

STRUCTURAL STUDIES OF INDUSTRIALLY
IMPORTANT PEROXO COMPOUNDS

A Thesis Submitted for the
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by

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A B S T R A C T

The work described in this thesis is mainly concerned with the structural characteristics of a series of inorganic peroxo compounds, in particular those which are used industrially or have some industrial interest. The techniques used include vibrational spectroscopy, with ^2H , ^{10}B and ^{11}B isotopic substitutions helping in the assignments of vibrational modes; ^{11}B nuclear magnetic resonance spectroscopy to show the existence of a peroxoborate species in solution; Raman and ^{13}C nuclear magnetic resonance spectroscopy and some electrochemical techniques to study the stability and equilibria of a percarbonate species in solution. Extensive use was made of single-crystal X-ray crystallographic methods and six structures were studied by this means. X-ray powder diffraction and electron spin resonance techniques have also been used.

During the course of this work salts of sodium, lithium, potassium, rubidium, caesium and ammonium peroxoborates were prepared and their vibrational spectra measured. Preparations of several analogues of hexa-aquomagnesium(II) bis(2-carboxylato-monoperoxybenzoic acid) were carried out in order to obtain crystals suitable for single-crystal X-ray studies.

Full X-ray structural determinations have been carried out on five inorganic compounds:

(i) Disodium tetrahydroxo-di- μ -peroxo-diborate tetrahydrate,
 $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (p. 17).

- (ii) Hexa-aquomagnesium(II)bis(2-carboxylato-monoperoxybenzoic acid), $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_5\text{O}_5)_2$ (p. 73).
- (iii) Tripotassium tris(2-carboxylato-monoperoxybenzoic acid) monohydrate, $3[\text{K}(\text{C}_8\text{H}_5\text{O}_5)] \cdot \text{H}_2\text{O}$ (p. 88).
- (iv) Sodium sulphate hemiperhydrate monohydrate, $\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (p. 103).
- (v) Potassium 4-sulphonato-monoperoxybenzoic acid, $\text{K}(\text{C}_7\text{H}_5\text{SO}_6)$ (p. 114).

A sixth structure, that of bis(triphenylphosphine)-peroxo-carbonato platinum(II), was also attempted but proved impossible to solve completely due to disorder of the peroxocarbonate moiety in the crystal (p. 46).

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ABBREVIATIONS AND SYMBOLS

Throughout this thesis various abbreviations have been used:

- DSS - 3-(Trimethylsilyl)-1-propanesulphonic acid, sodium salt hydrate, $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na} \cdot x\text{H}_2\text{O}$.
- MMPP - Hexa-aquomagnesium(II)bis(2-carboxylatomonoperoxybenzoic acid), $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_5\text{O}_5)_2$.
- KMPP - Tripotassium tris(2-carboxylato-monoperbenzoic acid)monohydrate, $\text{K}_3(\text{C}_8\text{H}_5\text{O}_5)_3 \cdot \text{H}_2\text{O}$.

Frequencies for infrared and Raman spectra are quoted in wave-numbers cm^{-1} . Bands obtained are described as s, strong; m, medium; w, weak; b, broad or sh, shoulder and v, very. Raman bands are also described as p, polarised or dp, depolarised for solution spectra.

^{13}C n.m.r. chemical shift values (δ) are quoted in ppm downfield relative to DSS ($\delta = 0.00$). DSS is the water soluble form of TMS (tetramethylsilane). ^{11}B n.m.r. chemical shift values are quoted in ppm downfield relative to $[\text{B}(\text{OH})_4]^-$ ($\delta = 0.00$).

C H A P T E R O N E

PEROXOBORATES

SECTION 1-1. INTRODUCTION

"Sodium perborate" is by far the most common industrial bleaching agent¹ incorporated in household packed detergent washing powders (one of the major U.K. household detergent contains "sodium percarbonate", $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$, instead). "Sodium perborate" has been given various formulae^{1,2,3,4,5,6,7} such as $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ and $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, the latter being frequently used throughout industry. It was not until 1961, when Hansson⁸ studied this industrial bleaching agent crystallographically, and later in 1978 when a more accurate crystal study⁹ was carried out that it was shown that the anion was a dimer, $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$, and that the formula was $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$. Further confusion has arisen because "sodium perborate" does not only exist as the hexahydrate; other hydrates have been reported,^{6,7,10,11} including the tetrahydrate and anhydrous salts. As before, each compound has also been known by various formulae (see note on nomenclature, page 15).

This Chapter is principally concerned with the preparation of peroxoborates and the study of their structure in both solid and solution states. The techniques used in this study include single-crystal X-ray crystallography for the structure determination of sodium peroxoborate tetrahydrate; Raman and infrared spectroscopy for the

vibrational spectra of the peroxoborates; ^{11}B nuclear magnetic resonance to study the peroxoborate species in solution and a short electron spin resonance investigation on sodium peroxoborate hexahydrate.

Nomenclature and Formulation.

The systematic name for $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$ is disodium tetrahydroxo-di- μ -peroxo-diborate(III) hexahydrate. We use in this chapter the more concise name "sodium peroxoborate hexahydrate" and adopt the convention of using "peroxoborate" to designate salts containing this $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$ anion. Where the nature of the anion is not certain the general term "perborate" is used.

It has become an established custom, particularly in patent and industrial publications, to use empirical formulae and trivial names for the various hydrates of $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$. In order to avoid confusion the various trivial names and formulae are tabulated (see Table 1-1-1).

Preparation of Peroxoborates

As well as the sodium peroxoborates, preparation of salts of a number of other alkali metal perborates have also been reported.^{6,7,12,13,14,15} These preparations were repeated in order to make products suitable for single crystal X-ray crystallographic studies. Microcrystalline samples of lithium and ammonium peroxoborates and amorphous powders of potassium, rubidium and caesium perborates were prepared, but none of these products was suitable for crystallographic study. It has been shown^{11,16,17,18,19} that of the different hydrates, sodium peroxoborate tetrahydrate is thermally more stable and less soluble in water than the hexahydrate. Using these differences an adaptation of a published method^{13,20} successfully yielded single-

Table 1-1-1

Nomenclature and Formulae of Various Sodium Peroxoborates.

True Formula	Empirical/ Industrial Formula	Trivial Name	Name Used Here
$\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$	$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$	Sodium perborate tetrahydrate	Sodium peroxoborate hexahydrate
$\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 4\text{H}_2\text{O}$	$\text{NaBO}_3 \cdot 3\text{H}_2\text{O}$	Sodium perborate trihydrate	Sodium peroxoborate tetrahydrate
$\text{Na}[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$	$\text{NaBO}_3 \cdot \text{H}_2\text{O}$	Sodium perborate monohydrate	Anhydrous sodium peroxoborate
	NaBO_3	Anhydrous sodium* perborate	

*Compound referred⁷ to but has not been characterised.

crystals of sodium peroxoborate tetrahydrate that were suitable for a full structure determination by X-ray crystallography. The unit cell and powder pattern data had been previously recorded.^{13,21} A microcrystalline sample of anhydrous sodium peroxoborate was prepared directly from the hexahydrate by heating the latter to 60°C. Figure 1-1-1 shows the XRD powder pattern observed for a sample of sodium peroxoborate hexahydrate heated from 20 to 100°C. It can be seen that at approximately 50°C a sudden structural change occurred. Up to 50°C the powder pattern observed is that of the hexahydrate, above 50°C the powder pattern observed is that of anhydrous peroxoborate so the structural change corresponds to the loss of all six molecules of water of crystallisation. It appears that the anhydrous salt is formed directly, without any intermediate hydrates being formed, suggesting that the structure of the tetrahydrate may be different from that of the hexahydrate.

SECTION 1-2. SINGLE CRYSTAL X-RAY CRYSTALLOGRAPHIC STUDIES.

X-Ray Crystal Structure of Disodium tetrahydroxo-di-μ-peroxo-diborate tetrahydrate (sodium peroxoborate tetrahydrate), $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 4\text{H}_2\text{O}$.

Suitable crystals of the title compound were prepared by leaving a saturated aqueous solution of sodium peroxoborate hexahydrate, in a closed vessel, for about eight weeks at 40°C. The resulting crystals were filtered off and dried in air. Accurate unit-cell dimensions were obtained by a least-squares calculation based on 7 reflections measured on a Nicolet R3m diffractometer using graphite monochromated Cu-K_α radiation.

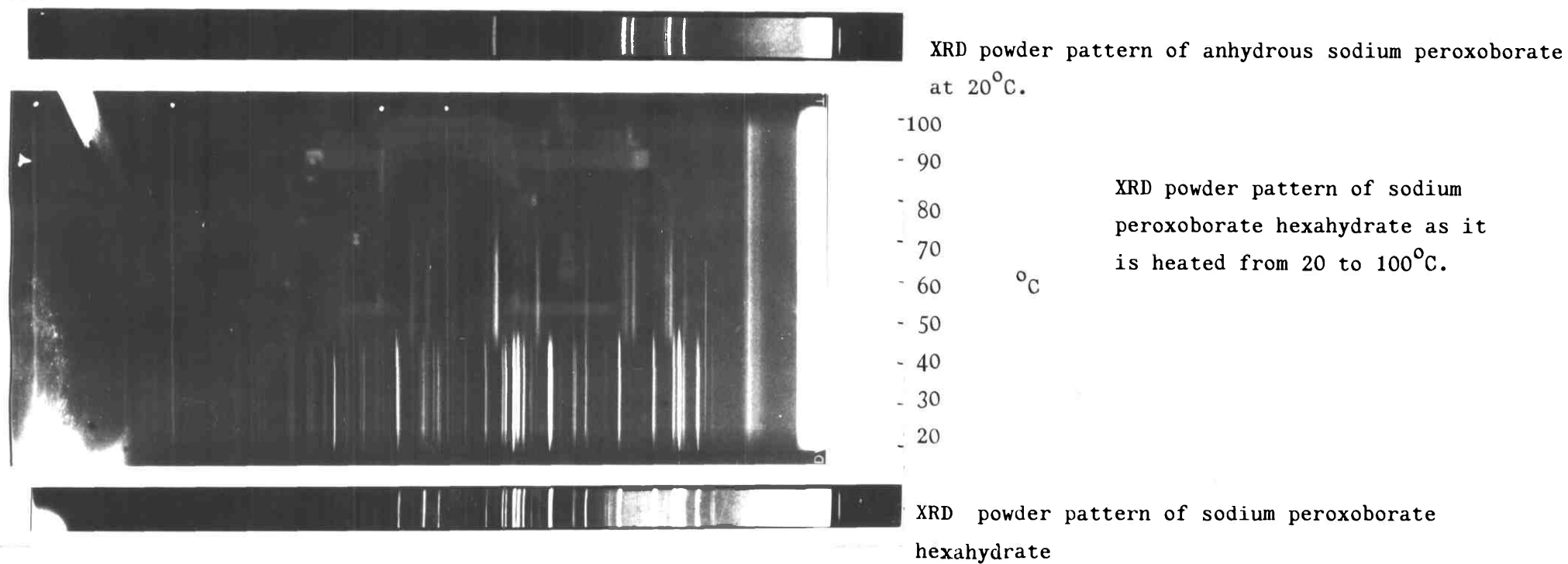


Figure 1-1-1. XRD powder pattern of sodium peroxoborate showing the sudden change in structure at approximately 50°C.

Crystal Data.

$B_2H_{12}Na_2O_{12}$, $M = 271.68$, triclinic, $a = 5.936(2)$, $b = 6.261(3)$, $c = 7.352(3)$, $\alpha = 104.52(3)^\circ$, $\beta = 97.58(3)^\circ$, $\gamma = 110.06(3)^\circ$ (at 18°C), $U = 241.2(2)\text{\AA}^3$, $Z = 1$, $F(000) = 137.99$, space group $P\bar{1}$ (No. 2), Cu-K_α radiation, $\lambda = 1.5418\text{\AA}$, $\mu(\text{Cu-K}_\alpha) = 24.52\text{ cm}^{-1}$, $D_c = 1.87\text{ g dm}^{-3}$.

A crystal of approximate size $0.1 \times 0.05 \times 0.05\text{ mm}$ was chosen for the study, and a layer of picture varnish was applied to prevent decomposition under X-rays. The ω scan technique was used and a total of 646 independent reflections were measured to $\theta = 57^\circ$ of which 56 were judged to be "unobserved" ($I < 3\sigma(I)$). After every 50 reflections the $0, \bar{1}, 1$ and $1, \bar{1}, 2$ reflections were monitored as reference reflections and their net count did not alter noticeably over the period of data collection (ca. 14 hours). The data were scaled by use of these reference reflections. The program system SHELXTL²² was used throughout for the solution and refinement of the structure, calculations being carried out on a Data General Eclipse S140 computer.

Locations of all the independent non-hydrogen atoms were found by direct methods and a few cycles of isotropic refinement with these atoms gave $R = 0.068$. The subsequent difference Fourier synthesis showed the locations of three of the hydrogen atoms. A further few cycles of refinement with all non-hydrogen atoms anisotropic gave $R = 0.040$, the difference Fourier synthesis showing the location of a fourth hydrogen atom. After a weighting scheme of the type $w = 1/(\sigma^2 F + |g|F^2)$, with g initially set at 0.0005 but allowed to refine to 0.00013 (by fitting $(F_o - F_c)^2$ to $(\sigma^2 F + |g|F^2)/k$, where k is a scale factor) further refinement resulted in an R factor of 0.036. When the four independent hydrogen atoms were included in the subsequent refinement, with all non-hydrogen atoms anisotropic R reached a value of 0.033 and the resulting difference Fourier synthesis showed that the two remaining

hydrogen atoms were disordered. After applying an empirical absorption correction, further refinement including the disordered hydrogen atoms at half occupancy resulted in the final R of 0.028. Table 1-2-1 lists the final atomic fractional coordinates, table 1-2-2 the atomic temperature factors and table 1-2-3 the bond lengths and angles, including those due to hydrogen bonding, and the coordination about the sodium atoms.

DISCUSSION.

This study has confirmed that the structure of the compound is made up of centrosymmetric $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$ anions, Na^+ cations and water molecules. The arrangement of the atoms in the cyclic anions are shown in Figure 1-2-1, and it is very similar to that found in the structure of the hexahydrate.^{9,23} The independent boron atoms are tetrahedrally coordinated, with two OH groups and two peroxide groups with mean B-O(OH) distance of $1.442\text{\AA}$ and mean B-O(O_2) distance of $1.499\text{\AA}$, both of which compare well with the hexahydrate (B-O(OH) = $1.442\text{\AA}$, B-O(O_2) = $1.495\text{\AA}$). These data are in contrast to those available for the borates^{24,25} $\text{Na}_3[\text{B}_3\text{O}_5(\text{OH})_2]$ and γHBO_2 where the mean B-O(OH) distance is longer than the mean B-O distance. However, in both borates the oxygen atom of the B-O is a bridging oxygen atom rather than a bridging peroxo group. The tetrahedral geometry about the boron atom is slightly distorted as the O-B-O angles range from $103.9(2)^\circ$ to $114.4(2)^\circ$. The B-O(2)-O(1) and $\text{B}^{\text{II}}\text{-O(1)-O(2)}$ angles of $110.5(2)^\circ$ and $108.3(1)^\circ$ respectively, are close to those expected for the sp^3 hybridisation of each oxygen atom. The O(1)-O(2) peroxo distance, $1.477(2)\text{\AA}$ is very close to the accepted²⁶ O-O single bond distance of $1.48\text{\AA}$ in hydrogen peroxide. The dihedral angle of the O-O bridge is 61° , and is much more acute than those found in other compounds²⁷ containing

Table 1-2-1

Fractional Atom Coordinates with Estimated Standard Deviations in
Parentheses for Sodium Peroxoborate tetrahydrate.

Atom	x	y	z
Na	0.1812(2)	0.8714(2)	0.8854(1)
B	0.2729(4)	0.4069(4)	0.5550(4)
O(1)	0.4924(3)	0.5870(3)	0.3368(2)
O(2)	0.3341(3)	0.6114(3)	0.4731(2)
O(3)	0.1511(3)	0.4714(3)	0.7049(2)
O(4)	0.1233(3)	0.1823(3)	0.4072(2)
O(5)	0.4375(3)	-0.0456(3)	0.2039(3)
O(6)	0.1757(3)	0.2596(3)	0.9950(3)
H(31)	0.017(5)	0.429(5)	0.663(4)
H(41)*	0.205	0.137	0.350
H(42)*	0.114	0.073	0.462
H(51)	0.458(5)	-0.137(5)	0.243(4)
H(52)*	0.508	0.081	0.320
H(53)*	0.352	0.014	0.263
H(61)	0.290(6)	0.361(6)	1.092(5)
H(62)	0.169(5)	0.325(5)	0.921(4)

* These atoms have a site population parameter of
0.5

Table 1-2-2
Anisotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for sodium Peroxoborate
Tetrahydrate with Estimated Standard Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	33(1)	29(1)	32(1)	10(1)	6(1)	9(1)
B	18(1)	22(1)	20(1)	10(1)	5(1)	8(1)
O(1)	18(1)	30(1)	19(1)	12(1)	9(1)	11(10)
O(2)	21(1)	27(1)	24(1)	13(1)	13(1)	12(1)
O(3)	19(1)	30(1)	22(1)	10(1)	8(1)	10(1)
O(4)	24(1)	23(1)	21(1)	5(1)	5(1)	4(1)
O(5)	45(1)	35(1)	39(1)	21(1)	18(1)	22(1)
O(6)	34(1)	28(1)	24(1)	11(1)	3(1)	6(1)
H(31)	32(8)					
H(41)	28(14)					
H(42)	39(15)					
H(51)	38(9)					
H(52)	64(18)					
H(53)	104(24)					
H(61)	48(9)					
H(62)	40(9)					

The anisotropic temperature factor exponent takes the form:-

$$-2^2 (h^2 a^2 U_{11} + k^2 b^2 U_{22} + \dots + 2hka^*b^*U_{12})$$

Table 1-2-3
Bond Lengths (Å) and Angles (°) for Sodium Peroxoborate Tetrahydrate
with Estimated Standard Deviations in Parentheses.

Sodium Ions

Na-O(3)	2.455(2)	Na-O(5) ^{III}	2.444(2)
Na-O(4) ^I	2.491(2)	Na-O(6) ^{IV}	2.374(2)
Na-O(5) ^{II}	2.409(2)	Na-O(6) ^V	2.365(2)
O(3)-Na-O(5) ^{II}	89.2(1)	O(3)-Na-O(4) ^I	84.2(1)
O(4) ^I -Na-O(5) ^{II}	100.5(1)	O(3)-Na-O(5) ^{III}	103.3(1)
O(3)-Na-O(6) ^{IV}	168.0(1)	O(4) ^I -Na-O(5) ^{III}	170.1(1)
O(4) ^I -Na-O(6) ^{IV}	84.4(1)	O(5) ^{III} -Na-O(6) ^{IV}	88.5(1)
O(5) ^{II} -Na-O(6) ^{IV}	88.9(1)	O(3)-Na-O(6) ^V	96.7(1)
O(5) ^{III} -Na-O(5) ^{II}	86.3(1)	O(4) ^I -Na-O(6) ^V	83.2(1)
O(5) ^{III} -Na-O(6) ^V	89.4(1)	O(5) ^{II} -Na-O(6) ^V	173.4(1)
O(6) ^{IV} -Na-O(6) ^V	85.9(1)		

Perborate Anion

B-O(2)	1.503(3)	B-O(3)	1.445(3)
B-O(4)	1.439(2)	B-O(1) ^{II}	1.494(3)
O(1)-O(2)	1.477(2)		
O(2)-B-O(3)	104.6(2)	O(2)-B-O(4)	111.3(2)
O(3)-B-O(4)	113.4(2)	O(2)-B-O(1) ^{II}	108.6(2)
O(3)-B-O(1) ^{II}	103.9(2)	O(4)-B-O(1) ^{II}	114.4(2)
O(2)-O(1)-B ^{II}	108.3(1)	B-O(2)-O(1)	110.5(2)

Hydrogen Bonds

O(3)...O(2) ^I	2.814	O(3)-H(31)...O(2) ^I	166
O(4)...O(4) ^{VI}	3.001	O(4)-H(42)...O(4) ^{VI*}	146
O(5)...O(1) ^{VII}	2.812	O(5)-H(51)...O(1) ^{VII}	175
O(5)...O(2) ^{II}	2.873	O(5)-H(52)...O(2) ^{II*}	168
O(6)...O(1) ^{VIII}	2.753	O(6)-H(61)...O(1) ^{VIII}	168
O(6)...O(3)	2.792	O(6)-H(62)...(3)	175
O(5)...O(4)	3.040	O(5)-H(53)...O(4)*	177
		O(5)...H(41)-O(4)*	170

*Involving atoms with site occupation parameter of 0.5

Table 1-2-3 (continued)

Superscripts denote the following symmetry operations:-

I	$-x, 1-y, 1-z$	V	$-x, 1-y, 2-z$
II	$1-x, 1-y, 1-z$	VI	$-x, -y, 1-z$
III	$x, 1+y, 1+z$	VII	$x, y-1, z$
IV	$x, 1+y, z$	VIII	$x, y, 1+z$

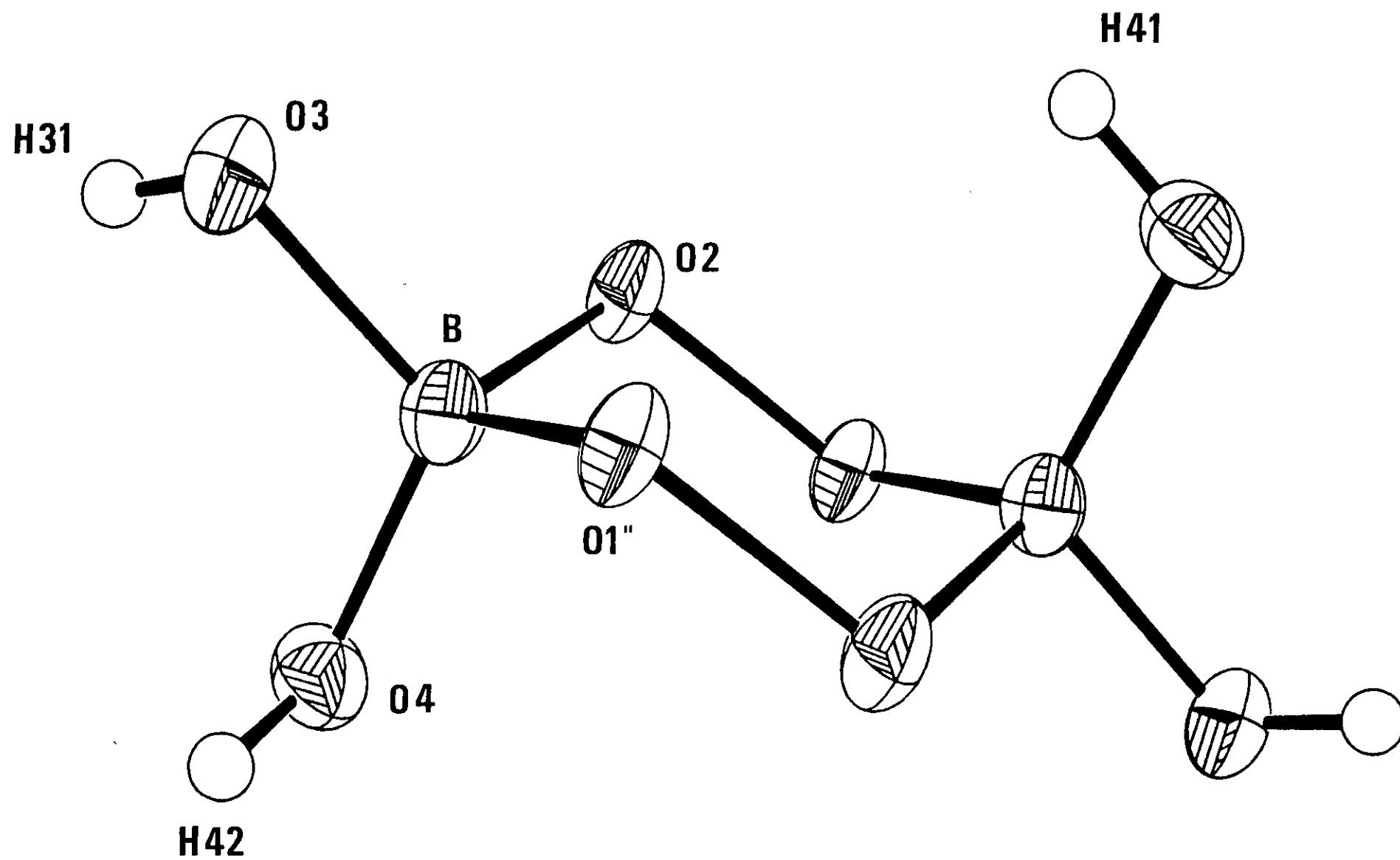


Figure 1-2-1. The cyclic peroxoborate anion, $[B_2(O_2)_2(OH)_4]^{2-}$.

O-O linkages, but compares well with that of the hexahydrate (60°). The acute angle is due to the chair conformation of the ring system and to the tetrahedral angles at the boron atoms. As in the hexahydrate the sodium ions are surrounded by six oxygen atoms in approximately octahedral coordination with mean Na-O distance of $2.423\text{\AA}$ (range $2.365(2)$ to $2.491(2)\text{\AA}$) and mean cis-O-Na-O angle of 90.0° (range $83.2(1)$ to $103.3(1)^\circ$).

The disorder within the structure which affects two of the hydrogen atoms is a consequence of the packing and occurs because, if no disorder is present, the hydrogen atom H(42) of one molecule is too close to the related H(42) of the next molecule, the $\text{H}(42)\text{--H}(42)^{\text{VI}}$ distance being $1.61\text{\AA}$. This means that $\text{H}(42)^{\text{VI}}$ is forced to take up the position of $\text{H}(41)^{\text{VI}}$. However, the position of H(41) is such that it lies too close to H(53) ($\text{H}(41)\text{--H}(53)$ distance $1.46\text{\AA}$) and so H(53) is accordingly forced to take up the position of H(52). Even though H(52) is involved in hydrogen-bonding it is still in a strained position with respect to O(5) and H(51) within the water molecule ($\text{H}(51)\text{--H}(52)$ of $1.25\text{\AA}$ and $\text{H}(51)\text{--O}(5)\text{--H}(52)$ of 96° ; expected^{28,29} values for free water of $1.60\text{\AA}$ and 105° respectively). Thus, if it is possible for H(52) to return to the position of H(53) then H(41) must be able to resort to the position of H(42) and it will do so. As a result of the disorder it is obvious that each cyclic anion must contain one H(42) type hydrogen and one H(41) type hydrogen atom (figure 1-2-1). The packing, taking disorder into account, can be seen in figure 1-2-2. The three dimensional network of hydrogen bonds is composed of 12 hydrogen bonds per formula unit, $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]\cdot 4\text{H}_2\text{O}$, with every hydrogen atom participating. However, it should be said that the hydrogen bonds involving H(41), H(42) and H(53) must only be weak as their O...O distances are between 2.90 and $3.04\text{\AA}$. In the hexahydrate,

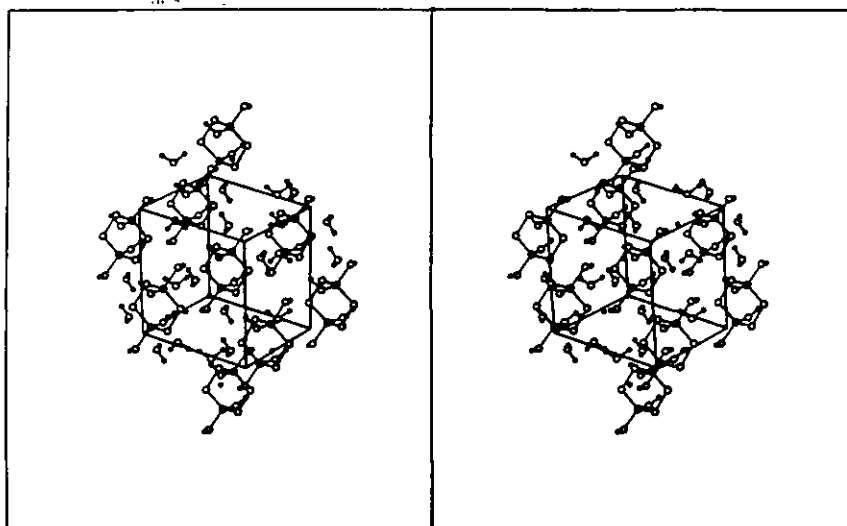


Figure 1-2-2. Stereoscopic view of sodium peroxoborate tetrahydrate.

unlike the tetrahydrate, not all the potential hydrogen-bonding hydrogen atoms are involved in hydrogen-bonding and, again unlike the tetrahydrate, the oxygen atoms of the peroxo bridge of the hexahydrate do not have four bonds (including the two hydrogen-bonds to each oxygen) associated with them, as would be expected for sp^3 hybridisation. Therefore, in the tetrahydrate not only are the peroxo oxygen atoms more tightly held in place than in the hexahydrate but the complete structure is held together more tightly by hydrogen bonding. This is likely to be the explanation of why the tetrahydrate is thermally more stable and less soluble than the hexahydrate.

SECTION 1-3. VIBRATIONAL SPECTROSCOPIC STUDIES.

(a) Salts containing the $[B_2(O_2)_2(OH)_4]^{2-}$ ion.

