)	H(181)	0.290	0.775	-0.012
	H(182)	0.400	0.725	-0.040
	H(183)	0.350	0.600	0.052
N(23)	H(23)	-0.117	0.275	0.588
C(25)	H(25)	-0.443	0.050	0.412
C(27)	H(271)	-0.253	0.315	0.720
	H(272)	-0.390	0.250	0.648
	H(273)	-0.300	0.115	0.720
C(28)	H(281)	-0.373	-0.175	0.104
	H(282)	-0.467	-0.030	0.152
	H(283)	-0.427	-0.225	0.216

Table 3:4 Bond lengths ($\text{\AA}$) and angles ($^\circ$) of the three molecules in the unit cell. E.S.D's in parentheses.

The $\text{Mn}(\text{H}_2\text{O})_6$ ion:

Mn-O(1) 2.166(4) Mn-O(2) 2.214(3) Mn-O(3) 2.160(4)

O(1)-Mn-O(2) 90.15(12) O(1)-Mn-O(3) 92.78(15)

O(2)-Mn-O(3) 94.96(12)

Since the Mn atom is on a centre of symmetry, the other co-ordination sphere angles are complements of the unique.

The 4,6-DMP ligands:

Ligand 1		Ligand 2	
N(11)-C(12)	1.358(5)	N(21)-C(22)	1.357(5)
C(12)-O(12)	1.248(5)	C(22)-O(22)	1.265(5)
C(12)-N(13)	1.378(6)	C(22)-N(23)	1.375(6)
N(13)-C(14)	1.347(6)	N(23)-C(24)	1.355(6)
C(14)-C(17)	1.507(7)	C(24)-C(27)	1.500(7)
C(14)-C(15)	1.351(6)	C(24)-C(25)	1.357(5)
C(15)-C(16)	1.405(7)	C(25)-C(26)	1.406(7)
C(16)-C(18)	1.493(6)	C(26)-C(28)	1.492(6)
C(16)-N(11)	1.325(6)	C(26)-N(21)	1.327(6)
C(16)-N(11)-C(12)	118.8(4)	C(26)-N(21)-C(22)	118.6(4)
N(11)-C(12)-N(13)	119.1(4)	N(21)-C(22)-N(23)	119.2(4)
N(11)-C(12)-O(12)	122.2(4)	N(21)-C(22)-O(22)	122.2(4)
O(12)-C(12)-N(13)	118.6(3)	O(22)-C(22)-N(23)	118.6(3)
C(12)-N(13)-C(14)	122.2(3)	C(22)-N(23)-C(24)	123.0(3)
N(13)-C(14)-C(15)	119.0(4)	N(23)-C(24)-C(25)	117.8(4)
N(13)-C(14)-C(17)	116.3(3)	N(23)-C(24)-C(27)	117.5(3)
C(17)-C(14)-C(15)	124.7(4)	C(27)-C(24)-C(25)	124.8(4)
C(14)-C(15)-C(16)	118.2(4)	C(24)-C(25)-C(26)	118.7(4)
C(15)-C(16)-N(11)	122.7(3)	C(25)-C(26)-N(21)	122.7(3)
C(15)-C(16)-C(18)	120.3(4)	C(25)-C(26)-C(28)	119.3(4)
C(18)-C(16)-N(11)	117.1(4)	C(28)-C(26)-N(21)	118.0(4)

Table 3:5 Least-squares planes calculations, with distances from the plane in $\text{\AA}$. E.s.d's in Parentheses.

Plane 1. Equation $-2.56x + 6.82y - 4.26z - 3.99 = 0$

Defining plane:

N(11) 0.009(7) C(12) -0.005(7) N(13) -0.001(5)

C(14) 0.004(8) C(15) -0.001(8) C(16) -0.006(7)

Not defining plane:

O(12) -0.020(5) C(17) 0.040(9) C(18) -0.050(9)

Plane 2. Equation $-2.32x + 6.91y - 4.15z + 0.50 = 0$

Defining plane:

N(21) -0.013(7) C(22) 0.023(7) N(23) -0.013(5)

C(24) -0.008(7) C(25) 0.019(8) C(26) -0.008(7)

Not defining plane:

O(22) 0.101(5) C(27) -0.033(8) C(28) -0.022(9)

Table 3:6. Hydrogen bonds. Distances in Å, angles in °
 , eesed in parentheses.

N(11)...O(1)	2.799(5) ¹	N(23)...O(12) ²	2.757(4)
O(22)...N(13) ²	2.855(5)	I...O(3)	3.473(3)
O(2)...O(22)	2.826(3)	O(1)...O(12) ³	2.803(5)
O(3)...N(21) ³	2.793(5)	O(2).....I	>3.5

H(10)-O(1)-H(20) 95.7(3) H(30)-O(2)-H(40) 122.0(3)

H(50)-O(3)-H(60) 110.4(3)

O(1)-H(10).....N(11) 155.6(2)

O(1)-H(20).....O(12) 145.9(2)

O(2)-H(30).....O(22) 176.6(2)

O(3)-H(50).....N(21) 177.5(3)

N(23)-H(23).....O(12) 166.0(3)

N(13)-H(13).....O(22) 169.2(2)

1 = x, 1+y, z 3 = -x, -y, -z

2 = x, y, 1+z

References.

1. K.Johns (1978) PhD Thesis, University of London.
2. M.Goodgame and K.Johns, J.Chem.Soc. Dalton (1977) 1680
3. B.A.Cartwright, C.D.Reynolds and A.C.Skapski. Acta Cryst B33 (1977) 1883
4. B.A.Cartwright, P.O.Langguth Jr., and A.C.Skapski Acta Cryst B35 (1979) 63
5. H.Montgomery, R.V.Chastain and E.C.Lingafelter Acta Cryst. 20 (1966) 731
6. 'Advanced Inorganic Chemistry'. F.A.Cotton and G.Wilkinson. Wiley Interscience, New York p590.
7. G.J.Pitt Acta Cryst 1 (1948) 168
8. D.Voet and A.Rich Progr.Nucl.Acids.Res.Mol.Biol. 10 (1970) 183
9. C.Singh Acta Cryst. 19 (1965) 861
10. C.E.Bugg, J.M.Thomas, M.Sundaralingam and S.T.Rao Biopolymers 10 (1971) 175

Chapter 4.

The crystal and molecular structure of
bis(1,3-Dimethyluracil)dichlorocopper(II).

Introduction.

1,3-Dimethyluracil (1,3-DMU) is a molecule which has both nitrogen positions blocked by methyl groups, and thus can only use exocyclic oxygens for binding to metals. Therefore any compound formed by the molecule is of obvious interest. As previously noted in chapter 1C, only weak metal-oxygen interaction in uracils has been characterized specifically (1). Work by Dr's M. Goodgame and K. Johns (2) led to the isolation of crystals of stoichiometry $\text{Cu}(1,3\text{-DMU})_2\text{Cl}_2$. Such a compound would be consistent with metal-oxygen binding, although the presence of bridging chlorine atoms could not be ruled out at this stage. A structural determination was therefore carried out (3).

Experimental

A hot saturated ethanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added to a hot solution of 7%-by-weight 1,3-DMU (4) in ethyl acetate, in a 1:2 Cu:1,3-DMU molar ratio. A clear, pale green solution was formed which was allowed to slowly evaporate to dryness over a period of ca. 4 weeks. This yielded a green fibrous crystalline material. From the mass of crystals so formed, a very small single fragment was isolated and was mounted with its 'c' axis parallel to the camera axis. It was measured at $0.033 \times 0.115 \times 0.308$ mm. Preliminary oscillation, Weissenberg and precession photographs gave approximate unit-cell dimensions and a triclinic space group, either $P1$ or $\overline{P}1$.

The crystal was then mounted on the diffractometer with its 'c' axis parallel to the ϕ axis. Accurate unit-cell dimensions were determined by measuring 28 high-angle ($\theta = 50^\circ - 60^\circ$) reflections and doing a least-squares calculation. This gave $a = 12.029(1)$, $b = 8.449(1)$, $c = 3.883(1)$ Å, $\alpha = 93.66^\circ(1)$, $\beta = 93.69(1)^\circ$, $\gamma = 101.27(1)^\circ$. Other crystal data are: $U = 384.99$ Å³, $z = 1$, $F(000) = 211$, $D(\text{calc}) = 1.79$ g/cm³, linear absorption coefficient $\mu = 54.99$ cm⁻¹, and absorption grid $10 \times 10 \times 10$. Microanalytical results are: Found C=33.79%, H=3.56%, N=13.80%, calculated for $\text{Cu}(\text{C}_6\text{H}_8\text{N}_2\text{O}_2)_2\text{Cl}_2$ are

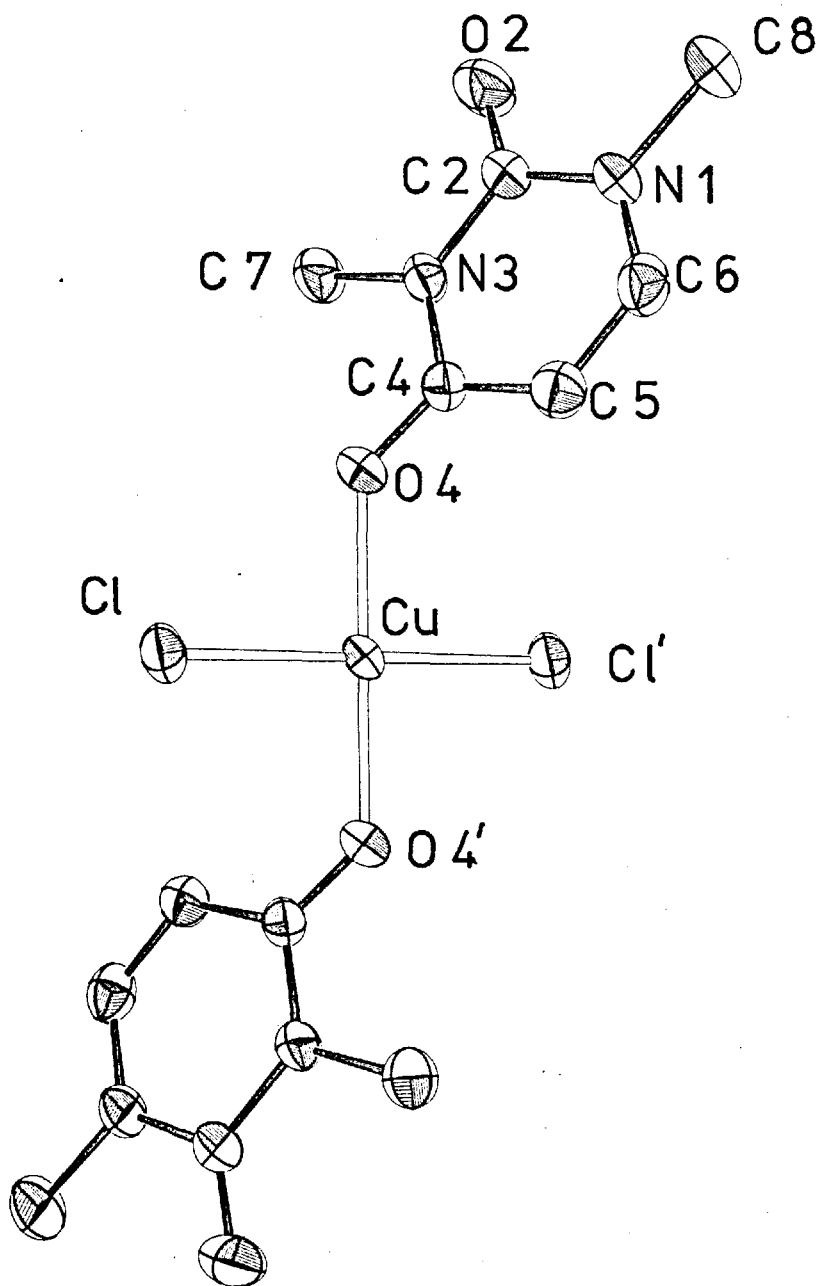


Figure 4:1 The molecule of bis(1,3-dimethyluracil)dichloro copper(II), with thermal ellipsoids scaled to include 50% probability.

C=34.75%, H=3.89%, N=13.57%. The molecular weight is $M=414.71$.

1155 reflections were measured, collecting at a rate of ca 300 reflections per day. The 3,4,0 reflection was monitored as a reference, and its nett count did not change during data collection. Data processing showed 221 reflections to have nett counts less than $2.58 \sigma I$; these were coded unobserved.

Solution and refinement of the structure.

A Patterson synthesis gave peaks corresponding to copper-other atom vectors, from which almost all of the structure could be seen. Reflection statistics suggested a centrosymmetric space group. A Fourier synthesis in $P\bar{1}$, with copper fixed at the origin, and a chlorine atom in a general position gave $R=0.35$. All the other atoms were easily located, and isotropic refinement gave $R=0.11$. Fully anisotropic refinement gave $R=0.057$, and correction for absorption further reduced R to 0.053. From the difference Fourier all the hydrogen atoms could be located. These were input as fixed-atom contributions with the temperature parameter of their parent atoms. Correction for anomalous dispersion for copper and chlorine, and application of the usual weighting scheme, with $F^*=13$, gave the final R of 0.034. Table 4:1 lists atomic co-ordinates, and Table 4:2 the anisotropic thermal parameters. Observed and calculated structure factor amplitudes are listed on page 72.

Description and discussion of the structure.

Figure 4:1 shows the molecule of bis(1,3-Dimethyluracil)dichlorocopper(II). The copper atom is co-ordinated to two trans chlorine atoms, and two trans exocyclic oxygen atoms, in a square-planar fashion. The Cu-O distance is $1.985(3) \text{ \AA}$, and Cu-Cl is $2.269(1) \text{ \AA}$. Both are typical of strong bonds to the copper atom, for example in a recently determined copper-formate structure (5), mean Cu-O is $1.959 \text{ \AA}$, and a literature mean of $2.30 \text{ \AA}$ for square-planar Cu-Cl has been reported (6).

The copper atom lies on a centre of symmetry and so its co-ordination geometry is strictly planar. The unique Cu-Cl-O angle is $88.5(1)^\circ$. At a distance of $2.983(3) \text{ \AA}$ in the

direction of the 'axis' of the square plane, are chlorine atoms of neighbouring molecules, giving a pseudo-elongated octahedral arrangement about the copper atoms.

Bond lengths and angles within the 1,3-DMU molecule are very similar to those found in 1,3-DMU itself (7). Table 4:3 lists the relevant bond lengths and angles. Of particular interest are the lengths of the carbonyl bonds, which in the title compound are 1.246(4) Å for C(4)-O(4), and 1.212(5) for C(2)-O(2), because these groups can be recognised using infra-red spectroscopy. This is responsive to changes of bond strength caused by oxygen interaction with external atoms. The change caused by strong binding to copper through O(4) is slight, as seen by comparing the values of 1.225(3) Å (C(2)-O(2)), and 1.227(3) Å for 1,3-DMU itself. The change, however, is significant, and shows the strength of the Cu-O(4) bond when compared with the related structure of bis-uracil-dichloromercury (II), (1). This compound has a C(4)-O(4) distance of 1.25(3) Å, which is not significantly greater than the 1.245(2) Å found in uracil itself (3). The i.r. spectrum reflects these small changes in bond lengths, but peak shifts are very small, ca 10 cm⁻¹, and require careful measurement in order to detect significant changes due to strong metal-oxygen binding (2,3).

The other interesting feature of the structure is a large Cu-O(4)-C(4) angle of 133.5(2)°, which may indicate some π -bonding of the oxygen to the copper. This would be consistent with the low ligand field found for uracil (2) and theoretical electron density calculations for uracil (9).

Table 4:4 gives least-squares planes calculations, and for the uracil base shows very little deviation from planarity, even for the exocyclic atoms of the ligand. The carbonyl oxygens are not significantly displaced from the plane. This is not the case in (1), in which O(4) is displaced 0.07 Å toward the mercury atom. The 1,3-DMU base makes an angle of 60.6° with the copper co-ordination plane, and the copper atom is 0.64 Å out of the uracil base plane.

No hydrogen bonding is possible, so packing of the molecules is probably determined by base-base stacking,

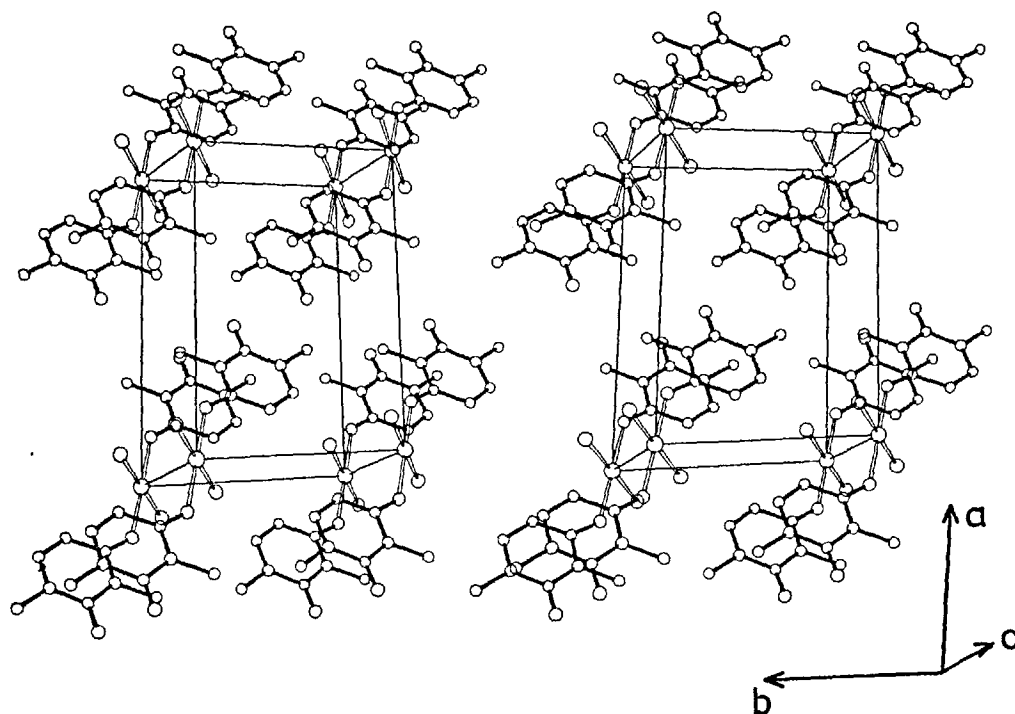


Figure 4:2 A stereoscopic view of the contents of the unit cell

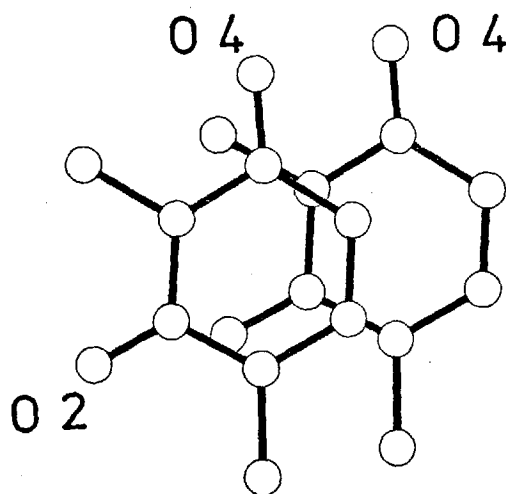


Figure 4:3 A view perpendicular to the pyrimidine base, showing the overlap of the uracil ligands.

and the chlorine atom occupation of the long axial sites about the copper. Figure 4:2 shows the arrangement of the molecules within the unit cell, and Figure 4:3 shows the overlap of the bases. This is at the expected 3.39 Å separation, and shows the alignment of C(2)-O(2) carbonyl bonds above the aromatic rings. This similar to that found in the free ligand structure. Figure 4:4 depicts a space filling drawing of the molecule.

The existence of strong copper-oxygen interaction must not necessarily be used to predict metal-O(4) interaction in nucleotides and nucleosides; for example the structure of dicopper-bispyridylamine-bis-5'UMP(10) shows only copper to phosphate-oxygen binding. On the other hand, care must be taken in the use of infra-red spectroscopy as a diagnostic tool for such binding.

It seems, however, that copper-O(4) binding must not be ruled out in cases where phosphate binding is not possible because of steric or other reasons. Thus more work on nucleic acid units is required before generalisations, concerning the binding sites of uracil-base nucleotides, can be made.

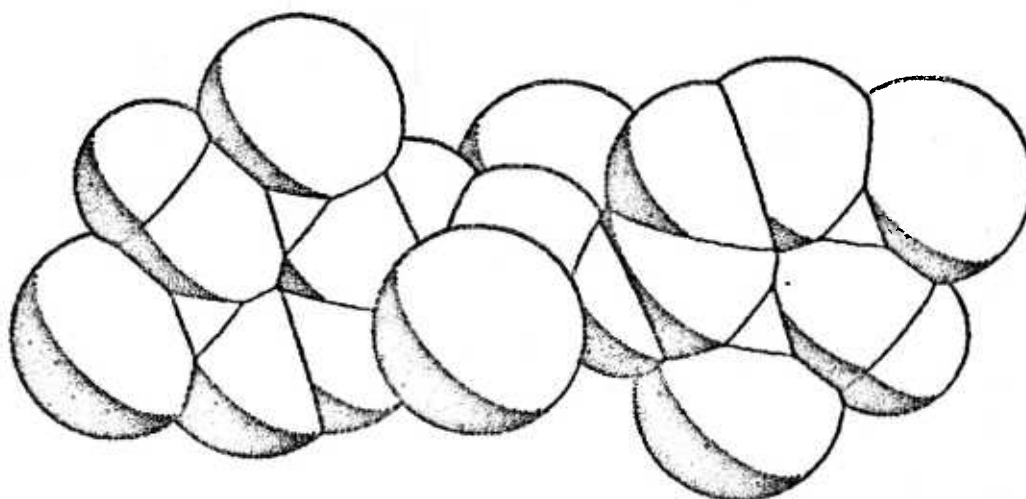


Figure 4:4 A space-filling diagram of the molecule (PLUT078)

Table 4:1 Atomic co-ordinates with estimated standard deviations in parentheses.

ATOM	x	y	z
Cu	0	0	0
Cl	0.0699(1)	0.1988(1)	0.4236(2)
N(1)	0.2927(3)	-0.4403(3)	-0.1482(8)
C(2)	0.3501(3)	-0.2942(4)	-0.2412(9)
O(2)	0.4409(2)	-0.2784(3)	-0.3669(8)
N(3)	0.2956(2)	-0.1642(3)	-0.1860(7)
C(4)	0.1918(3)	-0.1749(4)	-0.0478(9)
O(4)	0.1550(2)	-0.0473(3)	-0.0135(7)
C(5)	0.1390(3)	-0.3295(4)	0.0479(9)
C(6)	0.1908(3)	-0.4551(4)	-0.0025(10)
C(7)	0.3524(3)	-0.0067(4)	-0.2911(11)
C(8)	0.3444(4)	-0.5838(5)	-0.1946(13)

Unrefined hydrogen atom positions: the numbering is such that the first digit is that of the parent atom.

H(5)	0.061	-0.335	0.17
H(6)	0.161	-0.570	0.05
H(71)	0.400	-0.010	-0.47
H(72)	0.304	0.050	-0.36
H(73)	0.393	0.060	-0.12
H(81)	0.404	-0.585	0.00
H(82)	0.296	-0.685	-0.20
H(83)	0.375	-0.575	-0.40

Table 4:2 Anisotropic thermal parameters $\times 10^3$ ($\text{Cu} \times 10^4$), $\text{\AA}^2$ with estimated standard deviations in parentheses.

ATOM	U11	U22	U33	U12	U13	U23
Cu	274(4)	227(4)	426(5)	87(3)	31(3)	-84(3)
Cl	40(1)	22(1)	37(1)	3(1)	5(1)	-2(1)
N(1)	36(2)	22(2)	49(2)	12(1)	0(1)	1(1)
C(2)	32(2)	27(2)	41(2)	10(1)	3(2)	0(2)
O(2)	41(2)	44(2)	81(2)	17(1)	22(1)	2(1)
N(3)	30(1)	21(1)	39(2)	6(1)	6(1)	2(1)
C(4)	29(2)	25(2)	33(2)	6(1)	-2(1)	-3(1)
O(4)	32(1)	29(1)	58(2)	12(1)	6(1)	-6(1)
C(5)	34(2)	33(2)	39(2)	6(2)	6(2)	0(2)
C(6)	41(2)	28(2)	41(2)	3(2)	-3(2)	7(2)
C(7)	40(2)	27(2)	56(2)	7(2)	9(2)	9(2)
C(8)	52(3)	27(2)	79(3)	19(2)	-2(2)	0(2)

Table 4:3. Bond lengths ($\text{\AA}$) and angles ($^\circ$) with estimated standard deviations in parentheses.