The structure of the peroxoborate anion, $[B_2(O_2)_2(OH)_4]^{2-}$, is known to consist of a cyclic anion with a chair conformation of the B_2O_4 ring (see figure 1-2-1) and tetrahedral coordination around the boron. Little work^{10,14,30} has been done involving its vibrational spectra except that of Koberstein¹⁰ *et. al.* who measured the infrared and Raman spectra of sodium peroxoborate hexahydrate from 450 to 1300 cm^{-1} ; however, no frequencies were listed or assignments made but the spectra were reproduced. We present here more comprehensive results on the infrared and Raman spectroscopy of a number of peroxoborate compounds. Infrared and Raman spectra have been measured for sodium peroxoborate hexahydrate as well as for its ^2H , ^{10}B and ^{11}B isotopically substituted analogues; for the tetrahydrate and anhydrous sodium peroxoborates and for lithium and ammonium peroxoborates. In order to assign many of the vibrational bands, infrared and Raman spectra of sodium metaborate, $Na[B(OH)_4]$, had to be studied since the literature^{30,31,32,33} did not give satisfactory assignments of some of its vibrations. It was felt

that a thorough investigation should be carried out, so solution and solid state spectra were measured for $\text{Na}[\text{B}(\text{OH})_4]$ as well as for its ^2H , ^{10}B and ^{11}B isotopically substituted forms. No Raman studies of the solid have been previously reported except for one on the mineral teepelite,³⁴ $(\text{Na}_2[\text{B}(\text{OH})_4]\text{Cl})$, but there are data for alkaline solutions^{34,35,36,37} of $[\text{B}(\text{OH})_4]^-$ with normal and ^{18}O substitution; infrared studies of ^{10}B and ^{11}B substituted sodium metaborate have also been reported.³⁰ The observed frequencies and proposed assignments are listed in table 1-3-1a and b and table 1-3-2.

The O-O stretch at approximately 900 cm^{-1} is the strongest band in all peroxoborate spectra and as expected is little affected by any isotopic substitution. The assignment of the other bands were made by comparison of the sodium metaborate spectra with those of sodium peroxoborate hexahydrate. The symmetric B-(OH) stretches of the peroxoborate near 720 cm^{-1} do not shift on ^{10}B or ^{11}B substitution, as expected, but drop 12 cm^{-1} on deuteration, a similar effect being noted for the symmetric stretch (ν_1) in the metaborate. The asymmetric B-(OH) stretches of the peroxoborate, near 970 cm^{-1} , are affected by ^2H , ^{10}B and ^{11}B substitution as is the asymmetric stretch (ν_3) in the metaborate. Assignment of the other modes also follows the pattern established for the metaborate.

The sodium peroxoborate hexahydrate shows a strong band at 3470 cm^{-1} in the infrared spectrum and 3430 cm^{-1} in the Raman spectrum; however, the anhydrous sodium peroxoborate does not show these bands. The H_2O deformation band at 1675 cm^{-1} is also present in the hexahydrate but not in the anhydrous compound. Both these observations constitute good evidence for assignment of the ≈ 3360 and $\approx 3580\text{ cm}^{-1}$ bands in the Raman spectra to the OH vibrations of the peroxoborate anion since they appear in both the anhydrous and hexahydrate spectra. The vibrational

Table 1-3-1a

Raman and Infrared Spectra of Sodium Peroxoborate Hexahydrate.

		ν_{O-H}	δ_{B-O-H}	$\nu_{BO_2(OH)}^{as}$	ν_{O-O}	$\nu_{BO_2(O_2)}^{as}$	$\nu_{BO_2(OH)}^s$	γ_{B-OH}	$\nu_{BO(O_2)}^{vs}$	$\delta_{BO(OH)}$	$\delta_{BO(O_2)}$	Other Bands
$Na_2[B_2(O_2)_4(OH)_4] \cdot 6H_2O$	R	3535vs 3470s		974m	907vs	869w	719w		537vw	497w	308vw	790w
	IR	3620s 3430vs	1240w 1170s	1040s 990s	903w	925s 855s	720w	630		505w		1300w, 450, 405, 255
$Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$	R	3535vs 3470s		937m	906vs	869w	719w		540vw	497w	308vw	430
	IR	3620s 3430vs	1240s 1170s	1040s 990s	903w	920s 855s	720w	630vs, b	obsc.	505m 450w		405, 250
$Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$	R	3535vs 3470s		986m	906vs		719w		540vw	500vw		455
	IR	3620s 3430vs	1250w 1200s	1060s 1015s	930w	950s 862s	720w	630vs, b		510m 453w		410, 260
$Na_2[B_2(O_2)_2(OD)_4] \cdot 6D_2O$	R	2535m 2518w 2450vs			903w	880w	708w		500vw	500w	308	430w, 259w
	IR	2680s 2500vs	970vs	970vs	915w	885s 825s	720w	400s, b		obsc.		1120, 255

Table 1-3-1b

Raman and Infrared Spectra of Sodium metaborate.

Compound		$\nu_{\text{O-H}}$	$\delta_{\text{O-O-H}}$	$\nu_3 \left(\begin{smallmatrix} \text{as} \\ \text{BO} \end{smallmatrix} \right)$	$\nu_1 \left(\begin{smallmatrix} \text{s} \\ \text{BO} \end{smallmatrix} \right)$	$\gamma_{\text{B-OH}}$	$\nu_4 \left(\begin{smallmatrix} \delta \\ \text{BO} \end{smallmatrix} \right)$	$\nu_2 \left(\begin{smallmatrix} \delta \\ \text{BO} \end{smallmatrix} \right)$	Other Bands
Na [B(OH) ₄]	R	3385m		955s	739s	650vw	520vw	405w [~] 380w	500w
		3185s							
		3665s	1280w	1010s	740m	670s	520s	400sh	
Na [¹⁰ B(OH) ₄]	R	3400s	1180s	940s			505sh		
		3280s	1085s	910s					
		3285m		970w	740s	650vw			460w, 350w, 390w, 540w
Na [¹¹ B(OH) ₄]	R	3185s							
		3665s	1250s	1050s	735m	675s	520s	400	
		3400s	1170s	1015s					
[B(OH) ₄] ⁻ *	R	3280s	1050s	950m					
		3640s, p		950vb	744s, p		518w, dp	398vw	
[¹¹ B(OH) ₄] ⁻ *	R	3640s		947vb	744s, p		518w, dp	380vw	440
[¹⁰ B(OH) ₄] ⁻ *	R	3640s, p		950vb	744s, p		533w, dp	390	
[B(OD) ₄] ⁻ *	R	2646s, p			730s, p		490b	360b	

*Aqueous solution; other data for solids.

Table 1-3-2

Raman and Infrared Spectra of Alkali Metal and Ammonium Peroxoborates

		$\nu_{\text{O-H}}$ (H ₂ O)	$\nu_{\text{O-H}}$ (complex)	$\delta_{\text{B-OH}}$	ν_{as} BO ₂ (OH)	$\nu_{\text{O-O}}$	ν_{as} BO ₂ (O ₂)	ν_{s} BO ₂ (OH)	$\gamma_{\text{B-OH}}$	ν_{s} BO(OH)	$\delta_{\text{BO(OH)}}$	$\delta_{\text{BO(O}_2\text{)}}$	Other Bands
Na ₂ [B ₂ (O ₂) ₂ (OH) ₄].6H ₂ O	R	3470m	3535s 3360w		974m	907vs	869	719w		537vw	497w	308vw	1040w
	IR	3430b	3620s 3370s	1240w 1170m	1040s 990s	903vw	925s 855s	720w	630w		515b		1675(H ₂ O), 780w
Na ₂ [B ₂ (O ₂) ₂ (OH) ₄].4H ₂ O	R	3420m, b	3590m 3360		980m	900vs	870w	710w		540vw	500w	320vw	
	IR	3450m, b	3600s 3370s	1230w 1165m	1035s 990s	900vw	940m 860s	710w	640w		515wb		1675
Na ₂ [B ₂ (O ₂) ₂ (OH) ₄]	R		3565m 3360w		959m 992w	888vs		708w		549vw	495w	305m	421w, 250w
	IR		3580s 3370vs	1230w 1160m	1050s 1000s	890w	945s 850s	720vw	650m		505w		770w
Li ₂ [B ₂ (O ₂) ₂ (OH) ₄]	R		3435w 3309m		968m	884vs	830vw	730w		562vw	510w	320vw	1275v, 1115vw, 290w, 395, 410, 420m
	IR		3540s 3330s, b	1295w 1205s	1080s 995s	880w 880w	920m 840s	715w, b	665w		540m	365s	440m, 770m
(NH ₄) ₂ [B ₂ (O ₂) ₂ (OH) ₄]*	R		3480w 3430mb		920vw	878vs	860s	760vw 735w	610w	530vw	470vb	345w 330w	3200, 3060vb(NH ₄ ⁺), 1720 1690(NH ₄ ⁺), 1460 ⁴ , 1430 (NH ₄ ⁺)m, 1040m, 687w
Rb ₂ [B ₂ (O ₂) ₂ (OOH) ₂]*	R		3400vb			932vs 862b, w	770w	725w	680w 630w	490b			1130vw, 1065vw, 485vw, 408vw
Cs ₂ [B ₂ (O ₂) ₂ (OOH) ₂]*	R	obsc.	obsc.			932vs 860b, w	780w	721w	675vw	545vw			1130vw, 1060vw, 430w, 405w.
Na _{2n} [B ₂ (O ₂) ₃ (OH) ₂] _n .nH ₂ O*	R					908vs, b 870m, b		740m, b					

*Decomposes in infrared beam.

spectra of sodium peroxoborate tetrahydrate are essentially the same as those of sodium peroxoborate hexahydrate, as might be expected. The only difference appears to be the slight increase in band width of the vibration assigned to H_2O , probably due to the more extensive hydrogen-bonding in the tetrahydrate. The similarity of the lithium and ammonium peroxoborate spectra to those of sodium peroxoborate suggests that the basic structure of the peroxoborate anion is the same for all these compounds. Similarly, the absence of the $\sim 3450\text{ cm}^{-1}$ bands in the spectra of lithium and ammonium peroxoborates indicates that both these compounds are also anhydrous, which is borne out by analytical data. The structure of anhydrous lithium peroxoborate, which contains the cyclic $[B_2(O_2)_2(OH)_4]^{2-}$ anion, has been confirmed by a recent single-crystal X-ray structure determination.²³

(b) Salts Containing other Perborate Anions.

The Raman spectra of the amorphous potassium, rubidium and caesium perborates differ from the spectra of sodium peroxoborate hexahydrate in several ways (Table 1-3-2). The most obvious difference is that the spectrum of the sodium salt has only one strong band at $\sim 900\text{ cm}^{-1}$ whereas the potassium, rubidium and caesium salts appear to have two, both broader, at $\sim 860\text{ cm}^{-1}$ and $\sim 930\text{ cm}^{-1}$, suggesting that the structures of the anions in these salts may be different. The analyses of these compounds, which show that the $O_2^{2-}:B$ ratios are higher than 1:1, indicate that the two broad, strong Raman bands near 900 cm^{-1} could arise from O-O stretches. Although analyses of the potassium salt are variable, those of the rubidium and caesium salts correspond reasonably well to $Rb_2[B_2(O_2)_2(OOH)_2(OH)_2]$ and

peroxide, or a more complex moiety rather similar to that found for the anion of the solid compound by X-ray crystallography in sodium peroxoborate hexahydrate,⁹ sodium peroxoborate tetrahydrate and lithium peroxoborate.²³ Polarographic studies reported in the literature,³⁸ have suggested that a species other than metaborate is present.

Although $\text{Et}_2\text{O} \cdot \text{BF}_3$ is generally accepted³⁹ as the external reference for boron nuclear magnetic resonance spectroscopy, in this study metaborate, $[\text{B}(\text{OH})_4]^-$ was used since any solution containing a perborate species is also likely to contain some metaborate. Relative to $\text{Et}_2\text{O} \cdot \text{BF}_3$, metaborate has a chemical shift of $\delta = 1.1$. Figure 1-4-1 shows the spectrum of a metaborate reference solution prepared by adding excess sodium hydroxide to an aqueous solution of sodium tetraborate ("borax"), which as expected,^{40,41} contains one sharp resonance indicating the presence of just one boron containing species. When an aqueous solution of hydrogen peroxide is added to this metaborate solution a second feature is observed. Figure 1-4-2 shows a spectrum of the metaborate/hydrogen peroxide solution at pH 14. One peak of the spectrum, presumably due to metaborate, has the same chemical shift $\delta = 0$ as the reference solution but is less intense and becomes slightly broader. The appearance of the second feature seems to vary according to the pH of the solution. At pH 9 the spectrum produced is very complex and seems to contain many different resonances. As the pH is increased the second feature of the spectrum becomes gradually less complex until at pH > 13.5 the second feature appears as one slightly broad, resonance. The chemical shift of the second feature is down field, i.e., at higher frequency to the metaborate, which is consistent^{42,43} with the deshielding that would be caused by a group of greater electronegativity than OH (e.g., OOH^-). This suggests that the second resonance may be due to a species of the form $[\text{B}(\text{OOH})_x(\text{OH})_{4-x}]^-$,

Figure 1-4-1. ^{11}B n.m.r. spectrum of
metaborate $[\text{B}(\text{OH})_4]^-$.

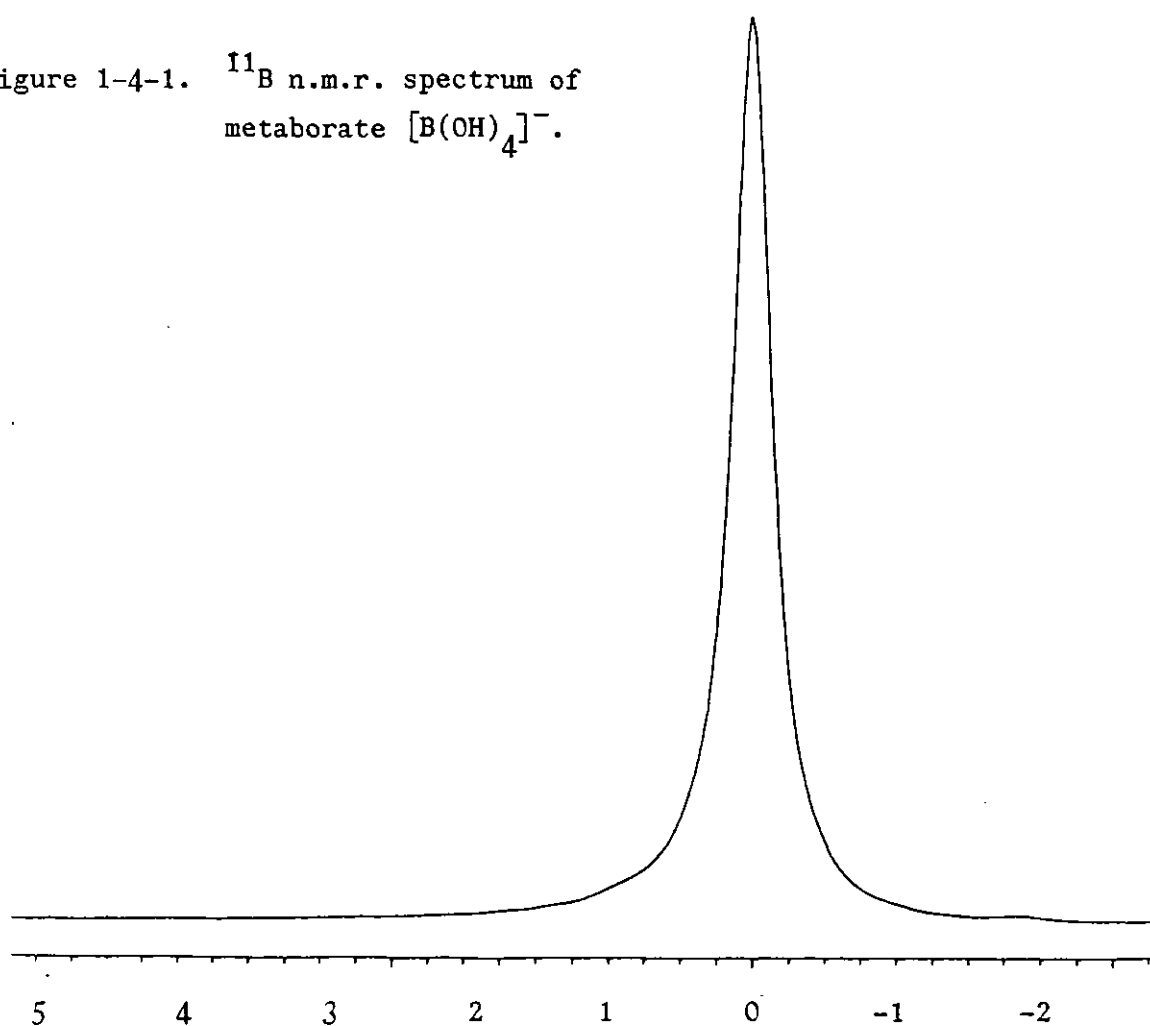
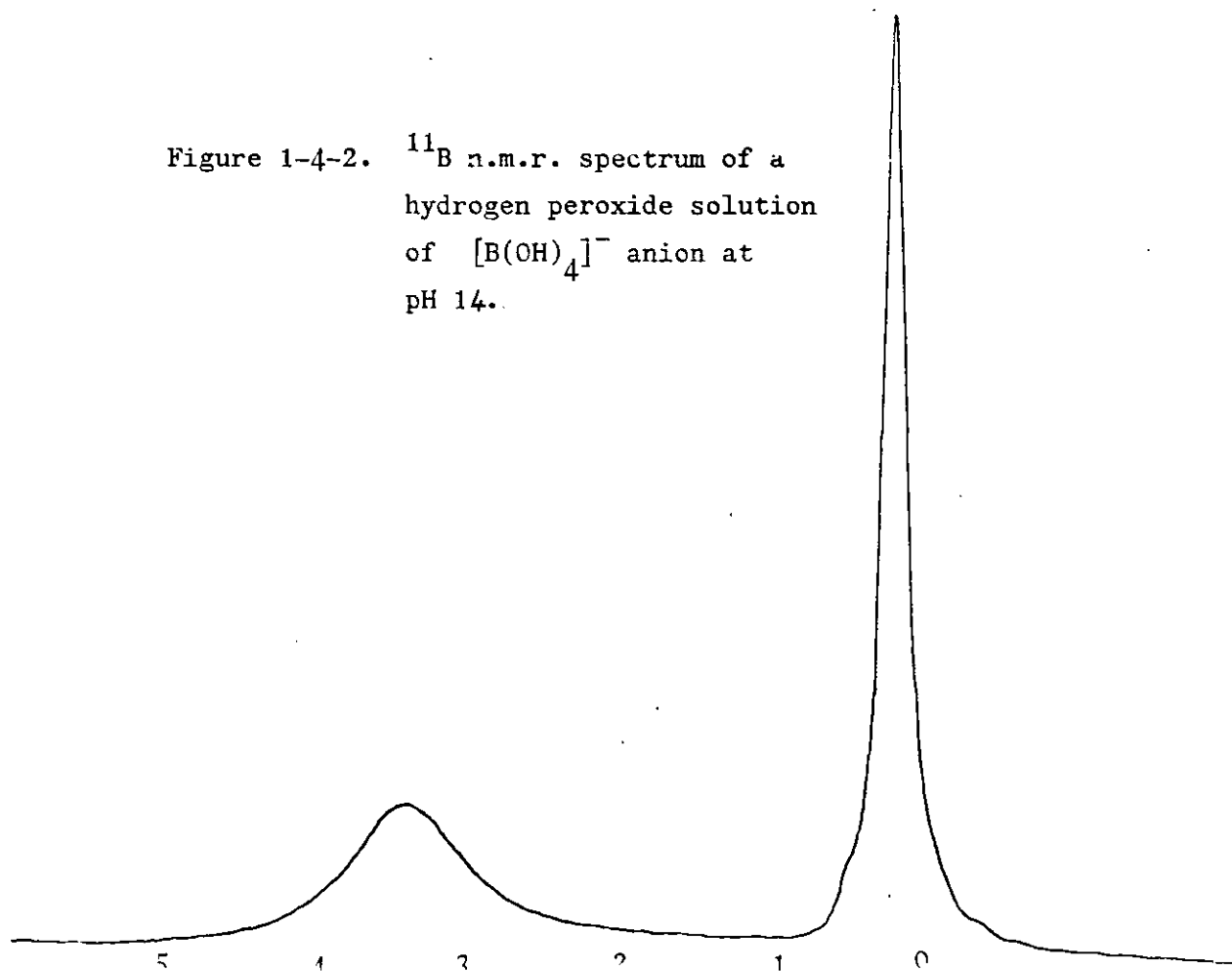


Figure 1-4-2. ^{11}B n.m.r. spectrum of a
hydrogen peroxide solution
of $[\text{B}(\text{OH})_4]^-$ anion at
pH 14..



where x depends on the degree of substitution of OH^- by OOH^- . Further work should be carried out in this area to ascertain whether the complexity of the second feature is due to differing degrees of substitution at different pH values.

Even though equilibrium constants have been quoted^{38,40,44} in the literature, ^{11}B n.m.r. could be used to ratify the reported values. However, in this study no work on the relaxation time of the different resonances has been carried out, thus no attempt has been made to use ^{11}B n.m.r. to evaluate an equilibrium constant for the system. Nevertheless, this n.m.r. work does suggest that peroxoborate persists in solution, i.e., it is not simply a mixture of metaborate and hydrogen peroxide. This contrasts with the situation for "sodium percarbonate", $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$, another common constituent of detergent washing powders; a solution of this contains almost entirely CO_3^{2-} and hydrogen peroxide. The ^{11}B n.m.r. data do not of course indicate what the structure in solution is, whether it is a dimer as in the solid state, or a monomer, e.g., $[\text{B}(\text{OH})_3\text{OOH}]^-$.

SECTION 1-5. ELECTRON SPIN RESONANCE STUDIES.

Electron spin resonance (e.s.r.) studies were carried out because previously reported work by Edwards, et al.⁴⁵ and Reitz⁴⁶ were in disagreement and it was thought that any information about radicals present might further confirm the structure of the peroxoborate species to be a cyclic anion.

Microcrystalline sodium peroxoborate hexahydrate gave no X-band e.s.r. signal at room temperature, so samples were heated to 55°C and 150°C then stored at -20°C , in order to produce radicals which are said to be found by such treatment.^{45,46} These samples were then used for

e.s.r. studies at room temperature. According to Edwards,⁴⁵ samples heated to 55° gave an e.s.r. signal, but we could not confirm this, possibly because any radicals formed may have recombined before the e.s.r. spectrum was measured. However, the sample heated to 150°C did give a signal, figures 1-5-1a,b, and c, with g values centred about $g = 2.012$. This spectrum was similar in appearance to that obtained by Edwards. The feature apparent in Figure 1-5-1c can be ascribed to the ozonide ion (O_3^-) as its shape and g-values resemble very closely those reported⁴⁷ for O_3^- . The small feature at 3325 G in figure 1-5-1b can be tentatively ascribed to the O_2^- ion as it shows striking similarities to the spectrum of O_2^- in sodium peroxide.⁵⁰ The work of Edwards⁴⁵ is in agreement with those assignments and he assigns the broad feature in figure 1-5-1a to some kind of unspecified combined form of oxygen. Reitz,⁴⁶ however, did not report the features seen in figures 1-5-1a and b, but he did observe an additional feature assigned to be a "primary radical structure of $BO_4^\bullet$ " which occurs at a g value of 2.0046. We did not observe this feature.

Further studies were carried out on a sample of sodium peroxoborate hexahydrate that had been irradiated by u.v. light but no signal was apparent. This experiment was undertaken because $K_2C_2O_6$ irradiated by u.v. light did show an e.s.r. signal.⁴⁸

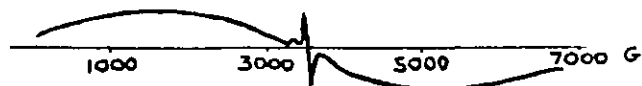
SECTION 1-6. PREPARATIONS.

Lithium peroxoborate, $Li_2[B_2(O_2)_2(OH)_4]$.

Three methods were used:

- (a) Lithium tetraborate (2.6 g, 0.01 moles) and lithium hydroxide, $LiOH \cdot H_2O$ (0.4 g, 0.01 moles) were dissolved in water (15 cm³). To this solution hydrogen peroxide (9 cm³, 30% w/v) was added. The solution was

1-5-1a



1-5-1b



1-5-1c

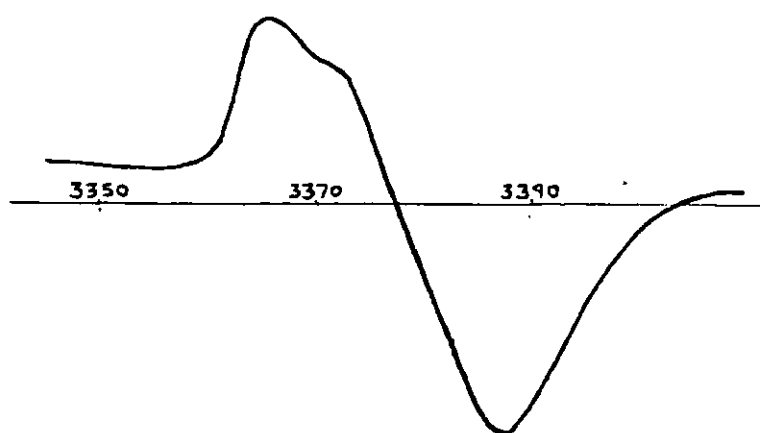


Figure 1-5-1. E.s.r. Spectra of Sodium Peroxoborate Hexahydrate After Heating to 150°C.

left to stand at 5°C for 3 days. When crystallisation did not occur, as was the case on some occasions, the product was precipitated out as microcrystals by addition of methanol. If the methanol was added too slowly a fine emulsion was produced; in such cases, the mixture can be left to stand for a further three days, after which time an oil separates out. Trituration with ether gave the product (Found: B, 12.6; H, 2.6; O_2^{2-} , 37.2%. $\text{B}_2\text{H}_4\text{Li}_2\text{O}_8$ requires B, 12.9; H, 2.4; O_2^{2-} , 38.2%).

(b) Lithium hydroxide monohydrate (0.8 g, 0.02 moles) and boric acid (1.2 g, 0.02 moles) were dissolved in hot water (15 cm^3). After cooling to room temperature hydrogen peroxide (2 cm^3 , 30% w/v) was added. The solution was left to stand at 5°C for two days. After addition of ethanol a sticky solid was produced. The mother liquor was decanted off and ethanol added again. The solution was left for a further day. This procedure was repeated several times until the product became crystalline. (Found: B, 12.9; H, 2.5; O_2^{2-} , 37.4%. $\text{B}_2\text{H}_4\text{Li}_2\text{O}_8$ requires B, 12.9; H, 2.4; O_2^{2-} , 38.2%).

(c) Lithium hydroxide monohydrate (0.8 g, 0.02 moles) and boric acid (1.2 g, 0.02 moles) were dissolved in hot water (15 cm^3). After cooling to room temperature methanol (10 cm^3) and hydrogen peroxide (5 cm^3 , 30% w/v) were added. The solution was left to stand at 5°C until crystallisation of the white microcrystalline solid was complete. (Found: B, 12.6; H, 2.4; O_2^{2-} , 37.6%. $\text{B}_2\text{H}_4\text{Li}_2\text{O}_8$ requires B, 12.9; H, 2.4; O_2^{2-} , 38.2%).

Sodium Peroxoborate Hexahydrate $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$.

Again three methods were used:

(a) Sodium tetraborate (3.8 g, 0.01 moles) and sodium hydroxide (0.4 g, 0.01 moles) were dissolved in water (60 cm³). The solution was cooled and hydrogen peroxide (9 cm³, 30% w/v) added. The solution was left to stand at 5°C until crystallisation of the white solid was complete. (Found: H, 5.2; O₂²⁻, 20.9%. $\text{B}_2\text{H}_{16}\text{Na}_2\text{O}_{14}$ requires H, 5.2; O₂²⁻, 20.8%).

(b) Oven dried boric oxide B_2O_3 (1.4 g, 0.02 moles) and sodium hydroxide (0.8 g, 0.02 moles) were dissolved in water (40 cm³). To the cold solution was added hydrogen peroxide (9 cm³, 30% w/v). The solution was left to stand at 5°C until crystallisation was complete. (Found: H, 5.2; O₂²⁻, 20.9%. $\text{B}_2\text{H}_{16}\text{Na}_2\text{O}_{14}$ requires H, 5.2; O₂²⁻, 20.8%).

(c) Boric acid (2.4 g, 0.04 moles) and sodium hydroxide (1.2 g, 0.03 moles) were dissolved in water (30 cm³). Hydrogen peroxide (9 cm³, 30% w/v) was added to the solution which was left to stand at 5°C until crystallisation was complete. (Found: H, 5.2; O₂²⁻, 20.7%. $\text{B}_2\text{H}_{16}\text{Na}_2\text{O}_{14}$ requires H, 5.2; O₂²⁻, 20.8%).

In all the above preparations the solid sodium peroxoborate hexahydrate could be precipitated with ethanol. The ¹⁰B and ¹¹B substituted forms were made via method c (using ¹⁰B and ¹¹B substituted boric acid), but with 1/4 value quantities. All products were filtered, then washed with ethanol and ether. The deuteriated sodium peroxoborate hexahydrate was made by method b, again using 1/4 the quantities, from NaO²H, ²H₂O and B_2O_3 .

Sodium Peroxoborate tetrahydrate, $\text{Na}_2[\text{B}_2(\text{O}_2)(\text{OH})_4]\cdot 4\text{H}_2\text{O}$.

The published methods^{13,20} all require a "seed" of the tetrahydrate; the following method was devised in order to avoid this. A saturated aqueous solution of sodium peroxoborate hexahydrate was prepared at 40°C such that there was some undissolved peroxoborate present. The solution was left to stand for several hours to check that the solution was in fact saturated. If the undissolved peroxoborate passed into solution more was added to the mixture. The flask was then stoppered and the mixture left for about eight weeks at 40°C, after which time sodium peroxoborate tetrahydrate crystals had formed. The crystals were filtered and dried in air. (Found: B, 8.0; H, 4.5; O_2^{2-} , 23.5%. $\text{B}_2\text{H}_{12}\text{Na}_2\text{O}_{12}$ requires B, 8.0; H, 4.5; O_2^{2-} , 23.6%). To ensure a successful preparation it is important that freshly prepared sodium peroxoborate hexahydrate should be used. It is also essential that perfectly clean flasks must be used otherwise at 40°C the peroxoborate solution will quickly decompose. Further samples of sodium peroxoborate tetrahydrate can be easily made by "seeding" sodium peroxoborate hexahydrate solutions with the tetrahydrate crystals, provided that the solution is kept at room temperature. At temperatures below 15°C the hexahydrate preferentially crystallises out.

Anhydrous Sodium Peroxoborate, $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$.

Sodium peroxoborate hexahydrate was heated to 60°C and then left in a desiccator to cool to room temperature. Any sample of anhydrous sodium peroxoborate, if left in air below 15°C, will convert to the hexahydrate. (Found: B, 10.4; H, 2.2; O_2^{2-} , 31.9. $\text{B}_2\text{H}_4\text{Na}_2\text{O}_8$ requires B, 10.8; H, 2.0; O_2^{2-} , 32.1%).

Sodium "Super Oxide" Perborate.

A sample of sodium "super oxide" perborate was supplied by Interlox Chemicals Ltd. (Found in these laboratories: B, 10.0; H, 1.6; O_2^{2-} , 45.0%. Found by Solvay et Cie for Interlox Chemicals Ltd., B, 9.8; H, 1.5; O_2^{2-} , 46.0%. $B_{2n}H_{4n}Na_{2n}O_{9n}$ requires B, 10.0; H, 1.9; O_2^{2-} , 44.5%).

Potassium Perborate

Boric acid (2.4 g, 0.04 moles) and potassium hydroxide (1.7 g, 0.03 moles) were dissolved in water (30 cm³). Hydrogen peroxide (9 cm³, 30% w/v) was added to the cold solution which was left to stand at 5°C. If no product formed, precipitation was induced by addition of excess ethanol. Other methods similar to those for the production of sodium peroxoborate hexahydrate were tried, but all methods gave an amorphous solid with variable analyses (typical analysis: B, 7 (+1); H, 2 (+0.5); O_2^{2-} , 45 (+2)%).

Rubidium peroxoborate, $Rb_2[B_2(O_2)(OOH)_2(OH)_2]$.

Rubidium hydroxide (1.03 g, 0.015 moles) and boric acid (0.8 g, 0.013 moles) were dissolved in water (20 cm³). To this solution hydrogen peroxide (3 cm³, 30% w/v) was added. The peroxoborate solution was left at 5°C until a fine powdery product formed. The solid gave a very weak XRD powder pattern. (Found: B, 6.4; H, 0.5; O_2^{2-} , 34.0%. $B_2H_4O_{10}Rb_2$ requires B, 6.1; H, 1.9; O_2^{2-} , 35.9%).

Caesium Peroxoborate, $\text{Cs}_2[\text{B}_2(\text{O}_2)_2(\text{OOH})_2(\text{OH})_2]$.

Caesium hydroxide (0.75 g, 0.005 moles) and boric acid (0.41 g, 0.007 moles) were dissolved in water (10 cm²). A product which gave a weak XRD powder pattern, was produced after several days at 5°C. (Found: B, 4.9; H, 1.2; O₂²⁻, 27.4. $\text{B}_2\text{H}_4\text{O}_{10}\text{Cs}_2$ requires B, 4.8; H, 0.9; O₂²⁻, 28.4%). The product often contained a carbonate impurity.

Ammonium Peroxoborate, $(\text{NH}_4)_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$.

Finely powdered boric acid (1.2 g, 0.02 moles) was dissolved in a mixture of water (15 cm³) and concentrated ammonia solution (2 cm³, sp. gr. 0.88). To this solution hydrogen peroxide (5 cm³, 30% w/v) was added. This solution was left at 5°C until crystallisation was complete. (Found: B, 12.8; C, 0.6; H, 6.1; N, 15.5; O₂²⁻, 37.4%. $\text{B}_2\text{H}_{12}\text{N}_2\text{O}_8$ requires B, 11.4; C, 0.0; H, 6.4; N, 14.8; O₂²⁻, 33.7%). This product always contained some carbonate as an impurity.

Sodium Metaborate, $\text{Na}[\text{B}(\text{OH})_4]$.

Boric oxide (0.7 g, 0.01 moles), boric acid (0.6 g, 0.01 moles) or sodium tetraborate (1.9 g, 0.005 moles) were dissolved in water (5 cm³) with an excess of sodium hydroxide (0.8 g, 0.02 moles). The solutions were heated then cooled to 5°C. The product was then precipitated with ethanol. The ¹⁰B and ¹¹B isotopically substituted forms were made via ¹⁰B and ¹¹B substituted boric acid and the deuteriated form via anhydrous boric oxide, ²H₂O and NaO²H; however, the solids for the isotopically substituted forms were produced by evacuating the solution to dryness rather than by precipitation. (Found: B, 10.6; H, 4.0%. BH_4NaO_4 requires B, 10.6; H, 4.0%). If the metaborate solution is left so that the product crystallises out, a hydrated product is formed.

CHAPTER TWO

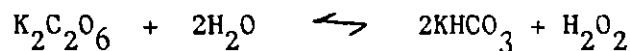
PERCARBONATES

INTRODUCTION

The term 'percarbonate' is rather loosely used, in the context of alkali metal salts, to describe any salt or compound made from hydrogen peroxide and an alkali metal carbonate or bicarbonate or an alkali metal hydroxide or peroxide with carbon dioxide and hydrogen peroxide. Such compounds may or may not be 'true' percarbonates (i.e., contain a C-O-O bond). Thus, 'sodium percarbonate' (used in one of the most popular commercial washing powder in Britain⁹) is not a 'true' percarbonate but simply a perhydrate, $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$, in which H_2O_2 molecules are hydrogen bonded to carbonate groups.^{51,52,53} This chapter is, however, principally concerned with 'true' percarbonates, in which a C-O-O bond is likely to be present.

A number of such percarbonates of the alkali metals have long been known, e.g., $\text{M}^{\text{I}}\text{HCO}_4$ ($\text{M} = \text{Na},^{54} \text{K},^{55,56} \text{Rb},^{57} \text{Cs}^{58}$), normally made by reaction of MOOH with carbon dioxide at low temperatures; $\text{M}_2^{\text{I}}\text{C}_2\text{O}_6$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) made by reaction of MOH with CO_2 in H_2O_2 ,^{54,55,58,59} by anodic oxidation of M_2CO_3 at low temperatures ($\text{M} = \text{K},^{60} \text{Rb},^{61} \text{Cs}^{61}$) or from elemental fluorine and M_2CO_3 at low temperatures ($\text{M}^{62} = \text{Na}, \text{K}, \text{and Rb}$). Finally, $\text{Li}_2(\text{CO}_4)$ has been reported, prepared by reaction of LiOH with H_2O_2 and CO_2 .⁶³ In earlier work in these laboratories⁴⁹ the vibrational spectra of solid MHCO_4 ($\text{M} = \text{Na}, \text{K}, \text{Rb}$) of $\text{M}_2\text{C}_2\text{O}_6$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$, including $\text{K}_2^{13}\text{C}_2\text{O}_6$) and of $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ were reported and structures suggested for these salts. There has also been some work

reported^{64,65,66,67,68,69} on the possible existence in solution of the $\text{C}_2\text{O}_6^{2-}$ ion, but most of this is in journals which are inaccessible or not available in translation. One author^{68,69,70} gives an equilibrium constant of 0.097 for the 'percarbonate' hydrolysis



determined⁶⁸ from the distribution of hydrogen peroxide between organic solvents and water. The same author^{69,70} also describes a method for the determination of rate constants by following the hydrolysis of $\text{K}_2\text{C}_2\text{O}_6$.

The mechanism of $\text{K}_2\text{C}_2\text{O}_6$ hydrolysis has been studied⁷¹ using H_2^{18}O which suggests that a C-O bond is cleaved rather than a O-O bond via a species such as CO_4^{2-} .

In this chapter we report a single crystal X-ray crystallographic study of a complex, $\text{Pt}(\text{CO}_4)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in which CO_4^{2-} is believed to be coordinated to platinum.⁷² We then report results of studies in the Raman and ^{13}C n.m.r. spectra of aqueous solutions containing HCO_3^- and CO_3^{2-} in the presence of excess hydrogen peroxide, and show that such mixtures contain a percarbonate species, possibly HCO_4^- or HCO_4^- in equilibrium with CO_4^{2-} . Finally, the results of some electrochemical studies on this system are presented.

SECTION 2-1. SINGLE CRYSTAL X-RAY CRYSTALLOGRAPHIC STUDIES.

Crystal structure of bis(triphenylphosphine)peroxocarbonate platinum(II).

The title compound was first prepared in 1969⁷³ and is the best characterised of the few known^{72,73,74,75} transition metal peroxocarbonate complexes.

As no successful single-crystal X-ray studies have been carried out on any of the true percarbonates it was felt that a further attempt to determine the structure of the platinum complex would be useful as it might prove the existence of the CO_4^{2-} moiety, albeit as a coordinated ligand. The title compound was prepared using the methods of Hayward, *et al.*⁷² by bubbling oxygen and carbon dioxide simultaneously through a solution of tetrakistriphenylphosphineplatinum(0) (2.0 g, 1.6 mmol) in dry benzene (50 cm³). The yellowish-green crystals were grown by the slow evaporation of a solution in toluene-dichloromethane (ratio 1:1) to give a compound of stoichiometry $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{PtCO}_4 \cdot \text{C}_7\text{H}_8$. If a benzene or a dichloromethane solvent were used instead of the mixed solvent the crystals produced tended to crumble rapidly, due to the loss of the more volatile benzene or dichloromethane of crystallisation. (Found: C, 57.4; H, 4.2; P, 7.2%. $\text{C}_{43}\text{H}_{36}\text{O}_4\text{P}_2\text{Pt}$ requires C, 59.1; H, 4.2; P, 7.1%).

Accurate unit-cell dimensions were obtained by a least-squares calculation based on 15 reflections measured on a Nicolet R3 m diffractometer using graphite monochromated Cu-K_α radiation.

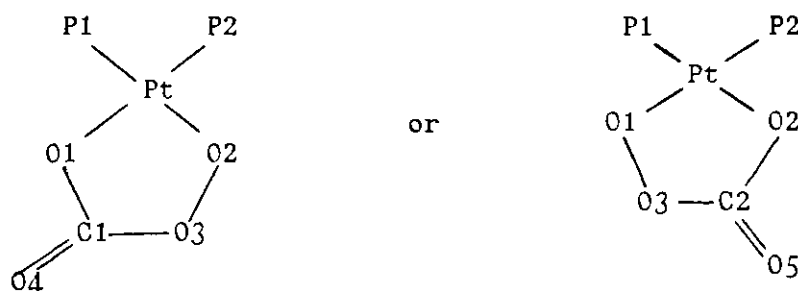
Crystal Data

$\text{C}_{43}\text{H}_{36}\text{O}_4\text{P}_2\text{Pt}$, $M = 873.8 \text{ g mol}^{-1}$, triclinic, $a = 10.801(2)$, $b = 12.537(3)$, $c = 15.802(4) \text{ \AA}$, $\alpha = 83.89(2)$, $\beta = 71.12(2)$, $\gamma = 68.37(2)^\circ$, $U = 1881.9(8) \text{ \AA}^3$, $Z = 4$, $F(000) = 883.8$, space group $\bar{P}1$ (No. 2) Cu-K_α radiation $\lambda = 1.5418 \text{ \AA}$, $\mu(\text{Cu-K}_\alpha) = 81.8 \text{ cm}^{-1}$.

A crystal of size 0.2 x 0.15 x 0.15 mm was chosen for the study and a coat of picture varnish was applied to the crystal to help prevent decomposition under the X-ray beam. The ω scan data collection technique was used and a total of 3865 unique reflections were observed to $\theta = 50^\circ$. The $\bar{1}, 1, 0$ and $0, 0, 2$ reflections were monitored as reference reflections every 50 reflections collected and their net count did not alter noticeably over the period of data collection (ca. 29 hours). The

data were scaled by use of these reference reflections. Program system SHELXTL²² was used throughout and all calculations were carried out on a Data General Eclipse S140 computer.

The location of the platinum atoms were found by Patterson synthesis. A few cycles of isotropic refinement gave $R = 0.31$. The subsequent difference Fourier synthesis gave the positions of the other atoms. The least squares refinement has reached an R value of 0.084 with an absorption correction having been applied. All non-hydrogen atoms were refined anisotropically apart from those in the solvent molecule of crystallisation. The refinement was stopped at this stage due to a difficulty arising from disorder in the structure. The position of the platinum atom and of the two triphenylphosphine groups have been accurately determined. The bond lengths and angles within the groups agree well with published^{76,77} data. However, the peroxocarbonate moiety showed disorder which, together with the possibility of some decomposition, made it practically impossible to solve that part of the structure completely. The disorder has arisen because, while the packing of the molecules is almost entirely determined by the bulky triphenylphosphine groups, the peroxocarbonate ring can be represented in two ways:



If the disorder was completely random, i.e., 50% present in each orientation, and there was no other affect then the Pt-O bond lengths would be the same. However, as they are different, (table 2-1-1), it

Table 2-1-1.

Selected Interatomic Bond Distances ($\text{\AA}$) and Bond Angles ($^{\circ}$).

Pt-P1	2.228(5)	C1-O1	1.18(5)
Pt-P2	2.282(8)	O2-O3	1.44(3)
Pt-O1	2.02(2)	C1-O3	1.39(4)
Pt-O2	1.89(2)	C1-O4	1.15(5)
		C2-O5*	1.26(2)

*For the disordered symmetry.

O1-Pt-O2	80.4(11)
Pt-O1-C1	101.1(17)
O1-C1-O3	113.1(26)
O1-C1-O4	128.1(32)
C1-O3-O2	117.2(20)
O3-O2-Pt	107.1(17)
O3-C1-O4	118.7(30)

appears that one form is more common than the other, even though there seems to be no obvious reason for this to be so. Any preferential decomposition of one form would further complicate the issue. Whilst this does not represent proof it demonstrates that coordinated CO_4^{2-} is likely to be present in the crystal. It may be useful to repeat the study at low temperature as this may reduce any decomposition and more importantly, will reduce the thermal vibration of the atoms which should make the solution of the structure more likely. Figure 2-1-1 shows the likely structure of the compound. One point worth noticing from figure 2-1-1 is the positions of the two aromatic rings at the front of the figure. It can be seen that they are orientated in parallel planes with a separation of 3.41Å. This compares^{76,77} well with what might be expected for such a contact.

SECTION 2-2. PERCARBONATES IN AQUEOUS SOLUTION.

Preliminary Raman and ^{13}C n.m.r. spectroscopy in these laboratories⁷⁸ suggested that aqueous solutions of bicarbonate between the pH range 7.5 and 9.5 (in which HCO_3^- and CO_3^{2-} would be present) reacted with excess hydrogen peroxide to give a 'percarbonate' species of unknown composition. We now extend these studies and, while still unable to give a precise formulation of the 'percarbonate', present more data and suggest what further research would help to elucidate its nature. Such work is important because washing powders containing 'sodium percarbonate' ($\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$) are used at approximately pH 9 and at this pH the H_2O_2 , CO_3^{2-} and HCO_3^- released by the detergent in solution may well produce some of the 'percarbonate' referred to in this section. Furthermore, the use of carbonate-bicarbonate buffers is

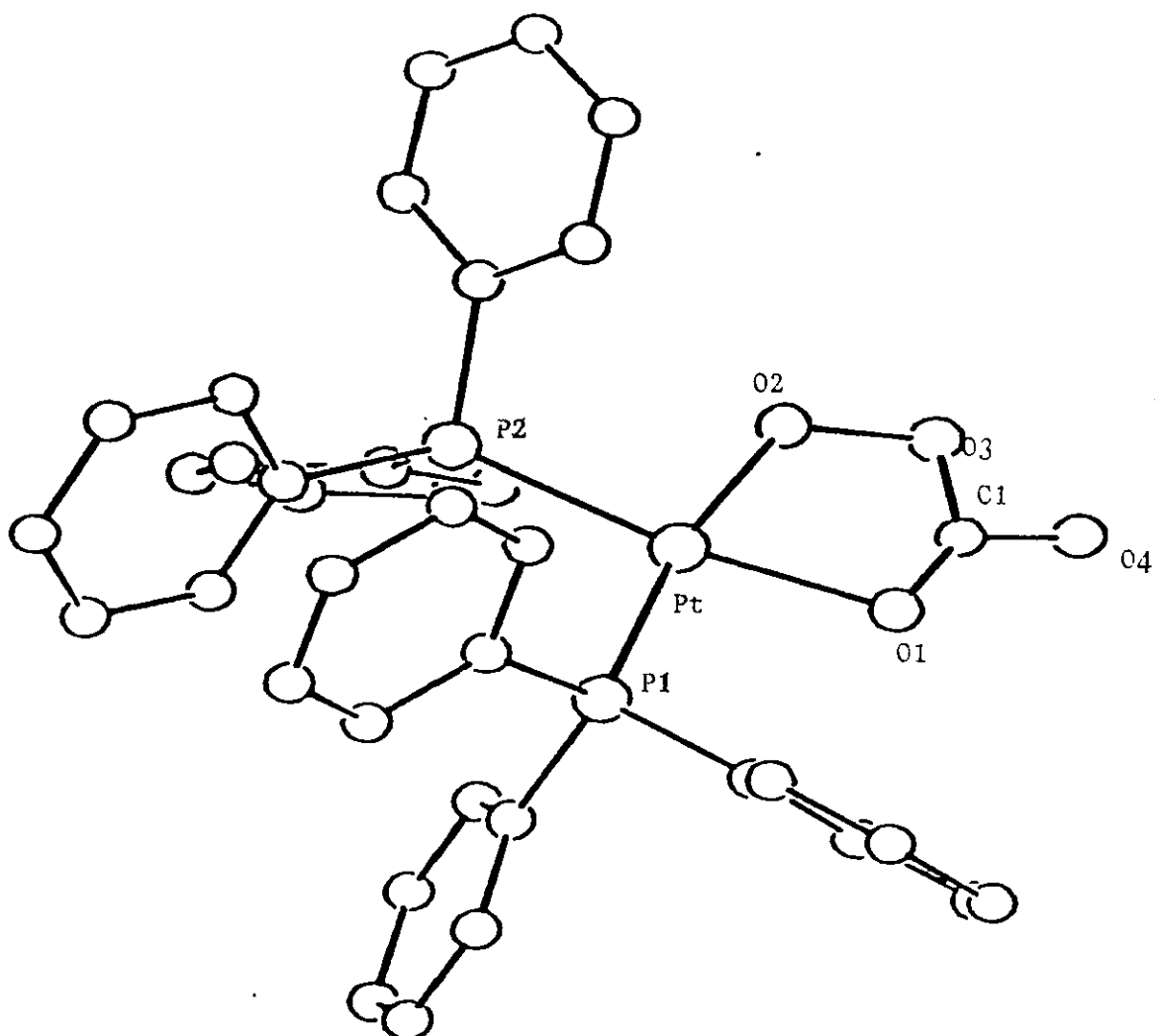


Figure 2-1-1(a). X-ray molecular structure of $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{PtCO}_4$ (not showing disorder).

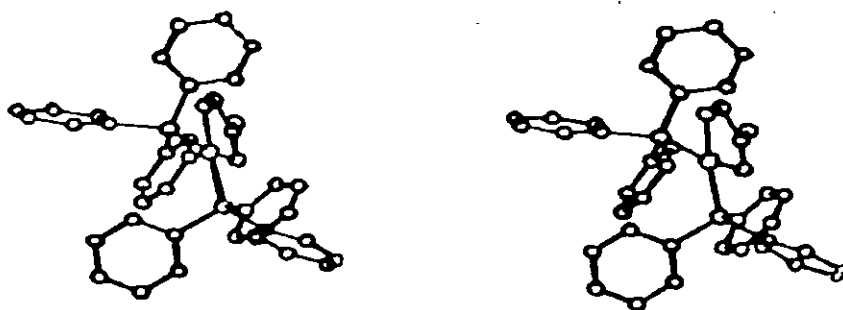


Figure 2-1-1(b). Stereoscopic view of a molecule of $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{PtCO}_4$.

relatively common with hydrogen peroxide, it being implicitly assumed that $\text{CO}_3^{2-}/\text{HCO}_3^-$ is inert with respect to hydrogen peroxide. Our work suggests that this latter assumption is untenable.

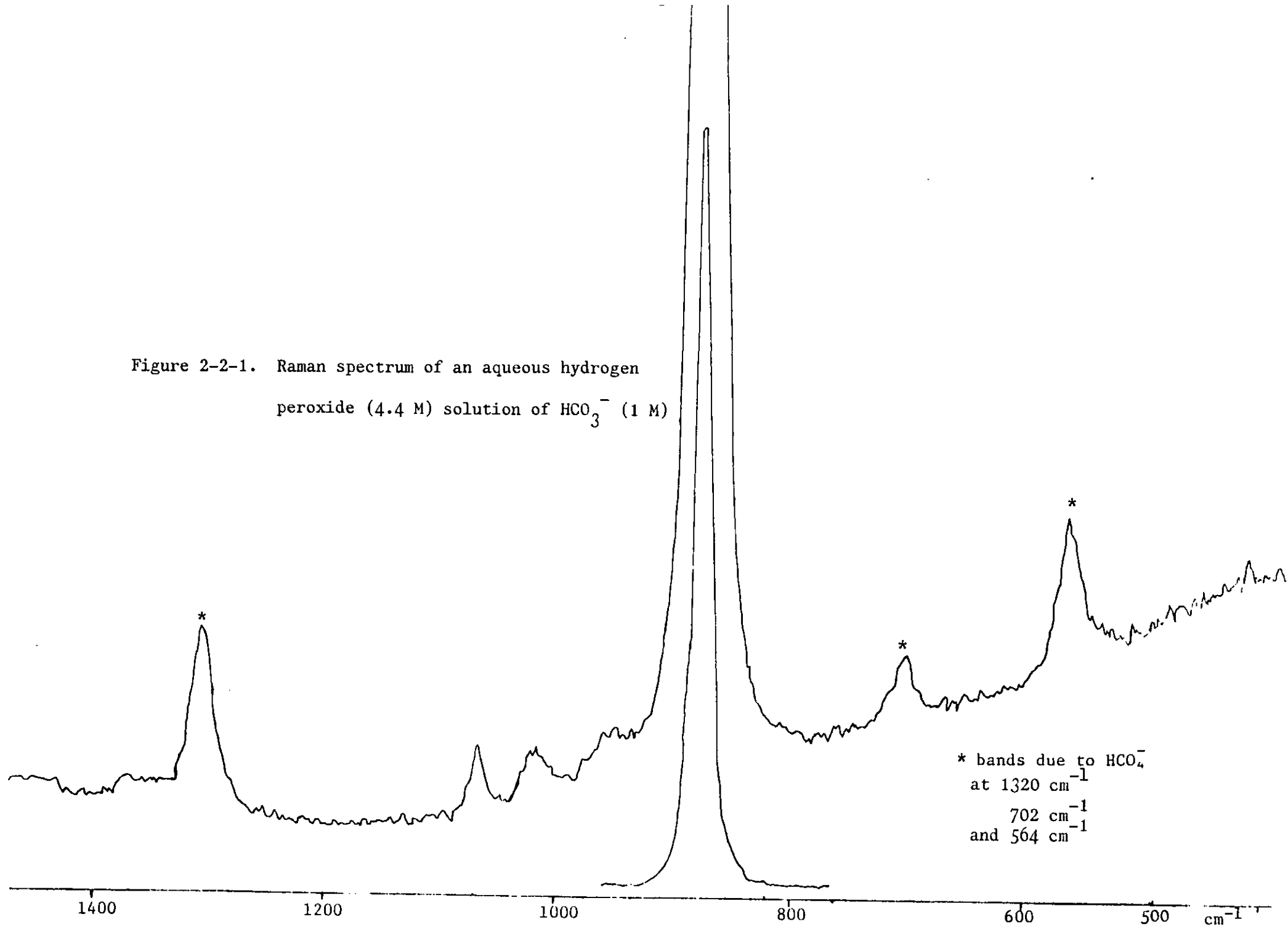
(a) Raman Data.

Earlier work in these laboratories⁷⁸ showed that a frozen solution of bicarbonate in excess hydrogen peroxide showed Raman active bands in the $600\text{--}1500\text{ cm}^{-1}$ region additional to those of CO_3^{2-} ^{79,80} (1063 cm^{-1} the symmetric C-O stretch and 680 cm^{-1} the O-C-O deformation) and HCO_3^- ^{80,81,82} (1302 , 1017 , 672 and 632 cm^{-1}). These new bands appeared at 1320 , 708 and 580 cm^{-1} and shifted to 1288 , 700 and 560 cm^{-1} on ^{13}C substitution,⁷⁸ thus suggesting that they arose from carbon containing species.

We have repeated and confirmed this work and have shown that such bands are present in mobile aqueous solutions (typically 1 M in HCO_3^- and 4.4 M in H_2O_2) at 20°C (figure 2-2-1). Raman data were obtained using a spinning cell with excitation at $5309\text{\AA}$ from a krypton ion laser (see Appendix B). The bands found (again, in addition to those attributable to CO_3^{2-} and HCO_3^-) were at 1320 , 702 and 564 cm^{-1} , in general agreement with values found⁷⁸ for the frozen solutions.

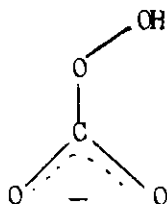
A comparison of the Raman spectra⁴⁸ of solid $\text{M}_2\text{C}_2\text{O}_6$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), $\text{K}_2^{13}\text{C}_2\text{O}_6$, MHCO_4 ($\text{M} = \text{Na}, \text{K}, \text{and Rb}$) and $\text{Li}_2\text{CO}_4 \cdot \text{H}_2\text{O}$ with the spectra of the solutions show that the Raman profile of MHCO_4 is similar to that of the solution 'percarbonate' species, though spectra of $\text{M}_2\text{C}_2\text{O}_6$ are also not markedly different from it. Using the assignment originally proposed for NaHCO_4 ,⁵⁶ we very tentatively assign the polarised band at 1320 cm^{-1} to a symmetric C=O stretch and those at 702 and 564 cm^{-1} to CO_3 deformation. A band associated primarily with an O-O stretch of a

Figure 2-2-1. Raman spectrum of an aqueous hydrogen peroxide (4.4 M) solution of HCO_3^- (1 M)



C-O-O moiety would be expected near 900 cm^{-1} , but this region is blacked out by the extremely strong Raman band at 880 cm^{-1} due to the excess hydrogen peroxide present in the solutions and so is not observed.

On the basis of this comparison of the Raman spectra of solid MHCO_4 with those of solutions of HCO_3^- in excess hydrogen peroxide we suggest that the three bands at 1320 , 702 and 564 cm^{-1} arise from an HCO_4^- ion; its structure in solution would presumably be:



Attempts to measure the infrared spectrum of the solution species were unsuccessful due to decomposition of the solution in the infrared beam; such data would be useful and complimentary to the Raman results, however, and could perhaps be obtained by using a low-temperature cell.

We also attempted to measure the Raman spectra of $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ solutions at different pH. Although the position of the 1320 , 702 and 564 cm^{-1} bands did not appear to vary with pH, they were not observable below pH 7.0 or above pH 9.5. Spectra from solutions outside this range were very noisy due to gas evolution and so data from them are not reliable. We also measured the Raman spectra of $\text{HCO}_3^-/\text{H}_2\text{O}_2$ solutions as a function of time (^{13}C n.m.r. data, reported below, indicated that the 'percarbonate' species was formed slowly (over a period of up to forty minutes). However, the intensities of the Raman bands which we assigned to HCO_4^- did not appear to increase with time. Laser excitation at 5309 , 5682 and 6471Å was used but in all cases the formation of 'percarbonate' appeared to be complete by the time the measurement was

made. A possible reason for this difference from the ^{13}C n.m.r. data is that the intense laser radiation used for the Raman experiments may have in some way increased the rate of 'percarbonate' formation.

(b) ^{13}C N.M.R. DATA.

(i) The $\text{CO}_3^{2-}/\text{HCO}_3^-$ System.