Superscripts denote the following symmetry operations:
($'$) $x, y, z-1$; ($''$) $-x, -y, -z$.

Cu-Cl 2.269(1) Cu-O(4) 1.985(3) Cu...Cl' 2.951(1)
Cl-Cu-O(4) 88.5(1) Cl-Cu...Cl' 95.2(1)
Cl-Cu-O(4)'' 91.5(1) O(4)-Cu...Cl' 83.3(1)
Cu-O(4)-C(4) 133.5(2)

The 1,3-Dimethyluracil molecule.

N(1)-C(2)	1.373(4)	C(2)-N(3)	1.397(5)
C(2)-O(2)	1.212(5)	N(3)-C(4)	1.379(5)
C(4)-C(5)	1.420(5)	C(4)-O(4)	1.246(4)
C(5)-C(6)	1.342(6)	C(6)-N(1)	1.370(5)
C(7)-N(3)	1.468(4)	C(8)-N(1)	1.474(5)

C(6)-N(1)-C(2)	121.9(3)	C(6)-N(1)-C(8)	119.1(3)
C(8)-N(1)-C(2)	119.0(3)	N(1)-C(2)-N(3)	115.3(3)
N(1)-C(2)-O(2)	122.8(3)	N(3)-C(2)-O(2)	121.9(3)
C(2)-N(3)-C(4)	124.6(3)	C(2)-N(3)-C(7)	117.1(3)
C(4)-N(3)-C(7)	118.3(3)	N(3)-C(4)-C(5)	116.7(3)
N(3)-C(4)-O(4)	116.7(3)	C(5)-C(4)-O(4)	126.6(3)
C(4)-C(5)-C(6)	119.2(3)	C(5)-C(6)-N(1)	122.3(3)

Conformation of the methyl groups:

C(2)N(1)C(8)H(81)	80.0	C(2)N(3)C(7)H(71)	26.9
C(2)N(1)C(8)H(82)	-160.5	C(2)N(3)C(7)H(72)	147.7
C(2)N(1)C(8)H(83)	-40.6	C(2)N(3)C(7)H(73)	-97.8

Table 4:4. Least-squares plane calculations for the uracil moiety. Distances from the plane are in $\text{\AA}$, with estimated standard deviations in parentheses.

Defining plane:

N(1)	-0.012(5)	C(2)	0.005(6)	N(3)	0.005(4)
C(4)	0.001(6)	C(5)	0.001(6)	C(6)	0.001(6)

Not in plane:

O(2)	0.003(5)	O(4)	0.000(4)	C(7)	-0.017(6)
C(8)	0.000(8)	Cu	-0.643		

The equation of the plane is given by:

$$4.59x + 0.48y + 3.40z - 0.64 = 0$$

References.

1. J.A.Carrabine and M.Sundaralingam. Biochem 10 (1971) 292.
2. M.Goodgame and K.W.Johns. J.C.S.Dalton (1977) 1680.
3. B.A.Cartwright, M.Goodgame, K.W.Johns and A.C.Skapski. Biochem. J. (1978) 337.
4. Made by the method of D.Davidson and D.Baudisch, J.Am.Chem.Soc. 48 (1926) 2379.
5. B.A.Cartwright, L.Couchman and A.C.Skapski Acta Cryst. B35 (1979) 824
6. B.J.Hathaway and D.E.Billing Co-ord. Chem. Rev. 5 (1970), 143
7. A.Banerjee, J.K.Dattagupta, W.Saenger and A.Rabczenko. Acta Cryst. B33 (1977) 90.
8. R.F.Stewart and L.H.Jensen. Acta Cryst. B23 (1967) 1102
9. I.Kulakowska, M.Geller, B.Lesnyg and K.L.Wier^zchowski. Biochim.Biophys.Acta 361 (1974) 119.
10. B.E.Fischer and R.Bau. Inorg. Chem. 17 (1978) 27

Chapter 5.

The crystal and molecular structure of the metal-nucleotide complex 5'-uridinemonophosphate cobalt(II).water.

Introduction.

Cobalt can be used to replace zinc and magnesium ions in some metal-activated enzyme systems, without the enzyme losing its activity. Since cobalt(II) is paramagnetic (normally high-spin d^7 with a magnetic moment of about 5 B.M.) it can be useful as a probe to study its immediate surroundings (1). An example of such an enzyme is terminal deoxynucleotidyl transferase (2), which adds on mono deoxy nucleotides to the end of a DNA chain. The enzyme is seriously inhibited by chelating ligands such as EDTA, and its rate of catalysis depends on the type of metal ion present. Purine nucleotides work best with magnesium, and pyrimidine nucleotides best with cobalt (3). The studies also show that anionic interactions can be important in enzyme reactions. It is thought that the mechanism for the reaction is dependant on the formation of a cation-nucleotide triphosphate complex, cleavage of phosphate from the NTP, and formation of a new link to the 3'OH of the end of the existing DNA. It is interesting to note that RNA's do not work very well; only two rNTP's can be incorporated per chain.

Differences between cobalt(II) and manganese(II) binding to various nucleotides have been reported structurally. The purine nucleotides have similar structures involving N(7) co-ordination and octahedral stereochemistry. These were $[\text{Co}(\text{5'GMP})(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}$ (4), $[\text{Mn}(\text{5'GMP})(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}$ (5) and $[\text{Co}(\text{5'IMP})(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (6). The pyrimidine nucleotide 5'CMP forms a tetrahedral compound with cobalt(II) involving N(3) and phosphate binding (7), but an octahedral complex with manganese(II), which has phosphate binding and O(2) co-ordination (8).

This would seem to suggest that nucleotide-base interaction is important in the enzyme process, as the rates seem to depend on how the metal is bound. This has been forwarded as a proposition by Eichorn(9).

Uracil nucleotides have a special interest, in that they

have no unprotonated nitrogens for metal co-ordination, and this has prompted work on compounds of 5'UMP with transition metals (10). This work led to the isolation of single crystals of 1:1 cobalt(II):5'UMP, and the structure determination by x-ray diffraction (11).

Experimental.

Crystals of the compound, henceforth referred to as COUMP, were made by slow evaporation of a solution of cobalt nitrate hexahydrate, and the sodium salt of uridine 5'monophosphate, in water at a pH of 6.3 (10,11). Crystals appeared after 3 weeks, and were filtered and washed with cold water. They were small, pink prismatic crystals of low optical quality and poor surface.

Preliminary oscillation, Weissenberg and precession photographs of a suitable crystal showed it to be monoclinic, space group C2 (No.5), with systematic absences $hkl, h+k=2n$. Measurement of 18 high-angle reflections on the diffractometer followed by least-squares refinement gave unit-cell parameters of $a=28.693(2)$, $b=14.393(1)$, $c=4.761(1)$ Å, $\beta = 90.96(2)^\circ$. These are similar to those reported by Mosset et. al. (12).

Other pertinent data were $Z=4$, $F(000)=1052$, $D_{obs}=1.73$ g/cm³ (floatation), $D_{calc}=1.71$, $M.W=507.18$ (for Co:UMP.7H₂O). Analysis results were ; Found C=21.12%, H=4.74%, N=5.45%; calculated for C₉ H₁₁ Co N₂ O₉ P: 7H₂O C= 21.31%, H=4.97% N=5.52%. The linear absorption coefficient was $\mu=92.0$ cm⁻¹.

The crystal was measured and mounted on the diffractometer with its 'c' axis parallel to the ϕ axis. Its dimensions were 0.08 x 0.09 x 0.25 mm. 1949 reflections to $\theta=70^\circ$ (CuK α , $\lambda = 1.5418\text{\AA}$) were measured by the diffractometer collecting at ca. 300 reflections per day. Of these 226 were coded as 'unobserved' as their nett count did not exceed $2.58 \sigma I$. Close inspection of the photograph showed that the crystal was twinned to about 10% of its volume; no correction was thought necessary as the twin reflections were widely separated from the main ones. The 11,5,0 reflection was monitored as a reference after every 50 reflections, and its nett count did not change significantly over the period of data collection. Lorentz and polarisation corrections were applied, and the reference used to scale the data. At

a later stage the data was corrected for absorption using a 10 x 10 x 10 grid.

Solution and refinement of the structure.

A sharpened, origin-removed Patterson synthesis of low-angle reflections to $\theta=45^\circ$ gave a peak at the origin, with a similar peak $3\text{\AA}$ either side along the y axis. A cobalt atom was fixed on the origin and used to compute a Fourier synthesis, giving $R=0.43$. Since the origin is a special position, in order to maintain a 1:1 Co:UMP ratio, another cobalt atom on a diad axis is required. This was located at about $3\text{\AA}$ along the y axis. Further cycles of least-squares refinement with delta-F syntheses located all but 4 of the expected non-hydrogen atoms, giving $R=0.11$ with data limited to 45° in θ . At this stage the data were corrected for absorption, the R for full data being 0.079.

5 possible sites for water molecules could be located, and so oxygen atoms were allocated these positions with fixed temperature factors of $U=0.07$ and allowed to refine occupancy. Full anisotropic refinement allowed location of the ^{ning}hydrogen atoms from the difference map and these were input as fixed-atom contributions with $U=0.04\text{\AA}^2$.

For final refinement a weighting scheme with $F^*=30.0$ was applied. Anomalous dispersion corrections for Co and P were added, the absolute configuration of the molecule being known from the sugar. Incidentally, the presence of an optically active compound forces the space group to be $C2$, not the alternative $C2/m$ or Cm . One reflection was removed from the data as it was thought to be suffering from extinction. The final agreement factor was $R=0.065$. The final difference synthesis shows some diffuse density in the region of the 'column' of water molecules and is best explained as the presence of loosely co-ordinated water of crystallisation within the structure. Table 5:1 lists refined atom co-ordinates, Table 5:2 the hydrogen atom positions, and Table 5:3 the anisotropic thermal parameters. Observed and calculated structure factor moduli are on pages 88 to 89.

Description of the structure.

The major feature of the crystal structure is a polymeric

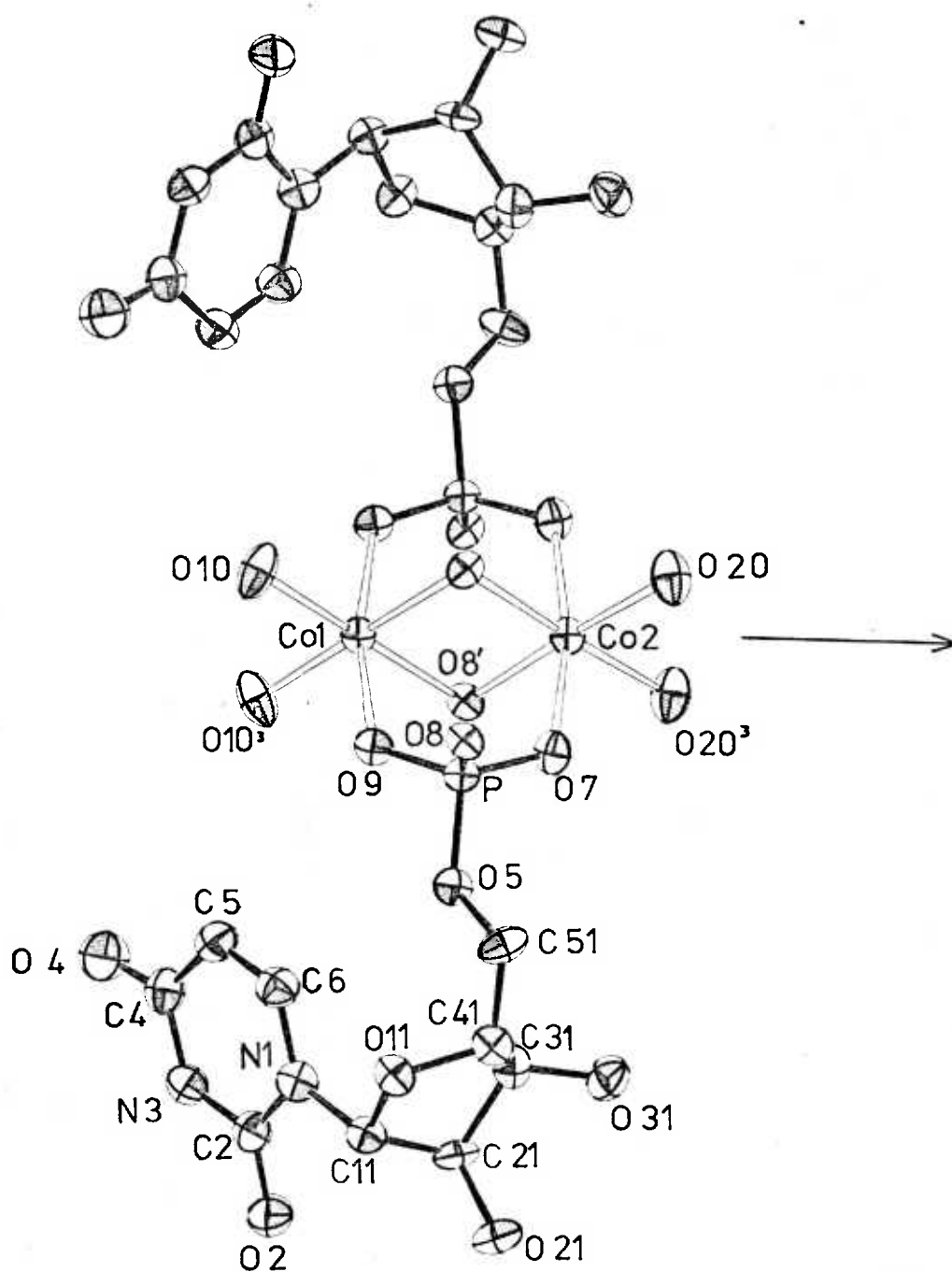


Figure 5:1. The monomer unit, showing the cobalt co-ordination, with thermal ellipsoids scaled to include 50% probability.

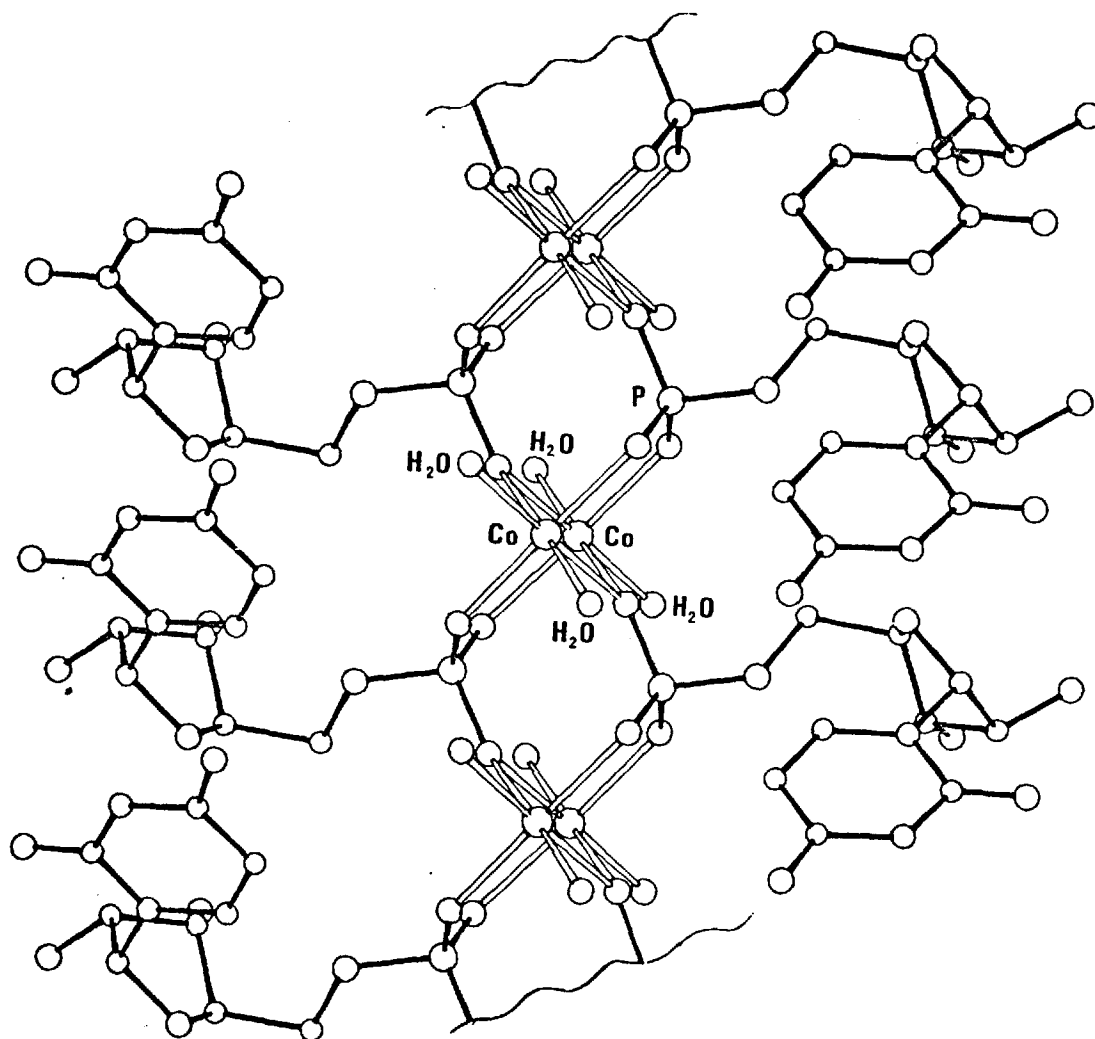


Figure 5:2 . The polymer chain, showing the phosphate links.

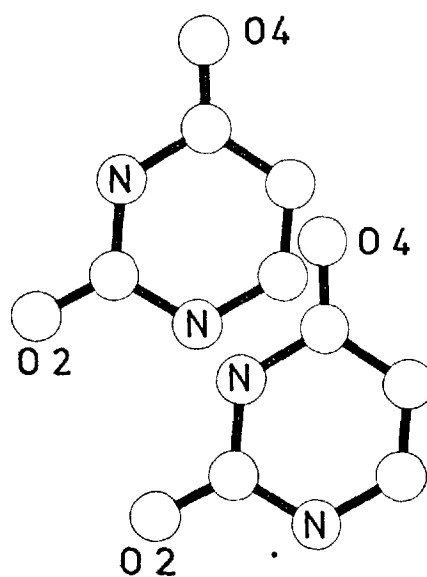


Figure 5:3 A view perpendicular to the uracil base, showing the unusual staggering, and no overlap.

chain running parallel to the 'c' axis of the unit-cell with a repeat distance of $4.761\text{\AA}$. The polymer is formed by pairs of cobalt atoms, linked by the phosphate groups of the 5'UMP nucleotide in such a way that the pairs of cobalt atoms lie on a crystallographic two-fold axis $2.992(2)\text{\AA}$ apart.

Figure 5:1 shows the monomer unit viewed down the 'c' axis and Figure 5:2 shows the polymer chain. Each of the cobalt atoms is octahedrally co-ordinated to 4 different phosphate groups and to 2 water molecules. Each phosphate group in turn links 4 different cobalt atoms, via two single Co-oxygen bonds and a bridging oxygen link. Thus every free oxygen on the phosphate group is involved in strong co-ordination to the metal.

Bond lengths and angles are given in Table 5:4. Co-O(?) bonds are in the range 2.03 to $2.16\text{\AA}$, with the independent Co-OH bonds of $2.076(9)$ and $2.103(9)\text{\AA}$.

The Uracil base is essentially planar, and its bond lengths and angles are closely related to those found in similar compounds containing uracil (13), and with uracil itself (14). The uracil base does not interact with the metal ion either directly or via a co-ordinated water molecule. A similar result has subsequently been found in the crystal structure of copper(II)5'UMP.dipyridylamine (15). This compares well with the title complex as far as 5'UMP parameters are concerned. Least-squares planes through the pyrimidine base are given in Table 5:5.

The sugar has a fairly typical conformation. Its internal bond lengths and angles are not exceptional, and its conformation can be described as C(3)' endo, which is a very common occurrence (16). A least-squares plane through the other 4 atoms shows clearly this deflection (table 5:5), and a view of the moiety is given in Figure 5:5. Torsion angles are given in Table 5:6, defined according to Saenger (17), and show the glycosidic bond to be anti, with a χ of 190° . This is typical of C(3)' endo puckered pyrimidine nucleosides and nucleotides (17). The conformation about the C(4)'-C(5)' bond is described as gauche,gauche, again normal for ribose sugars.

The packing of the molecule is shown in Figure 5:4, and is best thought of as chains of $(\text{Co}_2\text{ 5'UMP}_{24}\text{H}_2\text{O})_n$ linked to

each other by intra-molecular hydrogen bonds between the base and the 'sugar'. The 'columns' between the chains are filled with loosely co-ordinated water molecules. Not all the expected water molecules could be found, although the formula of $\text{CoS}^1\text{UMP} \cdot 7\text{H}_2\text{O}$ was confirmed by thermogravimetric analysis. It thus seems likely that some water is lost under X-rays, and that the remaining water is imprecisely fixed in the crystal structure.

The overlap of the uracil bases is shown in figure 5:3, and is somewhat unusual in that the $\text{C}=\text{O}(2)$ bond is not oriented immediately above the aromatic ring, but displaced to one side, so that no perpendicular overlap occurs. The interplanar spacing is still $3.3 \text{ \AA}$, typical of these systems. It appears likely that the Co-phosphate chain is forcing the repeat distance of the structure, rather than base stacking, and thus full overlap is prevented.

Figure 5:6 shows a space filling diagram of the 'polymer' to give some idea as to the shape of the molecule.

Discussion.

It seems likely that cobalt(II) will not interact directly with the uracil base, bearing in mind the difficulties in comparing solid state studies with in vivo environments. Powder diffraction has shown manganese²(II) to form an isomorphous compound (18), i.e. no uracil-manganese interaction. This is in contradiction to C^{13} N.M.R studies which suggest O(2) and O(4) proximity to the manganese ion (19), as well as phosphate binding. Studies with Cu(II) show the metal ion can interact with the ribose hydroxyl groups, and also with the base (20). Neither were observed in Cu(II) $\text{S}^1\text{UMPbypy}$ (13), and so metal interaction with the uracil bases must be considered unlikely if there are other sites available such as the phosphoester link in polynucleotides. More recent NMR work again suggests that copper binds close to N(3) of the uracil base (21), and in view of the structure of Cu(II)dimethyl uracil (Chapter 4) copper-O(4) binding cannot be ruled out. However, as a general rule it is unlikely for any metal ion to bind to the uracil base in a nucleic acid in preference to phosphate bonding.

Figure 5:4 A stereoscopic view of a section through the unit cell, clearly indicating the region of water in between the phosphate-metal chains.

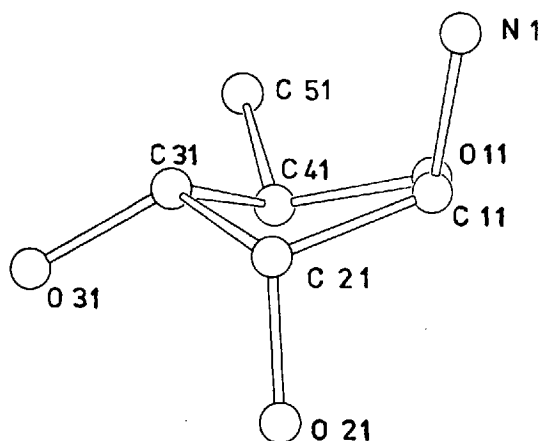
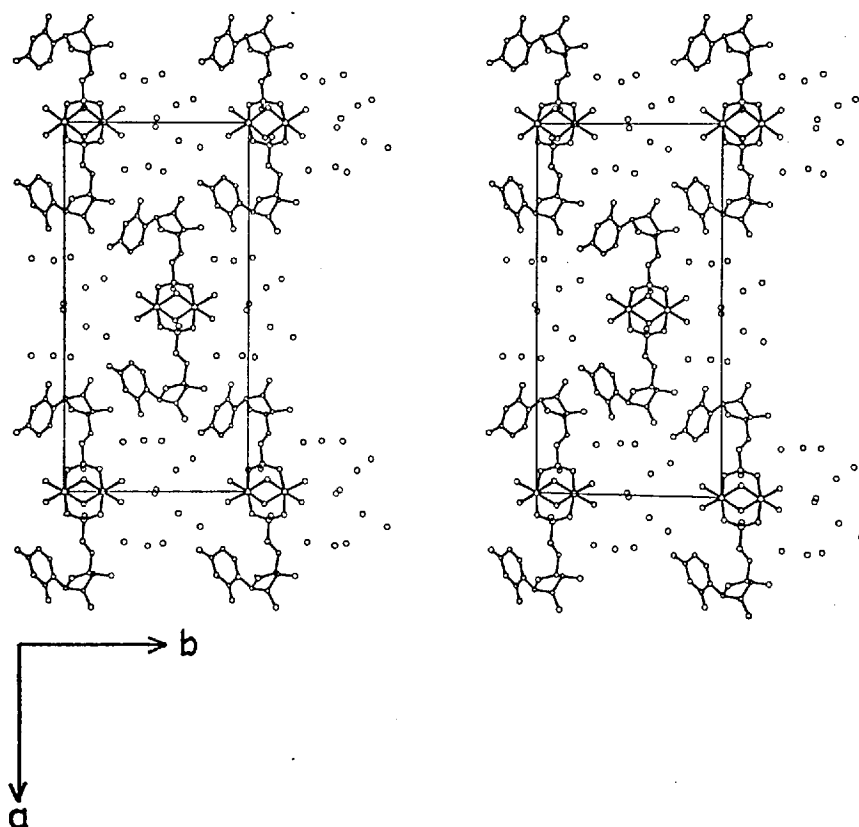


Figure 5:5 A view essentially parallel to the in-plane atoms of the sugar, depicting the 3' endo pucker.

Table 5:1 Fractional atomic co-ordinates of the non-hydrogen atoms, with estimated standard deviations in parentheses.

Atom	x	y	z	PP.
Co(1)	0	0	0	
Co(2)	0	0.20786(16)	0	
P	0.0601	0.1028(2)	0.4853(4)	
D(9)	0.0494(2)	0.0157(5)	0.3219(13)	
D(7)	0.0518(3)	0.1936(5)	0.3241(14)	
D(5)	0.1149(2)	0.0941(5)	0.5393(12)	
D(8)	0.0375(2)	0.1061(6)	0.7719(10)	
D(10)	-0.0365(3)	-0.1008(6)	0.2302(17)	
D(20)	-0.0338(3)	0.3101(6)	0.2270(17)	
D(30)	0.1273(3)	0.3189(7)	0.2628(26)	
D(40)*	0.067(1)	-0.282(1)	0.793(4)	0.61
D(50)*	0.118(1)	0.442(2)	0.772(5)	0.47
D(60)*	0.049(2)	0.613(5)	0.308(11)	0.18
D(70)*	-0.011(3)	0.496(5)	0.209(15)	0.15
D(80)*	0.132(1)	0.532(3)	0.194(9)	0.26
D(11)	0.2048(2)	0.0371(5)	0.7592(14)	
C(11)	0.2388(3)	0.0092(7)	0.5542(19)	
C(21)	0.2518(3)	0.0980(9)	0.3988(18)	
D(21)	0.2897(2)	0.1392(5)	0.5517(15)	
C(31)	0.2069(4)	0.1535(7)	0.4126(20)	
D(31)	0.2137(3)	0.2490(6)	0.3639(17)	
C(41)	0.1907(3)	0.1338(7)	0.7103(18)	
C(51)	0.1394(3)	0.1444(8)	0.7571(19)	
N(1)	0.2160(3)	-0.0598(7)	0.3622(19)	
C(2)	0.2446(4)	-0.1052(8)	0.1824(21)	
D(2)	0.2867(3)	-0.0868(6)	0.1710(19)	
N(3)	0.2246(3)	-0.1705(7)	0.0120(19)	
C(4)	0.1780(4)	-0.1934(8)	0.0047(23)	
D(4)	0.1639(3)	-0.2545(7)	-0.1605(19)	
C(5)	0.1496(4)	-0.1418(8)	0.1934(29)	
C(6)	0.1690(4)	-0.0804(8)	0.3610(23)	

* These atoms had fixed temperature factors of 0.07 $\text{\AA}^2$ and the population parameter refined.

Table 5:2 ² Unrefined hydrogen atom positions, input with U=0.04. Numbers refer to their parent atoms

Atom	x	y	z
H(3)	0.240	-0.197	-0.182
H(5)	0.113	-0.160	0.182
H(6)	0.157	-0.033	0.545
H(11)	0.271	-0.023	0.591
H(21)	0.269	0.090	0.218
H(31)	0.187	0.127	0.255
H(41)	0.183	0.167	-0.091
H(51)	0.131	0.227	0.745
H(52)	0.127	0.123	-0.055

Figure 5:6 A space-filling diagram showing the polymer chain, giving some idea as to the packing along 'c'.

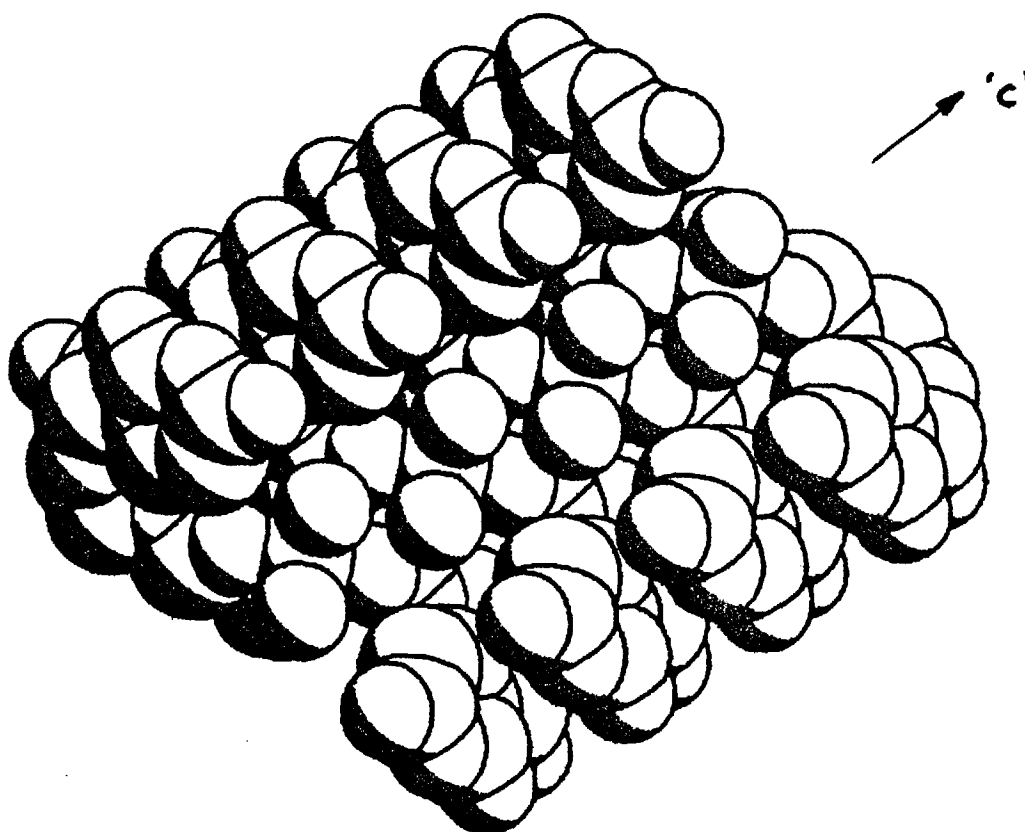


Table 5:3 Anisotropic temperature parameters of the refined atoms (Co, P $\times 10^4$, C, O, N $\times 10^3$) $\text{\AA}^2$ Estimated standard deviations in parentheses.

Atom	U11	U22	U33	U12	U13	U23
Co(1)	288(12)	243(11)	171(11)	0	-15(8)	0
Co(2)	295(12)	253(12)	195(11)	0	31(8)	0
P	231(10)	288(11)	161(9)	1(11)	20(6)	9(11)
O(9)	30(4)	33(4)	17(3)	1(3)	-3(3)	3(3)
O(7)	41(4)	31(4)	26(4)	-2(3)	1(3)	5(3)
O(8)	29(3)	30(3)	21(2)	4(3)	4(2)	4(3)
O(5)	29(3)	34(4)	24(3)	2(3)	1(2)	-6(3)
O(10)	64(6)	39(4)	34(4)	-21(4)	13(4)	-0(4)
O(20)	62(5)	35(4)	35(4)	6(4)	13(4)	-2(3)
O(30)	46(5)	54(6)	112(8)	-14(4)	4(5)	6(6)
O(11)	36(4)	36(3)	28(3)	5(3)	6(3)	5(3)
C(11)	29(4)	34(5)	25(4)	2(4)	4(3)	2(4)
C(21)	17(3)	47(6)	30(4)	-5(4)	1(3)	-11(5)
O(21)	26(3)	53(4)	44(4)	-11(3)	-1(3)	2(3)
C(31)	46(5)	31(5)	26(4)	-1(4)	-11(4)	-2(4)
O(31)	42(4)	37(4)	47(4)	-7(3)	7(3)	6(4)
C(41)	35(4)	36(5)	23(4)	2(4)	-1(3)	1(3)
C(51)	32(5)	52(6)	25(4)	-12(4)	-2(3)	-9(4)
N(1)	35(4)	38(5)	29(4)	1(4)	3(3)	0(4)
C(2)	35(5)	36(5)	34(5)	0(4)	5(4)	7(4)
O(2)	34(4)	45(4)	66(5)	-3(3)	14(4)	-3(4)
N(3)	34(4)	40(5)	42(5)	5(4)	5(4)	-3(4)
C(4)	44(6)	37(5)	39(5)	-1(4)	1(4)	-3(4)
O(4)	52(5)	54(5)	59(5)	2(4)	-4(4)	-22(4)
C(5)	34(5)	40(6)	69(8)	-4(5)	-1(5)	-13(5)
C(6)	32(5)	45(6)	40(6)	0(4)	9(4)	7(5)

Table 5:4 Interatomic bond lengths ($\text{\AA}$) and angles ($^\circ$) with estimated standard deviations in parentheses.

'=x,y,z-1;''=-x,y,1-z,'''=-x,y,-z ,iv x,y-1,z+1

Cobalt coordination.

Co(1).....Co(2)	2.992(2)		
Co(1)-O(9)	2.083(6)	Co(2)-O(7)	2.135(7)
Co(1)-O(10)	2.108(9)	Co(2)-O(20)	2.076(9)
Co(1)-O(8)'	2.169(7)	Co(2)-O(8)''	2.126(7)
O(9)-Co(1)-O(10)	91.8(3)	O(7)-Co(2)-O(20)	91.0(3)
O(9)-Co(1)-O(8)'	87.4(2)	O(7)-Co(2)-O(8)''	87.2(2)
O(9)-Co(1)-O(8)''	83.8(2)	O(7)-Co(2)-O(8)'''	85.2(2)
O(9)-Co(1)-O(9)'''	167.5(3)	O(7)-Co(2)-O(7)'''	169.0(3)
O(9)-Co(1)-O(10)'''	96.8(3)	O(7)-Co(2)-O(20)'''	96.8(3)
O(10)-Co(1)-O(8)'	178.6(3)	O(20)-Co(2)-O(8)''	177.5(3)
O(10)-Co(1)-O(8)''	88.2(3)	O(20)-Co(2)-O(8)'''	88.7(3)
O(10)-Co(1)-O(10)'''	93.0(3)	O(20)-Co(2)-O(20)'''	89.7(4)
O(8)'-Co(1)-O(8)''	90.5(3)	O(8)''-Co(2)-O(8)'''	92.9(3)
Co(1)-O(8)(iv)-Co(2)	88.3(2)		

Phosphate group.

P-O(5)	1.593(6)	P-O(8)	1.521(5)
P-O(7)	1.532(8)	P-O(9)	1.504(3)
O(9)-P-O(7)	115.1(4)	O(7)-P-O(8)	111.0(4)
O(9)-P-O(5)	102.1(4)	O(5)-P-O(8)	107.0(3)
O(7)-P-O(5)	107.0(4)	O(9)-P-O(8)	113.8(4)
Co(1)-O(9)-P	126.9(4)	Co(2)-O(7)-P	123.0(4)
Co(1)(iv)-O(8)-P	130.5(5)	Co(2)(iv)-O(8)-P	134.9(5)
P-O(5)-C(51)	123.1(6)		

Ribose sugar.

C(11)-C(11)	1.448(12)	O(11)-C(41)	1.467(12)
C(11)-C(21)	1.526(16)	C(21)-C(31)	1.518(14)
C(21)-O(21)	1.428(11)	C(31)-C(41)	1.525(13)
C(31)-O(31)	1.408(13)	C(41)-C(51)	1.501(13)
C(51)-O(5)	1.439(12)	N(1)-C(11)	1.494(14)
C(41)-O(11)-C(11)	110.1(7)	O(11)-C(11)-C(21)	105.5(8)
O(11)-C(11)-N(1)	107.7(8)	C(21)-C(11)-N(1)	111.6(7)
C(11)-C(21)-C(31)	101.9(7)	C(11)-C(21)-O(21)	106.9(7)
C(31)-C(21)-O(21)	113.4(9)	C(21)-C(31)-C(41)	102.4(8)
C(21)-C(31)-O(31)	112.8(9)	C(41)-C(31)-O(31)	112.3(8)
C(31)-C(41)-O(11)	103.7(7)	C(31)-C(41)-C(51)	115.8(8)
O(11)-C(41)-C(51)	110.0(8)	C(41)-C(51)-O(5)	108.1(7)

Uracil base.

N(1)-C(2)	1.364(14)	N(1)-C(6)	1.380(14)
C(2)-N(3)	1.362(14)	C(2)-O(2)	1.238(13)
N(3)-C(4)	1.379(14)	C(4)-C(5)	1.431(17)
C(5)-C(6)	1.310(17)	C(4)-O(4)	1.243(14)
C(6)-N(1)-C(2)	119.6(9)	C(6)-N(1)-C(11)	124.3(9)
C(2)-N(1)-C(11)	116.1(9)	N(1)-C(2)-N(3)	116.9(9)
N(1)-C(2)-O(2)	121.6(10)	N(3)-C(2)-O(2)	121.6(10)
C(2)-N(3)-C(4)	125.4(9)	N(3)-C(4)-C(5)	115.0(10)
N(3)-C(4)-O(4)	119.4(10)	C(5)-C(4)-O(4)	125.5(11)
C(4)-C(5)-C(6)	119.5(10)	C(5)-C(6)-N(1)	123.6(10)

Hydrogen bonds.

N(3)...O(31) ¹	2.789(12)	O(21)...O(4) ²	2.770(12)
O(2)...O(50) ³	2.77(2)	O(10)...O(40) ⁴	2.7(2)
O(40)...O(4) ⁵	2.80(2)	O(30)...O(31)	2.713(13)
O(60)...O(80)	2.71(7)	O(7)...O(30)	2.837(12)
O(20)...O(70)	2.76(7)		
O(40)...O(60) ⁶	2.79(6)		

$$\begin{aligned}
 1 &= 1/2 - x, -1/2 + y, -z \\
 2 &= 1/2 - x, 1/2 + y, -z \\
 3 &= 1/2 - x, -1/2 + y, 1 - z
 \end{aligned}$$

$$\begin{aligned}
 4 &= -x, y, 1 - z \\
 5 &= x, y, 1 - z \\
 6 &= x, 1 - y, z
 \end{aligned}$$

Table 5:5 Least-squares planes, with estimated standard deviations in parentheses. Distances are given in Å.

Uracil base. Equation $-4.307x + 10.094y - 3.305z + 2.727 = 0$

Defining plane:

N(1) $-0.005(9)$ C(2) $0.008(9)$ N(3) $-0.002(10)$

C(4) $-0.008(11)$ C(5) $0.012(13)$ C(6) $-0.006(11)$

Not defining plane.

O(2) $0.050(9)$ O(4) $-0.018(10)$ C(11) $-0.041(10)$

Ribose sugar. Equation $19.53x + 3.65y + 3.22z - 6.529 = 0$

Defining plane

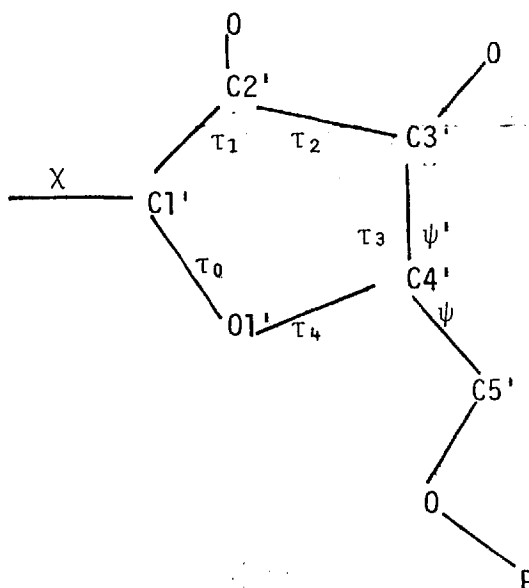
C(21) $0.029(12)$, C(11) $-0.048(10)$, O(11) $0.050(7)$, C(41) $-0.041(11)$

Not defining plane C(31) $-0.600(9)$

Table 5:6 Ribose sugar conformation, defined according to Saenger (17).

τ_0	8.8	$\chi(C11-N1)$	190 anti
τ_1	329	ψ_{OO}	295 gauche, gauche
τ_2	40	ψ_{OC}	51 about C(51)C(41)
τ_3	325	ψ'	83
τ_4	17		

Glycosidic bond O(11)C(11)N(1)C(2) $\chi = 190$ (anti)



10	122	118	12	193	190	5.1.4	5	764	744	8	110	114	
12	188	184	3	-3.1.4	3	1074	112	7	251	228	8	264	244
			1	711	688	9	262	257	11	814	5.7		
			3	205	207	7	124	130					
			5	130	136	8	251	243					
			7	114	120	11	87	80					
			11	454	477								
			11	322	327								
						6.1.4	0	197	201				
						2	252	256					
						4	130	131					
						8	171	159					
						12	140	197					
						10	784	47					
						12	140	197					
						7.1.4	7	884	78				
						1	224	251					
						3	240	252					
						5	456	427					
						7	116	94					
						11	124	127					
						8	104	107					
						10	124	127					
						12	124	127					
						8.1.4	8	140	124				
						10	230	227					
						15.1.4	1	378	360				
						3	178	204					
						5	136	152					
						7	121	120					
						9	238	226					
						18.1.4	9	111	111				
						17.1.4	1	181	181				
						8	104	91					
						11	212	213					
						10.1.4	1	402	402				
						2	188	181					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10	178	175					
						12	178	175					
						13.1.4	1	371	372				
						2	118	118					
						4	147	147					
						6	172	172					
						8	178	175					
						10							

References.

1. M. Hughes (1972) The inorganic chemistry of biological processes. pp80-91
2. F.J. Bollum (1974) The Enzymes (Ed. by P.D. Boyer) Vol X. 3rd Edition pp145-171.
3. K-I Kato, J.M. Goncalves, G.E. Houts and F.J. Bollum J. Biol. Chem. (1967) pp 2780-2789.
4. P. de Meester, D.M.L. Goodgame, T.J. Jones and A.C. Skapski C.R. Acad. Sci. Paris, Ser C 279 (1974) 667-669
5. P. de Meester, D.M.L. Goodgame, T.J. Jones and A.C. Skapski Biochem J. 139 (1974) 791-792
6. K. Aoki Bull. Chem. Soc. Japan 48 (1975) 1260-1271
7. J.R. Clark and J.D. Orbell J. Chem. Soc. Chem. Comm (1975) 697-3
8. K. Aoki J. Chem. Soc. Chem. Comm. (1976) 748-9
9. G.L. Eichorn Inorganic Biochemistry (1973) Vol 2 1210-1243
10. I. Jeeves PhD Thesis University of London (1976)
11. B.A. Cartwright, D.M.L. Goodgame, I. Jeeves and A.C. Skapski Biochim. Biophys. Acta 477 (1977) 195-198
12. A. Mosset, J.J. Bonnet and J. Galy C.R. Acad. Sci. Paris, Ser C 283 (1976) 127-9
13. D. Voet and A. Rich Progr. Nucl. Acid. Res. Mol. Biol. 10 (1970) 183-265
14. R.F. Stewart and L.H. Jensen Acta Cryst. 23 1102-1105
15. B.E. Fischer and R. Bau Inorg. Chem 17 (1978) 27-34
16. M. Sundaralingam Biopolymers 7 (1969) 821-860
17. W. Saenger Angew. Chem. Int. Eng. Ed. 12 1973 591-601
18. Dr R.S. Osborn, personal communication.
19. G. Kotowycz and O. Suzuki Biochem. 12 (1973) 3434-3439
20. N.A. Berger and G.L. Eichorn Biochem 10 (1971) 1857-1864
21. G. Kotowycz Can. J. Chem. 52 (1974) 924-929

Chapter 6

The crystal and molecular structure of the assymetrically bridged osmium dioxo complex Di-u-oxo-bis[(cyclohexane-1,2-diolato)oxo(quinuclidine) osmium(vi)], $[\text{OsO}_2(\text{C}_6\text{H}_{10}\text{O}_2)(\text{C}_7\text{H}_{13}\text{N})]_2$.

Introduction.

Osmium tetroxide forms adducts with a wide range of tertiary amines, giving compounds of formula $\text{OsO}_4 \cdot \text{L}_n$ (where n is 1 or 2). These greatly speed up the catalytic hydroxylation of alkenes to cis diols (1,2,3). They are also of considerable interest as models for the staining agents used in electron microscopy of plant tissue containing unsaturated alkaloids with tertiary amine units (4).

One such adduct is formed with quinuclidine, and has the stoichiometry $\text{OsO}_4 : \text{quinuclidine}$. This reacts with cyclohexene to form a compound of empirical formula $\text{OsO}_4 : \text{quinuclidine} : \text{cyclohexene}$ (5). This is diamagnetic, and thus expected to contain trans oxo ligands, and a suggested structure represented by fig 6:a.

For the d^2 electron configuration of osmium(VI) this would lead to the dxz and dyz orbitals forming

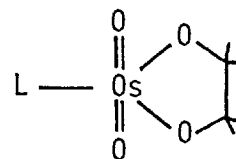


Figure 6:a

π -bonds to oxygen, leaving the

dx_y orbital non-bonding and

filled with the two 'd' elec-

trons. The vibrational spectra of the species, however, indicated a non-linear arrangement of the $\text{O}=\text{Os}=\text{O}$ unit (6), and since crystals suitable for X-ray study were available the determination was carried out (7).

Experimental.

Osmium tetroxide (1.0g) dissolved in 20 cm^3 of water was slowly added to a solution of quinuclidine hydrochloride (0.57g) in 10 cm^3 of water, the solution having been adjusted to pH7 with sodium hydroxide solution. The adduct formed as an orange precipitate, which was filtered, washed, and dried under vacuum. A solution of this adduct, $\text{OsO}_4 : \text{quinuclidine}$ (0.5g), in 10 cm^3 of diethyl ether was made up, to which 5 cm^3 of cyclohexene was added, and the mixture cooled to 0°C . Dark brown crystals of stoichiometry $\text{OsO}_4 :$

quinuclidine:cyclohexene were formed (5). Analysis results are ; Found C=35.03%, H=5.26%, N=3.06%. Calculated for C₁₃ H₂₃ N O₄ Os :C=34.09%, H=5.18%, N=3.13%.

Preliminary oscillation and Weissenberg photographs showed the crystals to be orthorhombic, space group Pbca (No.61), with unique systematic absence conditions 0kl, k=2n+1; h0l, l=2n+1; hk0, h=2n+1. A crystal, 0.14 x 0.12 x 0.26 mm. was mounted with its 'c' axis parallel to the ϕ axis of the diffractometer, and measurement of high-angle axial Cu K α_1 and K α_2 reflections gave unit-cell dimensions of :- a=23.394(1), b=10.303(1), c=11.743(1) Å. Other unit-cell parameters are Z=4 dimeric molecules, U=2830.4 Å³, F(000)=1728, D_{calc}= 2.10g/cm³, μ =174.49 cm⁻¹, MW=895.06. Data were collected using the usual procedures to a θ max of 55°, at 1000 reflections per day. 1794 unique reflections were measured, and processed in the usual way. During the later stages of refinement it was noted that some very weak reflections were calculating with extremely low F's. The data were then reprocessed using a sigma value of 3 to code the unobserved reflections in the hope of raising the threshold to include the 'dodgy' reflections. This resulted in 139 unobserved reflections. The 10,3,0 reflection was monitored as a reference; its nett count did not alter significantly over the period of data collection and it was used to scale the reflections. At a later stage the data was corrected for absorption using a 10 x 10 x 10 grid.

Solution and refinement of the structure.