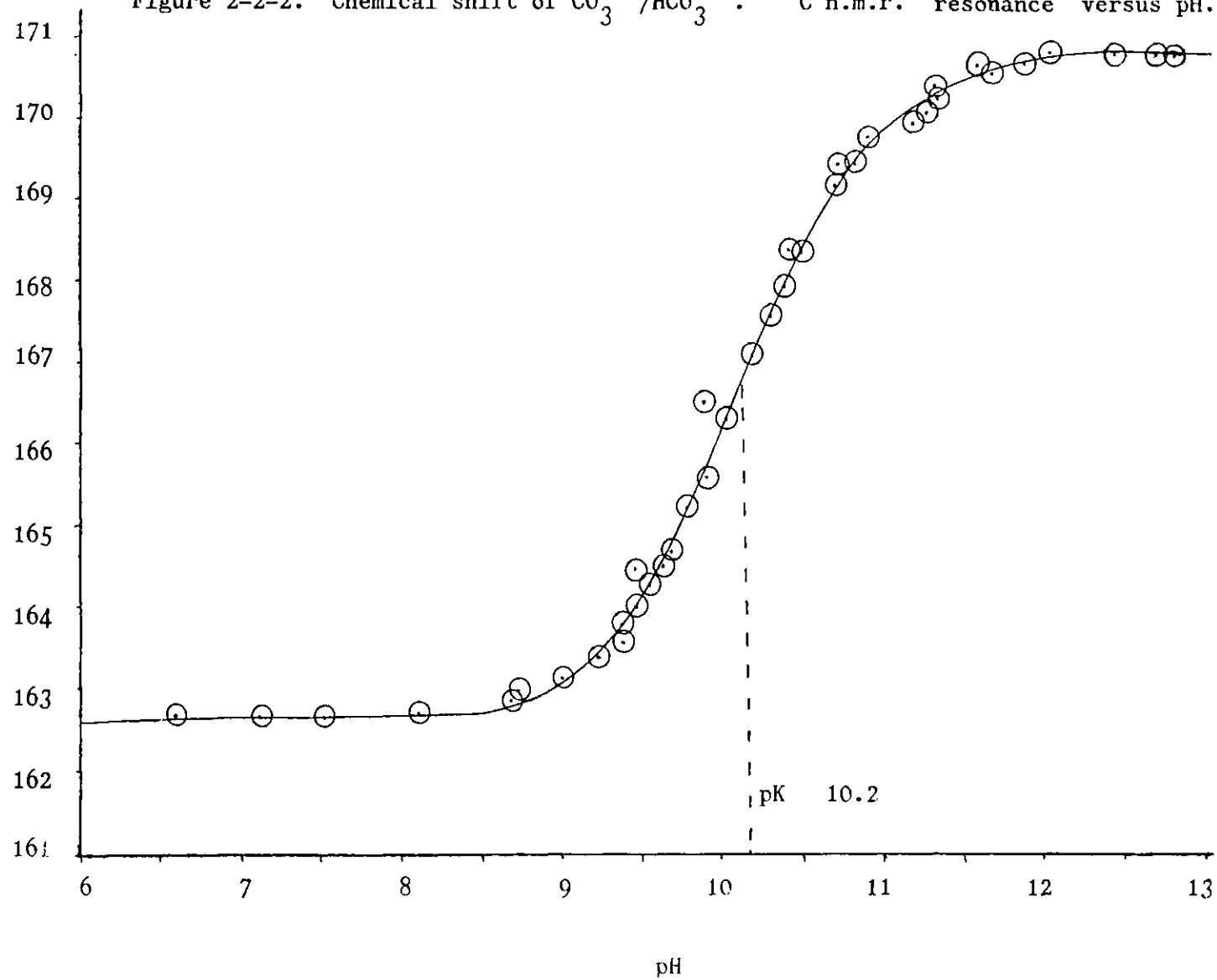
An aqueous solution of an alkali metal carbonate or bicarbonate or a mixture of both gives rise to one ^{13}C resonance only. An essentially pure carbonate solution (pH 12.0) gives a resonance at 170 ppm (relative to DSS) and an essentially pure bicarbonate solution (pH 8.0) gives a resonance at 163 ppm. Due to rapid proton exchange (in the n.m.r. time scale) between the carbonate and bicarbonate an aqueous solution containing both species gives rise to one resonance⁸³ at a position which depends on the proportions of each species and therefore on the pH of the solution. A resonance at 125.4 ppm, assigned⁸³ to $\text{CO}_2\text{.aq}$, occurs at low pH only and is not observed in these studies. Figure 2-2-2 shows the relative position of the carbonate/bicarbonate resonance at different values of pH. The mid point corresponds to the pK_a value (where $[\text{HCO}_3^-] = [\text{CO}_3^{2-}]$); we find $\text{pK}_a = 10.25$, in good agreement with the literature⁸⁴ value of 10.3. During the course of this part of the work some ^{13}C n.m.r. data were published⁸⁵ for this system, over a smaller pH range and with a less sensitive machine; the pK_a value found was 10.2.

(ii) The $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{H}_2\text{O}_2$ System.

Preliminary work in these laboratories⁷⁸ showed that, if excess hydrogen peroxide were added to the $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution over the pH range ca. 7-10, a new ^{13}C resonance near 160 ppm arose in addition to the existing $\text{CO}_3^{2-}/\text{HCO}_3^-$ resonance in the 170-163 ppm range. Typical spectra are shown in figure 2-2-3. As with the $\text{CO}_3^{2-}/\text{HCO}_3^-$ system, the

Figure 2-2-2. Chemical shift of $\text{CO}_3^{2-}/\text{HCO}_3^-$. ^{13}C n.m.r. resonance versus pH.

Chemical
Shift of
 $\text{CO}_3^{2-}/\text{HCO}_3^-$



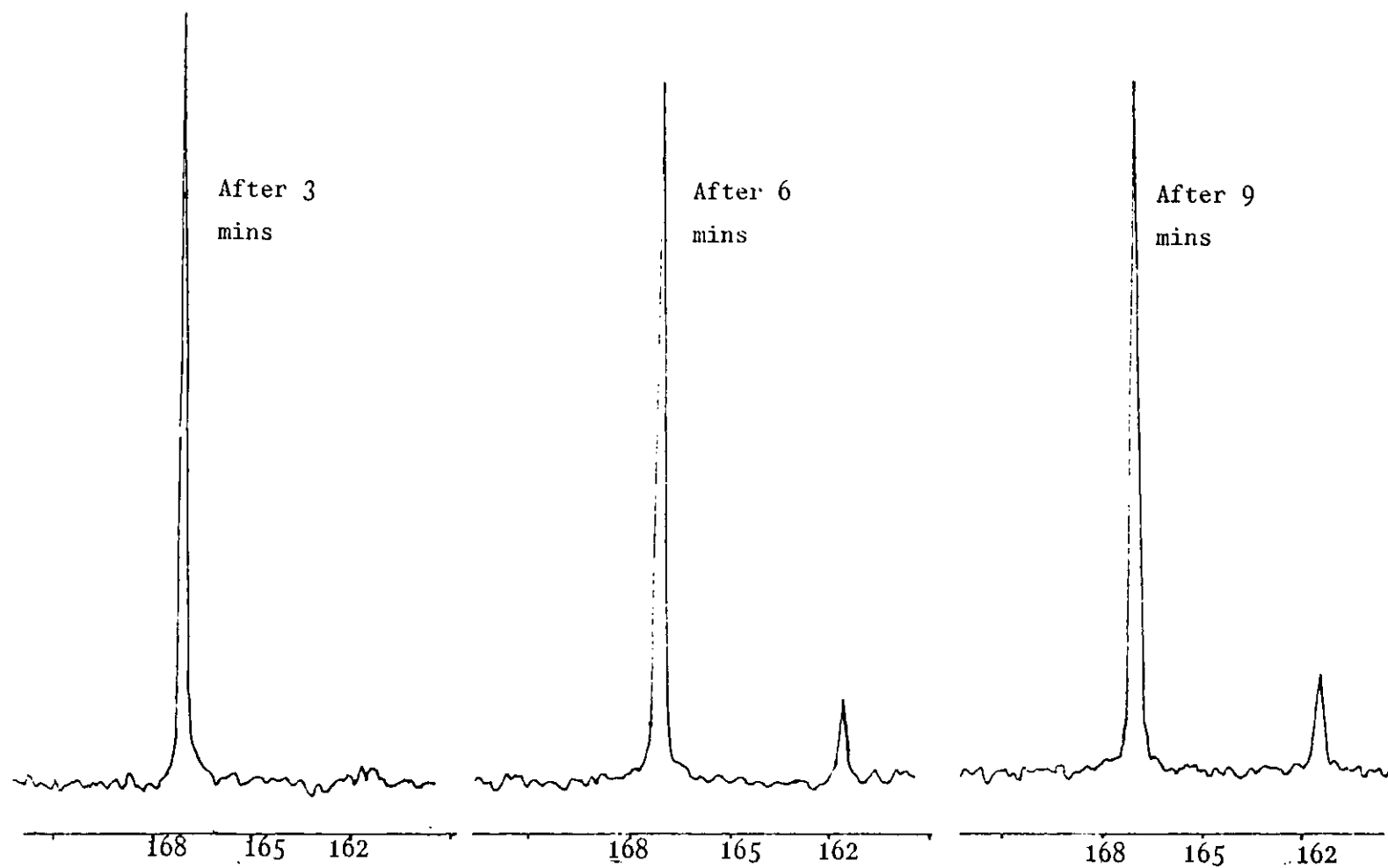


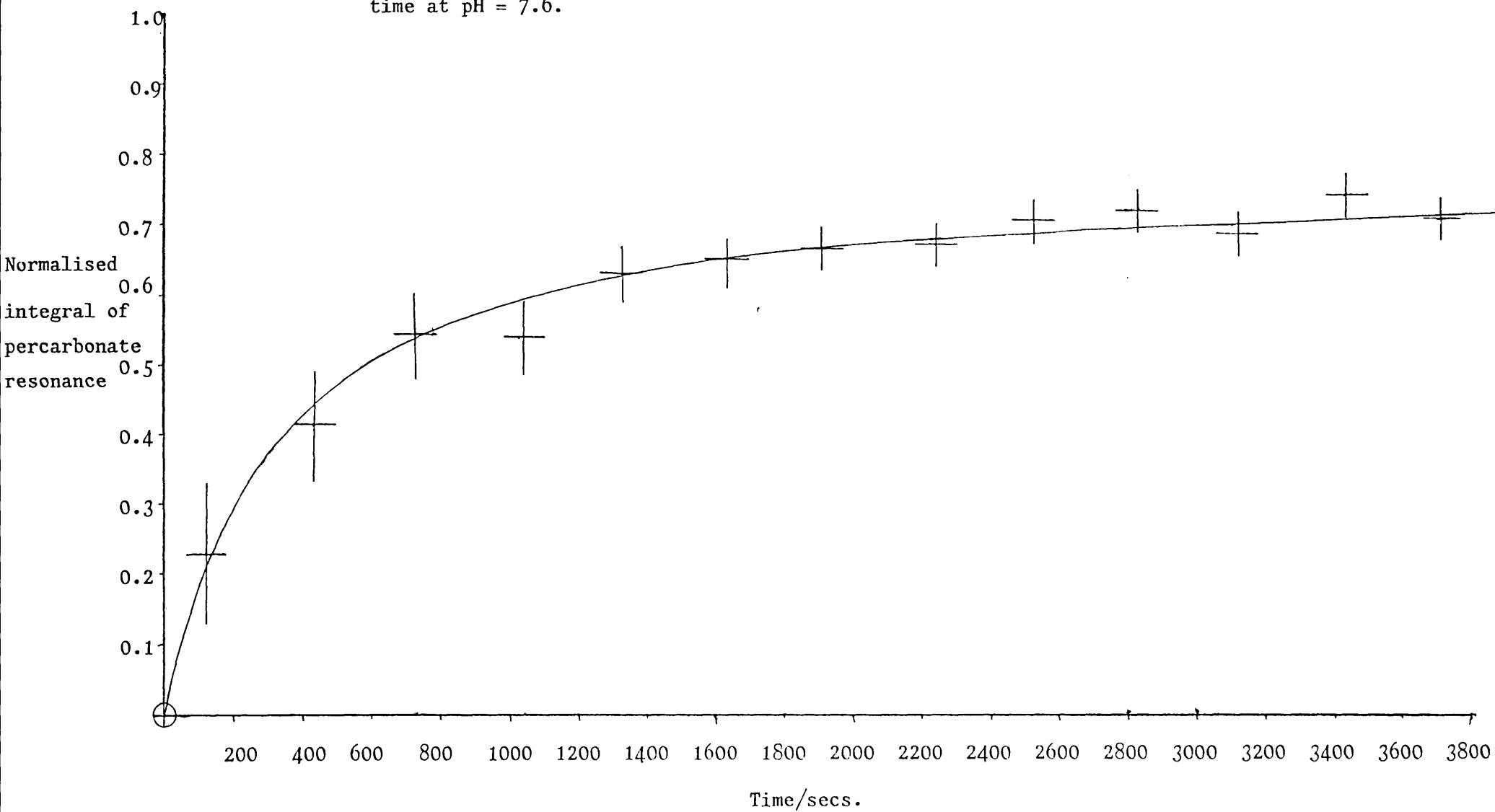
Figure 2-2-3. Typical ^{13}C n.m.r. spectra of an aqueous hydrogen peroxide (4.4 M) solution of H^{13}CO^- (0.1 M.) showing the growth of the percarbonate resonance with time.

position of this resonance was pH dependent, though not as markedly so as the $\text{CO}_3^{2-}/\text{HCO}_3^-$ resonance.⁸⁵ The early measurements were made on a Varian X 100 instrument which was only capable of producing useful spectra after one hour accumulation of data. Our present measurements, however, are from a Bruker WM 250 instrument which produces data in five minutes from enriched ^{13}C samples (90% enrichment). By using this instrument we have been able to make semi-quantitative measurements of the integrals of the two peaks (that at 163-170 ppm, due to $\text{CO}_3^{2-}/\text{HCO}_3^-$ and that near 160 ppm due to the 'percarbonate'). That these integrals are a reasonable measure of the concentrations of both $\text{CO}_3^{2-}/\text{HCO}_3^-$ and the percarbonate was ascertained by checking that the relaxation times of the two species were similar.

We find that the integral of the 'percarbonate' peak, and thus the concentration of the species giving rise to it (a) increases with time (figure 2-2-3, and 2-2-4) (b) is pH dependent (figures 2-2-5 and 2-2-6 and table 2-2-1) (c) has a certain dependence, at present only partially investigated, on the total carbon:hydrogen peroxide ratio (table 2-2-1).

(a) Time Dependence. Most of the measurements were made on solution 0.1 M in total carbon concentration and 4.4 M in hydrogen peroxide at 20°C; ^{13}C spectra were recorded every five minutes after two minutes of data accumulation. The $\text{CO}_3^{2-}/\text{HCO}_3^-$ peaks, of course, appear immediately but the 'percarbonate' peak near 161 ppm grows slowly (relative to the $\text{CO}_3^{2-}/\text{HCO}_3^-$ peak), reaching an apparent equilibrium after about forty minutes (see figure 2-2-4). Although rate plots were made and it appeared that the reaction was pseudo-first order in $\text{HCO}_3^-/\text{CO}_3^{2-}$, we have not established that the apparent equilibrium reached is a true one, i.e., no long term studies on the stability of the species have been carried out (due to shortage of time available on the n.m.r. instrument).

Figure 2-2-4. Change in integral (proportional to concentration) of percarbonate. ^{13}C n.m.r. resonance with time at pH = 7.6.



Chemical
shift of
percarbonate
(ppm)

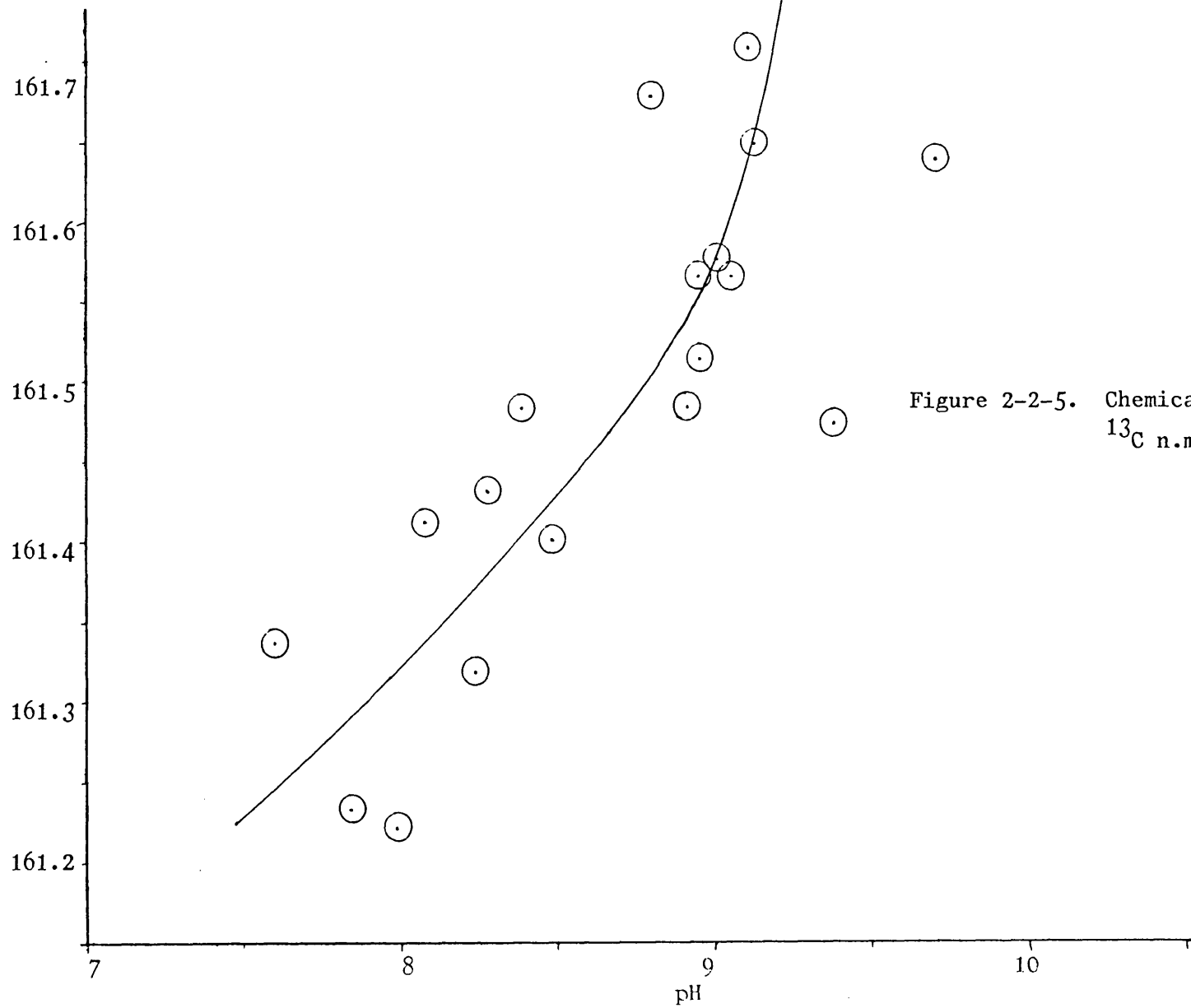


Figure 2-2-5. Chemical shift of percarbonate
 ^{13}C n.m.r. resonance versus pH.

Concentration
of percarbonate
 mol dm^{-3}

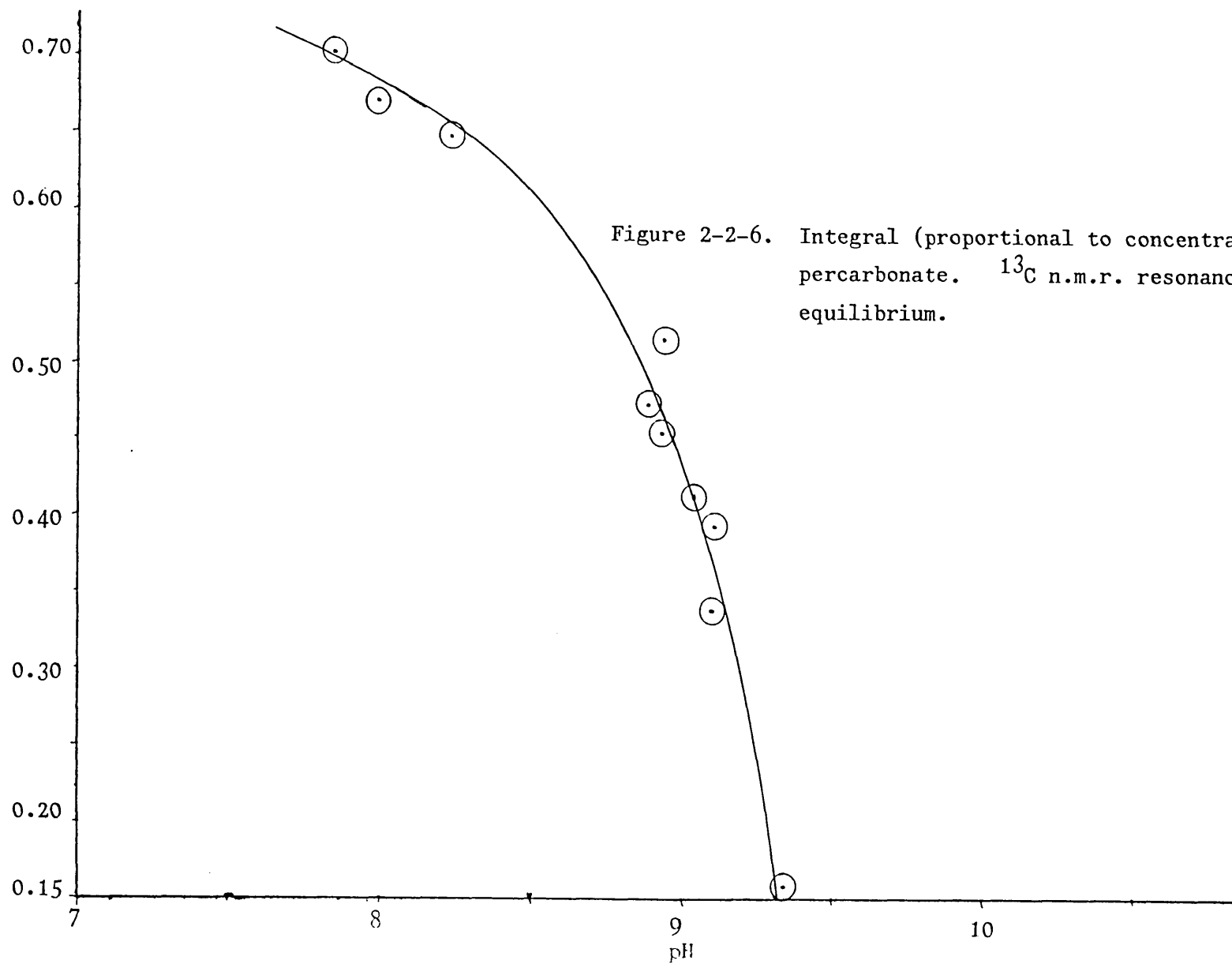


Table 2-2-1. ^{13}C n.m.r. data for the $\text{HCO}_3^-/\text{CO}_3^{2-}/\text{H}_2\text{O}$ system.

Total C moles dm^{-3}	H_2O_2 moles dm^{-3}	CHEMICAL SHIFT		pH	$[\text{H}^+]$ mol dm^{-3}	CONCENTRATION	
		$\text{CO}_3^{2-}/\text{HCO}_3^-$ ppm	percarb. ppm			$\text{CO}_3^{2-}/\text{HCO}_3^-$ mol dm^{-3}	percarb. mol dm^{-3}
0.1+0.01	4.4	162.94	161.26	7.8(5)	1.41×10^{-8} 1.0×10^{-8}	0.031	0.069
0.1	4.4	163.01	161.23			0.032	0.068
0.1	4.4	163.10	161.22			0.035	0.065
0.1	4.4	163.48	161.31			0.035	0.065
0.1	4.4	163.58	161.33	8.2(5)	5.62×10^{-9}	0.032	0.068
0.1	4.4	163.72	161.31			0.037	0.063
0.1	4.4	163.83	161.31			0.036	0.064
0.1	4.4	164.15	161.36			0.033	0.067
0.1	4.4	165.06	161.51	8.9(5)	1.12×10^{-9} 1.23×10^{-9}	0.040	0.060
0.1	4.4	165.51	161.55			0.050	0.050
0.1	4.4	166.22	161.50			0.056	0.044
0.1	4.4	166.25	161.49			0.054	0.046
0.1	4.4	166.66	161.55	9.0(5)	8.91×10^{-10} 7.59×10^{-10}	0.060	0.040
0.1	4.4	167.19	161.63			0.062	0.038
0.1	4.4	167.40	161.69			0.067	0.033
0.1	4.4	167.92	161.78			0.084	0.016

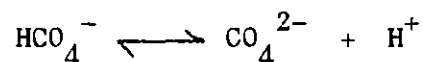
/continued.....

Table 2-2-1 (continued)

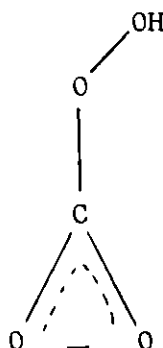
Total C moles dm ⁻³	H ₂ O ₂ moles dm ⁻³	CHEMICAL SHIFT		pH	[H ⁺] mol dm ⁻³	CONCENTRATION	
		CO ₃ ²⁻ / HCO ₃ ⁻ ppm	percarb. ppm			CO ₃ ²⁻ / HCO ₃ ⁻ mol dm ⁻³	percarb. mol dm ⁻³
0.2±0.01	4.4	163.35	161.33	7.6	2.51 x 10 ⁻⁸	0.075	0.125
0.201	4.4	167.01	161.75	9.2	6.31 x 10 ⁻¹⁰	0.13	0.071
0.24	4.4	165.99	161.56	9.0	1.0 x 10 ⁻⁹	0.131	0.109
0.28	4.4	166.52	161.62	9.7	2.0 x 10 ⁻¹⁰	0.231	0.049
0.31	3.73	166.16	161.66	8.8	1.58 x 10 ⁻⁹	0.165	0.143
0.32	4.4	165.24	161.46	9.4	3.98 x 10 ⁻¹⁰	0.178	0.141
0.38	4.4	164.35	161.39	8.5	3.16 x 10 ⁻⁹	0.164	0.216
0.38	4.4	165.07	161.47	8.9	1.26 x 10 ⁻⁹	0.214	0.166
0.398	4.4	163.93	161.40	8.1	7.94 x 10 ⁻⁹	0.164	0.234
0.398	4.4	164.32	161.58	7.2-8.2	6.3 x 10 ⁻⁹	0.191	0.207
0.398	4.4	164.36	161.42	8.3	5.01 x 10 ⁻⁹	0.19	0.208
0.398	4.4	164.40	161.47	8.4	3.98 x 10 ⁻⁹	0.171	0.227

(b) pH Dependence. Variation of pH of the solution (achieved by varying the ratio of carbonate to bicarbonate dissolved while maintaining a constant overall carbon concentration of 0.1 M) affects both the chemical shifts of the 'percarbonate' resonance and its integral relative to those of the $\text{CO}_3^{2-}/\text{HCO}_3^-$ peak; these effects are shown in figures 2-2-5 and 2-2-6 and the data listed in table 2-2-1.

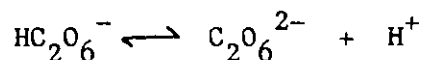
The change in chemical shift with pH suggests that the 'percarbonate' is undergoing rapid protonic exchange, just as in the $\text{CO}_3^{2-}/\text{HCO}_3^-$ system. This could well arise from an equilibrium such as:-



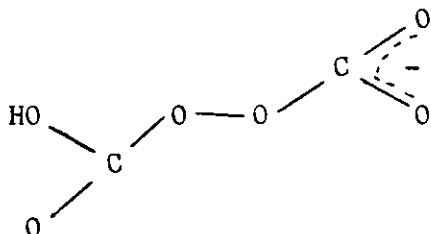
The fact that the actual variation in shift of the 'percarbonate' with pH (ca. 1 ppm for pH 8-9 compared with a shift of ca. 5 ppm for the $\text{CO}_3^{2-}/\text{HCO}_3^-$ system over the same pH range) suggests that the proton is more remote from the carbon atom than in the bicarbonate/carbonate system. Thus, a structure such as:



for HCO_4^- would be consistent with this observation; an equilibrium such as:



would also be possible though in this case a larger shift might be expected since the proton is presumably closer to the carbon nucleus.

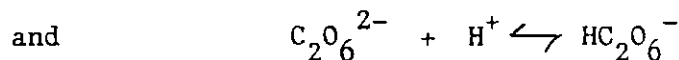
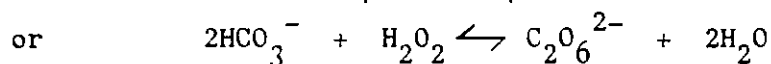
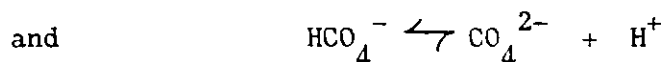
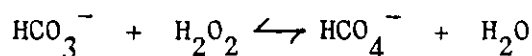


The integral of the 'percarbonate' resonances which we take to be a measure of its relative concentration, is pH dependent (figure 2-2-6 and table 2-2-1). The lowest pH at which the 'percarbonate' peak has been observed was 7.0, below which, because of CO_2 evolution, no reliable data could be obtained; from pH 7.5 to 9.5 the integral of the 'percarbonate' peak drops with increasing pH. Solutions above pH 9.5 are very unstable; extensive bubbling occurs and consequently useful n.m.r. data are then impossible to obtain. Nevertheless, there is no doubt that, with increasing pH, the ratio of 'percarbonate' to $\text{CO}_3^{2-}/\text{HCO}_3^-$ decreases. This observation suggests that the reacting carbon-containing species may be HCO_3^- rather than CO_3^{2-} since, as the pH increases from pH 8.0 (at which bicarbonate is the main species present) the carbonate concentration increases and the bicarbonate concentration decreases; even so, the pK of $\text{CO}_3^{2-}/\text{HCO}_3^-$ is 10.3^{83} so that in our solutions, there is always more bicarbonate than carbonate. The decline of the 'percarbonate' resonance above pH 9.5 may arise from competing decomposition of the species as it approaches its own pK ; it is well known⁸⁵ that organic per-acids tend to decompose near their pK_a values.

(c) Dependence on Carbon:H₂O₂ Ratio. We can offer little information on this since few studies have so far been carried out. The data of table 2-2-1 shows that there is some dependence but not a marked change in 'percarbonate' concentration with the change in this ratio.

Fitting the ¹³C Data.

We have attempted to fit the data of tables 2-2-1 and figures 2-2-3/2-2-6 to possible equilibria and reactions, e.g.,:



These attempts have been unsuccessful; clearly more extensive data are needed. On page 71 we outline the extra studies which should be carried out to help to solve this problem. At this point we note, however, that the ¹³C n.m.r. data are not inconsistent with an equilibrium such as $\text{CO}_4^{2-}/\text{HCO}_4^-$ being responsible for the 'percarbonate' resonance.

(c) Electrochemical Studies.

It has been reported that the polarographic reduction of H₂O₂ in water is affected by the presence of bicarbonate.^{64,65,66} Russian work⁶⁷ has also indicated that freshly prepared solutions prepared from K₂C₂O₆ in water exhibit a shoulder on the wave attributable to hydrogen peroxide. Since the use of carbonate-bicarbonate buffers with hydrogen peroxide is fairly common it is important to know whether there is any chemical interaction between hydrogen peroxide and bicarbonate or

carbonate; our Raman and ^{13}C n.m.r. studies described above indicate that there is such interaction, so we have carried out brief investigations on the electrochemical reduction of $\text{H}_2\text{O}_2/\text{HCO}_3^-$ solutions using first of all conventional polarography with a dropping mercury electrode and also with a rotating disc electrode assembly at which hydrogen peroxide is generated electrochemically.