A sharpened, origin-removed Patterson synthesis rapidly allowed allocation of unique osmium co-ordinates, and a difference Fourier gave R=0.22, from which all the other non-hydrogen atoms were located without difficulty. With the osmium refining anisotropically and all the other non-H atoms isotropically, R was 0.080. The application of various corrections made very little individual improvement, and the final fully anisotropic full-matrix least-squares refinement gave R=0.059. This included absorption corrected data, anomalous dispersion correction for Os, the insertion of hydrogen atoms as fixed-atom contributions, with U=0.04 Å², and removal of the strongest (2,0,0) reflection as suffering from extinction. The structure-factor listings (p102)

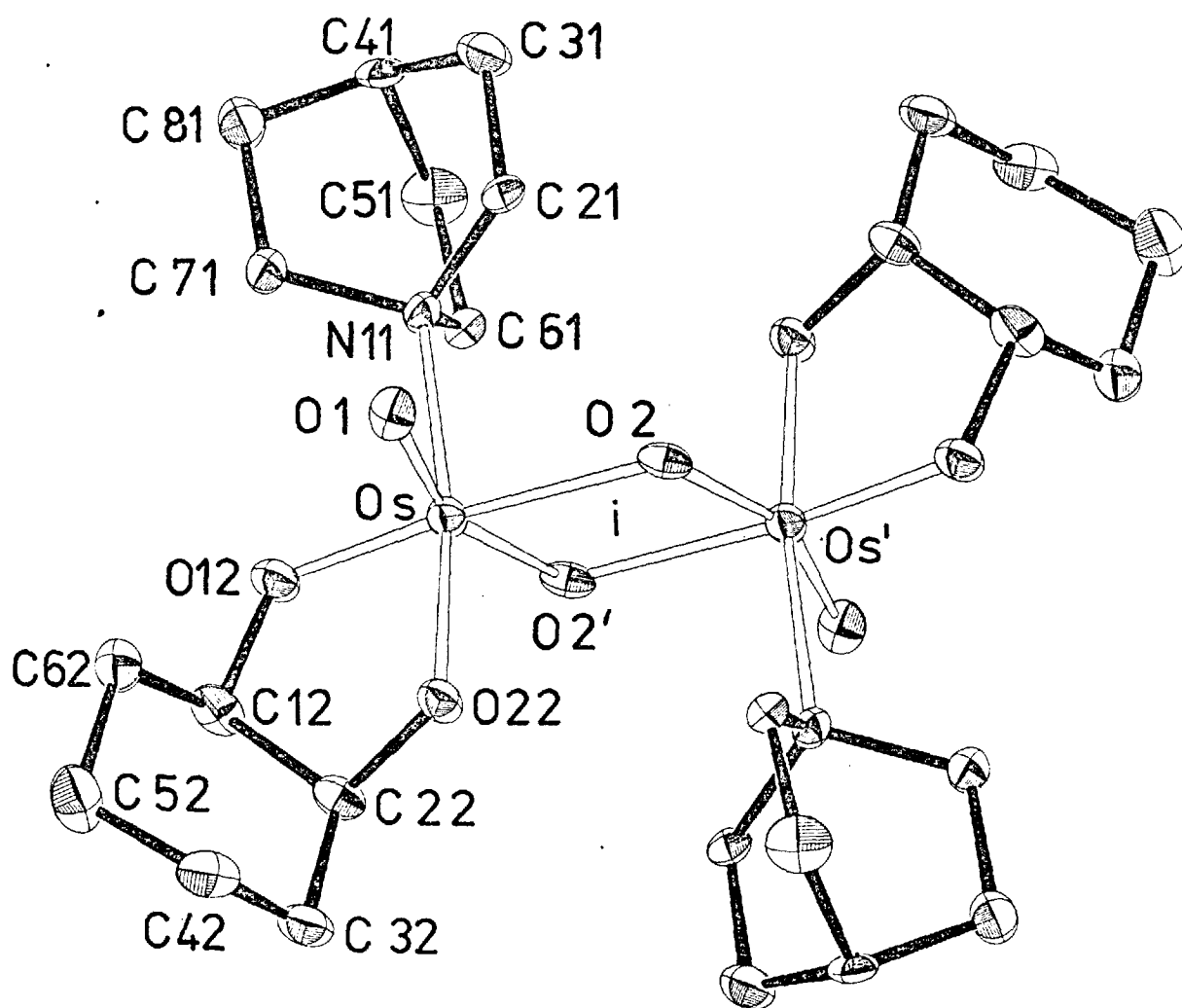


Figure 6:1 The dimeric molecule, with thermal ellipsoids scaled to include 30% probability.

show for about 25 weak observed reflections that F_{obs} is appreciably higher than F_{calc} . This might be due to slight disorder in the region of the quinuclidine moiety, where one rather long C-C bond is obtained. Final atomic co-ordinates are in Table 6:1, with anisotropic temperature parameters in Table 6:2. Calculated hydrogen atom positions are in Table 6:3.

Description and discussion of the structure

Figure 6:2 shows the dimeric molecule $[\text{OsO}_2(\text{O}_2\text{C}_6\text{H}_{10}\text{C}_7\text{H}_{13}\text{N})]_2$ in which the two monomers are held together through two oxygen bridges, and are related via a centre of symmetry. The Os_2O_2 bridge is unique in being asymmetric, with independent Os-O distances of 1.78(1) and 2.22(1) Å. The only other structure containing an asymmetric bridge is $[\text{Na}(\text{NH}_4)\text{MoO}_3(\text{C}_2\text{O}_4)]_n$ (10), where there is a single oxo linkage having Mo-O bonds of 1.873 and 2.230 Å. In the title compound the shorter bridge bond is slightly longer than the terminal oxo ligand (Os-O 1.73(1) Å). This compares with Os-O of 1.712 Å in OsO_4 itself (13), and is somewhat longer than the values found for Os-O apical bonds in some square-pyramidal osmium structures; eg 1.675 (7) Å in $\text{Os}_2\text{O}_4(\text{O}_2\text{C}_2(\text{CH}_3)_4)_2$ (8), and 1.670 Å for the diester compound $\text{OsO}(\text{O}_2\text{C}_2\text{H}_4)$ (9). Octahedral Os=O bonds have values of ca. 1.74 Å, eg 1.75(2) Å (ref14), 1.734 and 1.714 (ref15) and 1.73 and 1.75 Å (ref11).

Table 6:4 gives all the interatomic bond lengths and angles of the dimeric molecule. The two ester bonds are similar to those found for other osmium(VI) diolato species for example; 1.863(7) and 1.876(6) in ref.(8), 1.873(7) and 1.896(8) Å in ref(9). The longer bridge bond is obviously sufficient to hold the dimer intact during crystallisation. Its weakness can, however, be assessed by comparison with the 2.00 Å reported for an osmium(VI)-OH bond (12). The nitrogen bond to the quinuclidine unit at 2.23(1) Å is longer than normally found, but not exceptional, similar values of 2.164 and 2.173 Å found in $(\text{OsO}_2(\text{O-methylthymine}))\text{PS}_2$ (11).

The quinuclidine ligand has internal bond lengths similar to those reported in other structures containing it, eg dimethylbis(quinuclidine)magnesium (16). This has averages

for the three different types of bonds as N-C 1.501, C-C 1.569, and C-C bridgehead 1.547 Å. These compare with 1.50, 1.53 and 1.55 found in the title complex. (However the long C(41)-C(51) distance, and the thermal ellipsoids of these two atoms suggest that there may be a trace of disorder present).

The cyclohexane ring has a chair conformation, and again has typical interatomic bond lengths and angles. The ester oxygen-carbon distances, 1.45(2) and 1.48(2) Å, are slightly longer than the literature mean for 'organic' esters (1.426 ref.17). The increased length is consistent with similar findings for osmium diester complexes. Torsion angles for the cyclohexane ring and quinuclidine ligand are in Table 6:5.

The complex is known from molecular weight determinations to be monomeric in chloroform (found 465, calc 447), which indicates the breaking of the double oxo bridge. The vibrational spectra show two pairs of bands assignable to O=Os=O stretching; a polarised strong Raman band at 923 cm^{-1} with a weak i.r equivalent at 919 cm^{-1} ; and a weak depolarised Raman band at 881 cm^{-1} , having a strong i.r counterpart at 879 cm^{-1} . These have been assigned as V_{symm} and V_{asymm} O=Os=O stretches respectively, which indicates a non-linear O=Os=O unit (q.v. cis dioxo species (6)). From the observed solid state dimer it is likely that the monomer has a trigonal bipyramidal structure with terminal oxo ligands in the equatorial plane, and an axial quinuclidine ligand. Equatorial oxo ligands are known in $\text{RuO}_3(\text{OH}_2)$ (18), but not in any d^2 species at present.

The dimer can be seen to arise from the approach of two trigonal bipyramidal molecules in such a way as to open up the erstwhile O=Os=O angle, of ca. 120° , to 154° in the dimer, forming a long oxygen bridge linkage.

Figure 6:3 shows a view of the packing of the unit cell. Space filling diagrams (Figure 6:4) show the molecule to have an approximately ovoid shape. The crystallinity must be maintained by Van-der-Waals forces, there being no opportunity for hydrogen bonding.

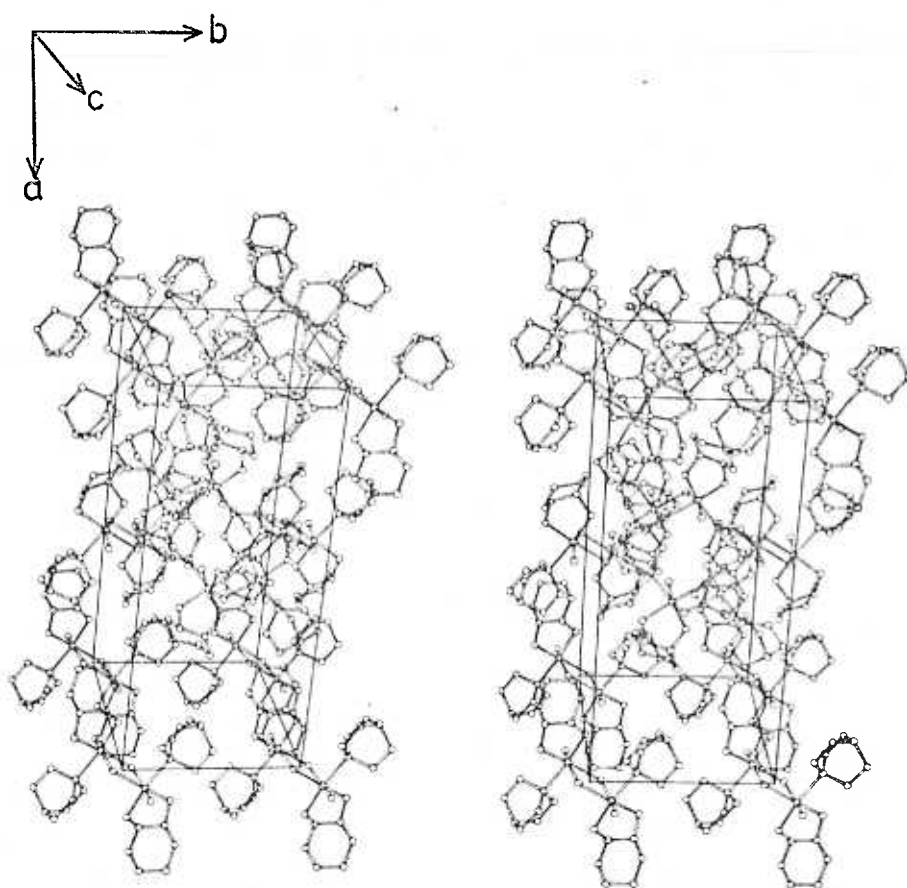


Figure 6:2 A stereoscopic view of the contents of the unit cell

Figure 6:3 A space-filling diagram of the dimer

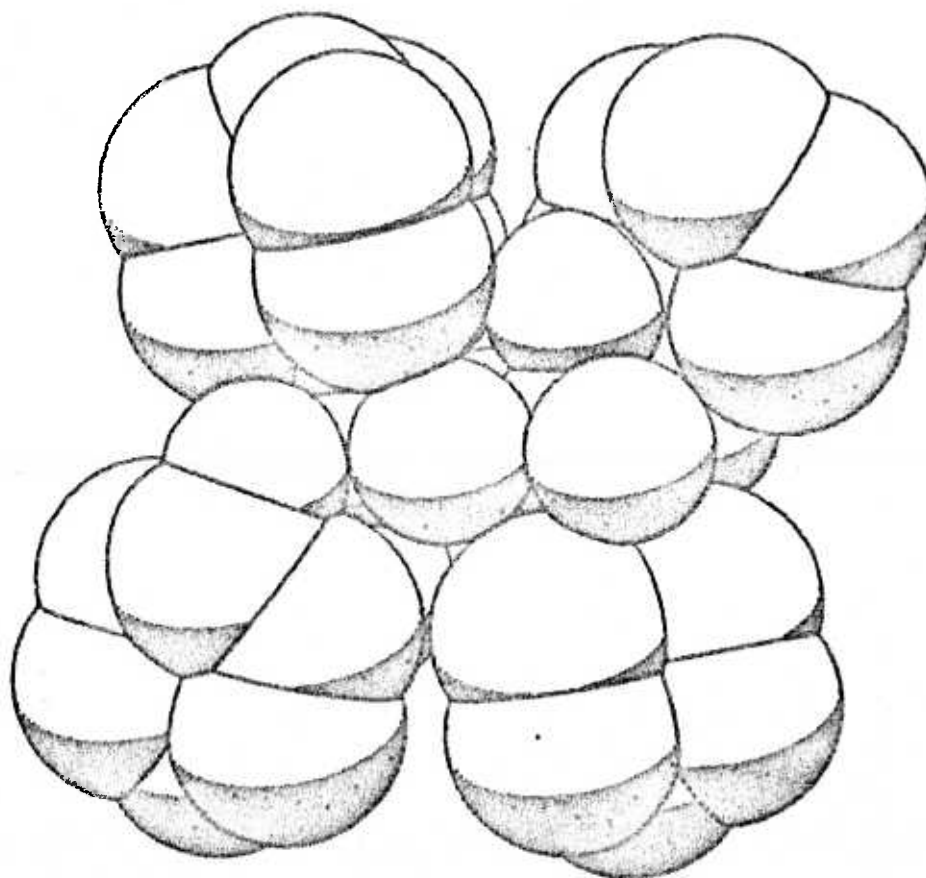


Table 6:1. Fractional co-ordinates of the non-hydrogen atoms, with estimated standard deviations in parentheses.

Atom	x	y	z
Os	0.03048(3)	0.11511(7)	0.07024(7)
O(1)	0.0171(5)	0.1191(11)	0.2151(9)
O(2)	-0.0195(4)	-0.0677(11)	0.0738(9)
O(12)	0.0745(4)	0.2669(12)	0.0452(11)
O(22)	0.1055(4)	0.0287(10)	0.0845(10)
C(12)	0.1359(7)	0.2466(18)	0.0695(18)
C(22)	0.1502(7)	0.1117(18)	0.0390(14)
C(32)	0.2088(7)	0.0654(19)	0.0689(21)
C(42)	0.2189(8)	0.0959(21)	0.1974(19)
C(52)	0.2099(9)	0.2393(22)	0.2217(22)
C(62)	0.1482(8)	0.2799(19)	0.1918(19)
N(11)	-0.0478(5)	0.2385(13)	0.0609(12)
C(21)	-0.0966(7)	0.1753(16)	0.1211(13)
C(31)	-0.1501(7)	0.2619(20)	0.1128(20)
C(41)	-0.1368(7)	0.3891(18)	0.0576(17)
C(51)	-0.1125(8)	0.3646(21)	-0.0686(18)
C(61)	-0.0638(7)	0.2695(17)	-0.0592(16)
C(71)	-0.0354(7)	0.3656(17)	0.1215(16)
C(81)	-0.0890(8)	0.4517(19)	0.1280(19)

Table 6:2 Anisotropic temperature factors, with estimated standard deviations in parentheses. Os $\times 10^4$, others $\times 10^3 \text{ \AA}^2$

Atom	U11	U22	U33	U12	U13	U23
Os	310(4)	335(4)	554(5)	19(3)	-26(3)	4(4)
O(1)	54(7)	51(7)	49(7)	7(6)	-20(6)	1(6)
O(2)	25(5)	60(7)	39(6)	12(5)	-2(5)	14(6)
O(12)	33(6)	51(7)	73(8)	2(6)	0(6)	0(7)
O(22)	33(6)	42(7)	64(8)	1(5)	-4(6)	5(6)
C(12)	35(9)	46(11)	87(15)	7(9)	-17(10)	22(11)
C(22)	34(9)	61(12)	44(10)	-1(9)	-2(8)	13(9)
C(32)	36(10)	55(12)	111(18)	4(9)	15(11)	6(13)
C(42)	52(12)	74(15)	77(14)	10(11)	13(11)	16(12)
C(52)	73(14)	65(14)	102(20)	-10(13)	-24(14)	6(14)
C(62)	55(12)	50(13)	90(16)	-3(10)	-1(12)	-9(12)
N(11)	36(7)	32(7)	55(9)	7(6)	-5(7)	-10(7)
C(21)	44(10)	45(10)	26(8)	1(8)	10(7)	-9(8)
C(31)	38(10)	56(12)	104(17)	1(10)	11(11)	3(12)
C(41)	44(10)	53(11)	73(13)	2(9)	37(10)	-12(11)
C(51)	62(13)	77(15)	70(13)	27(11)	-25(11)	22(12)
C(61)	43(9)	40(10)	59(12)	0(8)	10(9)	-16(9)
C(71)	41(10)	42(10)	63(12)	3(8)	-5(9)	-14(10)
C(81)	50(11)	51(12)	85(15)	-3(10)	-7(11)	-5(11)

Table 6:3 Calculated hydrogen atom positions.

The first two digits are those of the parent atom

Atom	x	y	z
H(12)	0.160	0.307	0.022
H(22)	0.146	0.104	-0.048
H(321)	0.212	-0.031	0.055
H(322)	0.239	0.111	0.021
H(421)	0.192	0.044	0.247
H(422)	0.260	0.071	0.221
H(521)	0.219	0.259	0.305
H(522)	0.238	0.293	0.175
H(621)	0.120	0.230	0.244
H(622)	0.142	0.375	0.207
H(211)	-0.104	0.088	0.035
H(212)	-0.086	0.161	0.203
H(311)	-0.181	0.215	0.067
H(312)	-0.166	0.278	0.191
H(41)	-0.173	0.443	0.052
H(511)	-0.144	0.331	-0.121
H(512)	-0.098	0.451	-0.103
H(611)	-0.075	0.187	-0.100
H(612)	-0.029	0.306	-0.101
H(711)	-0.021	0.346	0.201
H(712)	-0.004	0.413	0.030
H(811)	-0.103	0.459	0.210
H(812)	-0.081	0.541	0.099

Table 6:4 Interatomic bond lengths ($\text{\AA}$) and angles ($^\circ$) with estimated standard deviations in parentheses.

(i) refers to position $-x, -y, -z$

Osmium co-ordination.

Os-O(1)	1.730(11)	Os-O(22)	1.975(10)
Os-O(2)	2.217(11)	Os-N(11)	2.231(12)
Os-O(12)	1.895(12)	Os-O(2) ⁱ	1.779(11)
O(1)-Os-O(2)	84.6(5)	O(2)-Os-O(22)	94.8(4)
O(1)-Os-O(12)	103.4(5)	O(2)-Os-N(11)	93.0(4)
O(1)-Os-O(22)	95.1(5)	O(2)-Os-O(2) ⁱ	73.0(4)
O(1)-Os-N(11)	83.5(5)	O(12)-Os-O(22)	84.4(4)
O(1)-Os-O(2) ⁱ	156.2(5)	O(12)-Os-N(11)	88.1(5)
O(2)-Os-O(12)	172.0(5)	O(12)-Os-O(2) ⁱ	99.1(5)
O(22)-Os-N(11)	171.9(5)	O(22)-Os-O(2) ⁱ	94.9(5)
N(11)-Os-O(2) ⁱ	89.5(5)	Os-O(2)-Os ⁱ	107.0(5)

Cyclohexane moiety.

C(12)-O(12)	1.48(2)	C(12)-C(22)	1.47(3)
C(22)-C(32)	1.49(2)	C(22)-O(22)	1.45(2)
C(32)-C(42)	1.56(3)	C(42)-C(52)	1.52(3)
C(52)-C(62)	1.54(3)	C(62)-C(12)	1.50(3)
C(62)-C(12)-C(22)	114(2)	C(62)-C(12)-O(12)	110(1)
O(12)-C(12)-C(22)	108(1)	C(12)-C(22)-C(32)	117(2)
C(12)-C(22)-O(22)	108(1)	O(22)-C(22)-C(32)	113(1)
C(22)-C(32)-C(42)	108(2)	C(32)-C(42)-C(52)	111(2)
C(42)-C(52)-C(62)	111(2)	C(52)-C(62)-C(12)	110(2)
C(12)-O(12)-Os	112(1)	C(22)-C(22)-Os	110(1)

Quinuclidine moiety.

N(11)-C(21)	1.49(2)	N(11)-C(61)	1.49(2)
N(11)-C(71)	1.52(2)	C(21)-C(31)	1.54(2)
C(31)-C(41)	1.50(3)	C(41)-C(51)	1.61(3)
C(41)-C(81)	1.53(3)	C(51)-C(61)	1.51(3)
C(81)-C(71)	1.54(3)		
C(61)-N(11)-C(21)	110(1)	C(61)-N(11)-C(71)	108(1)
C(61)-N(11)-Os	112(1)	C(21)-N(11)-Os	111(1)
C(21)-N(11)-C(71)	107(1)	C(71)-N(11)-Os	108(1)
N(11)-C(21)-C(31)	110(1)	C(21)-C(31)-C(41)	111(1)
C(31)-C(41)-C(51)	110(2)	C(31)-C(41)-C(81)	107(2)
C(81)-C(41)-C(51)	108(1)	C(41)-C(51)-C(61)	108(2)
C(51)-C(61)-N(11)	114(1)	N(11)-C(71)-C(81)	111(1)
C(71)-C(81)-C(41)	109(2)		

(b)

Table 6:5 Torsion angles for the cyclohexane and quinuclidine moieties. Errors in the angles are ca. 1°.

Cyclohexane:

C(62)C(12)C(22)C(32)	-51	C(12)C(22)C(32)C(42)	51
C(22)C(32)C(42)C(52)	-56	C(32)C(42)C(52)C(62)	60
C(42)C(52)C(62)C(12)	-56	C(52)C(62)C(12)O(12)	172
O(12)C(12)C(22)O(22)	-45	C(62)C(12)C(22)O(22)	77

Quinuclidine:

N(11)C(21)C(31)C(41)	-6	C(21)C(31)C(41)C(51)	60
C(31)C(41)C(51)N(11)	-57	C(21)N(11)C(81)C(71)	128
N(11)C(81)C(71)C(41)	7	C(31)C(71)C(41)C(31)	-121
C(21)N(11)C(71)C(81)	-55	N(11)C(71)C(51)C(41)	-7
C(71)C(81)C(41)C(31)	63		

10/Fd 10/Fd

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64																																				

References.

1. M.L.Hair and P.L.Robinson J.Chem.Soc. (1960) 2775
2. R.Criegee, B.Marchand, and H.Wannowius Annalen 550 (1942) 99
3. M.J.Cleare, P.C.Hydes, W.P.Griffith, and M.J.Wright J.C.S.Chem.Soc. Dalton (1977) 941
4. Some Biological Techniques in Electron Microscopy (1970) p69
5. M.Schröder PhD Thesis, University of London (1978)
6. W.P.Griffith J.Chem.Soc.(A) (1969) 211.
7. B.A.Cartwright, W.P.Griffith, M.Schröder and A.C.Skapski J.Chem.Soc.Chem.Comme (1978) 853
8. F.L.Phillips and A.C.Skapski J.Chem.Soc.Dalton (1975) 2586 and references therein.
9. F.L.Phillips and A.C.Skapski Acta Cryst. B31(1975) 1814
- 10 L.O.Atovmyan and G.B.Bokii J.Struct.Chem(USSR) (1963) 4 524
- 11 T.J.Kistenmacher, L.G.Marzilli, and M.Rossi Bioinorg.Chem. 6 (1976) 347
- 12 J.M.Walters and E.R.Whittle (1971) Chem.Comm. 518
- 13 H.M.Seip and R.Stolevik Acta Chem.Scand. 20 (1960) 385
- 14 F.H.Kruse Acta Cryst. 14 (1961) 1035
- 15 T.Prange and C.Pascard Acta Cryst. B33 (1977) 621
- 16 J.Toney and G.D.Stucky J.Organometallic.Chem. 22 (1970) 241
- 17 Chem.Soc.Special Publ. No.18 (1965)
- 18 G.Nowogrocki, F.Abraham, J.Trehaux and D.Thomas Acta Cryst. B32 (1976) 2413

Chapter 7.

The crystal and molecular structure of
 u-cyclooctane-1,2-diolato-5,6-diolato-bis-
 (dioxodipyridine osmium(vi)) tetrahydrate.