(i) Polarography. The reduction of hydrogen peroxide in water with 1 M sodium chloride as a base electrolyte has been well studied⁸⁷; thus in 1 M NaCl, 10^{-2} M H_2O_2 gives a single wave at $E_{\frac{1}{2}} = -1.0$ V (vs. standard calomel electrode), see figure 2-2-7. In the absence of hydrogen peroxide, HCO_3^- or CO_3^{2-} in 1 M NaCl produces no reduction wave of their own, but if hydrogen peroxide (10^{-2} M) is added to a solution of 1 M KHCO_3 in 1 M NaCl a small extra wave superimposed on that of hydrogen peroxide itself is observed near $E_{\frac{1}{2}} = -0.4$ V (figure 2-2-8) in agreement with the literature.⁶⁶ Increasing the concentration of bicarbonate increases the height of the extra wave but the change is difficult to follow because the wave is obscured by that of hydrogen peroxide. We decided therefore to attempt a different electrochemical approach to the problem.

(ii) Rotating Ring/Disc Studies. Qualitative results have also been observed electrochemically using a rotating ring/disc electrode system. The theory behind this technique has been reported elsewhere⁸⁸ but generally it can be used in a similar way to polarography and can give information relating to the concentration of hydrogen peroxide in a solution. Using this apparatus it is possible to make hydrogen peroxide electrochemically

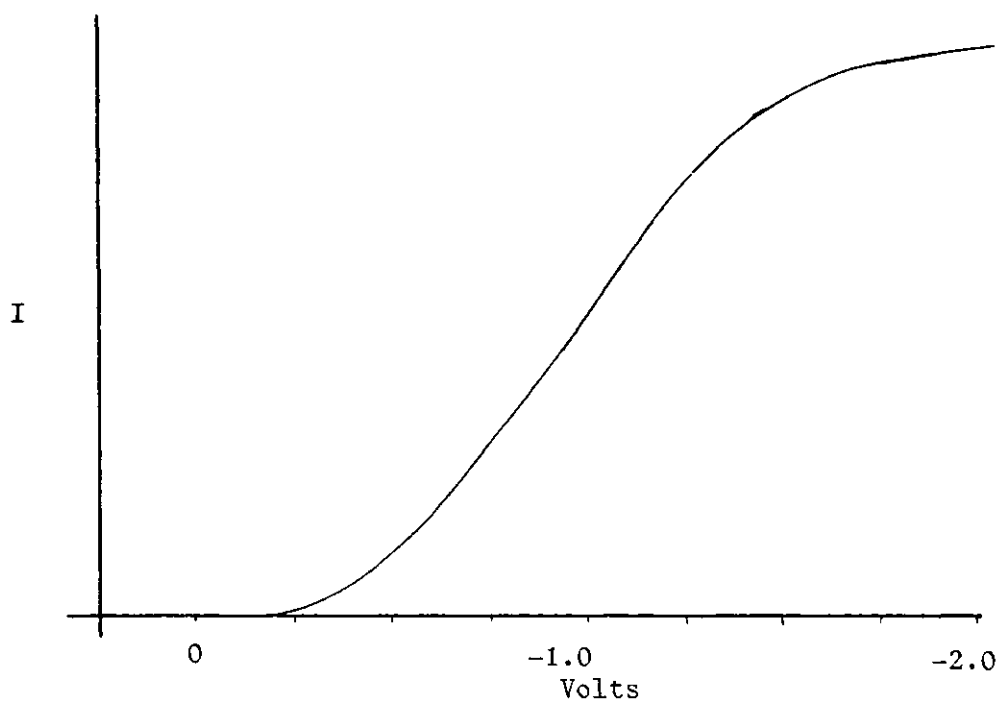


Figure 2-2-7. Polarogram of 10^{-2} M H_2O_2 in 1 M NaCl.

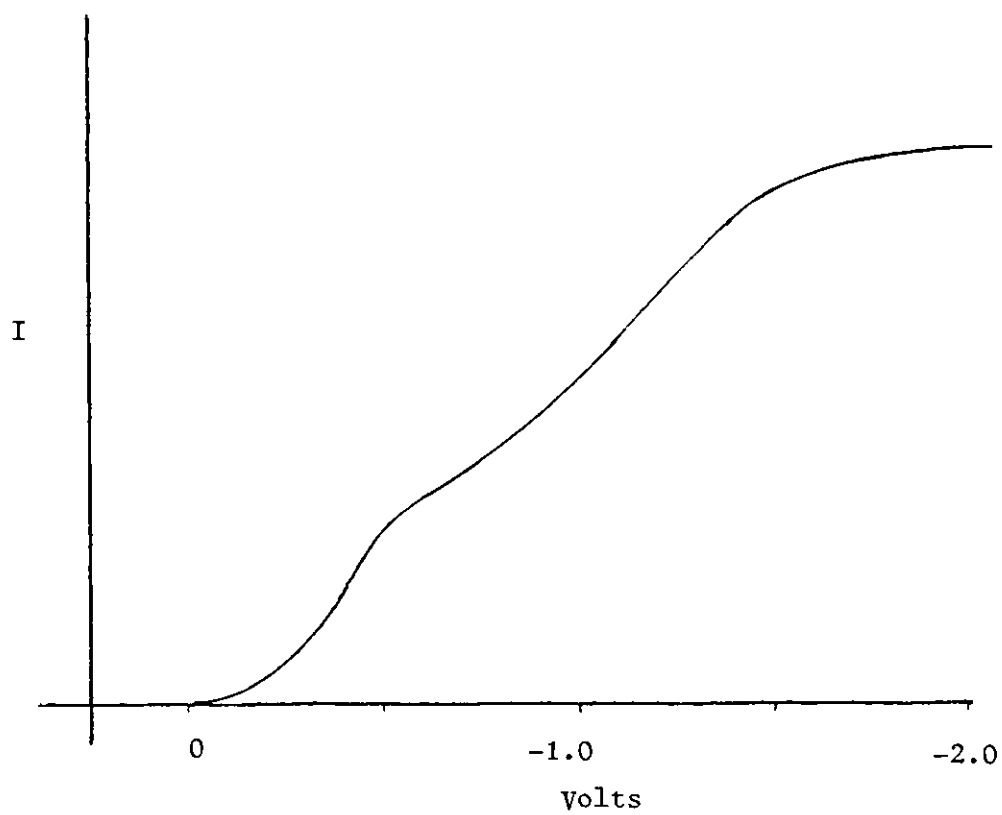
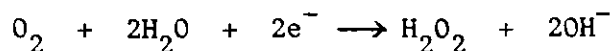


Figure 2-2-8. Polarogram of 10^{-2} M H_2O_2 in 1 M KHCO_3 /1 M NaCl.



and then to monitor the concentration of hydrogen peroxide actually present in the solution.

In standard 'blank' electrolyte, 0.1 M NaClO_4 (saturated with oxygen), the full amount of hydrogen peroxide produced is detected at the ring. However, if HCO_3^- is added to the blank electrolyte the amount of hydrogen peroxide detected is reduced. This indicates that some hydrogen peroxide produced is scavenged before it can be detected. Qualitative results have shown that increasing the bicarbonate concentration increases the amount of hydrogen peroxide scavenged, i.e., less hydrogen peroxide is detected. It also seems that at lower pH values in the range $7 < \text{pH} < 9$ again more hydrogen peroxide is scavenged. These observations compare well with those for ^{13}C n.m.r. spectroscopy (see above). Figure 2-2-9 shows the rotating ring/disc electrode.

The major problem associated with both electrochemical techniques is that they are too sensitive and tend to give inconsistent results. Metal catalysed decomposition may be the root cause of any inconsistency as metal contact cannot be avoided. Both electrochemical techniques rely on metal contact; mercury in the case of polarography and platinum for the rotating ring/disc electrode technique.

SECTION 2-3. CONCLUSIONS

(a) Nature of the 'percarbonate' species. The Raman, ^{13}C n.m.r. and the electrochemical studies show conclusively that a new species is formed from excess hydrogen peroxide and a carbonate-bicarbonate mixture in aqueous solution. The Raman data provide some evidence for this

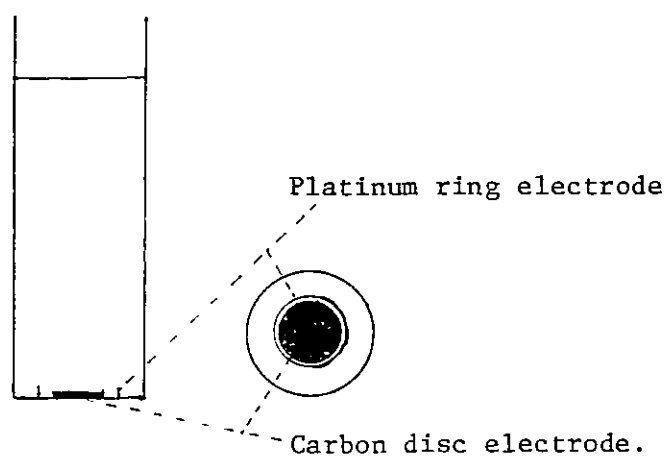
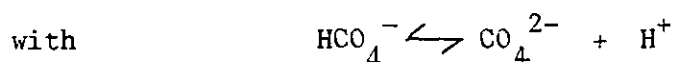
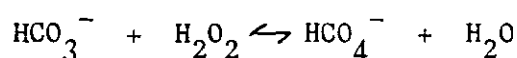


Figure 2-2-9. Rotating Ring/Disc Electrode.

N.B. The electrode is attached to a motor which rotates electrode with constant rotation speed. The spinning electrode is then lowered into the solution to be analysed, together with a Calomel reference electrode and a platinum counter electrode.

being HCO_4^- . The ^{13}C n.m.r. data also suggest the presence of a 'percarbonate' species, probably protonated (HCO_4^-) and show that the rate of its formation is relatively slow.

The fact that the new species is only formed in solutions where the $[\text{HCO}_3^-]$ concentration rather than $[\text{CO}_3^{2-}]$ concentration is high suggests that HCO_3^- is the reacting species and that the overall reaction is



being largely responsible for the observed change in chemical shift of the ^{13}C 'percarbonate' resonance with pH. The probability of attack by OOH^- , good nucleophile though it is, seems unlikely since both it and HCO_3^- bear similar charges and at the pH range 7-10 the amount of OOH^- present will be very low (pK for $\text{H}_2\text{O}_2 = 11.6^{89}$). Although nucleophilic attack by OOH^- has been observed at pH as low as 3,^{90,91} such attack has been on neutral, not negatively charged species.

(b) Further work. Further work on the system is clearly necessary; it has not been possible in this study to obtain sufficient time on our new multinuclear n.m.r. machine to carry out all the work that we would have wished. Possible lines of approach would be:

(i) study of the rate of formation of the new species with respect to pH, total carbon concentration and H_2O_2 concentration, using ^{13}C n.m.r.;

(ii) similar studies of the apparent rates of decomposition of the species (our present data, because of its incompleteness and inexactitude, can not tell us whether we are observing, in plots such as figure 2-2-4, a true equilibrium);

(iii) the use of sequestering agents (such as "Dequest") which stabilises aqueous hydrogen peroxide; it is possible that difficulty in observing 'percarbonate' above pH 9.5 is at least partly due to trace-metal catalysed decomposition of hydrogen peroxide;

(iv) study of the ^{13}C n.m.r. spectra of freshly prepared solutions made up from pure $\text{NaH}^{13}\text{CO}_4$ and $\text{Na}_2^{13}\text{C}_2\text{O}_6$, again as a function of pH time, and carbon and hydrogen peroxide concentrations.

(v) Extension of the vibrational spectroscopic work. It should be possible to monitor the formation of the 'percarbonate' by infrared (e.g., in the $1000\text{--}1600\text{ cm}^{-1}$ region using BaF_2 plates) using a low temperature cell. Raman data could also be extended by using greater pH variation, ^{13}C and ^2H substitution;

(vi) the use of differential scanning polarography should allow a more precise measurement of the 'percarbonate' wave in hydrogen peroxide/bicarbonate solutions.

C H A P T E R T H R E E

SALTS OF 2-CARBOXYLATO-MONOPERBENZOIC ACID

As mentioned previously, the two most important industrial bleaching agents currently used in washing powders are sodium "percarbonate" ($\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$) and sodium "perborate" ($\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$). As part of our chemical and structural studies^{9,49,51} on these and related compounds, in this chapter we report the structural characterisation of a novel bleaching agent, 'MMPP' ($[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_5\text{O}_5)_2$), first prepared by Interlox Chemicals Ltd.⁹² This salt, which is now being produced on an industrial scale for incorporation into washing powder, is very stable. In order to discover any structural reasons for this stability, attempts were made to prepare crystalline analogues. As a result, the single-crystal X-Ray structure of the potassium salt of 2-carboxylato-monoperbenzoic acid is also reported in this chapter.

SECTION 3-1. CRYSTAL STRUCTURE OF HEXA-AQUOMAGNESIUM(II) BIS(2-CARBOXYLATO-MONOPERBENZOIC ACID) $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_8\text{H}_5\text{O}_5)_2$.

The present study was undertaken to establish the stoichiometry and structure of the title compound.

The colourless plate-like crystals used in this study were prepared by a modification of the published^{92,93} procedure. A dry mixture of magnesium oxide (4.0 g, 0.1 moles) and phthalic anhydride (30 g, 0.2 moles) was slowly added to aqueous 30% w/v hydrogen peroxide solution (12.5 cm³, 0.1 moles) and the temperature was kept below 15°C at all times. The resulting mixture was filtered, washed with ethyl acetate and dichloromethane and then dried in air. (Found: C, 38.9; H, 4.5; O₂²⁻, 12.9%. C₁₆H₂₂MgO₁₆ requires C, 38.85; H, 4.48; O₂²⁻, 12.94%). Accurate unit-cell dimensions were obtained by a least-squares calculation based on 16 reflections measured on a Nicolet R3m diffractometer.

Crystal Data

C₁₆H₂₂MgO₁₆, M = 494.65, monoclinic, a = 13.053(3), b = 5.375(1), c = 14.931(2) Å, β = 90.44(2)°, (at 18°C), U = 1047.6(3) Å³, Z = 2, F(000) = 591.95, space group P2₁/a (No. 14), Cu-K_α radiation λ = 1.5418 Å, μ(Cu-K_α) = 17.5 cm⁻¹.

A crystal of size 0.2 x 0.1 x 0.05 mm was chosen for the study. The ω scan technique was used and a total of 1083 independent reflections were measured to θ = 50°, of which 276 were judged to be "unobserved" (I < 3σ(I)). The 0,0,3 and $\bar{1}$,1,1 reflections were monitored as reference reflections every 50 reflections and their net counts did not alter noticeably over the period of data collection (ca. 27 hours). The data were scaled by use of these reference reflections. Program system SHELXTL²² was used throughout for the solution and refinement of the structure, calculations being carried out on a Data General Eclipse S140 computer.

Locations of all the independent atoms, apart from hydrogen atoms, were found by direct methods and several cycles of isotropic refinement with these atoms gave R = 0.12. A further few cycles of refinement with all these atoms anisotropic gave R = 0.085. The subsequent difference

Fourier synthesis showed the possible locations of all the hydrogen atoms except for one of the hydrogen atoms on one of the molecules of water of crystallisation. After a weighting scheme of the type, $w = 1/(\sigma^2|F| + |g|F^2)$, g set at 0.0005, was applied, further refinement allowing g to refine resulted in R of 0.052 with the difference Fourier synthesis showing the positions of all the remaining independent hydrogen atoms. When the hydrogen atoms were included in the subsequent refinement, with all non-hydrogen atoms anisotropic, R reached the final value of 0.049. Table 3-1-1 lists the final atomic fractional coordinates, table 3-1-2 lists the atom temperature factors and table 3-1-3 lists the bond lengths and bond angles, including the coordination about the magnesium atom.

DISCUSSION

The crystal structure consists of magnesium atoms on centres of symmetry, each surrounded by six water molecules to give an octahedral coordination geometry. The other components in the structure are the 2-carboxylato-monoperbenzoic acid anions; there are two such anions per magnesium atom. The three-dimensional packing of these entities can be seen in the stereoscopic drawing figure 3-1-1.

The mean distance between the magnesium atoms and the coordinated oxygen atoms of the water molecules is $2.071\text{\AA}$ (range $2.039(4)$ to $2.106(\text{\AA})$), while the mean O-Mg-O cis angle is 90° (range $87.7(2)$ to $92.3(2)^\circ$). In the anions the bond lengths and angles compare well with the limited structural data available^{86,94,95} on peroxycarboxylic acids. In the 2-carboxylato moiety the two C-O distances are very similar to each other with a mean of $1.260\text{\AA}$ and the mean angle between them of O20-C21-O21 is $122.7(5)^\circ$. In the peroxycarboxylic group the O11-O12 peroxy bond distance is $1.442(5)\text{\AA}$, while the C11-O11 distance ($1.347(6)\text{\AA}$) is longer than the C-O (terminal) distance (C11-O10 distance of $1.207(7)\text{\AA}$).

Table 3-1-1
Fractional Atom Coordinates for MMPP with Estimated
Standard Deviations in Parentheses.

Atom	x	y	z
Mg(1)	1.0000	1.0000	0.5000
C(1)	0.6287(3)	1.0631(9)	0.1681(3)
C(2)	0.7138(3)	1.1305(9)	0.2187(3)
C(3)	0.7740(4)	1.3293(10)	0.1903(3)
C(4)	0.7502(4)	1.4560(11)	0.1132(4)
C(5)	0.6665(4)	1.3926(10)	0.0632(3)
C(6)	0.6059(4)	1.1940(10)	0.0894(3)
C(11)	0.5670(4)	0.8483(11)	0.1944(4)
C(21)	0.7475(4)	1.0020(10)	0.3027(3)
O(10)	0.5826(3)	0.7217(7)	0.2599(3)
O(11)	0.4881(3)	0.8087(7)	0.1375(2)
O(12)	0.4368(3)	0.5758(7)	0.1541(3)
O(20)	0.7060(2)	1.0553(7)	0.3764(2)
O(21)	0.8225(2)	0.8562(7)	0.2969(2)
O(1)	1.1387(3)	0.7997(8)	0.5008(3)
O(2)	0.9294(3)	0.7111(7)	0.4361(3)
O(3)	1.0318(3)	1.1614(8)	0.3775(3)
H(3)	0.833	1.378	0.225
H(4)	0.793	1.591	0.094
H(5)	0.650	1.485	0.010
H(6)	0.548	1.146	0.053
H(120)	0.402(4)	0.643(11)	0.203(4)
H(11)	1.195(4)	0.843(12)	0.541(4)
H(12)	1.157(4)	0.730(9)	0.457(3)
H(21)	0.883(4)	0.740(10)	0.384(4)
H(22)	0.938(5)	0.569(9)	0.452(5)
H(31)	1.028(5)	1.063(14)	0.327(5)
H(32)	1.091(5)	1.228(12)	0.394(4)

NB: Where no e.s.d. atoms have been fixed.

Table 3-1-2
Temperature Factors ($\text{\AA}^2 \times 10^3$) For MMPP with Estimated Standard
Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg(1)	35(1)	26(1)	27(1)	3(1)	5(1)	-2(1)
C(1)	33(3)	24(3)	24(3)	4(3)	9(2)	1(3)
C(2)	32(3)	22(3)	28(3)	4(3)	12(2)	3(3)
C(3)	42(3)	35(4)	33(3)	1(3)	4(3)	-2(3)
C(4)	51(4)	33(4)	39(3)	6(3)	13(3)	-7(3)
C(5)	66(4)	25(3)	30(3)	7(3)	9(3)	7(3)
C(6)	48(3)	35(3)	31(3)	-8(3)	1(3)	4(3)
C(11)	37(3)	33(4)	33(3)	1(3)	8(3)	6(3)
C(21)	36(3)	31(3)	30(3)	9(3)	-1(2)	-3(3)
O(10)	56(2)	47(3)	45(2)	10(2)	5(2)	-12(2)
O(11)	39(2)	47(3)	53(2)	5(2)	-6(2)	-12(2)
O(12)	53(2)	48(3)	62(3)	-12(2)	20(2)	-14(2)
O(20)	44(2)	45(3)	23(2)	-3(2)	10(2)	7(2)
O(21)	45(2)	44(3)	37(2)	9(2)	9(2)	17(2)
O(1)	43(2)	53(3)	34(2)	-11(2)	3(2)	8(2)
O(2)	50(2)	27(2)	36(2)	5(2)	-6(2)	-2(2)
O(3)	44(2)	42(2)	30(2)	-6(2)	9(2)	-10(2)
H(3)	$1.2U_{eq}$ C(3)					
H(4)	$1.2U_{eq}$ C(4)					
H(5)	$1.2U_{eq}$ C(5)					
H(6)	$1.2U_{eq}$ C(6)					
H(120)	66(16)					
H(11)	72(20)					
H(12)	35(18)					
H(21)	46(15)					
H(22)	115(32)					
H(31)	95(25)					
H(32)	75(23)					

Table 3-1-3

Bond Lengths (Å) and angles (°) for MMPP with estimated standard deviations in

parentheses. (Hydrogen atoms not included).

Mg(1) Environment (including symmetry related oxygen atoms).

Mg(1)-O(1)	2.106(4)	Mg(1)-O(2)	2.039(4)
Mg(1)-O(3)	2.069(4)	Mg(1)-O(1)'	2.106(4)
Mg(1)-O(2) ^I	2.039(4)	Mg(1)-O(3)'	2.069(4)
O(1)-Mg(1)-O(2)	89.9(2)	O(1)-Mg(1)-O(3)	92.3(2)
O(2)-Mg(1)-O(3)	89.9(2)	O(1)-Mg(1)-O(1)'	180.0
O(2)-Mg(1)-O(1) ^I	90.1(2)	O(3)-Mg(1)-O(1)'	87.7(2)
O(1)-Mg(1)-O(2) ^I	90.1(2)	O(2)-Mg(1)-O(2)'	180.0
O(3)-Mg(1)-O(2) ^I	90.1(2)	O(1)'-Mg(1)-O(2)'	89.9(2)
O(1)-Mg(1)-O(3) ^I	87.7(2)	O(2)-Mg(1)-O(3)'	90.1(2)
O(3)-Mg(1)-O(3) ^I	180.0	O(1)-Mg(1)-O(3)'	92.3(2)
O(3)-Mg(1)-O(3) ^I			

Superscript denotes symmetry operation; I 2-x, 2-y, 1-z

2-Carboxylato-Monoperoxybenzoic Acid Anion.

C(1)-C(2)	1.386(6)	C(1)-C(11)	1.463(7)
C(2)-C(3)	1.394(7)	C(2)-C(21)	1.495(7)
C(3)-C(4)	1.371(7)	C(11)-O(10)	1.207(7)
C(4)-C(5)	1.362(7)	C(11)-O(11)	1.347(6)
C(5)-C(6)	1.387(7)	C(21)-O(20)	1.263(6)
C(1)-C(6)	1.400(7)	C(21)-O(21)	1.257(6)
		O(11)-O(12)	1.442(5)
C(2)-C(1)-C(6)	119.4(4)	C(1)-C(11)-O(10)	124.9(5)
C(1)-C(2)-C(3)	119.0(4)	C(1)-C(11)-O(11)	112.1(4)
C(2)-C(3)-C(4)	120.8(5)	O(10)-C(11)-O(11)	123.0(5)
C(3)-C(4)-C(5)	120.8(5)	C(11)-O(11)-O(12)	112.5(4)
C(4)-C(5)-C(6)	119.7(5)	C(2)-C(21)-O(20)	120.0(4)
C(1)-C(6)-C(5)	120.3(5)	C(2)-C(21)-O(21)	117.0(4)
C(2)-C(1)-C(11)	120.1(4)	O(20)-C(21)-O(21)	122.7(5)
C(6)-C(1)-C(11)	120.5(4)		
C(1)-C(2)-C(21)	124.4(4)		
C(3)-C(2)-C(21)	116.5(4)		

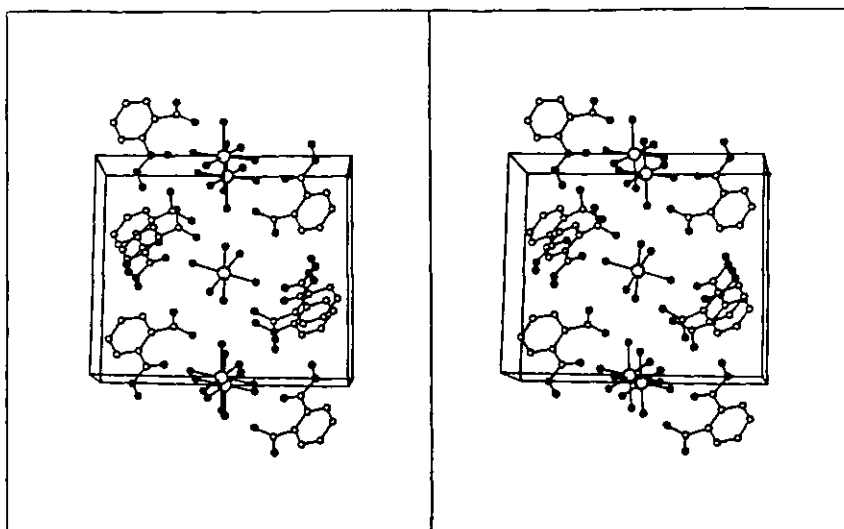
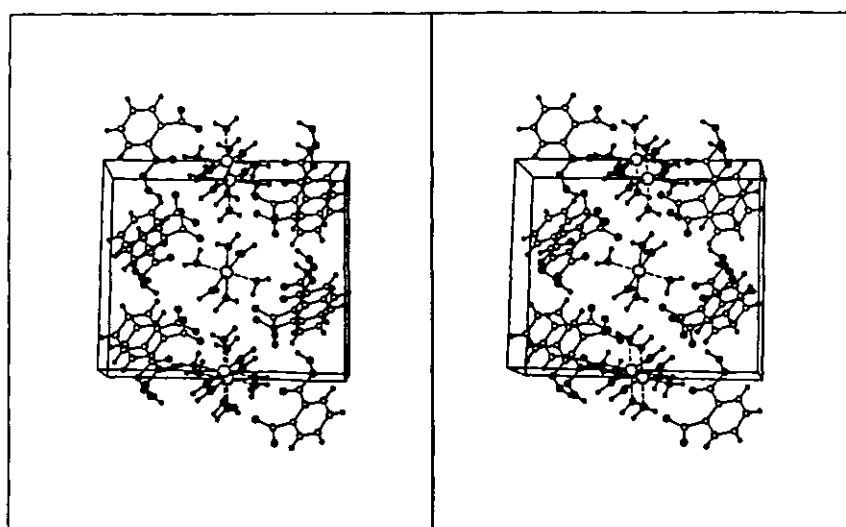


Figure 3-1-1. Two stereoscopic views showing the three-dimensional packing in 'MMPP'.



We have also shown that there is a hydrogen atom attached to the oxygen atom, O12, of the peroxy group with O12-H120 distance of $0.94(5)\text{\AA}$ and O11-O12-H120 angle of $91(3)^\circ$. The carboxylato group lies approximately normal to the plane of the six membered ring (dihedral angle 79.2°), while the peroxydicarboxylic acid group lies approximately within the plane (dihedral angle 8.6°). The torsion angle of the peroxy group is $102(3)^\circ$ which can be compared with the average dihedral angle of other compounds^{26,94,95,96} containing a peroxy group. An important feature of the structure is the network of hydrogen-bonds of the type O-H...O (O...O distances in the range 2.614 to 2.822Å), between the water molecules and oxygen atoms of the anions, and also between the anions themselves, involving the peroxy group hydrogen atoms. From the packing diagram, figure 3-1-1 it can be seen that the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra lie in layers sandwiched between layers of anions. Figure 3-1-2 shows this schematically, with planes A and A' representing layers of anions and the C planes represent layers of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ octahedra. The orientation of the anions within planes A and A' is such that there are interplanar hydrogen bonds between planes A and C and planes A' and C but there are no interplanar hydrogen-bonds between planes A and A'. It is worth noting that there are also hydrogen bonds between adjacent anions of the same layer. The result is that the structure is made up of layers of discrete 'sandwiches', each 'sandwich' containing a set of planes A, C and A' with a "three-dimensional" array of hydrogen bonds within each 'sandwich' but no hydrogen-bonds between one sandwich and the next. The lack of hydrogen-bonds between one 'sandwich' and the next might be expected to cause a weakness in the crystal structure. Figure 3-1-3 is an electron micrograph of a MMPP crystal at 1800 x magnification, showing

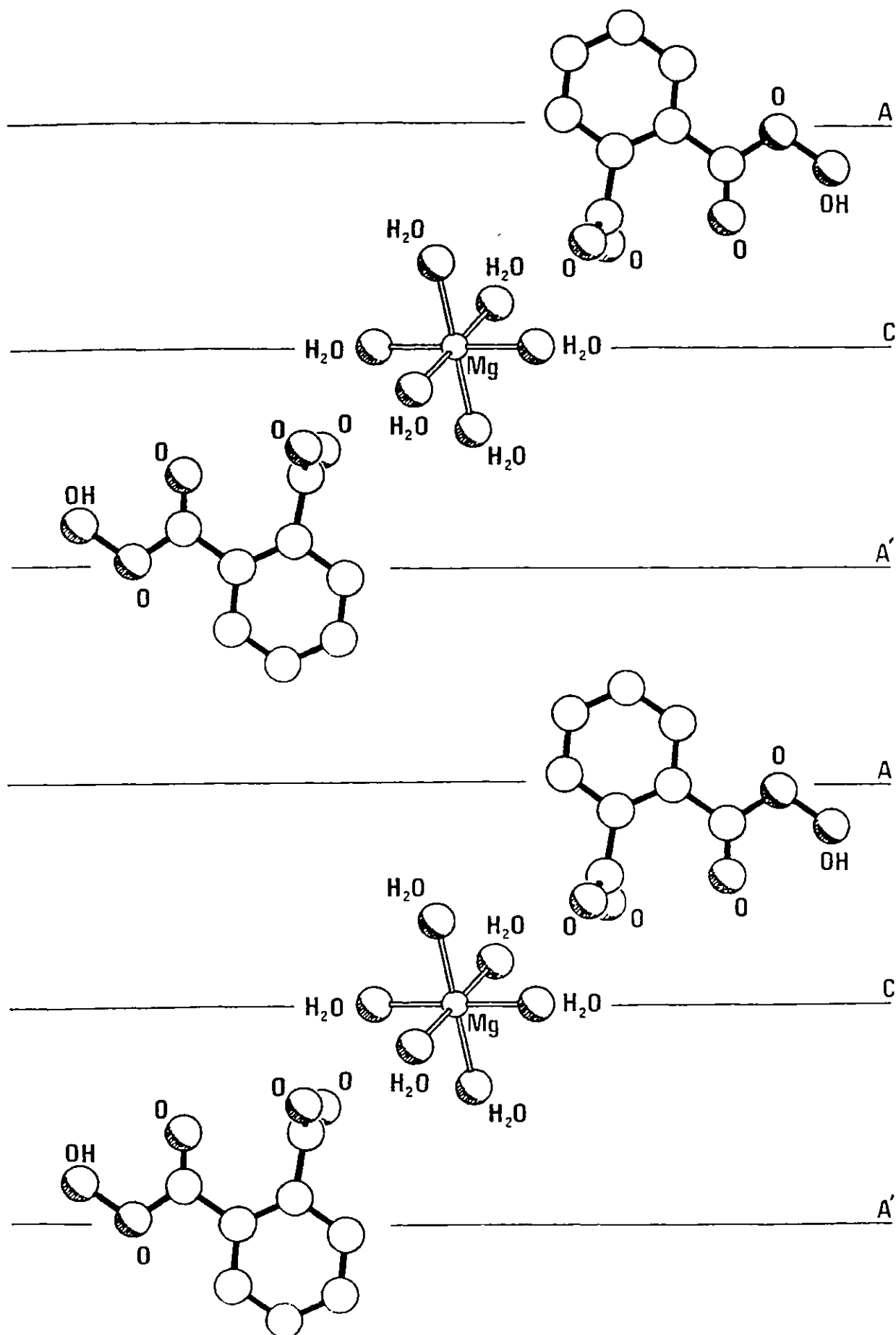


Figure 3-1-2. Schematic drawing of 'MMPP'. Planes A and A' represent layers of anions and C planes represent layers of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra.