Introduction.

In chapter 6 the outline of the preparation and use of osmium tetraoxide adducts was mentioned. OsO_4 with alkenes give products of stoichiometry $\text{OsO}_4:\text{O}_2\text{R}$, which are in fact dimeric, containing an OsO_2Os bridge, with each osmium coordinated in a square-base pyramidal fashion (1,2).

The presence of tertiary amines greatly accelerates the cis hydroxylation of double bonds for which osmium tetraoxide is classically known (3,4,5,6). This gives compounds of stoichiometry OsO_4RL_2 , where R is any alkene, or OsO_4RL for lower ligand concentrations. OsO_4 is widely used as a staining agent for electron microscopy of plant tissue (7), and the existence of both unsaturated compounds and tertiary amines in natural products prompts the study of such compounds. With dienes, the product depends on the ratio of OsO_4 to diene. With 2:1 OsO_4 :diene, products of stoichiometry $(\text{OsO}_4)_2\text{R}\cdot\text{Py}_4$ are formed in the presence of excess pyridine. A ratio of 1.50 OsO_4 :diene produces mono-osmium addition. During the course of this work the isolation of a crystalline complex with cyclooctadiene enabled the characterisation of the first osmium-diene complex to be carried out, by single crystal X-ray diffractometry.

Experimental.

(Chemistry from ref. 8)

A solution of osmium tetraoxide in ethanol containing 2.5 times the molar amount of pyridine was mixed with a diethyl etheric solution of 1,5-cyclooctadiene at 0.5 molar amount under nitrogen. Large black crystals were formed and washed with dry diethylether. Analysis of the crystals gave C=35.99% H=3.45%, N=5.57%. Calculated results were for the formula $(\text{OsO}_2)_2(\text{O}_4\text{C}_8\text{H}_{12})(\text{C}_5\text{H}_5\text{N})_4$: C=36.05% H=3.46% N=6.01% (8). On solution of the structure it was found that in the crystal under study there were 4 water molecules per cyclooctadiene, which would give calculated constitutions of C=33.46% H=3.98%, N=5.57%. It seems likely that the sample

used for analysis was dried beforehand.

Preliminary oscillation and Weissenberg photographs showed the crystals to be orthorhombic, with probable space group $P22_1$. The absence condition along the screw axis was not exactly observed, some very weak reflections with $l=2n+1$ being noted. The alternative orthorhombic space group, $P22_2$, did not allow sensible refinement, so $P22_1$ was confirmed on structure refinement. The presence of the weak axial reflections, if genuine, might be due to the disorder of one of the pyridine rings.

A crystal, $0.45 \times 0.35 \times 0.25$ mm, was mounted with its 'a' axis parallel to the ϕ axis of the diffractometer. Measurement of 9 high-angle Cu $K\alpha$ reflections followed by least-squares fitting gave unit-cell dimensions of :- $a=8.363(1)$, $b=14.546(1)$, $c=14.441(1)$ Å, $U=1756.8$ Å³. Other crystal parameters are orthorhombic, space group $P22_1$ (No. 17), $Z=2$ formula units, $MW=1005.04$ (C₂₈ H₄₀ N₄ O₁₂ Os₂), $F(000)=968$, $D_{calc}=1.90$ gm/cm³, $\mu(\text{CuK}\alpha)=142.2$ cm⁻¹.

1980 reflections were collected to $\theta=70^\circ$, at about 1000 reflections per day, of which 41 were considered as unobserved as their nett count was less than 2.5σ or 1. The 0,6,7 reflection was monitored as a reference every 50 reflections, and used to scale the data. Its nett count did not alter significantly over the period of data collection. The usual Lorentz and polarisation corrections were applied.

At a later stage the data were corrected for absorption by using a $10 \times 10 \times 12$ grid. Several runs were made in an attempt to account for the shape of the crystal, which had two curved faces. Although any description brought a great improvement over uncorrected data, differing details of the crystal description did not further improve agreement. Finally, the strongest 101 reflection was removed because its absorption correction was the largest, and very sensitive to the description of the curved faces.

Solution and refinement of the structure.

A sharpened, origin-removed Patterson synthesis gave the osmium co-ordinates easily, and confirmed the presence of 2 symmetry within the cell. This required that the diene must lie on a two-fold axis. A structure factor calculation with osmium only gave $R=0.17$, R for $P22_1$ being 0.39. From

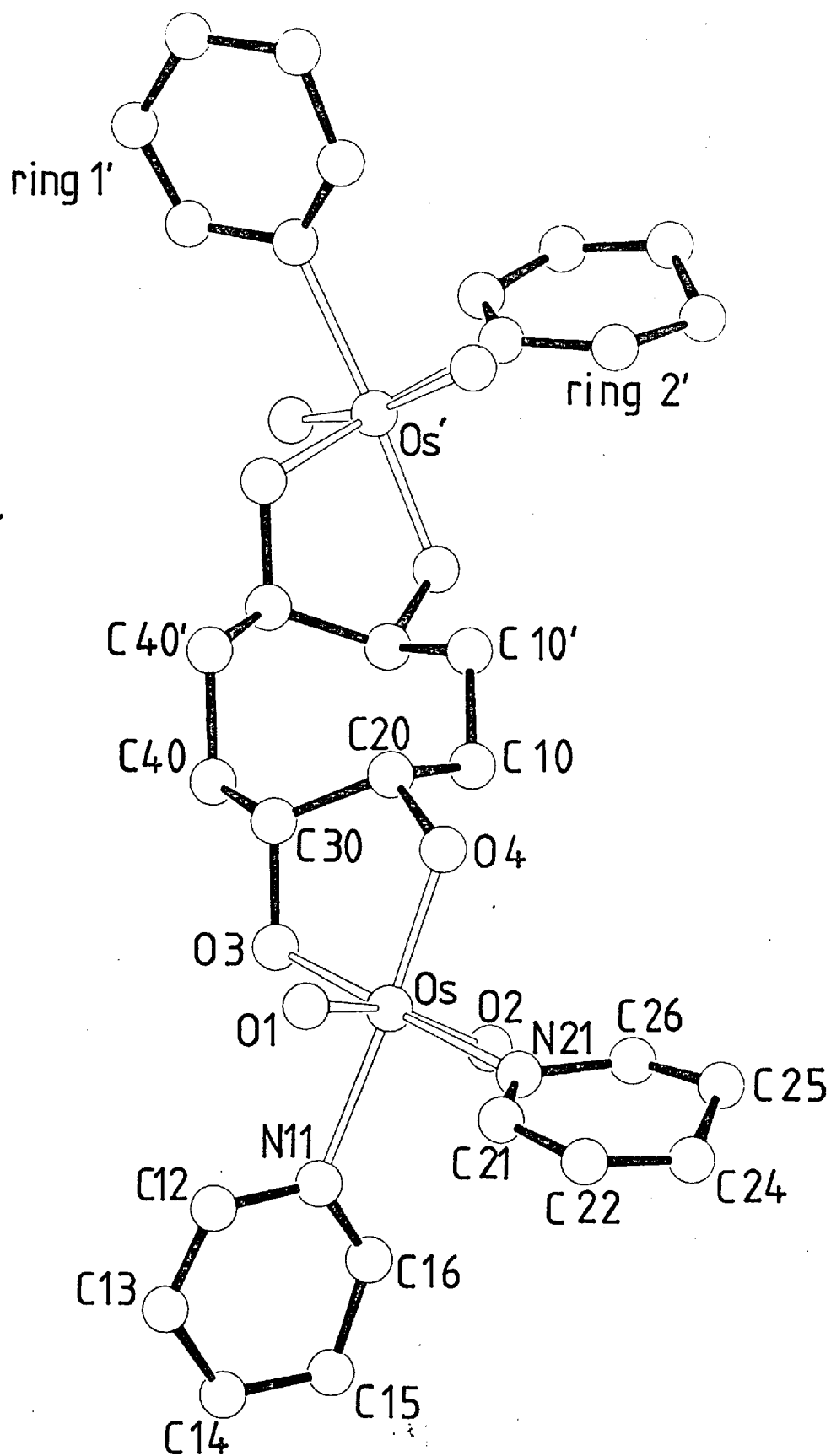


Figure 7:1 The molecule of cyclooctane-1,2-diolato-5,6-diolato-bis(dipyridinedioxo osmium(vi)).

the delta-Fourier synthesis most of the remaining non-hydrogen atoms could be determined, and a few cycles of isotropic refinement found all of the diene molecule and pyridine ligands, plus four isolated water molecules.

At this stage it was noted that one of the pyridines was refining with very high temperature factors and unusual bond lengths; attempts at refinement in different space groups proved unsuccessful. The conclusion is that there is some positional disorder of the pyridine which cannot be easily fitted to a simple alternative orientation of the groups.

Refinement using anisotropic temperature factors and absorption corrected data gave $R=0.069$. Application of anomalous dispersion correction for osmium gave $R=0.067$ and 0.064 for the two possible configurations of the molecule. Two strong reflections were flagged to be omitted as they were thought to be suffering from extinction. Application of the usual weighting scheme with $F^*=45$ gave the final R of 0.062 . This included calculated hydrogen atom positions for the cyclooctane ring and one of the pyridine ligands. They were given the isotropic temperature parameters of their parent atoms.

The final difference Fourier synthesis shows peaks close to the osmium of ca $1\text{e}\text{\AA}^{-3}$, which may reflect either absorption error, or some general disorder of the whole molecule.

Table 7:1 lists refined atomic co-ordinates, Table 7:2 anisotropic thermal parameters, and Table 7:3 calculated hydrogen atom positions. Observed and calculated structure factor amplitudes are on page 115.

Description and discussion of the structure.

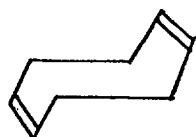
Figure 7:1 shows the molecule of cyclooctane-1,2-diolato-5,6-diolato-bis(dipyridinedioxoosmium(vi)). The molecule lies across a crystallographic diad, which passes perpendicular to the line joining the two osmium atoms. The osmium is octahedrally co-ordinated to two cis pyridine ligands, two trans oxo ligands, and two cis diolato oxygen atoms. The environment about each osmium atom is typical, and finds parallel in four monoalkene compounds: Adenosine bis(pyridine)osmate(vi) (9), an anthracene-bispyridine-dioxo compound (10), a methylamine-bispyridinedioxo comp-

ound (11), and a thymine bispypyridineoxo compound (12). The structure is the first reported osmium-diene compound.

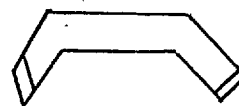
Internal bond lengths and angles are given in Table 7:4 from which it can be seen that the values are typical of six co-ordinate osmium (vi). Literature averages for the bonds are as follows: Os-N 2.14 Å, Os=O 1.73 Å, Os-O 1.96 Å (10,11), with the averaged values for the title complex of Os-N 2.19, Os=O 1.72, Os-O 1.95 Å. Care must be taken with conclusions from these values, however, as some distortion of the bond lengths may be caused by the disorder within the structure. Bond angles are unremarkable except for the O=Os=O angle of $163.5(7)^\circ$, which is significantly bent from the theoretical trans angle of 180.0° . Most other angles are within 5° of expected values for octahedral stereochemistry.

Bond lengths within the organic part of the molecule are typical and require no further comment within the limited accuracy of the determinations. The second pyridine ring shows signs of probable slight disorder, consistent with high temperature parameters for all but the nitrogen atom. The pattern of the thermal ellipsoids suggests both "bending" and "rotation" about the Os-N(21)-C(24) vector, pivoting at N(21). The mean bond lengths of this ring are slightly shorter, C-C 1.36 C-N 1.34, than the other ring which has C-C 1.39, C-N 1.30. This is typical of high thermal parameters, which in turn are consistent with positional disorder. (See Figure 7:2)

The conformation of the cyclooctane ring is given in table 7:5, and indicates a "trans" orientation of the erstwhile double bonds, with the two osmium diester linkages on opposite sides of the cyclooctane ring (see below).



Trans



Cis

Figure 7:2 A view showing thermal ellipsoids, at 30% probability. The disorder of the second ring is apparent.

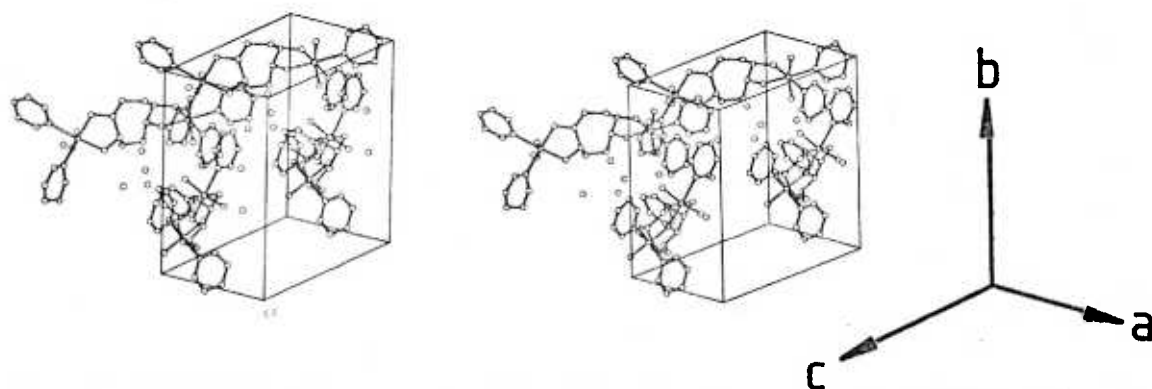
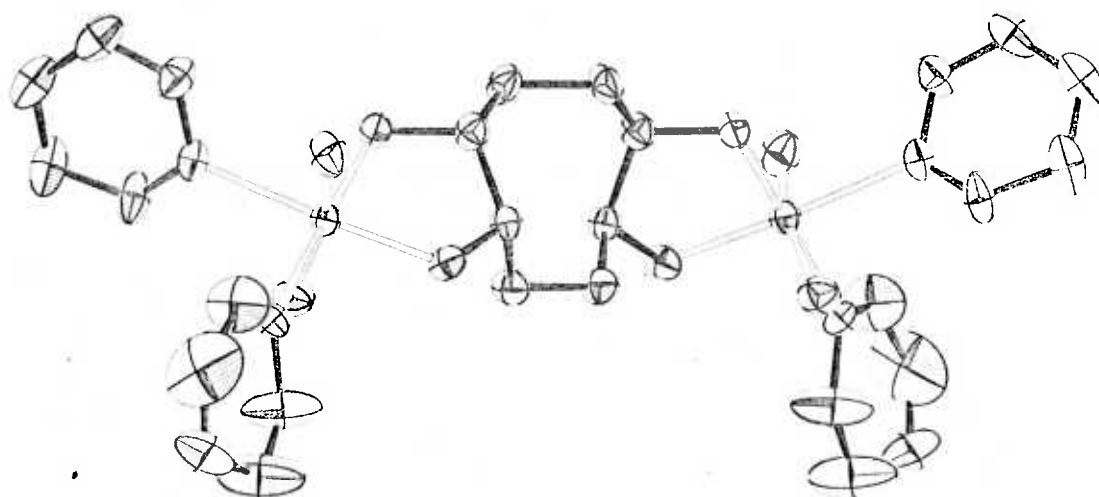


Figure 7:3 A stereoscopic packing diagram.

An interesting feature of the structure is the presence of two free water molecules. These are not co-ordinated to the metal atom, but hydrogen bond to the co-ordinated oxygen atoms at $2.74 \text{ \AA}$ (O(6)-O(4)), and $2.76 \text{ \AA}$ (O(5)-O(2)). Both the unique water molecules lie close to diads, but are reasonable distances apart, O(5)-O(5) 2.70 and O(6)-O(6) $2.75 \text{ \AA}$. The presence of the water is interesting in that no hydrolysis of the osmate ester has taken place to give a cis-diol. Such an observation is not unique, ref (11) reports a single unco-ordinated water molecule, but the ratio of two water molecules per double bond is twice that previously observed.

Figure 7:3 shows a packing diagram, from which it can be seen that the structure is maintained by two intra-molecular hydrogen bond links via the water molecules. There are no heavy atom contacts less than $3.0 \text{ \AA}$. Apart from the hydrogen bonds the shortest hydrogen-heavy atom contact is $2.3 \text{ \AA}$ between O(4) and H(15). There is nothing obvious to account for the disorder of one of the pyridine moieties. Figure 7:4 is a space-filling diagram of the molecule, without the water molecules included.

Figure 7:4 A space filling drawing of the molecule.

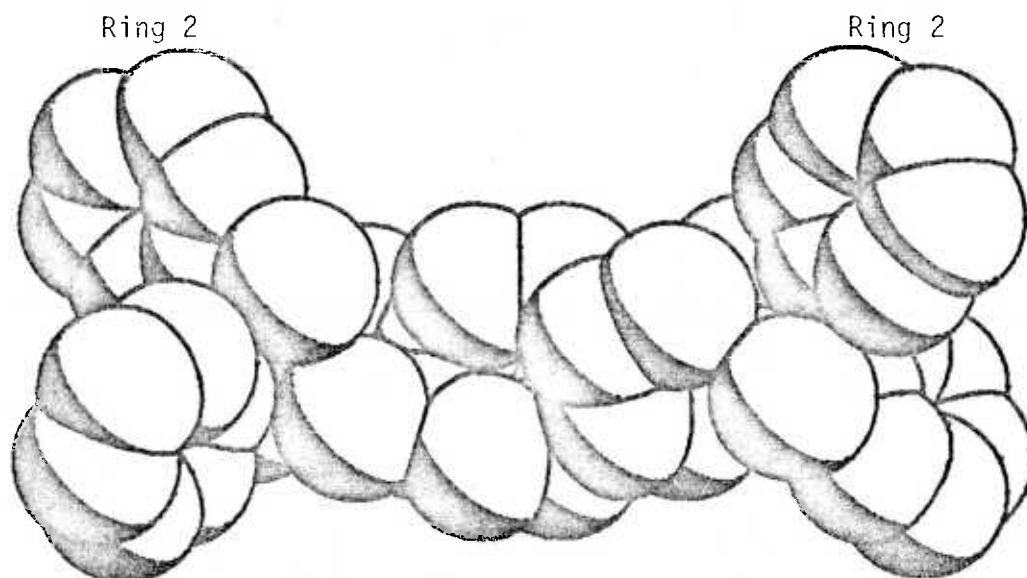


Table 7:1 Fractional atomic coordinates with estimated standard deviations in parentheses.

Atom	x	y	z
Os	0.21713(7)	0.21372(4)	0.01480(4)
O(1)	0.1327(22)	0.1473(10)	0.0956(10)
O(2)	0.3400(19)	0.2935(7)	-0.0431(10)
O(3)	0.2112(15)	0.1239(8)	-0.0851(9)
O(4)	0.0177(15)	0.2598(7)	-0.0370(7)
O(5)	0.5761(37)	0.3427(20)	-0.1674(17)
O(6)	-0.1812(29)	0.4092(13)	-0.0260(14)
C(10)	0.0466(23)	0.2846(11)	-0.2039(11)
C(20)	-0.0164(21)	0.2194(10)	-0.1271(10)
C(30)	0.0534(22)	0.1250(12)	-0.1289(12)
C(40)	0.0739(24)	0.0767(12)	-0.2186(12)
N(11)	0.4453(15)	0.1540(10)	0.0633(9)
C(12)	0.4446(24)	0.0636(14)	0.1001(16)
C(13)	0.5757(39)	0.0272(15)	0.1234(17)
C(14)	0.7266(30)	0.0721(19)	0.1143(17)
C(15)	0.7324(26)	0.1596(21)	0.0772(17)
C(16)	0.5778(22)	0.1923(16)	0.0532(14)
N(21)	0.2234(23)	0.3170(9)	0.1234(10)
C(22)	0.2097(60)	0.3015(20)	0.2122(15)
C(23)	0.2173(93)	0.3678(31)	0.2771(18)
C(24)	0.2418(76)	0.4527(20)	0.2529(42)
C(25)	0.2198(74)	0.4777(13)	0.1540(26)
C(26)	0.2295(54)	0.4076(17)	0.0993(28)

Table 7:2 Anisotropic temperature factors, with e.s.d.'s in parentheses. Os x 10000, rest x 1000 $\text{\AA}^2$

Atom	U11	U22	U33	U12	U13	U23
Os	425(4)	415(4)	316(4)	1(2)	-28(2)	13(2)
O(1)	77(8)	83(8)	55(7)	-6(8)	-11(8)	-4(8)
O(2)	73(8)	53(6)	50(6)	-6(6)	3(7)	10(6)
O(3)	43(5)	53(5)	55(6)	4(5)	-8(6)	5(5)
O(4)	66(6)	45(4)	29(4)	11(5)	-4(5)	-1(4)
O(5)	124(20)	200(22)	102(13)	24(20)	43(16)	47(18)
O(6)	133(15)	95(11)	93(14)	39(12)	-1(14)	-3(11)
C(10)	67(10)	49(7)	43(7)	-3(8)	-4(8)	-1(7)
C(20)	55(8)	46(7)	33(6)	2(7)	-9(6)	-2(6)
C(30)	56(9)	57(8)	42(8)	6(7)	-5(8)	-3(7)
C(40)	70(10)	62(8)	46(7)	18(9)	-22(10)	-6(8)
N(11)	43(6)	66(8)	43(6)	6(6)	-4(5)	5(7)
C(12)	59(10)	69(10)	71(11)	9(9)	1(10)	20(11)
C(13)	99(7)	85(13)	65(11)	29(13)	1(14)	13(12)
C(14)	74(12)	105(14)	71(12)	37(13)	10(12)	23(13)
C(15)	51(10)	139(18)	61(11)	14(12)	-1(9)	25(14)
C(16)	38(7)	104(14)	56(9)	2(9)	3(8)	26(11)
N(21)	66(8)	48(6)	49(7)	2(7)	-15(8)	-16(6)
C(22)	204(37)	120(20)	37(8)	-4(3)	-13(15)	11(11)
C(23)	372(71)	214(36)	50(14)	82(54)	-64(26)	-42(19)
C(24)	234(54)	79(16)	244(38)	-1(28)	-102(46)	-69(24)
C(25)	283(57)	79(14)	101(22)	-15(23)	75(36)	2(16)
C(26)	203(34)	59(12)	145(27)	3(19)	81(32)	18(15)

Table 7:3 Calculated hydrogen atom positions. The first two digits refer to the parent atom.

Atom	x	y	z
H(101)	0.159	0.260	-0.228
H(102)	0.072	0.347	-0.177
H(20)	-0.132	0.209	-0.143
H(30)	-0.001	0.086	-0.085
H(401)	0.166	0.108	-0.255
H(402)	0.109	0.012	-0.207
H(12)	0.336	0.034	0.103
H(13)	0.574	-0.036	0.152
H(14)	0.835	0.043	0.137
H(15)	0.843	0.199	0.066
H(16)	0.567	0.252	0.021

Table 7:4 Interatomic bond lengths ($\text{\AA}$) and angles($^\circ$), with estimated standard deviations in parentheses.
(') = $-x$, y , $-1/2-z$.

Os-O(1)	1.672(15)	Os-O(2)	1.761(14)
Os-O(3)	1.948(12)	Os-O(4)	1.947(12)
Os-N(11)	2.210(13)	Os-N(21)	2.172(14)
O(1)-Os-O(2)	163.5(7)	O(1)-Os-O(3)	96.8(6)
O(1)-Os-O(4)	96.1(7)	O(1)-Os-N(11)	85.2(7)
O(1)-Os-N(21)	84.6(6)	O(2)-Os-O(3)	96.0(6)
O(2)-Os-O(4)	95.2(6)	O(2)-Os-N(11)	84.6(6)
O(2)-Os-N(21)	82.7(6)	O(3)-Os-O(4)	85.7(5)
O(3)-Os-N(11)	89.6(5)	O(3)-Os-N(21)	178.4(5)
O(4)-Os-N(11)	175.2(5)	O(4)-Os-N(21)	93.5(6)
N(11)-Os-N(21)	91.3(6)		
C(10)-C(20)	1.55(2)	C(20)-C(30)	1.49(2)
C(20)-O(4)	1.45(2)	C(30)-C(40)	1.48(2)
C(30)-O(3)	1.46(2)	C(10)-C(10)'	1.54(2)
C(40)-C(40)'	1.53(3)		
C(10)-C(20)-C(30)	115(1)	C(10)-C(20)-O(4)	109(1)
O(4)-C(20)-C(30)	108(1)	C(20)-C(30)-C(40)	120(1)
C(20)-C(30)-O(3)	111(1)	C(40)-C(30)-O(3)	106(1)
C(40)'-C(40)-C(30)	115(2)	C(10)'-C(10)-C(20)	116(1)
C(20)-O(4)-Os	112(1)	C(30)-O(3)-Os	110(1)

N(11)-C(12)	1.35(3)	N(21)-C(22)	1.31(3)
C(12)-C(13)	1.32(4)	C(22)-C(23)	1.35(5)
C(13)-C(14)	1.43(4)	C(23)-C(24)	1.30(6)
C(14)-C(15)	1.38(4)	C(24)-C(25)	1.49(7)
C(15)-C(16)	1.42(3)	C(25)-C(26)	1.29(4)
C(16)-N(11)	1.25(2)	C(26)-N(21)	1.36(3)
C(16)-N(11)-C(12)	117(2)	C(26)-N(21)-C(22)	115(2)
N(11)-C(12)-C(13)	123(2)	N(21)-C(22)-C(23)	124(3)
C(12)-C(13)-C(14)	119(2)	C(22)-C(23)-C(24)	120(4)
C(13)-C(14)-C(15)	120(2)	C(23)-C(24)-C(25)	118(4)
C(14)-C(15)-C(16)	112(2)	C(24)-C(25)-C(26)	113(3)
C(15)-C(16)-N(11)	129(2)	C(25)-C(26)-N(21)	127(4)

Hydrogen bonds.