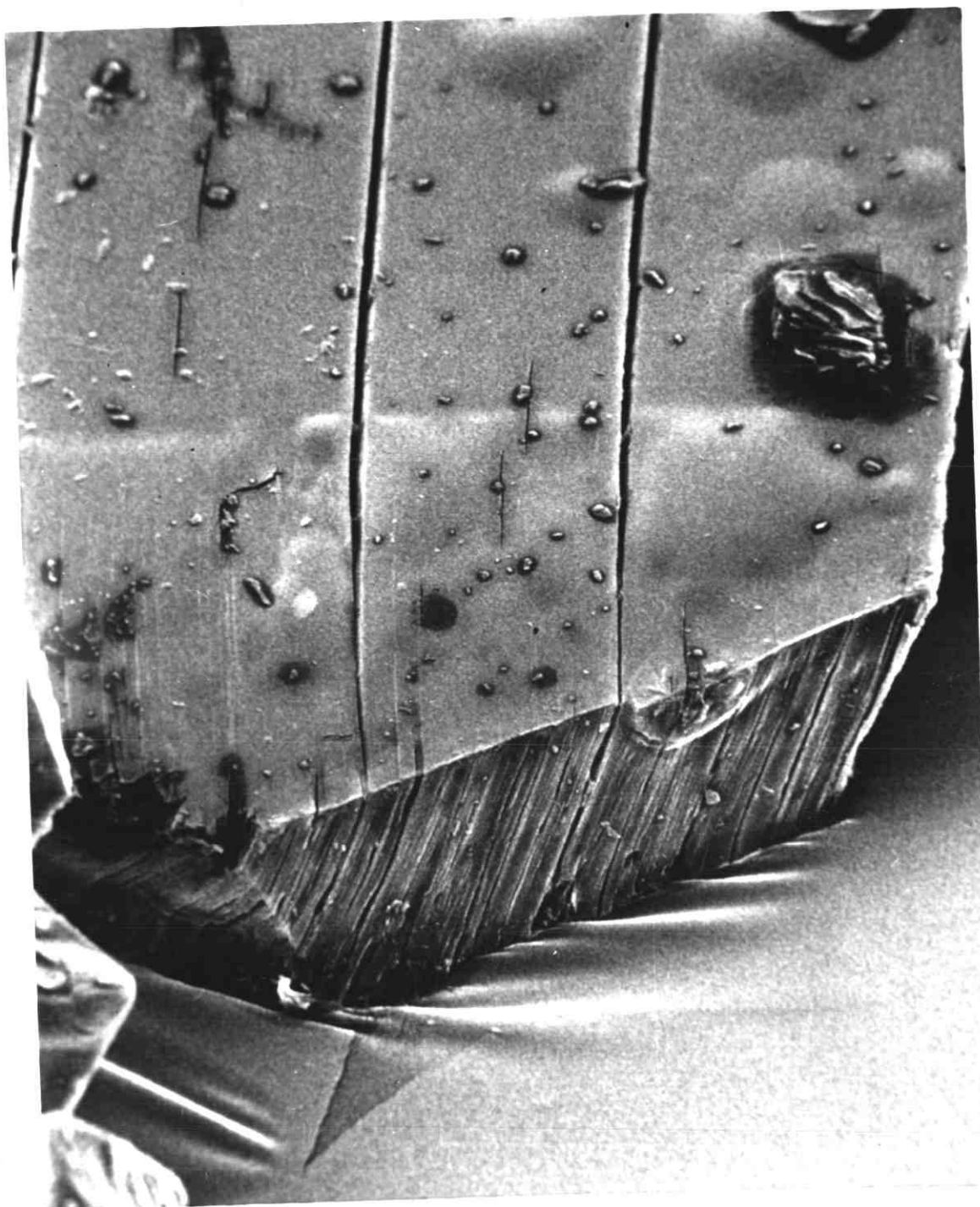


Figure 3-1-3. Electron micrograph of a MMPP crystal at 1800 x magnification, showing the parallel nature of the fractures in the crystal.

Table 3-1-4
Hydrogen-bonding distances (Å) and angles (°) for MMPP.

O(1)...O(20) ^I	2.832	O(1)-H(11)...O(20) ^{II}	175
O(1)...O(20) ^{II}	2.809	O(1)-H(12)...O(20) ^{III}	159
O(2)...O(21)	2.614	O(2)-H(21)...O(21)	166
O(3)...O(10) ^{II}	2.790	O(3)-H(31)...O(10) ^{III}	148
O(3)...O(20) ^{III}	2.737	O(3)-H(32)...O(20) ^{IV}	153
O(12) ^{II} ...O(21)	2.637	O(21) ^{III} -H(120) ^{III} ...O(21)	157

Superscripts denote the following symmetry operations:

I 2-x, 2-y, 1-z

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

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

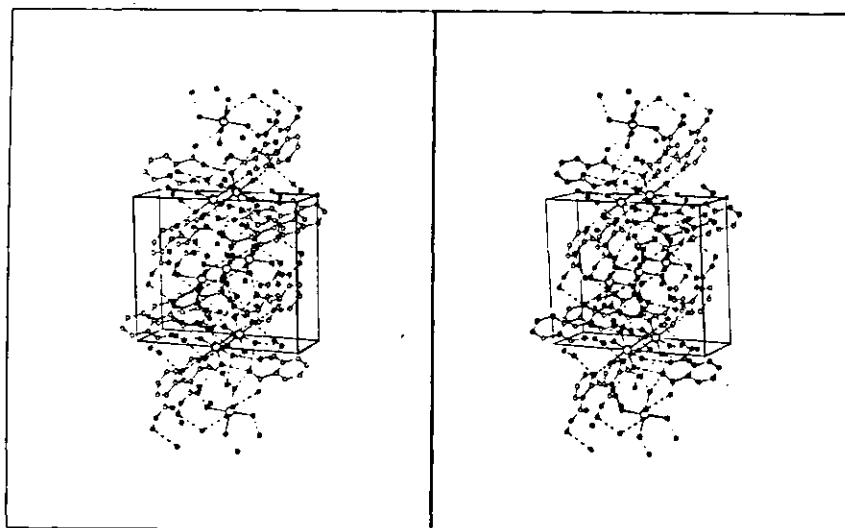


Figure 3-1-4. Stereoscopic view of MMPP showing the extensive hydrogen-bonding.

fractures in the crystal. The parallel nature of the fractures could easily be explained by the crystal fracturing along the planes between each 'sandwich'.

Hydrogen bonding distances and angles are given in table 3-1-4. Figure 3-1-4 shows the hydrogen bonding in the structure, the hydrogen-bonds being represented by dashed bonds.

SECTION 3-2. ANALOGUES OF 'MMPP'.

Further to the structure determination of 'MMPP' attempts were made to prepare analogues of it, consisting of either different cations or different analogous anions, the hope being that the products would form crystals suitable for single-crystal X-ray studies. Table 3-2-1 gives the purity and appearance of the analogues produced. The analogues were prepared by adaptations of the method^{92,93} used to prepare 'MMPP', the main changes in procedure resulting from the differences in the starting materials used with respect to phase and water solubility.

As can be seen from table 3-2-1 only two products consisted of crystalline material and of these only the potassium salt was suitable for single-crystal X-ray studies (see section 3-3). The sodium salt was not suitable because of its microcrystalline nature and its temperature instability.

The preparation of these salts followed one of three different routes (see table 3-2-1):

Method (i) Phthalic anhydride (15.1 g, 0.1 moles) was slowly added to a 15% w/v hydrogen peroxide solution (26 cm³, 0.1 moles) cooling when necessary in order to keep the temperature below 20°C. To this, rather thick, mixture 10 M alkali-metal hydroxide solution (10 cm³, 0.1 moles) was added dropwise, with continual stirring. The products were formed with evolution of heat and simultaneously began to dry out. Water was

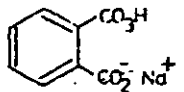
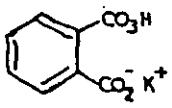
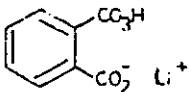
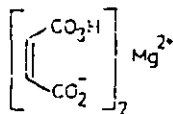
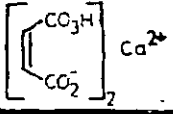
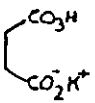
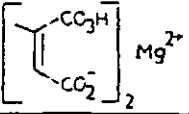
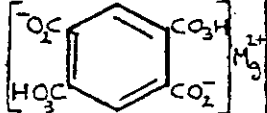
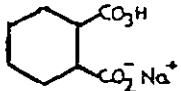
POTENTIAL PRODUCT	ANHYDRIDE USED IN PREPARATION	PURITY	APPEARANCE	METHOD USED
	PHTHALIC	60%	MICRO-CRYSTALLINE	i
	PHTHALIC	90%	VERY CRYSTALLINE	i
	PHTHALIC	50%	POWDERY	ii
	MALEIC	58%	FINE POWDER	ii
	MALEIC	40%	FINE POWDER	ii
	SUCCINIC	NO PRODUCT	FINE POWDER	i
	CITRACONIC	30%	FINE POWDER	iii
	PYROMELLITIC	35%	FINE POWDER	ii
	HEXAHYDRO-PHTHALIC	22%	FINE POWDER	i

Table 3-2-1. Analogues of 'MMPP'

added, when necessary, to keep the products moist while they were forming. The products were filtered, washed with ethyl acetate and then air dried. Sodium and potassium 2-carboxylato-monoperbenzoic acid (i.e., sodium and potassium salts of monoperoxyphthalic acid) were made by this method. Preparations of the potassium salt of monoperoxysuccinic acid and the sodium salt of monoperoxyhexahydrophthalic acid were also carried out using this method. Note, however, that succinic and hexahydrophthalic anhydride respectively were used instead of phthalic anhydride, in these latter preparations

Method (ii) Maleic anhydride (10 g, 0.1 moles) and magnesium oxide (2.1 g, 0.05 moles) were mixed as the dry materials and then added in small portions, with stirring, to a 30% w/v hydrogen peroxide solution (13 cm^3 , 0.1 moles) which was kept below 20°C throughout the addition. The product formed as a thick slurry and was then filtered and washed with ethyl acetate before being air dried. This method yielded the magnesium salt of monoperoxymaleic acid. Calcium carbonate was used instead of magnesium oxide to produce the calcium salt of monoperoxymaleic acid. This method was also used to prepare the lithium salt of monoperoxyphthalic acid and the magnesium salt of monoperoxypyromellitic acid. The lithium salt was made from lithium hydroxide, $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.1 moles) and phthalic anhydride (15.1 g, 0.1 moles); the magnesium salt was made from magnesium oxide (0.1 moles) and pyromellitic anhydride (0.1 moles).

Method (iii) Citraconic anhydride (11.4 g, 0.1 moles) was added dropwise to a 20% w/v hydrogen peroxide solution (22 cm^3 , 0.1 moles). The mixture was stirred very fast in order to form an emulsion of the two immiscible liquids. Magnesium oxide (2.1 g, 0.05 moles) was then added in portions, and during the additions the mix became one phase. After continual

stirring a fine powdery product formed which was filtered, washed with ethyl acetate and air-dried. The resulting product contained approximately 30% of the magnesium salt of monoperoxydicarboxylic acid.

SECTION 3-3. CRYSTAL STRUCTURE OF TRIPOTASSIUM TRIS(2-CARBOXYLATO-MONOPEROXYDICARBOXYLIC ACID) MONOHYDRATE, $K_3(C_8H_5O_5)_3 \cdot H_2O$.

This study was undertaken essentially to highlight the structural factors affecting the stability of 'MMPP'. The white crystals used for the study were prepared as previously mentioned by a modification of the procedure^{92,93} used to prepare 'MMPP'. To a 30% w/v hydrogen peroxide solution (20 cm³) was added phthalic anhydride (0.1 moles, 15.1 g) portionwise, stirring constantly. Potassium hydroxide (5.7 g, 0.1 moles) in water (12 cm³) was then added dropwise, the temperature being kept below 10°C. The resulting solution was left to stand at 20°C for one hour and then slowly cooled to 10°C, the product crystallising out with the cooling. The crystals were filtered off, washed with ethyl acetate and dichloromethane and then dried in air. (Found: C, 42.5; H, 2.6; O₂²⁻, 14.0%. C₂₄H₁₇K₃O₁₆ requires C, 42.47; H, 2.5; O₂²⁻, 14.14%).

Accurate unit-cell dimensions were obtained by a least-squares calculation based on 15 reflections measured on a diffractometer.

Crystal Data.

$K_3H_{17}C_{24}O_{16}$, $M = 678.69$, triclinic, $a = 8.028(1)$, $b = 13.584(2)$, $c = 14.228(2)$ Å, $\alpha = 115.18(1)$, $\beta = 90.63(2)$, $\gamma = 95.50(1)^\circ$ (at 18°C), $U = 1395.3(4)$ Å³, $Z = 2$, $F(000) = 685.95$, space group $P\bar{1}$ (No. 2) Cu-K $_{\alpha}$ radiation $\lambda = 1.5418$ Å, $(Cu-K_{\alpha}) = 51.07$ cm⁻¹.

A crystal of approximate size 0.1 x 0.1 x 0.1 mm was chosen for the study. The ω scan technique was used and a total of 3519 independent reflections were measured to $\theta = 55^\circ$ on a Nicolet R3m diffractometer system. The 0, $\bar{1}$, 1 and 2,0, $\bar{2}$ reflections were monitored as reference

reflections every 50 reflections measured. Their net count did not alter noticeably for the first 2900 reflections but began to decrease for the last 600 reflections measured. Those last 600 reflections were removed and the remaining 2919 reflections, of which 688 were judged to be 'unobserved', were scaled by use of the reference reflections. Program system SHELXTL²² was used throughout for the solution and refinement of the structure, calculations being carried out on a Data General Eclipse S140 computer. Locations of the three independent potassium atoms were found by direct methods and a few cycles of isotropic refinement with these atoms gave $R = 0.56$. The resulting difference Fourier synthesis showed the location of four oxygen atoms and four carbon atoms. Isotropic refinement with these atoms gave $R = 0.49$ and the subsequent difference Fourier synthesis showed up four more oxygen atoms and three more carbon atoms. The difference Fourier synthesis resulting from further isotropic refinement ($R = 0.44$) gave the positions of all the remaining non-hydrogen atoms. However, it was clear that some disorder was associated with the water molecule. Several cycles of isotropic refinement of all non-hydrogen atoms gave $R = 0.136$. Further refinement with all non-hydrogen atoms anisotropic gave $R = 0.085$. After an empirical absorption correction was applied R reached 0.061 on further anisotropic refinement. The resulting difference Fourier synthesis showed one of the hydrogen atom positions. At this point a weighting scheme of the type $w = 1/(\sigma^2|F| + |g|F^2)$ with g allowed to refine from 0.0005, was applied and the subsequent refinement gave $R = 0.059$ with the difference Fourier synthesis showing the remaining peroxy group hydrogen atoms. From this difference Fourier it was possible to see the disorder of the water molecule. To help fully describe the disorder the site occupation factors for the two possible water molecule oxygen atom positions were allowed to refine; this refinement together with all atoms

anisotropic, except for the hydrogen atoms and the oxygen atoms of the disordered water molecule gave $R = 0.055$ and site occupation factors for the disordered water oxygen atoms of 0.72 and 0.28. The difference Fourier synthesis also gave the positions of the remaining hydrogen atoms. When all the independent atoms were included in the next refinement, with all non-hydrogen atoms anisotropic and the site occupation factors of the atoms of the disordered water molecule fixed, R reached its final value of 0.048. It must be noted, however, that from the difference Fourier synthesis of the final refinement it was possible to see some trace of disorder, though not describable, about one of the 2-carboxylato-monoperbenzoic acid anions adjacent to the disordered water molecule. Table 3-3-1 and 3-3-2 lists the final fractional atomic coordinates, table 3-3-3 lists the atom temperature factors and table 3-3-4 lists the bond lengths and bond angles including the hydrogen bonding distances and angles, and the coordination about the potassium atoms.

DISCUSSION

The crystal structure consists of three independent potassium cations, three independent 2-carboxylato-peroxybenzoic acid anions and one independent water molecule. Figures 3-3-1, 3-3-2, and 3-3-3 show the three anions and figure 3-3-4 shows the three-dimensional packing of the structure.

In the anions the bond lengths and angles agree well with the literature^{94,95} and with those found for 'MMPP'. As is the case with 'MMPP' in the carboxylato moieties the two C-O distances are very similar to each other with a mean distance of $1.254\text{\AA}$ and a mean O-C-O angle of 125.9° . In the peroxy acid group the mean O-O peroxy distance is $1.453\text{\AA}$.

Table 3-3-1

Fractional Atom Coordinates for KMPP with Estimated Standard Deviations
 Parentheses (Non-Hydrogen Atoms).

Atom	x	y	z
K(1)	0.5302(2)	-0.1923(1)	0.2283(1)
K(2)	-0.0163(2)	0.2734(1)	0.7191(1)
K(3)	0.2499(2)	-0.0008(1)	0.4990(1)
C(11)	0.5625(7)	0.2339(4)	0.3952(4)
C(12)	0.6071(7)	0.2843(4)	0.5018(4)
C(13)	0.6838(8)	0.3907(4)	0.5464(5)
C(14)	0.7084(9)	0.4482(5)	0.4863(5)
C(15)	0.6600(9)	0.4009(5)	0.3834(5)
C(16)	0.5898(8)	0.2939(4)	0.3370(4)
C(111)	0.4968(7)	0.1169(4)	0.3454(4)
C(121)	0.5610(10)	0.2280(4)	0.5713(4)
O(110)	0.5206(5)	0.0494(3)	0.3768(3)
O(111)	0.4035(5)	0.0940(3)	0.2579(3)
O(112)	0.3548(6)	-0.0225(3)	0.2001(3)
O(120)	0.6777(5)	0.2107(3)	0.6192(3)
O(121)	0.4078(5)	0.2042(3)	0.5784(3)
C(21)	0.4190(9)	0.5737(5)	0.8972(4)
C(22)	0.3580(8)	0.6703(4)	0.9669(4)
C(23)	0.4449(10)	0.7702(5)	0.9803(5)
C(24)	0.5906(11)	0.7740(7)	0.9283(6)
C(25)	0.6483(11)	0.6798(10)	0.8628(7)
C(26)	0.5658(11)	0.5805(7)	0.8470(5)
C(211)	0.3404(10)	0.4644(5)	0.8730(5)
C(221)	0.2030(9)	0.6748(4)	1.0270(5)
O(210)	0.3450(9)	0.3852(4)	0.7883(4)
O(211)	0.2630(6)	0.4564(3)	0.9503(4)
O(212)	0.1914(7)	0.3427(3)	0.9170(4)
O(220)	0.0647(6)	0.6411(4)	0.9737(3)
O(221)	0.2236(6)	0.7121(4)	1.1215(3)
C(31)	0.0073(7)	-0.1568(4)	0.6848(4)
C(32)	0.0511(7)	-0.0463(4)	0.7492(4)
C(33)	0.1123(8)	-0.0148(5)	0.8496(4)
C(34)	0.1198(9)	-0.0920(6)	0.8884(5)
C(35)	0.0713(9)	-0.2004(6)	0.8266(5)
C(36)	0.0155(8)	-0.2338(5)	0.7252(5)
C(311)	-0.0465(7)	-0.1913(4)	0.5740(4)
C(321)	0.0322(7)	0.0420(4)	0.7115(4)
O(310)	-0.0086(5)	-0.1420(3)	0.5229(3)
O(311)	-0.1482(5)	-0.2864(3)	0.5372(3)
O(312)	-0.1886(6)	-0.3283(3)	0.4267(3)
O(320)	-0.1172(5)	0.0557(3)	0.6951(3)
O(321)	0.1598(5)	0.0945(3)	0.7022(3)
O(1)	0.0140(12)	0.5035(6)	0.2396(7)
O(2)	0.8995(25)	0.4740(14)	0.8089(15)

Table 3-3-2

Fractional atomic coordinates and isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for KMPP with estimated standard deviations in parentheses (hydrogen atoms).

Atom	x	y	z	U
H13	0.7199(8)	0.4247(4)	0.6188(5)	67
H14	0.7603(9)	0.5224(5)	0.5178(5)	84
H15	0.6749(9)	0.4423(5)	0.3431(5)	80
H16	0.5592(8)	0.2601(4)	0.2638(4)	64
H112	0.247(5)	-0.029(6)	0.229(5)	93
H23	0.4037(10)	0.8373(5)	1.0261(5)	80
H24	0.6496(12)	0.8432(7)	0.9391(6)	102
H25	0.7481(11)	0.6826(10)	0.8271(7)	119
H26	0.6092(10)	0.5154(7)	0.8008(5)	94
H212	0.1027	0.3487	0.9555	310
H33	0.1498(8)	0.0608(5)	0.8928(4)	73
H34	0.1595(9)	-0.0694(6)	0.9592(5)	86
H35	0.0763(9)	-0.2532(6)	0.8545(5)	83
H36	-0.0179(8)	-0.3099(5)	0.6821(5)	65
H312	-0.261(7)	-0.276(4)	0.431(5)	88
H1	-0.071(10)	0.483(8)	0.277(6)	101
H2	-0.021(12)	0.457(7)	0.170(3)	101
H3	0.897(34)	0.496(16)	0.753(10)	75
H4	0.941(26)	0.539(9)	0.867(9)	75

NB. Where no e.s.d. the variable has been fixed.

Table 3-3-3.

Anisotropic temperature factors ($\text{\AA}^2 \times 10^2$) for KMPP with estimated standard deviations in parentheses (non-hydrogen atoms).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	60(1)	48(1)	42(1)	18(1)	-7(1)	-2(1)
K(2)	63(1)	37(1)	54(1)	15(1)	-11(1)	-1(1)
K(3)	51(1)	22(1)	36(1)	12(1)	-5(1)	0(1)
C(11)	36(4)	38(3)	47(3)	21(3)	0(3)	3(3)
C(12)	39(4)	34(3)	48(3)	18(3)	1(3)	4(3)
C(13)	72(5)	26(3)	56(4)	16(3)	-8(3)	-7(3)
C(14)	91(6)	42(3)	76(5)	29(3)	3(4)	-10(4)
C(15)	89(6)	57(4)	73(5)	44(4)	11(4)	5(4)
C(16)	69(5)	51(4)	47(3)	28(3)	-1(3)	1(3)
C(111)	47(5)	41(3)	32(3)	15(2)	3(3)	10(3)
C(121)	66(6)	19(3)	24(3)	0(2)	-5(3)	5(3)
O(110)	65(3)	33(2)	44(2)	13(2)	-11(2)	4(2)
O(111)	71(3)	49(2)	39(2)	16(2)	-14(2)	-4(2)
O(112)	71(4)	51(2)	43(2)	6(2)	-6(2)	-8(2)
O(120)	60(3)	46(2)	47(2)	22(2)	-8(2)	6(2)
O(121)	46(3)	37(2)	46(2)	20(2)	-1(2)	-6(2)
C(21)	64(6)	55(4)	40(3)	15(3)	-8(3)	1(3)
C(22)	64(5)	44(3)	35(3)	14(3)	-17(3)	-3(3)
C(23)	97(7)	60(4)	44(4)	27(3)	-16(4)	-11(4)
C(24)	94(8)	98(6)	65(5)	46(5)	-24(5)	-33(5)
C(25)	84(8)	152(9)	78(6)	72(6)	-2(5)	-27(7)
C(26)	74(7)	111(6)	53(4)	34(4)	12(4)	24(5)
C(221)	112(7)	53(4)	56(4)	20(4)	-18(4)	14(4)
C(221)	64(6)	39(3)	52(4)	17(3)	0(4)	-1(3)
O(210)	17(6)	61(3)	80(4)	-8(3)	17(4)	12(3)
O(211)	113(4)	44(2)	61(3)	19(2)	-19(3)	-17(2)
O(212)	116(5)	51(3)	82(3)	18(2)	-11(3)	8(3)
O(220)	67(4)	91(3)	58(3)	39(2)	-9(2)	-2(3)
O(221)	77(4)	93(3)	35(2)	4(2)	-2(2)	-7(3)
C(31)	32(4)	46(3)	49(3)	24(3)	-4(3)	4(3)
C(32)	43(5)	43(3)	42(3)	22(3)	-1(3)	5(3)
C(33)	70(6)	67(4)	45(4)	24(3)	-12(3)	6(4)
C(34)	82(6)	86(5)	56(4)	43(4)	-10(4)	11(4)
C(35)	82(6)	83(5)	72(5)	60(4)	0(4)	13(4)
C(36)	53(5)	55(4)	71(4)	44(3)	3(3)	6(3)
C(311)	45(5)	31(3)	51(3)	20(3)	3(3)	8(3)
C(321)	51(4)	34(3)	27(3)	6(2)	-2(3)	2(3)
O(310)	64(3)	36(2)	39(2)	17(2)	-6(2)	-7(2)
O(311)	74(3)	38(2)	58(3)	24(2)	-14(2)	-11(2)
O(312)	77(4)	37(2)	55(2)	14(2)	-10(2)	5(2)
O(320)	47(3)	41(2)	52(2)	22(2)	-10(2)	0(2)
O(321)	55(3)	42(2)	52(2)	19(2)	1(2)	-6(2)
O(1)	82(9)	55(4)	91(6)	2(4)	-10(5)	2(5)
O(2)	45(15)	62(10)	66(11)	12(8)	1(10)	20(9)

Table 3-3-4.

Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) with Estimated Standard

Deviations in Parentheses.