O(4)....O(6)	2.74(2)	O(2)....O(5)	2.76(2)
O(6)....O(6) ²	2.75(4)	O(5)....O(5) ¹	2.70(4)

Torsion angles.

C(10)-C(10)C(20)C(30)	89.7	C(10)C(20)C(30)C(40)	-42.6
C(20)C(30)C(40)C(40) [*]	-49.0	C(20)C(10)C(10) [*] C(20)	-93.9
C(30)C(40)C(40) [*] C(30) ¹	117.2		

$$1 = -x, y, 1/2 - z$$

$$2 = x, 1 - y, -z$$

References.

1. F.C. Phillips and A.C. Skapski J.Chem.Soc.Dalton 1976 2586
2. F.C. Phillips and A.C. Skapski Acta Cryst. B31 (1975) 1814
3. R.Criegee, B.Marchand, H.Wannowius Annalen 99 (1942) 550
4. L.R.Subboraman, J.Subboraman and E.J.Behrman Inorg.Chem. 11 (1972) 262
5. F.B.Daniel, E.J.Behrman J.Amer.Chem.Soc. 97 (1975) 7352
6. R.L.Clarke, E.J.Behrman Inorg.Chem. 14 (1975) 1425
7. Some Biological Techniques in Electron Microscopy (1970) p69.
8. M.Schroder PhD Thesis (1978) University of London.
9. J.F.Conn, J.J.Kim, F.L.Suddath, P.Blattmann, A.Rich. J.Amer.Chem.Soc. 96 (1974) 7152
10. T.Prange and C.Pascard Acta Cryst. B33 (1977) 621
11. T.J.Kistenmacher, L.G.Marzilli and M.Rossi Bioinorg. Chem. 6 (1976) 347
12. S.Neidle and D.I.Stuart Biochim.Biophys.Acta 418 (1976) 226

Appendix A.

The crystal and molecular structure of
tris-diethylmalonato-iron(III).

Introduction.

Studies on the compounds of high oxidation states of iron have been carried out by the workers of the inorganic research group of Professor Wilkinson, with the view to trapping and characterising a complex. Experimental work involving β -diketones and Iron(III) chloride in inert atmospheres led to the isolation of an unstable, brown crystalline substance of suspected constitution $\text{Fe}(\text{diethylmalonate})_2\text{Cl}_2$ (1). Since crystals were available, an X-ray structure determination was carried out in order to elucidate the nature of the environment about the iron atom.

Experimental.

The compound crystallized as long brown fibres, with easy cleavage along the fibre direction. For X-ray study they were mounted in 0.3mm Lindemann tubes under nitrogen.

Preliminary oscillation and Weissenberg photographs gave systematic absence conditions of hkl , $h+k=2n+1$; $h0l$, $l=2n+1$. monoclinic. These are consistent with either space group Cc or $C2/c$. The latter was confirmed by refinement.

A crystal $0.16 \times 0.26 \times 1.3$ mm was mounted on the diffractometer with its c needle axis parallel to the ϕ axis, and also aligned along the length of the capillary tube. 14 high-angle $\text{CuK}\alpha_1$ reflections were measured and analysed by a least-squares procedure. The resulting unit-cell parameters did not correctly drive the diffractometer, and it was found that the a axis had changed slightly by $0.01\text{\AA}$. Recalculation gave actual unit-cell parameters of $a=19.176(4)$, $b=11.918(2)$, $c=13.911(4)$ $\text{\AA}$, $\beta=115.36(2)^\circ$, space group $C2/c$, $Z=4$ formula units, $U=2703.5$ $\text{\AA}^3$, $M=533.31$, $F(000)=1124$, formula $\text{C}_{21}\text{H}_{33}\text{FeO}_{12}$, $d_{\text{calc}}=1.31$ g/cm^3 , $\mu=53.89\text{cm}^{-1}$

1706 independent reflections were measured on the diffractometer, collecting at ca 600 per day to a θ max of 55° , of which 213 were considered unobserved with I less than 2.5σ .

0.1. The $11,3,0$ reflection was monitored as a reference every 50 reflections and used to scale the data. Its nett count remained significantly constant during the 3 days of

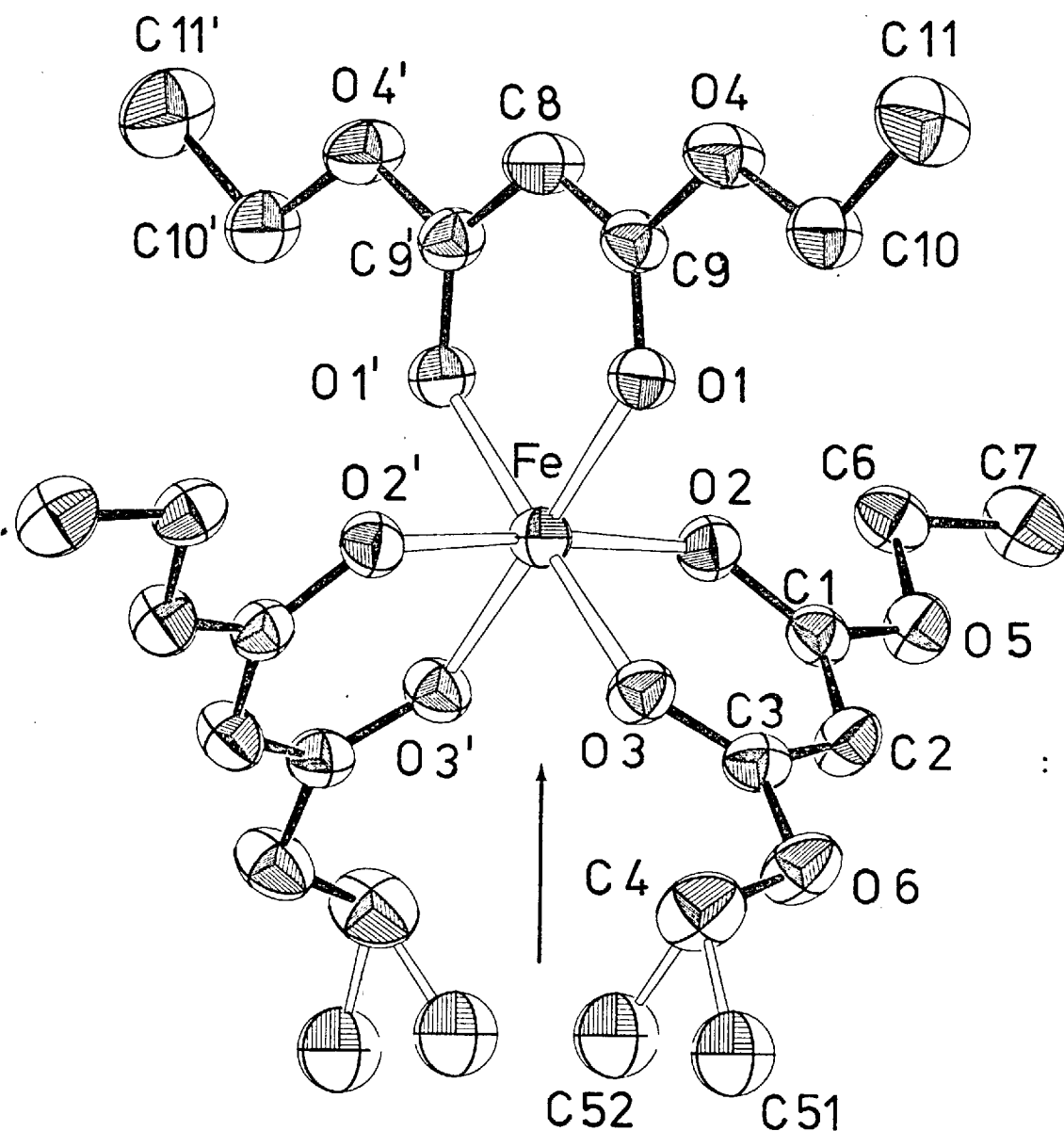


Figure A:1 A view roughly parallel to the pseudo three-fold axis of the iron, with thermal ellipsoids scaled to include 30% probability. The disordered C51 and C52 atoms have dummy isotropic spheres.

data collection. Lorentz and polarisation corrections were applied in the usual manner. At a later stage the data was corrected for absorption using a $10 \times 10 \times 12$ grid.

Solution and refinement of the structure.

Statistical analysis of the data gave a centric distribution, consistent with space group $C2/c$. This suggested that the molecule ought to lie on a special position, either a centre of symmetry or a two-fold axis. A sharpened, origin-removed Patterson synthesis located the iron atom on a diad and a structure factor calculation gave $R=0.55$. From the corresponding Fourier difference synthesis the co-ordinated oxygen atoms could be located, giving $R=0.45$. Location of the remaining non-hydrogen atoms proved to be rather difficult, successive cycles of isotropic least-squares refinement with new atom positions producing only very gradual reductions in R . The location of all the heavy atoms gave $R=0.100$, with anisotropic refinement giving $R=0.079$. The use of absorption corrected data gave $R=0.078$, and application of the usual weighting scheme with $F^*=35$, and inclusion of anomalous scattering corrections for iron gave $R=0.055$. The final R with calculated hydrogen atoms input as fixed atom contributions, with the isotropic temperature factors of their parent atoms, was 0.050. The $-4,0,2$ reflection was thought to be suffering from extinction and removed.

Table A:1 lists refined atom co-ordinates, Table A:2 anisotropic thermal parameters, and Table A:3 calculated hydrogen atom positions. Observed and calculated structure factor amplitudes are listed on page 129 & 130.

Description and discussion of the structure.

Figure A:1 shows the molecule of tris-diethylmalonato-iron(III). This is the first reported complex of a malonic ester, and the first example of a chelating malonate group. The iron atom lies on a two-fold axis which also passes through the central carbon atom of one of the three chelating diethyl malonate ligands. The iron is octahedrally co-ordinated by the carbonyl oxygens of the chelating diethyl malonate ligands, and has approximate 32 point symmetry (D_3). The diethyl malonate ligands are approximately planar with the exception of the terminal C5 methyl atom of one of

the ethyl groups. This shows positional disorder between two sites of equal occupancy, both of which are out of the mean plane of the rest of that malonate ligand. The planes of the three malonate ligands are mutually perpendicular, and the overall shape of the molecule is analogous to that found for trisacetylacetonatoiron(III), $\text{Fe}(\text{acac})_3$, (2). Table A:4 lists interatomic bond lengths and angles, and Table A:5 gives best planes through the diethylmalonate ligands.

The three independent iron-oxygen distances are closely similar, having a mean of 1.991 Å. The related complex of iron(III) with acac has a mean iron(III)-O distance of 1.994 Å (2,3,4). The other bond lengths and angles are as expected for the diethyl malonate ligands. A comparison of some bond lengths and angles between the title complex, $\text{Fe}(\text{acac})_3$ complexes and unco-ordinated malonate esters is given in Table A:6. This shows the expected lengthening of the carbonyl bond from 1.204 in the free esters to 1.253 Å in the co-ordinated ligand, and a corresponding shortening of the C-C bonds from 1.506 Å to 1.336 Å. These values are consistent with delocalisation of the double bond system which occurs on proton loss from the malonate ester. Other noticeable changes are the closing of the O=C-O angle from 123.5° to 113°, and a corresponding increase of O=C-C to 127° from 123.5°. The latter angle in acac complexes is not as high, but this is probably due to the ester linkage on the carbonyl carbon, rather than a methyl group.

The carbonyl bond length is shorter than that in acac complexes, which should increase the nucleophilic nature of the carbon atom. This will also be increased relative to the acac complexes by virtue of an oxygen, rather than a methyl, substituent. The C-O ester bond is significantly longer than that in the unco-ordinated malonates (1.339 to 1.325 Å) thus the combination of all these factors suggests that the co-ordinated malonate should be much more susceptible to nucleophilic attack at the carbonyl oxygen. Such attack, for example by water, would lead to hydrolysis of the ester bond.

The nucleophilic site is also less sterically restricted than the corresponding site in the free malonate, as evidenced by the increased O-C-C angle from 111.5° to 114.9°, and

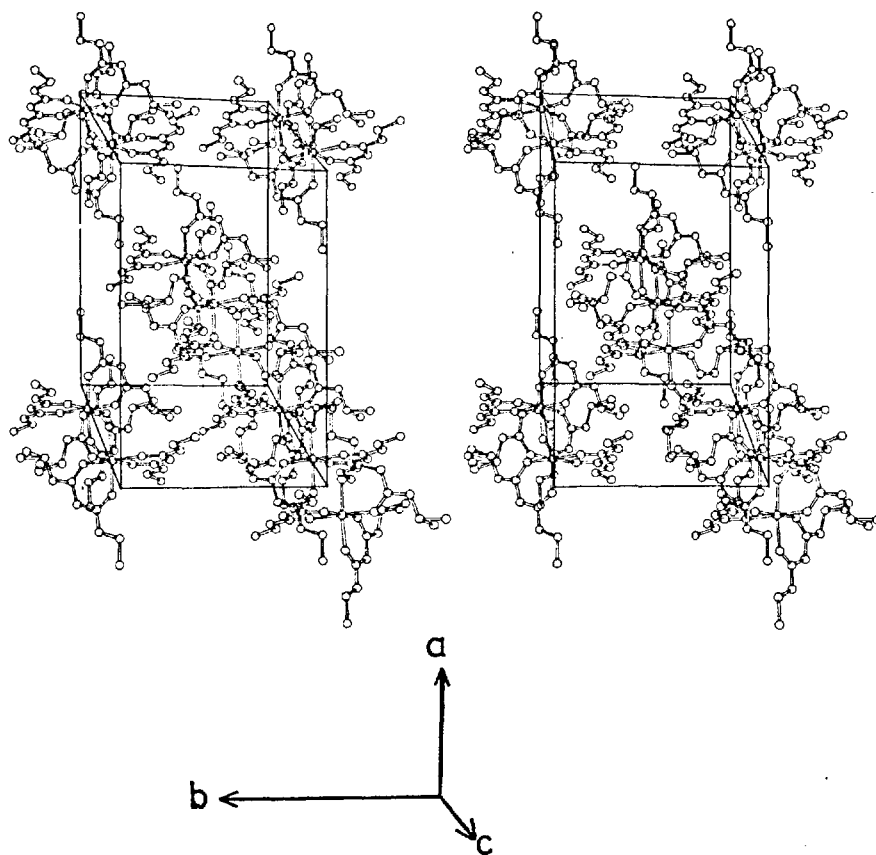


Figure A:2 A stereoscopic view of the contents of the unit cell.

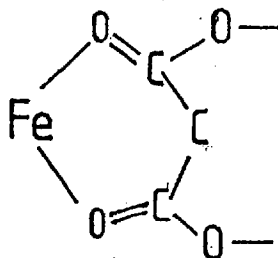
the restriction of movement of the whole ligand caused by binding to the iron atom. These factors may help to account for the instability of the complex, which is all the more remarkable when one considers that iron(III)(acac)_3 is one of the most stable iron(III) complexes known.

Figure A:2 shows the contents of the unit cell. The rather awkward shape of the molecule may cause packing difficulties, and may be responsible for the disorder of C(5). However, there are no short C-C(5) contacts either intra or inter molecularly, and either position of C(5) could be accommodated in one molecule.

Figure A:3 shows a space filling diagram, which serves to indicate the relative ease of approach to the carbonyl carbon atom.

Table A:6.

A comparison between the title complex, co-ordinated acetyl acetates, and unco-ordinated malonic esters. The data were obtained from the Cambridge Crystallographic Data Centre, searching for the following fragment:



The references for the iron acetates are given, but since 30 different malonic ester containing compounds were found they have not been listed. Only data with R less than 0.07 has been included.

	Fe-O	O=C	O-C	C-C	O=C-O	O=C-C	O-C-C	C-C-C
Title	1.983	1.245	1.347	1.384	117.5°	127.7°	114.9°	122.2°
comp.	1.995	1.261	1.335	1.384	118.4°	126.7°	115.1°	121.3°
	1.983	1.253	1.335	1.391	118.0°	126.9°	114.7°	
Mean	1.990	1.253	1.339	1.386	118.0°	127.1°	114.9°	121.3°
Acac	1.995	1.271		1.417		124.7°		124.6
Malonates		1.204	1.225	1.306	122.5	123.5	111.5	

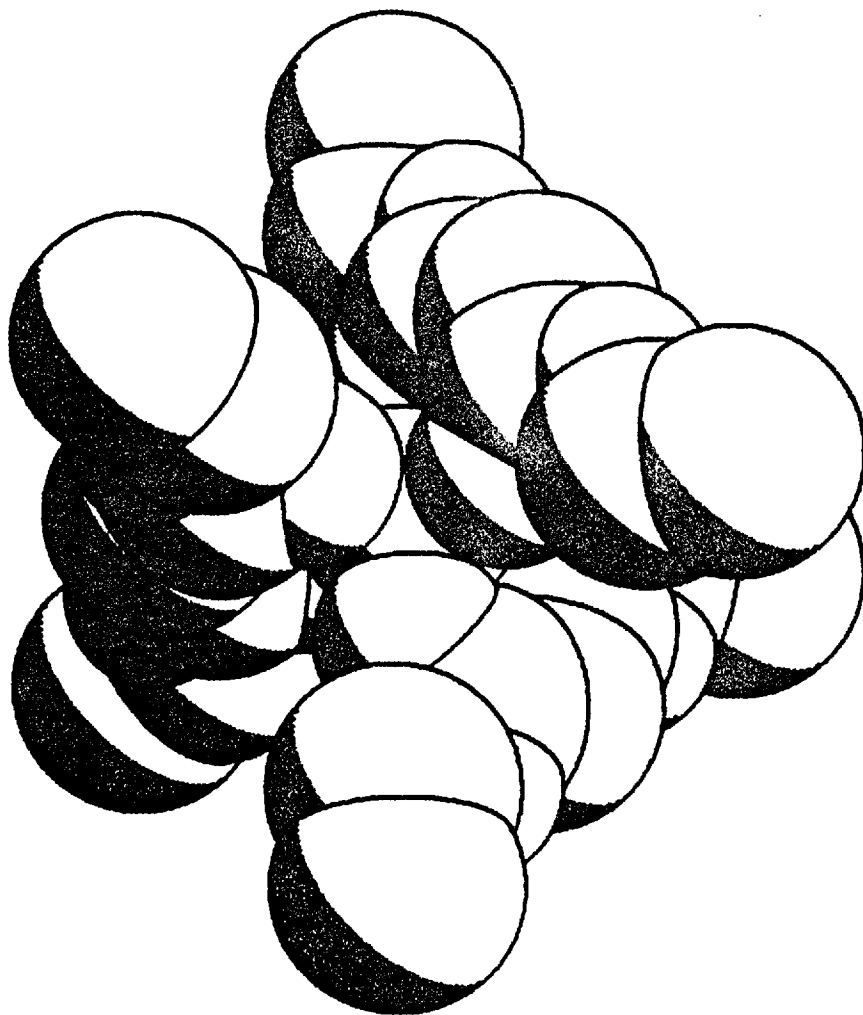


Figure A:3 A space filling diagram of the complex.

Table A1:1 Fractional coordinates of the non-hydrogen atoms with standard deviations in parentheses.

Atom	x	y	z
Fe	0	0.01009(7)	1/4
O(1)	0.0498(2)	0.1308(2)	0.3579(2)
O(2)	0.0987(2)	0.0032(2)	0.2216(2)
O(3)	0.0507(2)	-0.1059(2)	0.3627(2)
O(4)	0.0908(2)	0.2995(2)	0.4277(2)
O(5)	0.2181(2)	-0.0553(2)	0.2309(2)
O(6)	0.1364(2)	-0.2378(3)	0.4605(3)
C(1)	0.1589(2)	-0.0618(3)	0.2634(3)
C(2)	0.1710(3)	-0.1416(4)	0.3417(3)
C(3)	0.1158(3)	-0.1580(3)	0.3856(3)
C(4)	0.0765(4)	-0.2706(5)	0.4933(5)
C(51)*	0.0920(9)	-0.3777(11)	0.5467(15)
C(52)*	0.0322(10)	-0.3643(11)	0.4349(17)
C(6)	0.2092(3)	0.0264(4)	0.1485(4)
C(7)	0.2865(3)	0.0222(4)	0.1350(5)
C(8)	0	0.2920(5)	1/4
C(9)	0.0460(2)	0.2341(3)	0.3434(3)
C(10)	0.1420(3)	0.2423(4)	0.5270(4)
C(11)	0.1922(4)	0.3276(6)	0.6034(4)

* Atom C(5) is disordered, but refines satisfactorily in two positions, with site population parameters of 0.5

Table A2 Anisotropic temperature factors, with estimated standard deviations in parentheses. Fe x 10⁴, others x 10³ Å²

Atom	U11	U22	U33	U12	U13	U23
Fe	572(6)	502(5)	581(6)	0	209(4)	0
O(1)	65(2)	53(2)	53(2)	-3(1)	13(1)	1(1)
O(2)	58(2)	61(2)	60(2)	1(1)	24(1)	9(1)
O(3)	64(2)	59(2)	69(2)	7(1)	34(2)	11(1)
O(4)	100(2)	60(2)	51(2)	-8(2)	11(2)	-3(1)
O(5)	64(2)	72(2)	69(2)	4(1)	36(2)	11(2)
O(6)	90(2)	74(2)	91(2)	20(2)	55(2)	35(2)
C(1)	57(2)	54(2)	52(2)	-6(2)	20(2)	-6(2)
C(2)	64(3)	68(3)	71(3)	14(2)	33(2)	17(2)
C(3)	69(3)	48(2)	57(2)	-0(2)	26(2)	5(2)
C(4)	109(4)	88(4)	101(4)	12(3)	65(3)	32(3)
C(51)	135(11)	98(9)	188(15)	32(8)	105(11)	78(10)
C(52)	151(13)	78(8)	233(19)	-46(9)	121(14)	-36(11)
C(6)	81(3)	64(3)	61(3)	-12(2)	33(2)	0(2)
C(7)	99(4)	92(3)	87(4)	-17(3)	57(3)	-3(3)
C(8)	101(5)	53(3)	59(4)	0	17(4)	0
C(9)	65(2)	56(3)	51(2)	-5(2)	20(2)	-4(2)
C(10)	85(3)	72(3)	56(3)	-4(2)	12(2)	-1(2)
C(11)	138(5)	112(4)	64(3)	-21(4)	6(3)	-5(3)

Table A3 Calculated hydrogen atom positions. The first digit refers to the parent atom (1st two for C(10),C(11)).

Atom	x	y	z
H(71)	0.292	-0.058	0.107
H(72)	0.285	0.081	0.082
H(73)	0.334	0.038	0.205
H(61)	0.163	0.005	0.079
H(62)	0.200	0.102	0.170
H(2)	0.222	-0.189	0.368
H(8)	0	0.379	1/4
H(111)	0.222	0.296	0.671
H(112)	0.232	0.360	0.575
H(113)	0.157	0.392	0.606
H(101)	0.107	0.204	0.558
H(102)	0.176	0.184	0.515
H(41)*	0.075	-0.212	0.552
H(42)*	0.020	-0.271	0.437
H(43)*	0.102	-0.289	0.577
H(44)*	0.036	-0.206	0.488

* Hydrogens on C(4) have two sets of positions which correspond to the two methyl positions of C(5), and were given half occupancy.

Table A4 Interatomic bond lengths (Å) and angles (°),
with estimated standard deviations in parentheses.

(¹) = - x, y, 1/2 - z.