<u>K(1) Environment</u>			
K(1)-O(121) ^I	2.864(1)	K(1)-O(321) ^I	2.670(1)
K(1)-O(120) ^I	2.831(4)	K(1)-O(110)	3.065(3)
K(1)-O(210) ^I	2.812(1)	K(1)-O(112)	2.977(5)
K(1)-O(221) ^{II}	2.771(1)		
O(121) ^I -K(1)-O(120) ^I	45.9(1)	O(210) ^I -K(1)-O(221) ^{II}	97.5(2)
O(121) ^I -K(1)-O(210) ^I	64.8(1)	O(210) ^I -K(1)-O(321) ^I	86.1(2)
O(121) ^I -K(1)-O(221) ^{II}	117.6(1)	O(210) ^I -K(1)-O(110)	142.6(1)
O(121) ^I -K(1)-O(321) ^I	73.7(1)	O(210) ^I -K(1)-O(112)	166.8(1)
O(121) ^I -K(1)-O(110)	81.0(1)	O(221) ^{II} -K(1)-O(321) ^I	168.7(1)
O(121) ^I -K(1)-O(112)	125.8(1)	O(221) ^{II} -K(1)-O(110)	111.9(1)
O(120) ^I -K(1)-O(210) ^I	86.8(2)	O(221) ^{II} -K(1)-O(112)	71.0(1)
O(120) ^I -K(1)-O(221) ^I	75.7(1)	O(321) ^I -K(1)-O(110)	69.6(1)
O(120) ^I -K(1)-O(321) ^I	115.3(1)	O(321) ^I -K(1)-O(112)	104.0(1)
O(120) ^I -K(1)-O(110)	79.0(1)	O(110)-K(1)-O(112)	50.4(1)
O(120) ^I -K(1)-O(112)	96.2(1)		
<u>K(2) Environment</u>			
K(2)-O(120) ^{III}	2.697(4)		
K(2)-O(231) ^{IV}	2.779(1)	K(2)-O(210)	3.083(1)
K(2)-O(312) ^V	2.954(5)	K(2)-O(321)	2.851(1)
K(2)-O(212)	2.990(6)	K(2)-O(310) ^V	3.152(1)
K(2)-O(320)	2.863(1)	*K(2)-O(1) ^V	2.828(9)
		*K(2)-O(2) ^{III}	2.630(17)
O(120) ^{III} -K(2)-O(221) ^{IV}	77.8(1)	*O(312) ^V -K(2)-O(1) ^V	68.4(2)
O(120) ^{III} -K(2)-O(312) ^V	102.7(1)	*O(312) ^V -K(2)-O(2) ^{III}	91.1(5)
O(120) ^{III} -K(2)-O(212)	148.2(2)	O(212)-K(2)-O(320)	95.6(1)
O(120) ^{III} -K(2)-O(320)	72.7(1)	O(212)-K(2)-O(210)	47.6(2)
O(120) ^{III} -K(2)-O(210)	161.3(2)	O(212)-K(2)-O(321)	72.1(1)
O(120) ^{III} -K(2)-O(321)	113.5(1)	O(212)-K(2)-O(310) ^V	139.8(1)
O(120) ^{III} -K(2)-O(310) ^V	68.6(1)	*O(212)-K(2)-O(1) ^V	88.8(2)
*O(120) ^{III} -K(2)-O(1) ^V	95.1(2)	*O(212)-K(2)-O(2) ^{III}	83.6(5)
"O(120) ^{III} -K(2)-O(2) ^{III}	88.0	O(320)-K(2)-O(210)	122.6(2)

Table 3-3-4 (continued)

$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(312)^{\text{V}}$	162.7(1)	$0(320)\text{-K}(2)\text{-}0(321)$	45.9(1)
$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(212)$	70.4(1)	$0(320)\text{-K}(2)\text{-}0(310)^{\text{V}}$	79.9(1)
$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(320)$	72.2(1)	$*((320)\text{-K}(2)\text{-}0(1))^{\text{V}}$	163.2(2)
$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(210)$	115.7(1)	$*0(320)\text{-K}(2)\text{-}0(2)^{\text{III}}$	141.8(5)
$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(321)$	100.7(1)	$0(210)\text{-K}(2)\text{-}0(321)$	78.1(1)
$0(221)^{\text{IV}}\text{-K}(2)\text{-}0(310)^{\text{V}}$	141.4(1)	$0(210)\text{-K}(2)\text{-}0(310)^{\text{V}}$	101.7(1)
$*0(221)^{\text{IV}}\text{-K}(2)\text{-}0(1)^{\text{V}}$	94.2(2)	$*((210)\text{-K}(2)\text{-}0(1))^{\text{V}}$	71.8(2)
$*0(221)^{\text{IV}}\text{-K}(2)\text{-}0(2)^{\text{III}}$	71.6(5)	$*0(210)\text{-K}(2)\text{-}0(2)^{\text{III}}$	84.5(4)
$0(312)^{\text{V}}\text{-K}(2)\text{-}0(213)$	108.1(1)	$0(321)\text{-K}(2)\text{-}0(310)$	76.8(1)
$0(312)^{\text{V}}\text{-K}(2)\text{-}0(320)$	124.8(1)	$*0(321)\text{-K}(2)\text{-}0(1)^{\text{V}}$	149.9(2)
$0(312)^{\text{V}}\text{-K}(2)\text{-}0(210)$	60.5(1)	$*0(321)\text{-K}(2)\text{-}0(2)^{\text{III}}$	155.6(4)
$0(312)^{\text{V}}\text{-K}(2)\text{-}0(321)$	95.0(1)	$*0(310)^{\text{V}}\text{-K}(2)\text{-}0(1)^{\text{V}}$	106.9(2)
$0(312)^{\text{V}}\text{-K}(2)\text{-}0(310)^{\text{V}}$	49.9(1)	$*0(310)^{\text{V}}\text{-K}(2)\text{-}0(2)^{\text{III}}$	123.9(5)
<u>K(3) Environment.</u>			
$\text{K}(3)\text{-}0(121)$	2.692(1)	$\text{K}(3)\text{-}0(110)$	3.003(4)
$\text{K}(3)\text{-}0(321)$	2.757(1)	$\text{K}(3)\text{-}0(310)$	2.813(1)
$\text{K}(3)\text{-}0(120)^{\text{I}}$	2.749(3)	$\text{K}(3)\text{-}0(11)^{\text{I}}$	2.847(4)
$\text{K}(3)\text{-}0(320)^{\text{V}}$	2.711(1)	$\text{K}(3)\text{-}0(310)^{\text{V}}$	2.972(1)
$0(121)\text{-K}(3)\text{-}0(321)$	75.1(1)	$0(120)^{\text{I}}\text{-K}(3)\text{-}0(110)$	81.4(1)
$0(121)\text{-K}(3)\text{-}0(120)^{\text{I}}$	138.4(1)	$0(120)^{\text{I}}\text{-K}(3)\text{-}0(310)$	73.2(1)
$0(121)\text{-K}(3)\text{-}0(320)^{\text{V}}$	109.9(1)	$0(120)^{\text{I}}\text{-K}(3)\text{-}0(110)^{\text{I}}$	73.6(1)
$0(121)\text{-K}(3)\text{-}0(110)$	62.3(1)	$12120)^{\text{I}}\text{-K}(3)\text{-}0(310)^{\text{V}}$	135.2(1)
$0(121)\text{-K}(3)\text{-}0(310)$	145.7(1)	$0(320)^{\text{V}}\text{-K}(3)\text{-}0(110)$	72.1(1)
$0(121)\text{-K}(3)\text{-}0(110)^{\text{I}}$	88.1(1)	$0(320)^{\text{V}}\text{-K}(3)\text{-}0(310)$	88.9(1)
$0(121)\text{-K}(3)\text{-}0(310)^{\text{V}}$	73.0(1)	$0(320)^{\text{V}}\text{-K}(3)\text{-}0(110)^{\text{I}}$	1465(1)
$0(321)\text{-K}(3)\text{-}0(120)^{\text{I}}$	129.7(1)	$0(320)^{\text{V}}\text{-K}(3)\text{-}0(310)^{\text{V}}$	63.0(1)
$0(321)\text{-K}(3)\text{-}0(320)^{\text{V}}$	139.1(1)	$0(110)\text{-K}(3)\text{-}0(310)$	151.7(1)
$0(311)\text{-K}(3)\text{-}0(110)$	135.5(1)	$0(110)\text{-K}(3)\text{-}0(110)^{\text{I}}$	93.4(1)
$0(311)\text{-K}(3)\text{-}0(310)$	72.2(1)	$0(110)\text{-K}(3)\text{-}0(310)^{\text{V}}$	97.3(1)
$0(321)\text{-K}(3)\text{-}0(110)^{\text{I}}$	71.9(1)	$0(310)\text{-K}(3)\text{-}0(110)^{\text{I}}$	91.3(1)
$0(321)\text{-K}(3)\text{-}0(310)^{\text{V}}$	81.4(1)	$0(310)\text{-K}(3)\text{-}0(310)^{\text{V}}$	92.2(1)
$0(120)^{\text{I}}\text{-K}(3)\text{-}0(320)^{\text{V}}$	74.3(1)	$0((10)\text{-K}(3)\text{-}0(310)^{\text{V}}$	150.5(1)

Table 3-3-4 (continued)

2-Carboxylato-monoperbenzoic Acid AnionsAnion 1.

C(11)-C(12)	1.398(7)	C(11)-C(111)	1.476(7)
C(12)-C(13)	1.392(7)	C(12)-C(121)	1.516(9)
C(13)-C(14)	1.387(11)	C(111)-O(110)	1.208(8)
C(14)-C(15)	1.359(10)	C(111)-O(111)	1.346(7)
C(15)-C(16)?	1.372(8)	C(121)-O(120)	1.250(7)
C(11)-C(16)	1.394(10)	C(121)-O(121)	1.257(6)
		O(111)-O(112) Δ	1.449(6)
C(12)-C(11)-C(16)	119.1(4)	C(11)-C(111)-O(110)	126.2(5)
C(11)-C(12)-C(13)	119.5(6)	C(11)-C(111)-O(111)	110.5(5)
C(12)-C(13)-C(14)	119.8(5)	O(110)-C(111)-O(111)	123.3(4)
C(13)-C(14)-C(15)	120.9(6)	C(111)-C(111)-O(112)	11.8
C(11)-C(15)-C(16)	119.9(7)	C(12)-C(121)-O(120)	117.7(6)
C(15)-C(16)-C(11)	120.6(6)	C(12)-C(121)-O(121)	117.6(6)
C(12)-C(11)-C(111)	119.6(6)	O(120)-C(121)-O(121)	124.7(6)
C(16)-C(11)-C(111)	121.2(5)		
C(11)-C(12)-C(121)	121.4(4)		
C(13)-C(12)-C(121)	119.0(5)		

Anion 2

C(21)-C(22)	1.404(8)	C(21)-C(211)	1.450(9)
C(22)-C(23)	1.399(9)	C(22)-C(221)	1.509(10)
C(23)-C(24)-	1.399(12)	C(211)-O(210)	1.231(7)
C(24)-C(25)	1.351(13)	C(211)-O(211)	1.300(10)
C(25)-C(26)	1.371(15)	C(221)-O(220)	1.267(8)
C(26)-C(21)	1.400(11)	C(221)-O(221)	1.221(7)
		O(221)-O(212)	1.464(6)
C(22)-C(21)-C(26)	119.4(6)	C(21)-C(211)-O(210)	124.2(8)
C(21)-C(22)-C(23)	117.9(6)	C(21)-C(211)-O(211)	113.7(5)
C(22)-C(23)-C(24)	121.1(6)	O(210)-C(211)-O(211)	122.1(7)
C(23)-C(24)-C(25)	119.8(9)	C(211)-O(211)-O(212)	108.6(4)
C(24)-C(25)-C(26)	120.7(9)	C(22)-C(221)-O(220)	116.2(5)
C(25)-C(26)-C(21)	121.0(7)	C(22)-C(221)-O(221)	116.8(6)
C(22)-C(21)-C(211)	124.4(6)	O(220)-C(221)-O(221)	127.0(7)
C(26)-C(21)-C(211)	116.2(6)		
C(21)-C(22)-C(221)	124.9(5)		
C(23)-C(22)-C(221)	117.2(5)		

Table 3-3-4 (continued)

Anion 3.

C(31)-C(32)	1.392(6)	C(31)-C(311)	1.486(8)
C(32)-C(33)	1.374(8)	C(32)-C(321)	1.526(9)
C(33)-C(34)	1.384(12)	C(311)-O(310)	1.204(8)
C(34)-C(35)	1.368(9)	C(3110)-O(311)	1.350(6)
C(35)-C(36)	1.371(10)	C(321)-O(320)	1.265(7)
C(36)-C(31)	1.397(10)	C(321)-O(321)	1.233(7)
		O(211)-O(312)	1.446(6)
C(32)-C(31)-C(36)	119.4(5)	C(31)-C(311)-O(310)	125.9(4)
C(31)-C(32)-C(33)	119.8(6)	C(31)-C(311)-O(311)	110.6(5)
C(32)-C(33)-C(34)	120.0(5)	O(310)-C(111)-O(311)	123.5(5)
C(33)-C(34)-C(35)	120.5(7)	C(311)-O(311)-O(312)	112.0(4)
C(34)-C(35)-C(36)	120.3(8)	C(32)-C(321)-O(320)	115.3(5)
C(356)-(36)-C(31)	119.9(5)	C(32)-C(321)-O(321)	118.6(5)
C(32)-C(31)-C(311)	119.6(6)	O(320)-C(321)-O(321)	126.1(6)
C(36)-C(31)-C(311)	121.0(4)		
C(31)-C(32)-C(321)	121.7(5)		
C(33)-C(32)-C(321)	118.6(5)		

Water Molecule*

O1-H1	0.96(10)	H1-O1-H2	102(7)
O1-H2	0.94(5)		
O2 H3	0.95(20)	H3-O2-H4	104
O2-H4	0.95(8)		

Hydrogen Bonding Distances (°) and Angles(°).

O(112)...O(320) ^V	2.556	O(112)-H(112)...O(320) ^V	156
O(212)...O(220) ^{IV}	2.560	O(212)-H(212)...O(220) ^{IV}	179
O(312)...O(221) ^V	2.572	O(312)-H(312)...O(121) ^V	170
*O(1)...O(220) ^{VII}	2.849	O(1)-H(2)...O(220) ^{VII}	173
*O(2)...O(220) ^{VI}	2.690	O(2)-H(4)...O(220) ^{VI}	164

Superscripts denote the following symmetry operations;

I 1-x, -y, 1-z	III x-1, y, z	V -x, -y, 1-z	VII -x, 1-y, 1-z
II x, y-1, z-1	IV -x, 1-y, 2-z	VI 1+x, y, z	

*NB. Due to disorder, O(1) and O(2) (and associated hydrogen atoms) will not be present at the same time.

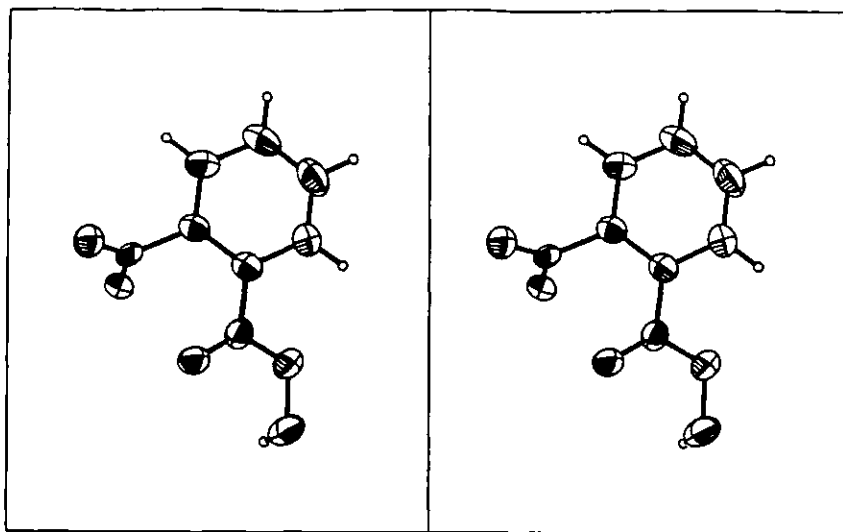


Figure 3-3-1. Stereoscopic view of KMPP, Anion 1

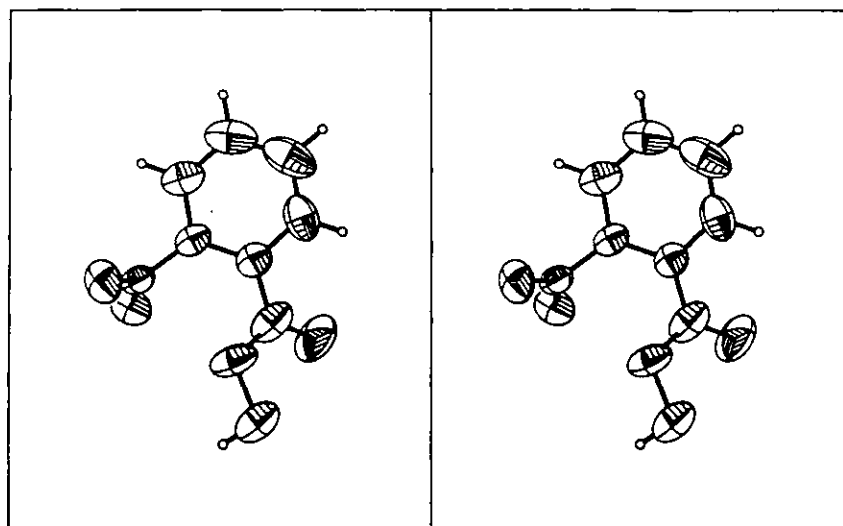


Figure 3-3-2. Stereoscopic view of KMPP, Anion 2

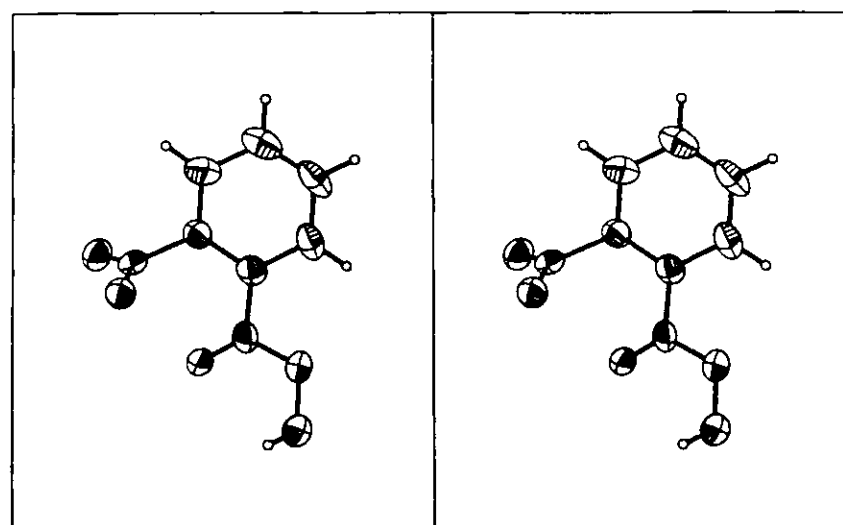


Figure 3-3-3. Stereoscopic view of KMPP, Anion 3

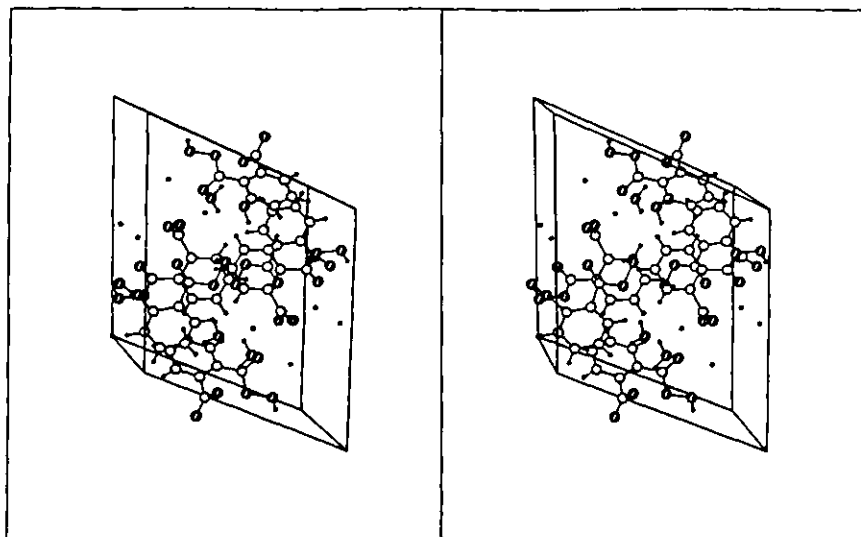


Figure 3-3-4. A stereoscopic view of the packing in the 'KMPP' structure.

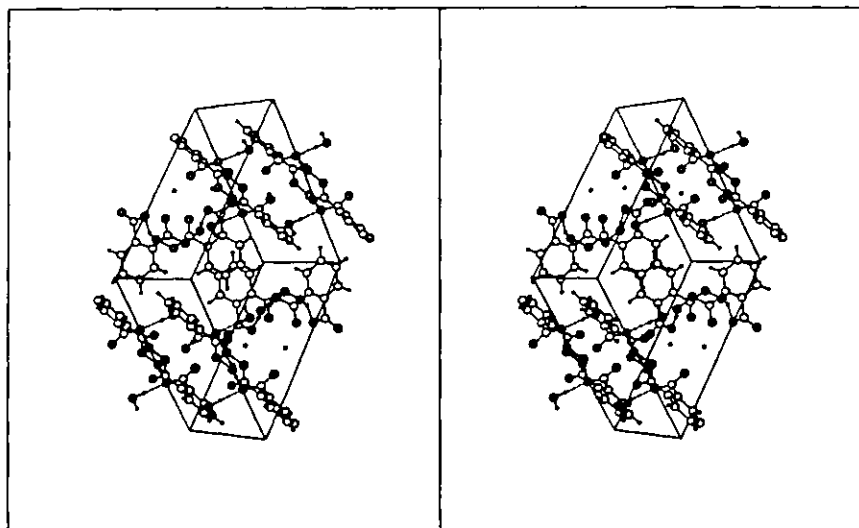


Figure 3-3-5. A stereoscopic view of 'KMPP' showing the hydrogen bonding.

(range 1.446(6) to 1.454(6)Å). This compares well with those reported for other compounds containing a peroxy group,²⁶ and as expected the C-O(peroxy) distance (mean 1.335Å) is longer than the C-O(terminal) distance mean value of 1.214Å. We have shown that there are hydrogen atoms attached to the terminal peroxy oxygen atoms, mean O-H distance of 0.94Å and mean O-O-H angle of 100°; again this compares well with 'MMPP' as does the torsion angle of the peroxy groups, mean 105.4°. It differs from 'MMPP' in that the carboxylato group does not lie normal to the plane of the six membered rings (mean dihedral angle of 113.9°) and the peroxycarboxylic acid group does not lie within the plane (mean dihedral angle 27.7°). However, as in 'MMPP' the peroxycarboxylic acid group and the carboxylato group do lie approximately normal to each other so that there is the minimum of steric interaction between the two groups.

In 'MMPP' and other peroxycarboxylic acids^{86,94,95} the peroxy-acid group is arranged such that the more bulky O-O moiety of the group is furthest away from the carboxylato group. This is also true for two of the anions in the potassium salt structure. However, in one of the anions, (anion 2, see figure 3-2-2) the peroxy acid group has been rotated through 180°, with the result that the O-O moiety is nearer to the carboxylato group. These differences between the magnesium and potassium salts in respect of the carboxylato and peroxycarboxylic acid groups can only be explained by the hydrogen bonding. Unlike in 'MMPP', the potassium salt does not have a complex network of hydrogen bonds which would tend to hold the structure together; in fact there is a rather different situation in which the hydrogen bonds tend to separate the structure into sets of 'dimers'. The hydrogen bonding is shown in a stereoscopic packing diagram, figure 3-3-5. In figure 3-3-5 it can be seen that one anion 2 is intermolecularly hydrogen-bonded to a similar anion so that the two anions lie almost within the same plane, whereas

anions 1 and 3 are hydrogen-bonded together so that they lie on top of each other. Both fractions of the disordered water molecule are also involved in one hydrogen-bond, to one of the anions (anion 2). The hydrogen-bonding involving the water molecule probably accounts for the slight disorder that may be present in anion 2, which is reflected by the somewhat higher temperature factors associated with some atoms of this anion.

SECTION 3-4. STRUCTURAL DIFFERENCES AFFECTING STABILITY OF MAGNESIUM AND POTASSIUM SALTS OF 2-CARBOXYLATO-MONOPERBENZOIC ACID.

Many different tests for stability of both compounds have been carried out in the research laboratories of Laporte Ind. Ltd. The most important of these, as far as industry is concerned, are impact sensitivity, active oxygen loss and sensitivity to water. On all counts the magnesium compound appears to be the more stable, especially with respect to impact and temperature sensitivity. By examination of the crystal structures of the two compounds it seems that the main structural reason for these differences must be attributed to the differences in hydrogen bonding. In the magnesium compound the hydrogen-bonding is extensive, holding the whole structure together, whereas in the potassium compound the hydrogen bonding is less significant and therefore does not really have the same stabilising effect. It should also be said that in the potassium compound the water of crystallisation, being disordered, is not so tightly hydrogen bonded and therefore may more easily be lost, which would in turn weaken the structure of the crystal. The increased impact sensitivity of the potassium compounds may also partially be due to the conformation of the peroxy-carboxylic acid group in anion 2, being

in a "metastable" state, i.e., it is rotated through 180° from its apparently more common orientation, as in the other two anions of the potassium compound.

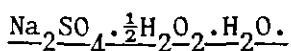
C H A P T E R F O U R

SODIUM SULPHATE HEMIPERHYDRATE MONOHYDRATE

Just like many compounds crystallise from aqueous solutions as hydrates, containing differing amounts of water of crystallisation, so some compounds will crystallise from aqueous hydrogen peroxide solution, with hydrogen peroxide of crystallisation to give "perhydrates". Sodium percarbonate, $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$, is one such compound.^{51,78} Some compounds can crystallise out with both hydrogen peroxide and water of crystallisation; the title compound is of this type and in this Chapter we verify the fact by single crystal X-ray crystallographic techniques. A brief study of the vibrational spectra is also reported for the compound.

SECTION 4-1. SINGLE CRYSTAL X-RAY CRYSTALLOGRAPHIC STUDIES.

Crystal Structure of Sodium Sulphate Hemiperhydrate Monohydrate,



The colourless crystals were prepared by slow evaporation in air of a dilute solution of anhydrous sodium sulphate in aqueous hydrogen peroxide (15% w/v) using the published procedure.^{78,97} After filtering,

the crystals were washed with ethanol and diethyl ether and dried in air. (Found: H, 1.5; O_2^{2-} , 9.0; S, 18.1%. $H_3Na_2O_6S$ requires H, 1.7; O_2^{2-} , 9.0; S, 18.1%).

Accurate unit-cell dimensions were obtained by a least-squares calculation based on 21 reflections measured on a Nicolet R3m diffractometer using graphite-monochromated $Cu-K_{\alpha}$ radiation.

Crystal Data

$H_3Na_2O_6S$, $M = 177.06$, orthorhombic, $a = 7.034(2)$, $b = 8.279(2)$, $c = 34.771(10)\text{\AA}$, $U = 2024.9(9)\text{\AA}^3$ (at 18°C), $Z = 8$, $F(000) = 1392$, space group $F2dd$ (No. 43), $Cu-K_{\alpha}$ radiation $\lambda = 1.5418\text{\AA}$, $\mu(Cu-K_{\alpha}) = 71.1\text{ cm}^{-1}$, $D_c = 1.16\text{ g cm}^{-3}$.

A crystal of approximate size $0.4 \times 0.3 \times 0.3\text{ mm}$ was chosen for the study, and a coat of picture varnish was applied to the crystal to help prevent loss of hydrogen peroxide under X-rays. The ω -scan technique was used for intensity data collection and a total of 346 independent reflections were measured to $\theta = 57^\circ$. The 1,1,7 and 2,2,2 reflections were monitored as reference reflections every 50 reflections and their net count did not alter noticeably over the period of data collection (ca. 24 hours). The data were scaled by use of these reference reflections. The program system SHELXTL²² was used throughout for the solution and refinement of the structure, calculations being carried out on a Data General Eclipse S140 computer.

Positions of one sodium atom, one sulphur and four oxygen atoms of the SO_4^{2-} group were found by direct methods, and a few cycles of isotropic refinement with these atoms gave $R = 0.34$. The subsequent difference Fourier synthesis showed the location of the second independent sodium atom. A further few cycles of isotropic refinement gave $R = 0.22$ with the difference Fourier synthesis showing the location of the oxygen atoms of the hydrogen peroxide (astride a 2 fold axis) and

of the water molecules. Further isotropic refinement gave $R = 0.045$. A few cycles of refinement with the sulphur, oxygen and sodium atoms anisotropic gave $R = 0.034$ and the resulting difference Fourier synthesis showing possible hydrogen atom positions. After applying a weighting scheme of the type, $w = 1/(\sigma^2|F| + |g|F^2)$, g set at 0.0005, further refinement resulted in an R of 0.03. When the three independent hydrogen atoms were included in the subsequent refinement, with all non-hydrogen atoms anisotropic, R reached a value of 0.029. After correcting for extinction ($F^* = F_{\text{calc}} / (1 + 0.002 \times F_{\text{calc}}^2 / \sin(2\theta))^{0.25}$ where $x = 1.3(3) \times 10^{-3}$) further refinement resulted in the final R of 0.027. Table 4-1-1 lists the final atomic fractional coordinates, Table 4-1-2 lists the temperature factors of all atoms and Table 4-1-3 lists the bond lengths and bond angles, including the hydrogen-bonding distances and angles and the coordination about the sodium atoms.

DISCUSSION

The structure is made up of sodium ions and units containing two sulphate groups, two water molecules and one hydrogen peroxide molecule held together by hydrogen bonds (see figure 4-1-1). We note that only one of the hydrogen atoms of the water molecules participates in the hydrogen bonding. The three dimensional packing of all the component entities can be seen in the stereoscopic drawings figures 4-1-2 and 4-1-3.

The sodium ions are surrounded by six oxygens in approximately octahedral coordination with mean Na(1)-O distances of $2.417\text{\AA}$ (range $2.351(4)$ to $2.543(4)\text{\AA}$) and a mean Na(2)-O distance of $2.459\text{\AA}$ (range $2.338(3)$ to $2.554(5)\text{\AA}$). The sulphate ion has S-O bond lengths and angles which are within the range usually found^{98,99} with mean S-O distance of $1.467\text{\AA}$ (range $1.457(4)$ to $1.484(4)\text{\AA}$); the S-O(3) and S-O(4)

Table 4-1-1

Fractional Atom Coordinates with Estimated Standard Deviations
in Parentheses for Sodium Sulphate Hemiperhydrate Monohydrate.