Fe-O(1)	1.988(3)	Fe-O(2)	1.995(3)	Fe-O(3)	1.988(3)
O(1)-Fe-O(2)	91.0(1)	O(1)-Fe-O(3)	90.4(1)		
O(1)-Fe-O(1) ¹	87.3(1)	O(1)-Fe-O(2) ¹	92.4(1)		
O(1)-Fe-O(3) ¹	177.6(1)	O(2)-Fe-O(3)	88.4(1)		
O(2)-Fe-O(2) ¹	175.3(1)	O(2)-Fe-O(3) ¹	88.3(1)		
O(3)-Fe-O(3) ¹	91.9(1)				

O(1)-C(9)	1.245(5)	C(9)-C(8)	1.384(5)
C(9)-O(4)	1.347(5)	O(4)-C(10)	1.456(5)
C(10)-C(11)	1.468(7)	O(2)-C(1)	1.261(5)
C(1)-C(2)	1.384(6)	C(2)-C(3)	1.391(8)
C(3)-O(3)	1.253(5)	C(3)-O(6)	1.335(5)
O(6)-C(4)	1.448(8)	C(4)-C(51)	1.412(15)
C(4)-C(52)	1.434(15)	C(1)-O(5)	1.335(6)
O(5)-C(6)	1.453(6)	C(6)-C(7)	1.494(9)
Fe-O(1)-C(9)	128.3(2)	O(1)-C(9)-C(8)	127.7(4)
C(9)-C(8)-C(9) ¹	120.3(5)	O(1)-C(9)-O(4)	117.5(3)
C(9)-O(4)-C(10)	116.7(3)	O(4)-C(10)-C(11)	107.6(4)
Fe-O(2)-C(1)	127.7(3)	O(2)-C(1)-C(2)	126.7(5)
C(1)-C(2)-C(3)	122.2(4)	C(2)-C(3)-O(3)	126.9(4)
C(3)-O(3)-Fe	127.8(3)	O(2)-C(1)-O(5)	118.4(4)
C(1)-O(5)-C(6)	117.9(3)	O(5)-C(6)-C(7)	106.3(4)
O(3)-C(3)-O(6)	118.0(5)	C(3)-O(6)-C(4)	117.9(4)
O(6)-C(4)-C(51)	112.7(9)	O(6)-C(4)-C(52)	106.9(11)

Table A:5 Least squares planes, with distances from the planes in Å, e.s.d's in parentheses.

Plane 1, Equation $17.45x - 9.16z + 2.29 = 0$

*=symop -x,y,1/2-z

Defining plane:

C(11)	0.116(5)	C(10)	-0.059(4)	O(4)	-0.043(3)
C(9)	-0.053(4)	O(1)	-0.118(3)	C(8)	0
C(9)*	0.053(4)	O(11)*	0.118(3)	O(4)*	0.043(3)
C(10)*	0.059(4)	C(11)	-0.116(5)		

Not defining plane Fe 0 (by symmetry)

Plane 2, Equation $3.21x + 8.03y + 7.91z - 2.11 = 0$

Defining plane:

C(7)	0.052(4)	C(6)	-0.056(4)	O(5)	-0.031(2)
C(1)	-0.016(3)	O(2)	-0.018(2)	C(2)	0.001(4)
C(3)	0.040(3)	O(3)	0.069(2)	O(6)	0.058(3)
C(4)	-0.099(2)				

Not defining plane:

Fe	-0.054(1)	C(51)	-0.52(1)	C(52)	-1.50(1)
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Appendix B.

The following two structures were done as part of the supervision of third year undergraduate students at Imperial College. Most of the photographic work was under the direct supervision of Dr Skapski. I was responsible for data collection, and practical aspects of the computing procedures.

I would like to thank Paul and Lorraine for their interest and help.

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X-ray Crystal Structure of the Acetone Solvate of Tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III): A Complex Involving Three Four-Membered Rings with Nitrogen and Sulphur as Donor Atoms

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Abstract

$\text{Co}(\text{C}_6\text{H}_7\text{N}_2\text{S})_3 \cdot (\text{CH}_3)_2\text{CO} \cdot \text{C}_{18}\text{H}_{21}\text{CoN}_6\text{S}_3 \cdot \text{C}_3\text{H}_6\text{O}$, is monoclinic with $a = 8.292(1)$, $b = 16.604(1)$, $c = 18.167(1)$ Å, $\beta = 90.34(1)^\circ$, space group $P2_1/n$, $Z = 4$. Refinement with 3137 counter reflexions gave $R = 0.044$. A chelate mode of binding *via* N and S atoms is found for the 4,6-dimethylpyrimidine-2-thionato ligands. These bidentate groups are arranged round the Co atom such that the three S atoms are *cis* to each other giving a facial octahedral complex of approximate C_3 point symmetry. A mean distance of 2.259 Å is found for Co–S, and the mean Co–N length is 1.979 Å. Distortion caused by the limited bite of the ligands is reflected in S–Co–N angles of *ca* 72.5° . The acetone molecules are neither coordinated nor hydrogen-bonded to the complex.

Introduction

While interest in S as a site for binding metals to naturally occurring substances containing thiolated chelates is well established (Eisenberg, 1970; Cox & Darken, 1971), as is that in S and N bidentate ligands (Ali & Livingstone, 1974), there is a paucity of structural information for the latter complexes (Fletcher & Skapski, 1972; Heitner & Lippard, 1974; Sletten & Apeland, 1975). An understanding of these interactions is important in work involving metal ions and complexes which are used as probes to study the conformation of such naturally occurring molecules in solution (Heitner & Lippard, 1974).

As part of a programme of structural studies on metal complexes with pyrimidine-based ligands (e.g. Cartwright, Reynolds & Skapski, 1977) we have studied the crystal structure of a Co complex with 4,6-dimethylpyrimidine-2-thionato ligands, especially as recent X-ray work on a Co complex of the parent ligand pyrimidine-2-thione, $\text{Co}(\text{pym}2\text{S})_2\text{Cl}_2$, has revealed only a very weak Co–S interaction (McConway, 1975). We find the title compound to

be a facial chelate complex with relatively strong Co–S and Co–N bonds. This is the first compound involving three four-membered rings with N and S as donor atoms, and preliminary details of the structure have been reported (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977).

Experimental

Tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) was prepared from cobalt(II) perchlorate hexahydrate and 4,6-dimethylpyrimidine-2-thione (in a 1:3 molar ratio) in a warm acetone solution (Cartwright, Goodgame, Jeeves, Langguth & Skapski, 1977). Chemical analysis indicated that the dark-green prismatic crystals contained acetone of solvation in a Co:acetone ratio of 1:1.

Photographs showed the crystals to be monoclinic, with systematic absences $h0l: h + l = 2n + 1$, and $0k0: k = 2n + 1$. These absences uniquely determine the space group as $P2_1/n$. A crystal $0.19 \times 0.13 \times 0.05$ mm was mounted with a parallel to the ϕ axis on a Siemens off-line four-circle automatic diffractometer, and measurement of 19 high-angle α_1 reflexions, followed by least squares, gave $a = 8.292(1)$, $b = 16.604(1)$, $c = 18.167(1)$ Å, $\beta = 90.34(1)^\circ$, $U = 2501.2$ Å³. Other crystal data are: $D_o = 1.43$ (by flotation), $D_c = 1.42$ Mg m^{−3} for $Z = 4$ and a formula of $\text{C}_{21}\text{H}_{27}\text{CoN}_6\text{OS}_3$, $M_r = 534.6$, $F(000) = 1116$, $\mu(\text{Cu } K\alpha) = 7.70$ mm^{−1}.

Intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at a take-off angle of 3° , a Ni β -filter, and a Na(Tl)I scintillation counter. The θ – 2θ scan technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 3142 independent reflexions were measured to $\theta = 55^\circ$; of these, 901 were considered to be unobserved with $I < 2.58 \sigma(I)$. The 085 reflexion was monitored as a reference every 50 reflexions and its net count did not alter noticeably. This reflexion was used to scale the data, and Lorentz and polarization corrections were applied. At a later

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stage the data were corrected for absorption (Busing & Levy, 1957) with a $10 \times 10 \times 10$ grid, and with crystal path lengths determined by the procedure of Coppens, Leiserowitz & Rabinovich (1965).

Solution and refinement of the structure

An origin-removed Patterson synthesis resulted in a solution for the Co atom to give $R = 0.56$. Difference syntheses and isotropic refinement located the remaining non-hydrogen atoms and reduced R to 0.104. The data were now corrected for absorption and refinement as previously gave $R = 0.090$. Inclusion of the anomalous-dispersion correction and refinement of all atoms with anisotropic temperature factors resulted in $R = 0.066$. From a difference map all the H atoms were located. These were included as fixed-atom contributions with the isotropic temperature factors of their parent C atoms to give $R = 0.046$. Introduction of a weighting scheme and the removal of five strong low-angle reflexions most affected by extinction reduced R to its final value of 0.044. The final difference synthesis was featureless. Table 1 lists the coordinates of the non-

Table 1. Atomic coordinates with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Co(1)	0.62213 (10)	0.70916 (5)	0.29437 (5)
S(10)*	0.70406 (18)	0.60369 (9)	0.22623 (8)
N(11)	0.7863 (5)	0.6497 (3)	0.3530 (3)
C(12)	0.8248 (7)	0.5927 (4)	0.3032 (3)
N(13)	0.9383 (6)	0.5364 (3)	0.3107 (3)
C(14)	1.0198 (7)	0.5376 (4)	0.3747 (4)
C(15)	0.9847 (7)	0.5926 (4)	0.4293 (3)
C(16)	0.8634 (7)	0.6494 (4)	0.4182 (3)
C(17)	1.1501 (7)	0.4754 (4)	0.3837 (4)
C(18)	0.8179 (8)	0.7104 (4)	0.4748 (3)
S(20)	0.41613 (18)	0.64278 (9)	0.34751 (9)
N(21)	0.5261 (5)	0.7819 (3)	0.3682 (3)
C(22)	0.4068 (7)	0.7335 (4)	0.3933 (3)
N(23)	0.2963 (6)	0.7534 (3)	0.4427 (3)
C(24)	0.3083 (7)	0.8286 (5)	0.4696 (3)
C(25)	0.4245 (8)	0.8820 (4)	0.4465 (4)
C(26)	0.5353 (7)	0.8578 (4)	0.3936 (3)
C(27)	0.1849 (9)	0.8521 (5)	0.5267 (4)
C(28)	0.6623 (9)	0.9132 (4)	0.3652 (4)
S(30)	0.47373 (16)	0.76438 (10)	0.20199 (8)
N(31)	0.7646 (5)	0.7822 (3)	0.2387 (2)
C(32)	0.6608 (7)	0.8074 (4)	0.1849 (3)
N(33)	0.6938 (5)	0.8537 (3)	0.1276 (3)
C(34)	0.8486 (7)	0.8797 (4)	0.1252 (3)
C(35)	0.9614 (7)	0.8579 (4)	0.1767 (4)
C(36)	0.9189 (7)	0.8084 (4)	0.2349 (3)
C(37)	0.8902 (8)	0.9336 (4)	0.0622 (4)
C(38)	1.0351 (7)	0.7833 (5)	0.2923 (4)
O(1)	0.2780 (9)	0.5745 (5)	0.0425 (4)
C(2)	0.2476 (11)	0.5757 (7)	0.1063 (6)
C(3)	0.1353 (13)	0.6334 (9)	0.1381 (7)
C(4)	0.3118 (18)	0.5173 (9)	0.1603 (8)

* Atoms of the ligands are numbered (*mn*) where *m* is the ligand number, and *n* is the atom number within each ligand.

Table 2. Fractional coordinates of the H atoms

Each atom has a number which corresponds, except for the last digit, to that of the parent C atom.

	<i>x</i>	<i>y</i>	<i>z</i>
H(151)	1.060	0.603	0.476
H(171)	1.100	0.428	0.378
H(172)	1.200	0.475	0.444
H(173)	1.235	0.500	0.356
H(181)	0.840	0.773	0.456
H(182)	0.710	0.703	0.500
H(183)	0.900	0.703	0.524
H(251)	0.435	0.935	0.473
H(271)	0.250	0.908	0.553
H(272)	0.080	0.873	0.498
H(273)	0.160	0.810	0.578
H(281)	0.650	0.970	0.378
H(282)	0.770	0.885	0.364
H(283)	0.640	0.923	0.316
H(351)	1.085	0.873	0.173
H(371)	0.875	0.905	0.016
H(372)	1.025	0.953	0.078
H(373)	0.800	0.983	0.067
H(381)	1.050	0.728	0.289
H(382)	1.005	0.785	0.340
H(383)	1.130	0.810	0.280
H(31)	0.100	0.675	0.089
H(32)	0.025	0.613	0.156
H(33)	0.190	0.675	0.184
H(41)	0.425	0.518	0.138
H(42)	0.350	0.540	0.211
H(43)	0.270	0.458	0.160

hydrogen atoms, while the unrefined positions of the H atoms are given in Table 2.[†]

The weighting scheme was that suggested by Hughes (1941) where $w = 1$ for $F < F^*$, $w^{1/2} = F^*/F$ for $F \geq F^*$, with $F^* = 58$ as the optimum value. Its introduction appreciably improved the e.s.d.'s of atomic parameters. Scattering factors of Cromer & Waber (1965), and for H of Stewart, Davidson & Simpson (1965), were used; the anomalous-dispersion corrections for Co and S were from Cromer & Liberman (1970). The July 1974 update of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used, least-squares refinement being carried out by means of CRYLSQ. Most of the calculations were performed on the University of London CDC 7600 computer; steering-tape generation, data processing and structural illustrations were performed on the Imperial College CDC 6400 machine.

Description of the structure and discussion

The crystal structure consists of molecules of tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III) and acetone.

[†] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33885 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1 shows the structure of the complex, and the thermal ellipsoids of the non-hydrogen atoms (Johnson, 1965). The more important bond lengths and angles in both molecules are given in Table 3.

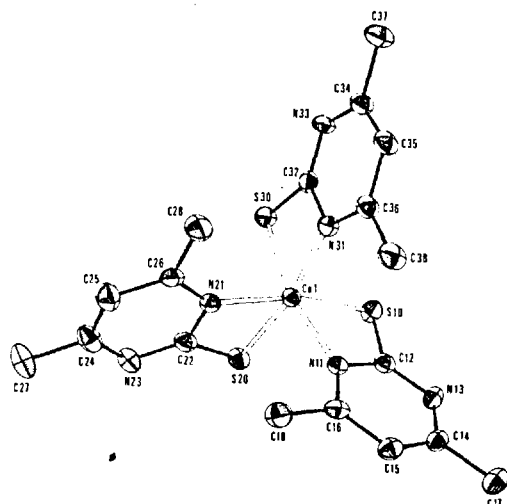


Fig. 1. Molecular structure of tris(4,6-dimethylpyrimidine-2-thionato)cobalt(III). Thermal-vibration ellipsoids are scaled to enclose 30% probability.

A distorted octahedral coordination is found for Co, with the three 4,6-dimethylpyrimidine-2-thionato ligands binding in a chelating mode *via* N and S atoms. The three S atoms are *cis* to each other giving a facial complex, with the plane of the S atoms nearly parallel to that of the N donor atoms, the angle between the two planes being 0.8°. A *cis* configuration of the S atoms can be rationalized on the grounds that it allows maximum π back-bonding to S, because the orbitals of the three S atoms can overlap different metal orbitals. The energy difference between *cis* and *trans* forms, however, is small and steric factors often cause the *trans* variant to be formed (Heitner & Lippard, 1974).

As can be seen from Fig. 1, the complex has approximate C_3 point symmetry, and the three bidentate ligands give it a propeller-like shape with a blade angle of incidence of *ca* 54°, this being the mean angle between the ring planes and the planes of the S and the N atoms.

Table 3 shows that the distortion of the coordination from octahedral is quite severe. The S—Co—N angles of 72.4–72.6° show the greatest deviations, with N—Co—N angles of 99.8–102.5° and S—Co—N *trans* angles of 164.7–167.4°. A similar, though slightly smaller, degree of strain can be seen in tris(*O*-ethyl

Table 3. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

						Mean	
Co(1)—S(10)	2.252 (2)	Co(1)—S(20)	2.255 (2)	Co(1)—S(30)	2.269 (2)	Co(1)—S(m0)	2.259
Co(1)—N(11)	1.986 (5)	Co(1)—N(21)	1.976 (5)	Co(1)—N(31)	1.975 (5)	Co(1)—N(m1)	1.979
S(10)—C(12)	1.724 (6)	S(20)—C(22)	1.723 (6)	S(30)—C(32)	1.738 (6)	S(m0)—C(m2)	1.728
N(11)—C(12)	1.351 (7)	N(21)—C(22)	1.356 (7)	N(31)—C(32)	1.365 (7)	N(m1)—C(m2)	1.357
C(12)—N(13)	1.333 (7)	C(22)—N(23)	1.328 (8)	C(32)—N(33)	1.320 (8)	C(m2)—N(m3)	1.327
N(13)—C(14)	1.342 (8)	N(23)—C(24)	1.344 (9)	N(33)—C(34)	1.355 (8)	N(m3)—C(m4)	1.347
C(14)—C(15)	1.381 (9)	C(24)—C(25)	1.377 (10)	C(34)—C(35)	1.369 (9)	C(m4)—C(m5)	1.376
C(15)—C(16)	1.392 (8)	C(25)—C(26)	1.393 (9)	C(35)—C(36)	1.386 (9)	C(m5)—C(m6)	1.390
C(16)—N(11)	1.342 (7)	C(26)—N(21)	1.344 (7)	C(36)—N(31)	1.354 (7)	C(m6)—N(m1)	1.347
C(14)—C(17)	1.502 (8)	C(24)—C(27)	1.513 (10)	C(34)—C(37)	1.495 (9)	C(m4)—C(m7)	1.503
C(16)—C(18)	1.494 (9)	C(26)—C(28)	1.493 (9)	C(36)—C(38)	1.476 (9)	C(m6)—C(m8)	1.488
O(1)—C(2)	1.188 (13)	C(2)—C(3)	1.459 (16)	C(2)—C(4)	1.477 (18)		
S(10)—Co(1)—N(11)	72.58 (14)	S(20)—Co(1)—N(21)	72.47 (14)	S(30)—Co(1)—N(31)	72.47 (14)	S(30)—Co(1)—N(m1)	72.35 (13)
S(10)—Co(1)—S(20)	94.99 (7)	S(10)—Co(1)—S(30)	94.12 (7)	S(20)—Co(1)—S(30)	94.12 (7)	S(20)—Co(1)—S(m0)	96.05 (6)
S(10)—Co(1)—N(31)	90.72 (14)	S(20)—Co(1)—N(11)	92.63 (14)	S(30)—Co(1)—N(21)	92.63 (14)	S(30)—Co(1)—N(m1)	92.06 (14)
N(11)—Co(1)—N(21)	102.54 (19)	N(11)—Co(1)—N(31)	99.76 (18)	N(21)—Co(1)—N(31)	102.53 (19)	N(21)—Co(1)—N(m1)	102.53 (19)
S(10)—Co(1)—N(21)	166.56 (15)	S(20)—Co(1)—N(31)	167.44 (14)	S(30)—Co(1)—N(11)	164.73 (14)	S(30)—Co(1)—N(m1)	164.73 (14)
Co(1)—S(10)—C(12)	79.2 (2)	Co(1)—S(20)—C(22)	79.4 (2)	Co(1)—S(30)—C(32)	79.5 (2)	Co(1)—S(m0)—C(m2)	79.5 (2)
Co(1)—N(11)—C(12)	98.8 (3)	Co(1)—N(21)—C(22)	99.4 (4)	Co(1)—N(31)—C(32)	100.3 (3)	Co(1)—N(m1)—C(m2)	100.3 (3)
Co(1)—N(11)—C(16)	142.8 (4)	Co(1)—N(21)—C(26)	141.6 (4)	Co(1)—N(31)—C(36)	142.4 (4)	Co(1)—N(m1)—C(m6)	142.4 (4)
C(12)—N(11)—C(16)	118.4 (5)	C(22)—N(21)—C(26)	118.7 (5)	C(32)—N(31)—C(36)	117.1 (5)	C(m2)—N(m1)—C(m6)	117.1 (5)
S(10)—C(12)—N(11)	109.3 (4)	S(20)—C(22)—N(21)	108.7 (4)	S(30)—C(32)—N(31)	107.8 (4)	S(m0)—C(m2)—N(m1)	107.8 (4)
S(10)—C(12)—N(13)	124.3 (5)	S(20)—C(22)—N(23)	125.2 (5)	S(30)—C(32)—N(33)	124.7 (4)	S(m0)—C(m2)—N(m3)	124.7 (4)
N(11)—C(12)—N(13)	126.4 (5)	N(21)—C(22)—N(23)	126.0 (5)	N(31)—C(32)—N(33)	127.5 (5)	N(m1)—C(m2)—N(m3)	127.5 (5)
C(12)—N(13)—C(14)	115.5 (5)	C(22)—N(23)—C(24)	115.3 (5)	C(32)—N(33)—C(34)	114.5 (5)	C(m2)—N(m3)—C(m4)	114.5 (5)
N(13)—C(14)—C(15)	121.6 (5)	N(23)—C(24)—C(25)	122.6 (6)	N(33)—C(34)—C(35)	122.3 (6)	N(m3)—C(m4)—C(m5)	122.3 (6)
N(13)—C(14)—C(17)	116.3 (5)	N(23)—C(24)—C(27)	116.1 (6)	N(33)—C(34)—C(37)	116.2 (5)	N(m3)—C(m4)—C(m7)	116.2 (5)
C(15)—C(14)—C(17)	122.1 (6)	C(25)—C(24)—C(27)	121.3 (7)	C(35)—C(34)—C(37)	121.5 (6)	C(m5)—C(m4)—C(m7)	121.5 (6)
C(14)—C(15)—C(16)	119.9 (5)	C(24)—C(25)—C(26)	119.3 (6)	C(34)—C(35)—C(36)	120.2 (5)	C(m4)—C(m5)—C(m6)	120.2 (5)
C(15)—C(16)—N(11)	118.1 (5)	C(25)—C(26)—N(21)	118.1 (5)	C(35)—C(36)—N(31)	118.4 (5)	C(m5)—C(m6)—N(m1)	118.4 (5)
C(15)—C(16)—C(18)	122.9 (5)	C(25)—C(26)—C(28)	122.0 (6)	C(35)—C(36)—C(38)	122.6 (5)	C(m5)—C(m6)—C(m8)	122.6 (5)
N(11)—C(16)—C(18)	118.9 (5)	N(21)—C(26)—C(28)	119.9 (5)	N(31)—C(36)—C(38)	119.1 (5)	N(m1)—C(m6)—C(m8)	119.1 (5)
O(1)—C(2)—C(3)	122.6 (10)	O(1)—C(2)—C(4)	124.0 (10)	C(3)—C(2)—C(4)	113.4 (10)		

dithiocarbonato)cobalt(III) where the corresponding angles are *ca* 76, 96 and 165° (Merlino, 1969). The relatively acute chelate angles are due to the strain involved in having a four-membered ring with the metal, and the difference between the two arises from the somewhat smaller bite of the thionato ligand as against that of the thiocarbonato.

The Co—S lengths are in the range 2.252–2.269 Å (mean 2.259 Å), in good agreement with means of 2.277 Å in tris(*O*-ethyl dithiocarbonato)cobalt(III) (Merlino, 1969), and 2.258 Å (Merlino, 1968) and 2.267 Å (Brennan & Bernal, 1969) in $[\text{Co}(\text{dtc})_3]$ (dtc = *N,N*-diethyldithiocarbamate). Co—N distances are in the range 1.975–1.986 Å (mean 1.979 Å). As expected, this is appreciably shorter than the 2.098 Å in $[\text{Co}(\text{pyrimidine-2-thione})_2\text{Cl}_2]$ (McConway & Rogers, 1975; McConway, 1975), as the latter is a Co^{II} complex. Although no $\text{Co}^{\text{III}}-\text{N}$ (pyrimidine) distance is available for comparison, the value is similar to the 1.979 Å in $[\text{Co}(\text{TPP})(\text{piperidine})_2]^+$ and the 1.983 Å in $[\text{Co}(\text{TPP})(\text{imidazole})_2]^+$ (Ibers, Lauher & Little, 1974), where TPP = $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin dianion. Given the strain necessarily present in a four-membered chelate ring both the Co—S and Co—N distances correspond to quite strong bonds.

The S—C length is also an indication of the strength of the Co—S bond. Its values range from 1.723–1.738 Å (mean 1.728 Å). Fig. 2 shows a comparison of four related pyrimidine-2-thione and pyridine-2-thione systems, and it can be seen that in (a) and (b) where chelate bonding takes place the C—S length is 1.73–1.74 Å, while in $[\text{Co}(\text{pyrimidine-2-thione})_2\text{Cl}_2]$ where

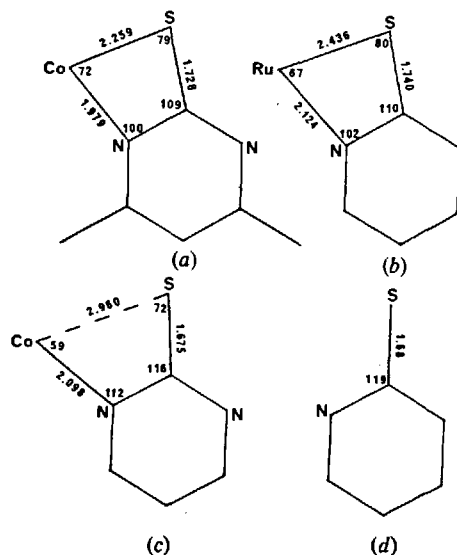


Fig. 2. A comparison of some average bond lengths (Å) and bond angles (°) in four related ligand systems: (a) title complex, (b) $\text{Ru}(\text{pyridine-2-thionato})_2(\text{PPh}_3)_2$ (Fletcher & Skapski, 1972), (c) $\text{Co}(\text{pyrimidine-2-thione})_2\text{Cl}_2$ (McConway & Rogers, 1975; McConway, 1975), (d) pyridine-2-thione (Penfold, 1953).

the Co—S interaction is at best weak and also in free pyridine-2-thione this length is *ca* 1.68 Å. In the tetrahedral complex $[\text{Zn}(1\text{-methylpyrimidine-2-thione})_4](\text{ClO}_4)_2$ (Skapski & Woode, 1979) C—S is 1.659 Å, again with insignificant *M*—S interaction. Another indication of the strength of metal—ligand bonding in these systems is the distortion from *ca* 120° of the S—C(*m2*)—N(*m1*) and Co—N(*m1*)—C(*m2*) angles. In Fig. 2(c) this distortion is relatively small, especially for the more rigid S—C(*m2*)—N(*m1*) angle, while it is much greater for the title compound with a mean S—C(*m2*)—N(*m1*) angle of 108.6°. Here the strain seems to be taken up by the whole four-membered ring rather than at one atom, although, as expected, the distortion is greatest at the donor N atom with a mean Co—N(*m1*)—C(*m2*) angle of 99.5°.

Although the crystal structure of the free ligand is not known, the C—N and C—C bonds are typical of those found in heterocyclic rings. In all three ligands the

Table 4. Planarity of groups of atoms in the structure and distances (Å) from the least-squares planes

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space. Atoms not defining planes are marked with asterisks.

Ring(1n): $5.62x + 10.39y - 7.07z = 8.66$					
N(11)	0.017	C(12)	-0.007	N(13)	-0.007
C(14)	0.011	C(15)	-0.001	C(16)	-0.013
		Co(1)*	0.126	S(10)*	-0.027
		C(17)*	0.033	C(18)*	-0.036
Ring(2n): $5.02x - 5.30y + 13.19z = 3.34$					
N(21)	0.010	C(22)	0.000	N(23)	-0.009
C(24)	0.007	C(25)	0.003	C(26)	-0.011
		Co(1)*	-0.096	S(20)*	-0.076
		C(27)*	0.016	C(28)*	-0.042
Ring(3n): $-2.00x + 13.34y + 9.92z = 11.28$					
N(31)	-0.003	C(32)	0.007	N(33)	-0.007
C(34)	0.005	C(35)	-0.001	C(36)	0.000
		Co(1)*	-0.140	S(30)*	-0.024
		C(37)*	0.015	C(38)*	0.003
Acetone: $6.35x + 10.26y + 3.17z = 7.80$					
O(1)	-0.006	C(2)	0.016	C(3)	-0.005
C(4)	-0.005				

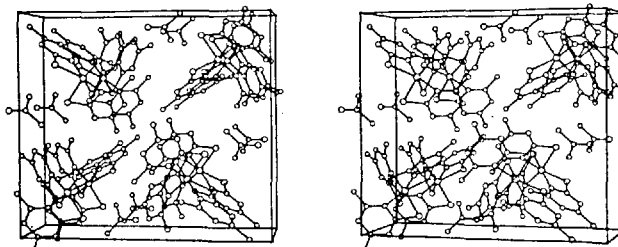


Fig. 3. Stereoscopic drawing showing packing of the complex and the acetone solvate molecules. The *b* axis is vertical, *c* is to the right and *a* is into the page, from an origin in the bottom left-hand corner.

shortest bond is C(m2)—N(m3). This is consistent with a lessening of double-bond character in the C—S bonds, and with the direction of bending of the C—S bonds out of their normal positions.

Table 4 shows that the pyrimidine rings are satisfactorily planar, while some of the exocyclic atoms, e.g. S(20), show a slight departure from the plane. The maximum distance of the Co atom from a ring plane is 0.14 Å.

Packing of the two molecular species in the unit cell is shown in Fig. 3 (Johnson, 1965). Solvate acetone molecules are only loosely held as indicated by temperature parameters which are much higher than those of atoms in the complex. The whole structure is held together by van der Waals forces. There is no possibility of hydrogen bonding between acetone and the ligands since the only potential sites on the rings, N(m3), are deprotonated.

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References

- ALI, M. A. & LIVINGSTONE, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132.
- ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* **B27**, 1325–1337.
- BRENNAN, T. & BERNAL, I. (1969). *J. Phys. Chem.* **73**, 443–445.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- CARTWRIGHT, B. A., GOODGAME, D. M. L., JEEVES, I., LANGGUTH, P. O. JR & SKAPSKI, A. C. (1977). *Inorg. Chim. Acta*, **24**, L45–L46.
- CARTWRIGHT, B. A., REYNOLDS, C. D. & SKAPSKI, A. C. (1977). *Acta Cryst.* **B33**, 1883–1887.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- COX, M. & DARKEN, J. (1971). *Coord. Chem. Rev.* **7**, 29–58.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- EISENBERG, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.
- FLETCHER, S. R. & SKAPSKI, A. C. (1972). *J. Chem. Soc. Dalton Trans.* pp. 635–639.
- HEITNER, H. I. & LIPPARD, S. J. (1974). *Inorg. Chem.* **13**, 815–822.
- HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
- IBERS, J. A., LAUHER, J. W. & LITTLE, R. G. (1974). *Acta Cryst.* **B30**, 268–272.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MC CONWAY, J. C. (1975). PhD thesis, Univ. of London.
- MC CONWAY, J. C. & ROGERS, D. (1975). Unpublished work.
- MERLINO, S. (1968). *Acta Cryst.* **B24**, 1441–1448.
- MERLINO, S. (1969). *Acta Cryst.* **B25**, 2270–2276.
- PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 707–713.
- SKAPSKI, A. C. & WOODE, K. A. (1979). *Acta Cryst.* **B35**, 59–62.
- SLETTEN, E. & APELAND, A. (1975). *Acta Cryst.* **B31**, 2019–2022.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

A Square-Pyramidal Copper Complex Containing both Monodentate and *anti-syn* Bridging Formate Groups: Crystal Structure of *catena-μ-Formato-formatobis(pyridine)copper(II) Monohydrate*

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Abstract

Crystals of the title complex, $\text{Cu}(\text{HCO}_2)_2 \cdot (\text{pyridine})_2 \cdot \text{H}_2\text{O}$, are orthorhombic with $a = 9.731$ (1), $b = 14.391$ (1), $c = 10.302$ (1) Å, space group *Pnma*, $Z = 4$. The structure was refined to $R = 0.043$ for 1420 independent reflections. Both independent formate groups and the Cu atom lie on a mirror plane, and the complex has a polymeric chain structure. One formate is monodentate and the other bridges in an *anti-syn* fashion. Thus each Cu atom is coordinated to three formate groups and to two pyridine molecules. Coordination about Cu is essentially square-pyramidal, the base consisting of two *trans* pyridine N atoms ($\text{Cu}-\text{N} = 2.025$ Å) and two formate O atoms (mean $\text{Cu}-\text{O} = 1.959$ Å), while the apical atom is from a bridging formate with a relatively long $\text{Cu}-\text{O}$ of 2.313 Å. The water molecules are not coordinated, but are attached by hydrogen bonds to individual chains.

Introduction

Many Cu-carboxylate complexes have a dimeric structure based on that of $[\text{Cu}(\text{acetate})_2 \cdot \text{H}_2\text{O}]_2$ (van Niekerk & Schoening, 1953; de Meester, Fletcher & Skapski, 1973), and show antiferromagnetic coupling, the nature of which is still a subject of debate (Catterick & Thornton, 1977). One such dimer is the emerald-green complex $[\text{Cu}(\text{HCO}_2)_2(\text{pyridine})]_2$ which has μ_{eff} of 1.15 BM (Gillard, Harris & Wilkinson, 1964). It can be obtained by heating a blue complex of formula $\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2 \cdot \text{H}_2\text{O}$, which has μ_{eff} of 1.88 BM, characteristic of magnetically normal Cu d^9 compounds. The structure of the latter complex was not known, and a number of possibilities could be envisaged, given that the stoichiometry allowed up to seven potential coordinating atoms per Cu atom. We have, therefore, determined its structure by X-ray diffraction, and find the complex to be a five-coordinate polymeric species with the water not coordinated to the metal.

Experimental

Crystals of the title complex were obtained by the method of King (1930) as modified by Goodgame (1977). Cupric formate (5 g) was dissolved in 1-propanol (40 ml) containing pyridine (10 ml) on a hot plate, and the solution filtered and allowed to cool. The resulting blue needles were washed with a little cold 1-propanol.

Photographs showed the needles to be orthorhombic with systematic absences $0kl: k + l = 2n + 1$, and $hk0: h = 2n + 1$. These are consistent with space groups *Pn2₁a* and *Pnma*. Successful refinement showed the latter to be correct. Measurement of high-angle α_1 and α_2 reflections on a diffractometer gave $a = 9.731$ (1), $b = 14.351$ (1), $c = 10.302$ (1) Å, $U = 1438.7$ Å³ (at 283 K). $D_o = 1.52$ (by flotation), $D_c = 1.52$ Mg m⁻³ for $Z = 4$ and a formula $\text{C}_{12}\text{H}_{14}\text{CuN}_2\text{O}_5$, $M_r = 329.8$, $F(000) = 676$, $\mu(\text{Cu K}\alpha) = 2.38$ mm⁻¹.

A crystal $0.33 \times 0.13 \times 0.08$ mm was mounted with a parallel to the ϕ axis of a Siemens off-line automatic four-circle diffractometer. Intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at a

Table 1. Atomic coordinates with e.s.d.'s in parentheses

	x	y	z
Cu(1)	0.11500 (6)	$\frac{1}{4}$	0.14374 (6)
C(1)	0.0615 (4)	0.4410 (3)	0.2303 (4)
C(2)	0.0728 (5)	0.5363 (3)	0.2388 (5)
C(3)	0.1594 (5)	0.5825 (3)	0.1559 (4)
C(4)	0.2310 (6)	0.5309 (3)	0.0662 (5)
C(5)	0.2142 (5)	0.4354 (3)	0.0621 (4)
C(6)	0.1390 (5)	$\frac{1}{4}$	−0.1291 (5)
C(7)	0.3000 (4)	$\frac{1}{4}$	0.3529 (4)
N(1)	0.1316 (3)	0.3906 (2)	0.1438 (3)
O(1)	0.3937 (3)	$\frac{1}{4}$	0.2743 (3)
O(2)	0.0535 (3)	$\frac{1}{4}$	−0.0365 (3)
O(3)	0.2636 (4)	$\frac{1}{4}$	−0.1209 (4)
O(4)	0.1730 (3)	$\frac{1}{4}$	0.3267 (3)
O(5)*	0.0329 (6)	0.2855 (5)	0.5562 (5)

* The water is disordered and this atom has a site population parameter of 0.5.

take-off angle of 4.0° , a Ni β -filter, and a Na(Tl)I scintillation counter. The θ - 2θ scan technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 1424 independent reflections were measured to $\theta = 70^\circ$, and of these 294 were considered to be unobserved with $I < 2.58\sigma(I)$. The 055 reflection was monitored as a reference every 50 reflections, and its net count did not alter noticeably. The data were scaled with the reference reflection, and Lorentz and polarization corrections applied.

At a later stage the data were corrected for absorption (Busing & Levy, 1957), with a $10 \times 10 \times 8$ grid and crystal path lengths determined by the vector analysis procedure (Coppens, Leiserowitz & Rabinovich, 1965).

Solution and refinement of the structure

An April 1974 version of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the solution and refinement of the structure. The calculations were carried out on the University of London CDC 7600 computer with CRYLSQ used in the refinement. Steering tape generation, data processing and structural illustrations were done with the Imperial College CDC 6500/Cyber 174 machines.

An origin-removed Patterson synthesis showed the position of the Cu atom to give $R = 0.37$, and all other non-hydrogen atoms were located from a difference synthesis. Both formate groups and the Cu atom were on a mirror plane, while the water O atom was disordered, close to but significantly off the mirror plane. It was given a site population parameter of 0.5, and isotropic refinement in $Pnma$ reduced R to 0.084. Anisotropic refinement gave $R = 0.060$. After absorption correction, refinement gave $R = 0.054$. All the H atoms were located from a difference synthesis, and their inclusion as a fixed-atom contribution, with isotropic temperature factors of their parent C or O atoms, reduced R to 0.048. Introduction of a weighting scheme, an anomalous-dispersion correction, and the

removal from refinement of four strong low-angle reflections thought to be suffering from extinction gave the final R of 0.043. Refinement in $Pn2_1a$ resulted in only a negligible improvement in R and produced unacceptable divergence in the geometry of the two pyridine molecules.

The weighting scheme (Hughes, 1941) was $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 19$ as the optimum value. Scattering factors were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965); the anomalous-dispersion corrections for Cu were from Cromer & Liberman (1970). Table 1 lists the atomic coordinates; the unrefined coordinates of the H atoms are given in Table 2.[†]

Description of the structure and discussion

Fig. 1 shows the structure, which consists of a chain in which each Cu atom is bonded to two pyridine molecules, a monodentate formate group, and to two formate groups which bridge in an *anti-syn* fashion; the water molecules are not coordinated to the metal. The chain runs in the a direction, and translation along the chain is by a combination of a 2_1 screw axis and an a glide. The more important interatomic distances and bond angles are given in Table 3.

[†] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33968 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates of the H atoms

Single-digit atomic numbers are the same as those of the parent C atoms; H(51) and H(52) are attached to O(5) and have site population parameters of 0.5.

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	-0.008	0.400	0.296
H(2)	-0.013	0.557	0.308
H(3)	0.179	0.653	0.163
H(4)	0.296	0.560	0.000
H(5)	0.279	0.387	0.004
H(6)	0.100	0.250	-0.221
H(7)	0.325	0.250	0.442
H(51)	0.058	0.273	0.475
H(52)	-0.058	0.260	0.563

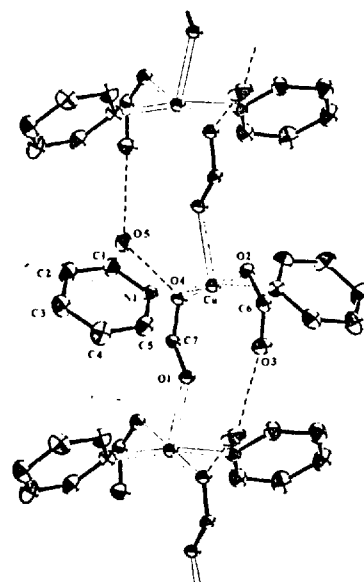


Fig. 1. Part of the chain structure of $\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2 \cdot \text{H}_2\text{O}$. Dashed lines indicate the hydrogen bonds which attach the water molecules to the chain. Thermal vibration ellipsoids are scaled to enclose 20% probability.

Both the crystallographically independent formate groups and also the Cu atom lie on a mirror plane, and Cu has an essentially square-pyramidal coordination. The base of the pyramid is formed by two *trans* pyridine N and two formate O atoms, one from a monodentate formate group and one from a bridging formate; the apex is an O atom from a second symmetry-related bridging group.

The Cu—N lengths are 2.025 Å; two basal Cu—O distances are 1.951 and 1.967 Å, the shorter of these two being to a monodentate formate. As expected, the apical Cu—O bond is weaker, with a length of 2.313 Å. On the side opposite to the apex the octahedral position is blocked by two formate O atoms at 3.03 and 3.09 Å from the Cu atom. Of the two links formed by the bridging formate, the *syn* link corresponds to the short basal bond, and the *anti* to the longer apical bond.

A distance of 0.066 Å of the Cu atom from the least-squares plane through the four basal atoms (Table 4) is unusually small for a square-pyramidal Cu complex, and in fact the two basal O atoms are fractionally further out of the plane in the apical direction. This distortion clearly arises because of the bridging groups, for which the angle O(apical)—Cu—O(basal) is 85.3°, with the Cu—O(apical) bond 4.1° from the normal to the basal plane.

anti-syn bridging by formate groups was originally postulated by Martin & Waterman (1959), and since

then only a few structures have been found which incorporate this type of bridge system. All of these are Cu complexes.

A formate complex, anhydrous Cu(HCO₂)₂ (Barclay & Kennard, 1961), and an acetate complex Cu(acetate)Br(NH₃)₂ (Belicchi Ferrari, Calzolari Capacchi, Gasparri Fava & Nardelli, 1972), both have the carboxylate bridge linking square-pyramidal coordinations base-to-base. In Cu(HCO₂)₂(H₂O)₂, one of the formate groups bridges in an *anti-syn* mode between octahedral Cu atoms (Bukowska-Strzyżewska, 1965). The only structure similar to that of the title complex is of μ -formato-(diethylenetriamine)copper(II) formate (Davey & Stephens, 1971) where the bridge links base-to-apex. In this compound the angle between the Cu—O(apical) bond and the normal to the base is 7.8°.

Both the formate groups are asymmetric, with C—O distances of 1.216 and 1.266 Å for formate centred on C(6), and 1.220 and 1.265 Å for that centred on C(7). The shortest of these bond lengths is associated with the non-coordinated O atom, while the other short distance is to the O atom involved in the long apical Cu—O bond. The two longer C—O distances are to O atoms involved in the strong basal Cu—O bonds.

Table 4 shows that the pyridine ring is closely planar, with the Cu atom ca 0.1 Å out of the ring plane. The plane of the pyridine ring is inclined 58.5° to that of the basal plane of the Cu coordination. Bond lengths and angles within the ring are typical of those found in other pyridine-containing compounds.

The disordered water molecule occupies one of two positions close to the mirror plane. It is associated with an individual chain by two O—H...O hydrogen bonds, of length 2.75 and 2.78 Å, to formate O atoms. As can be seen in Figs. 1 and 2 this hydrogen-bonding probably plays an important role in providing a secondary link in the chain to counterbalance the snaking covalently bonded strand.

Table 3. *Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

Superscripts refer to atoms in the following positions:
(I) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (II) $x, \frac{1}{2} - y, z$; (III) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

(a) Metal coordination			
Cu(1)—O(2)	1.951 (3)	Cu(1)—O(4)	1.967 (3)
Cu(1)—N(1)	2.025 (3)	Cu(1)—O(1 ^I)	2.313 (3)
Cu(1)...O(1)	3.027 (3)	Cu(1)...O(3)	3.087 (4)
N(1)—Cu(1)—N(1 ^{II})	170.87 (11)	O(2)—Cu(1)—O(4)	178.78 (13)
N(1)—Cu(1)—O(1 ^I)	94.24 (8)	N(1)—Cu(1)—O(2)	91.41 (8)
O(2)—Cu(1)—O(1 ^I)	93.54 (12)	N(1)—Cu(1)—O(4)	88.68 (8)
O(4)—Cu(1)—O(1 ^I)	85.25 (12)		
(b) Formate groups			
C(6)—O(3)	1.216 (7)	C(7)—O(1)	1.220 (5)
C(6)—O(2)	1.266 (6)	C(7)—O(4)	1.265 (5)
Cu(1)—O(2)—C(6)	121.0 (3)	Cu(1 ^{III})—O(1)—C(7)	117.0 (3)
O(2)—C(6)—O(3)	127.1 (5)	Cu(1)—O(4)—C(7)	119.0 (3)
		O(1)—C(7)—O(4)	126.1 (4)
(c) Pyridine ring			
C(1)—C(2)	1.375 (6)	C(4)—C(5)	1.381 (6)
C(2)—C(3)	1.371 (7)	C(5)—N(1)	1.329 (5)
C(3)—C(4)	1.374 (7)	N(1)—C(1)	1.335 (5)
Mean C—C	1.375	Mean C—N	1.332
N(1)—C(1)—C(2)	122.7 (4)	C(4)—C(5)—N(1)	122.1 (4)
C(1)—C(2)—C(3)	119.4 (4)	C(1)—N(1)—C(5)	118.0 (3)
C(2)—C(3)—C(4)	118.0 (4)	Cu(1)—N(1)—C(1)	119.9 (2)
C(3)—C(4)—C(5)	119.7 (4)	Cu(1)—N(1)—C(5)	122.0 (2)
(d) Hydrogen bonds			
O(4)...O(5)	2.777 (6)	O(4)—H(51)—O(5)	161
O(3)...O(5 ^{III})	2.751 (7)	O(3)—H(52)—O(5 ^{III})	157

Table 4. *Planarity of groups of atoms in the structure and distances (Å) from the least-squares planes*

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space.

$7.31x - 1.50y + 6.72z = 1.34$					
N(1)	0.006	C(1)	-0.001	C(2)	-0.004
C(3)	0.003	C(4)	0.002	C(5)	-0.006
Not defining plane: Cu(1) 0.096					
$9.29x - 3.07z = 0.69$					
N(1)	0.087	O(2)	-0.085	O(4)	-0.089
N(1 ^{II})	0.087				
Not defining plane: Cu(1) -0.066, O(1 ^I) -2.374					

Superscripts have the same meaning as in Table 3.

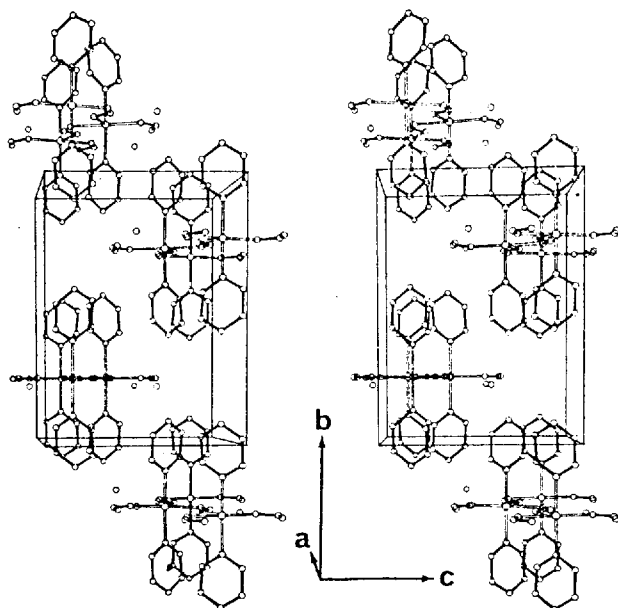


Fig. 2. A stereoscopic pair of drawings showing the packing of the chains in the structure. View is approximately down the length of the chains, and for the sake of clarity only one of each pair of disordered water molecules is drawn.

Fig. 2 (Johnson, 1965) shows how the chains are packed in the cell. Since cross-linking of chains by hydrogen bonds is not present, the forces holding them together are essentially of the van der Waals type. Although pairs of pyridine rings from different chains lie parallel across centres of symmetry, the perpendicular distance between them is >4 Å, much greater than the *ca* 3.3 Å typical of structures where base stacking occurs.

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References

- ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* **B27**, 1325–1337.
- BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* pp. 3289–3294.
- BELICCHI FERRARI, M., CALZOLARI CAPACCHI, L., GASPARRI FAVA, G. & NARDELLI, M. (1972). *J. Cryst. Mol. Struct.* **2**, 291–297.
- BUKOWSKA-STRZYŻEWSKA, M. (1965). *Acta Cryst.* **19**, 357–362.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- CATTERICK, J. & THORNTON, P. (1977). *Adv. Inorg. Chem. Radiochem.* **20**, 291–362.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DAVEY, G. & STEPHENS, F. S. (1971). *J. Chem. Soc. A*, pp. 103–106.
- GILLARD, R. D., HARRIS, D. M. & WILKINSON, G. (1964). *J. Chem. Soc.* pp. 2838–2840.
- GOODGAME, D. M. L. (1977). Unpublished work.
- HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KING, H. J. S. (1930). *J. Chem. Soc.* pp. 2307–2319.
- MARTIN, R. L. & WATERMAN, H. (1959). *J. Chem. Soc.* pp. 1359–1370.
- MEESTER, P. DE, FLETCHER, S. R. & SKAPSKI, A. C. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2575–2578.
- NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY 72 system. Technical Report TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.