Atom	x	y	z
S	0.3922	0.2369(1)	0.3117(1)
Na(1)	0.1190(3)	0.0439(2)	0.2544(1)
Na(2)	0.2014(3)	0.1428(2)	0.4062(1)
O(1)	0.4123(6)	0.0886(3)	0.2891(1)
O(2)	0.2146(6)	0.3158(4)	0.3011(1)
O(3)	0.3935(5)	0.1946(4)	0.3526(1)
O(4)	0.5540(6)	0.3467(4)	0.3035(1)
O(5)	0.6867(7)	0.3656(4)	0.3937(1)
O(6)	0.8281(6)	0.1919(4)	0.2657(1)
H(6)	0.751(9)	0.248(7)	0.279(2)
H(51)	0.625(11)	0.311(8)	0.382(2)
H(52)	0.737(11)	0.320(7)	0.409(2)

Table 4-1-2

Temperature Factors ($\text{\AA}^2 \times 10^3$) for Sodium Sulphate Hemiperhydrate Monohydrate with Estimated Standard Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	13(1)	12(1)	9(1)	1(1)	0(1)	1(1)
Na(1)	14(1)	18(1)	18(1)	2(1)	-0(1)	-0(1)
Na(2)	32(1)	19(1)	17(1)	-4(1)	2(1)	0(1)
O(1)	24(2)	16(2)	22(2)	-8(1)	0(2)	2(2)
O(2)	21(2)	30(2)	21(2)	8(2)	3(2)	7(2)
O(3)	19(2)	21(2)	17(2)	2(1)	-3(2)	0(2)
O(4)	23(2)	20(2)	17(2)	-1(1)	8(2)	-5(2)
O(5)	33(2)	18(2)	30(2)	3(1)	11(2)	-4(2)
O(6)	23(2)	27(2)	24(2)	0(2)	1(2)	3(2)
H(6)	44(20)					
H(51)	84					
H(52)	75					

Table 4-1-3.

Bond lengths (Å) and angles (°) for sodium sulphate hemiperhydrate
with estimated standard deviations in parentheses.

(a) Hydrogen peroxide molecule.

O(6)-O(6) ^I	1.456(7)	O(6)-H(6)	0.85(6)
O(6) ^I -O(6)-H(6)	93(4)		

(b) Sulphate ion.

S-O(1)	1.464(3)	S-O(2)	1.457(4)
S-O(3)	1.465(3)	S-O(4)	1.484(4)
O(1)-S-O(2)	108.9(2)	O(1)-S-O(3)	108.6(2)
O(2)-S-O(3)	111.0(2)	O(1)-S-O(4)	109.7(2)
O(2)-S-O(4)	109.5(2)	O(3)-S-O(4)	109.2(2)

(c) Na (1) environment.

Na(1)-O(1)	2.419(4)	Na(1)-O(1) ^{II}	2.368(4)
Na(1)-O(2) ^I	2.351(4)	Na(1)-O(4) ^{III}	2.405(4)
Na(1)-O(6) ^{IV}	2.418(5)	Na(1)-O(6) ^{II}	2.543(4)
O(1)-Na(1)-O(1) ^{II}	156.0(1)	O(1)-Na(1)-O(2) ^I	95.2(1)
O(1) ^{II} -Na(1)-O(2) ^I	83.1(1)	O(1)-Na(1)-O(4) ^{III}	85.0(1)
O(1) ^{II} -Na(1)-O(4) ^{III}	91.3(1)	O(2) ^I -Na(1)-O(4) ^{III}	166.4(1)
O(1)-Na(1)-O(6) ^{IV}	124.3(1)	O(1) ^{II} -Na(1)-O(6) ^{IV}	79.6(1)
O(2) ^I -Na(1)-O(6) ^{IV}	97.2(1)	O(4) ^{III} -Na(1)-O(6) ^{IV}	93.9(1)
O(1)-Na(1)-O(6) ^{II}	76.2(1)	O(1) ^{II} -Na(1)-O(6) ^{II}	79.8(1)
O(2) ^I -Na(1)-O(6) ^{II}	89.3(1)	O(4) ^{III} -Na(1)-O(6) ^{II}	77.5(1)
O(6) ^{IV} -Na(1)-O(6) ^{II}	157.5(2)		

(d) Na (2) environment.

Na(2)-O(3)	2.341(4)	Na(2)-O(1) ^V	2.514(3)
Na(2)-O(2) ^{VI}	2.458(4)	Na(2)-O(3) ^V	2.550(3)
Na(2)-O(5) ^{III}	2.388(3)	Na(2)-O(5) ^{VII}	2.554(5)
O(3)-Na(2)-O(1) ^V	123.1(1)	O(3)-Na(2)-O(2) ^{VI}	95.4(1)
O(1) ^V -Na(2)-O(2) ^{VI}	78.0(1)	O(3)-Na(2)-O(3) ^V	79.5(1)
O(1) ^V -Na(2)-O(3) ^V	56.0(1)	O(2) ^{VI} -Na(2)-O(3) ^V	116.5(1)
O(3)-Na(2)-O(5) ^{III}	93.3(1)	O(1) ^V -Na(2)-O(5) ^{III}	140.2(1)
O(2) ^{VI} -Na(2)-O(5) ^{III}	83.7(1)	O(3) ^V -Na(2)-O(5) ^{III}	158.9(1)
O(3)-Na(2)-O(5) ^{VII}	84.1(1)	O(1) ^V -Na(2)-O(5) ^{VII}	119.4(1)
O(2) ^{VI} -Na(2)-O(5) ^{VII}	159.5(1)	O(3) ^V -Na(2)-O(5) ^{VII}	83.6(1)
O(5) ^{III} -Na(2)-O(5) ^{VII}	75.8(1)		

Table 4-1-3 (continued)(e)Hydrogen bonding.

O(6)...O(4)	2.661	O(5)...O(3)	2.880
O(6)-H(6)-O(4)	170	O(5)-H(51)-O(3)	166

Superscripts denote the following symmetry operations:

I	$x, \frac{1}{2}-y, \frac{1}{2}-z$	V	$x-\frac{1}{4}, \frac{1}{4}+y, \frac{3}{4}-z$
II	$x-\frac{1}{2}, -y, \frac{1}{2}-z$	VI	$\frac{3}{4}+x, y-\frac{1}{4}, \frac{3}{4}-z$
III	$x-\frac{1}{2}, y-\frac{1}{2}, z$	VII	$x-\frac{3}{4}, y-\frac{1}{4}, \frac{3}{4}-z$
IV	$x-1, y, z$		

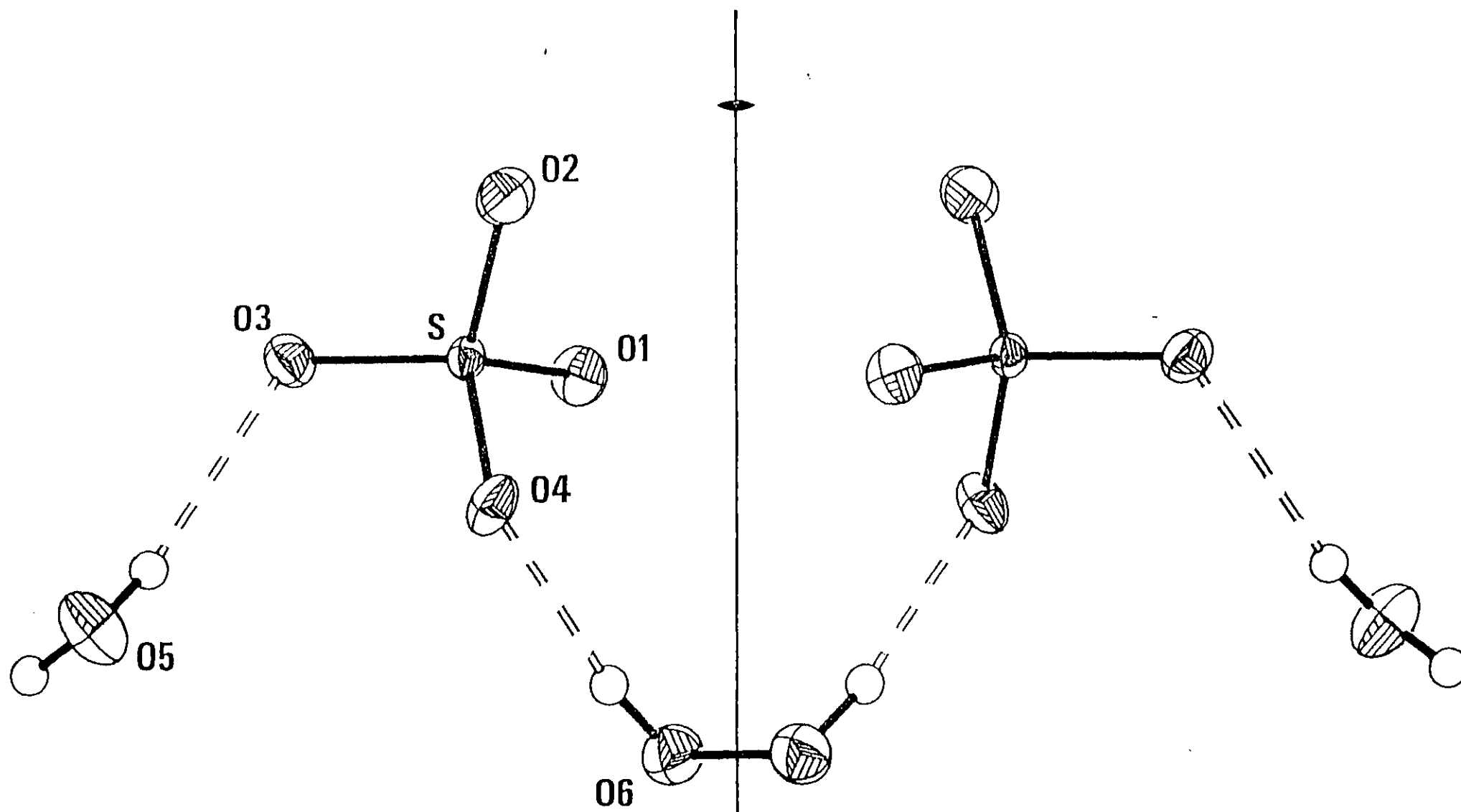


Figure 4-1-1-. Structure of the units present in sodium sulphate hemiperhydrate monohydrate

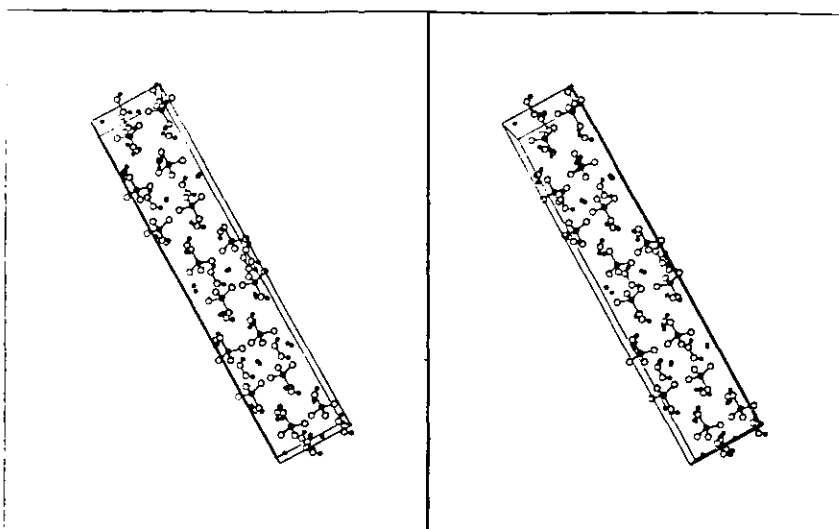


Figure 4-1-2. A stereoscopic view of the packing within the sodium sulphate hemiperhydrate monohyrate structure.

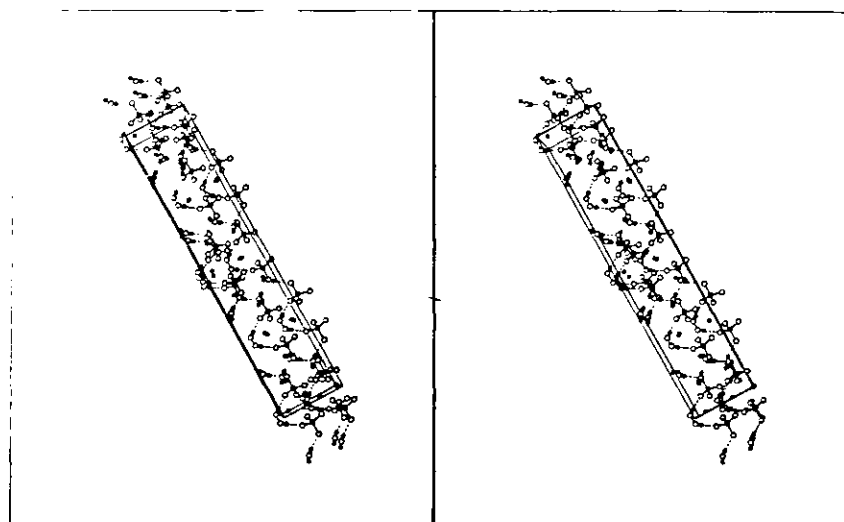


Figure 4-1-3. A stereoscopic view showing the hydrogen bonding within the sodium sulphate hemiperhydrate monohyrate structure.

being the longest bond distances as both O(3) & O(4) are involved in the hydrogen bonding. The mean O-S-O angle is 109.5° (range $108.6(2)$ to $111.0(2)^\circ$). The hydrogen peroxide molecule lies astride a two-fold axis and has an O-O distance of $1.456(7)\text{\AA}$; this compares well with published values for free hydrogen peroxide³⁶ and for other perhydrates.^{26,51,99} The dihedral angle of the hydrogen peroxide of 100.5° is within the literature^{26,100} range of $80\text{--}110^\circ$, and fits the model proposed by Hunt et al.¹⁰⁰ for the dihedral angle of lowest potential. The hydrogen peroxide molecule is fairly tightly hydrogen bonded to one of the oxygen atoms, O(4), of the sulphate group, with O(6)...O(4) distance of $2.661\text{\AA}$ and O(6)-H(6)-O(4) angle of 170° . The hydrogen bond involving the water of crystallisation, O(5)...O(3) has a hydrogen-bonding distance of $2.880\text{\AA}$ and O(5)-H(51)-O(3) angle of 165° .

SECTION 4-2. VIBRATIONAL SPECTRA.

Infrared and Raman spectra have been measured for the title compound and the observed bands are listed in Table 4-2-1. The ^2H -substituted compound data were measured by D.P. Jones.⁷⁸ Assignments for the sulphate ion agree with those reported,^{101,102} and as expected for a skewed (C_2) hydrogen peroxide molecule all six modes are active in the Raman and infrared. There are no unusual features arising from the spectra; however, very strong bands are present at 3515 and 3412 cm^{-1} in the Raman and 3522 and 3415 cm^{-1} in the infrared spectra supporting the X-ray crystallographic evidence that one hydrogen of the water of crystallisation is not involved in hydrogen-bonding.

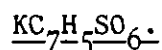
Table 4-2-1
Vibrational Spectra Data for Sodium Sulphate
Hemiperhydrate Monohydrate.

$\text{Na}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}^*$		Assignments	
Infrared	Raman	SO_4^{2-} Modes	H_2O_2 Modes
3522vs (2600)	3515s (2620)		$\nu_{\text{O-H}}, \text{H}_2\text{O}$
3415vs (2505)	3412s (2520)		$\nu_{\text{O-H}}, \text{H}_2\text{O}$
3280s (2410)			
3120s	3115w		ν_1
2800vs (2250)	2815m (2275)		ν_3
1645vs (1210)	(1212vw)		H_2O
1440vs (obsd.)	1460vw		ν_2
1335w (obsd.)			ν_6
	1200w (1192)		
	1185w (1181)		
1150vsb (1150)	1135w (1131)	ν_3	
1070vsb (1070)	1085w (1084)	ν_3	
	1075w (1054)	ν_3	
980vs (984)	985vs (986)	ν_1	
872s (874)	875s (878)		ν_3
830m			ν_4
635sh (638)	635w (640sh)	ν_4	
610vs (620)	620w (624m)		
475s (475)	455m (457)	ν_2	

*Values in parentheses are for ^2H -substituted compounds.⁷⁸

C H A P T E R F I V E

X-RAY CRYSTAL STRUCTURE OF POTASSIUM 4-SULPHONATO-PERBENZOIC ACID



In order to understand the factors responsible for the stability of materials used in washing powders it is useful to know the structures of new compounds produced which, although they may have appropriate chemical properties, may not be commercially viable. The title compound is such a material, which seems especially stable but is unlikely to be used industrially on anything like the same scale as "sodium perborate", "sodium percarbonate" or "MMPP".

The colourless crystals used for the determination were supplied by Interlox Chemicals Ltd. and were prepared in their research laboratories. Accurate unit-cell dimensions were obtained by a least-squares calculation based on 17 reflections measured on a Nicolet R3m diffractometer system using graphite monochromated Cu-K $_{\alpha}$ radiation.

Crystal Data

$\text{C}_7\text{H}_5\text{KO}_6\text{S}$, $M = 256.27$, orthorhombic, $a = 8.478(2)$, $b = 11.400(3)$, $c = 9.654(3)\text{\AA}$, $U = 933.1(4)\text{\AA}^3$ (at 18°C), $F(000) = 516$, space group $\text{Pca}2_1$ (No. 29), Cu-K $_{\alpha}$ radiation $\lambda = 1.5418\text{\AA}$, $\mu(\text{Cu-K}_{\alpha}) = 72.5\text{ cm}^{-1}$, $D_c = 1.82\text{ g dm}^{-3}$.

A crystal of size $0.1 \times 0.15 \times 0.15\text{ mm}$ was chosen for the study. A coat of picture varnish was applied to the crystal to help prevent decomposition under X-rays. The ω scan technique was used and a total

of 462 independent reflections were measured to $\theta = 50^\circ$. The $2,0,\bar{1}$ and $0,0,2$ reflections were monitored as reference reflections every 50 reflections measured. Their net count did not alter noticeably over the period of data collection (ca. 21 hours). The data were scaled by use of these reflections. The program system SHELXTL²² was used throughout for the solution and refinement of the structure, calculations being carried out on a Data General Eclipse S140 computer.

A Patterson synthesis gave the location of the potassium atom and possible vectors to the sulphur and one oxygen atom. A few cycles of isotropic refinement with these three atoms gave $R = 0.36$ and the subsequent difference Fourier synthesis showed the location of the six carbon atoms of the aromatic ring as well as three oxygen atoms. A further few cycles of isotropic refinement gave $R = 0.196$ with the difference Fourier synthesis showing the remaining carbon and oxygen atoms. A few cycles of refinement with the potassium, carbon and oxygen atoms anisotropic gave $R = 0.051$ and the resulting difference Fourier synthesis showed the hydrogen atom positions. Further refinement with all non-hydrogen atoms anisotropic gave $R = 0.040$. After a weighting scheme of the type $w = 1/(\sigma^2|F| + |g|F^2)$, g set at 0.0005, was applied, refinement allowing g to refine to 0.0006 resulted in a final $R = 0.039$.

Table 5-1-1 lists the final atomic fractional coordinates, Table 5-1-2 lists the atom temperature factors and Table 5-1-3 lists the bond lengths and bond angles of the anion, including the hydrogen bonding distance and angle.

DISCUSSION

The crystal structure consists of potassium cations and 4-sulphonato-perbenzoic acid anions (figure 5-1-1) and there is one anion per potassium cation. The three-dimensional packing can be seen in figure

Table 5-1-1
Fractional Atomic Coordinates for Potassium 4-Sulphonato-
Perbenzoic Acid with Estimated Standard Deviations in Parentheses.

Atom	x	y	z
K(1)	0.2468(4)	0.0574(2)	0.0000
C(1)	0.1155(9)	-0.2973(8)	0.2768(12)
C(2)	0.2044(12)	-0.3466(9)	0.3825(12)
C(3)	0.2104(10)	-0.4660(8)	0.3954(12)
C(4)	0.1294(10)	-0.5391(8)	0.3044(10)
C(5)	0.0392(12)	-0.4879(8)	0.2017(10)
C(6)	0.0316(11)	-0.3690(8)	0.1882(11)
C(40)	0.1445(12)	-0.6657(8)	0.3264(13)
S(1)	0.1086(2)	-0.1428(2)	0.2556(5)
O(1)	0.0311(11)	-0.0989(7)	0.3811(10)
O(2)	0.2701(6)	-0.1048(5)	0.2531(12)
O(3)	0.0266(13)	-0.1193(7)	0.1344(11)
O(40)	0.2123(9)	-0.7130(6)	0.4198(9)
O(41)	0.0677(9)	-0.7254(5)	0.2253(9)
O(42)	0.0762(7)	-0.8506(5)	0.2458(14)
H(2)	0.2612(12)	-0.2975(9)	0.4459(12)
H(3)	0.2718(11)	-0.5000(8)	0.4687(12)
H(5)	-0.0190(12)	-0.5367(8)	0.1389(10)
H(6)	-0.0325(11)	-0.3350(8)	0.1167(11)
H(42)	-0.055(9)	-0.870(7)	0.244(13)

Table 5-1-2

Temperature Factors ($\text{\AA}^2 \times 10^3$) for Potassium 4-Sulphonato-perbenzoic
 Acid with Estimated Standard Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	47(1)	47(1)	52(1)	2(2)	0(1)	-1(2)
C(1)	27(4)	57(5)	32(7)	-5(6)	2(5)	-4(4)
C(2)	60(6)	52(6)	44(6)	-2(6)	0(6)	-6(5)
C(3)	46(6)	52(6)	38(6)	7(6)	-4(5)	4(5)
C(4)	38(5)	44(6)	42(7)	-1(5)	7(5)	3(5)
C(5)	57(6)	40(5)	42(6)	1(5)	-5(5)	3(5)
C(6)	36(5)	56(6)	39(5)	14(5)	1(5)	3(5)
C(40)	61(6)	36(6)	43(6)	-2(6)	14(6)	10(5)
S(1)	43(1)	37(1)	54(1)	-1(2)	-5(3)	2(1)
O(1)	79(7)	48(5)	80(6)	-18(5)	21(6)	5(5)
O(2)	29(3)	55(3)	109(5)	16(8)	7(7)	-2(3)
O(3)	100(8)	48(5)	82(6)	0(5)	-54(6)	4(5)
O(40)	83(6)	51(5)	71(5)	10(5)	-8(5)	2(4)
O(41)	73(4)	37(4)	63(7)	5(4)	-6(4)	-1(3)
O(42)	60(4)	42(4)	87(6)	-4(6)	8(7)	2(3)
O(2)	1.2 U_{eq} C(2)					
H(3)	1.2 U_{eq} C(3)					
H(5)	1.2 U_{eq} C(5)					
H(6)	1.2 U_{eq} C(6)					
H(42)	1.2 U_{eq} O(42)					

Table 5-1-3
Bond Lengths (Å) and angles (°) for Potassium 4-Sulphonato-
Perbenzoic Acid with Estimated Standard Deviations in
Parentheses (hydrogen atoms not included).

Perbenzoic acid-4-Sulphonate Anion.

C(1)-C(2)	1.387(15)	C(1)-S(1)	1.772(9)
C(2)-C(3)	1.367(14)	S(1)-O(1)	1.466(9)
C(3)-C(4)	1.392(13)	S(1)-O(2)	1.436(5)
C(4)-C(5)	1.381(14)	S(1)-O(3)	1.389(11)
C(5)-C(6)	1.364(13)	C(4)-C(40)	1.466(13)
C(1)-C(6)	1.381(14)	C(40)-O(40)	1.198(14)
		C(40)-O(41)	1.356(13)
		O(41)-O(42)	1.443(8)
C(2)-C(1)-C(6)	119.6(9)	C(1)-S(1)-O(1)	105.0(5)
C(1)-C(2)-C(3)	119.5(9)	C(1)-S(1)-O(2)	105.7(3)
C(2)-C(3)-C(4)	121.3(9)	C(1)-S(1)-O(3)	107.7(5)
C(3)-C(4)-C(5)	118.2(8)	O(1)-S(1)-O(2)	109.8(6)
C(4)-C(5)-C(6)	121.0(9)	O(1)-S(1)-O(3)	113.9(5)
C(1)-C(6)-C(5)	120.4(9)	O(2)-S(1)-O(3)	114.0(7)
C(2)-C(1)-S(1)	120.4(8)	C(4)-C(40)-O(40)	126.5(10)
C(6)-C(1)-S(1)	120.0(8)	C(4)-C(40)-O(41)	110.3(9)
C(3)-C(4)-C(40)	117.1(9)	O(40)-C(40)-O(41)	123.1(8)
C(5)-C(4)-C(40)	124.7(9)	C(40)-O(41)-O(42)	112.0(8)

Hydrogen bonding distance and angle.

O(42)...O(2) ^I	2.644	O(42)-H(42)...O(2) ^I	179
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Superscript denotes the following symmetry operation

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

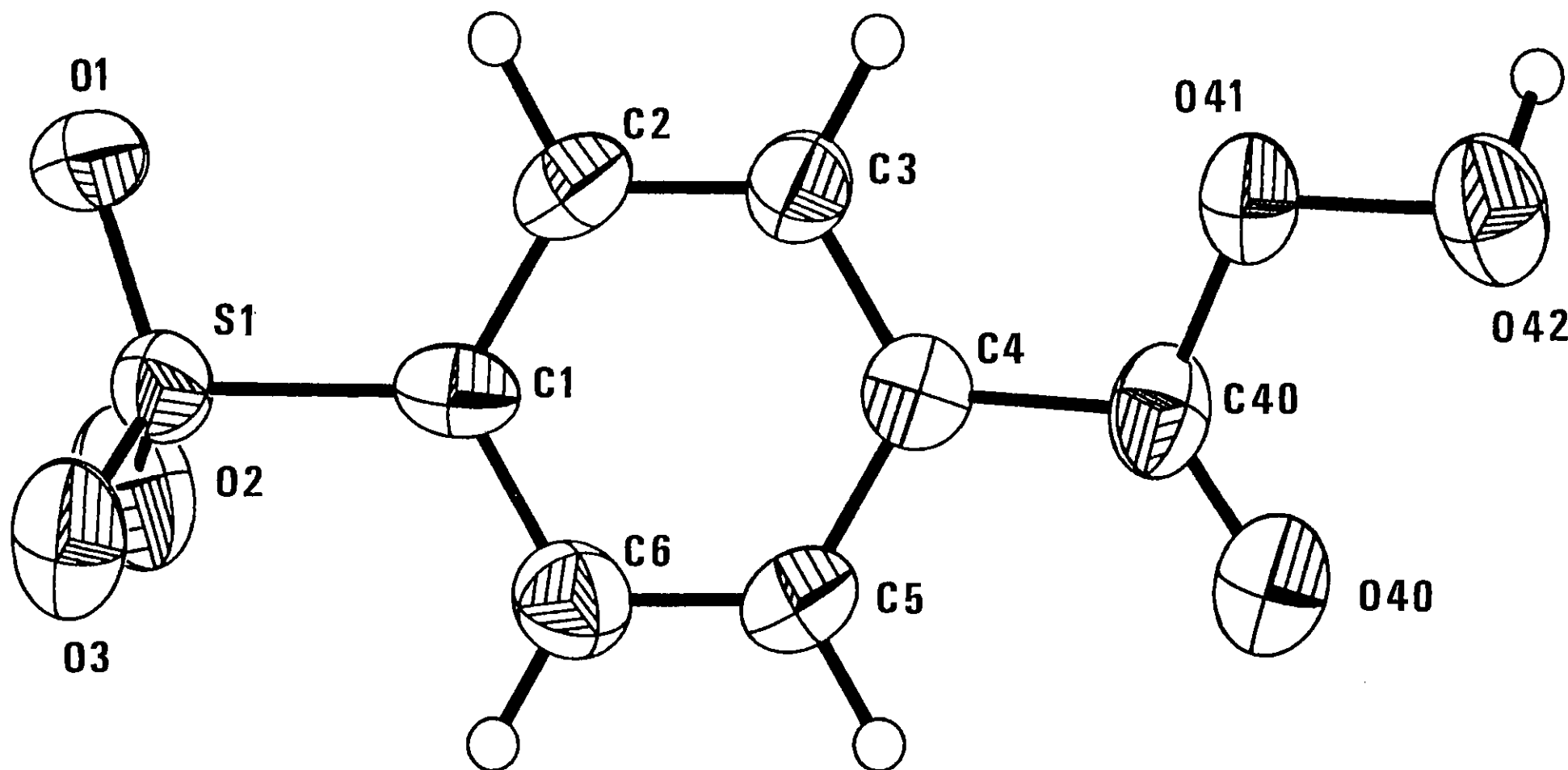


Figure 5-1-1. The 4-sulphonato-perbenzoic acid anion.

5-1-2. The bond lengths and bond angles of the peroxy-acid group and the aromatic ring of the anion agree well with those observed for "MMPP" and "KMPP" (see Chapter 3). In the peroxy-acid group the O41-O42 peroxy bond distance is $1.443(8)\text{\AA}$ (accepted distance²⁶ $1.44\text{\AA}$). As expected^{93,94,95} the C-O(peroxy) distance (C40-O41 of $1.356(13)\text{\AA}$) is longer than the C-O(terminal) distance (C40-O40 of $1.198(14)\text{\AA}$). As in the "MMPP" and "KMPP" structures there is a hydrogen atom attached to the terminal peroxy oxygen atom, O42. The peroxy-acid group lies approximately within the plane of the aromatic ring of the anion (dihedral angle 5.0°), again similar to that found in "MMPP" but the torsion angle is larger at 131.5° , however, this still fits the model proposed by Hunt.¹⁰⁰ The average S-O distance of $1.430\text{\AA}$ (range $1.389(11)$ to $1.466(9)\text{\AA}$) and the average angle at the sulphur atom of 109.4° (range $105.0(5)$ to $114.0(7)^\circ$) compares well with that expected¹⁰³ for a sulphonate substituent, as does the C-S distance of $1.772(9)\text{\AA}$. As might be expected, the hydrogen atom of the peroxy group is involved in a hydrogen bond of the type O-H...O (O...O distance of $2.644\text{\AA}$). The hydrogen bond links oxygen atom O42 of the peroxy group to one of the oxygen atoms, O2, of the sulphonate group of an adjacent anion. The hydrogen-bonding is shown in the three dimensional packing diagram, Figure 5-1-2, where it can be seen that the hydrogen bonding results in the formation of parallel chains of anions such that the hydrogen bonds run in the direction of the a axis whereas the anions themselves lie in the direction of the b axis. Apart from the fact that the hydrogen atom of the peroxy acid group is involved in hydrogen bonding, as in the other related compounds studied in this thesis, there seems to be no other structural feature particularly aiding the stability of the structure. It therefore seems very likely that hydrogen bonding is an

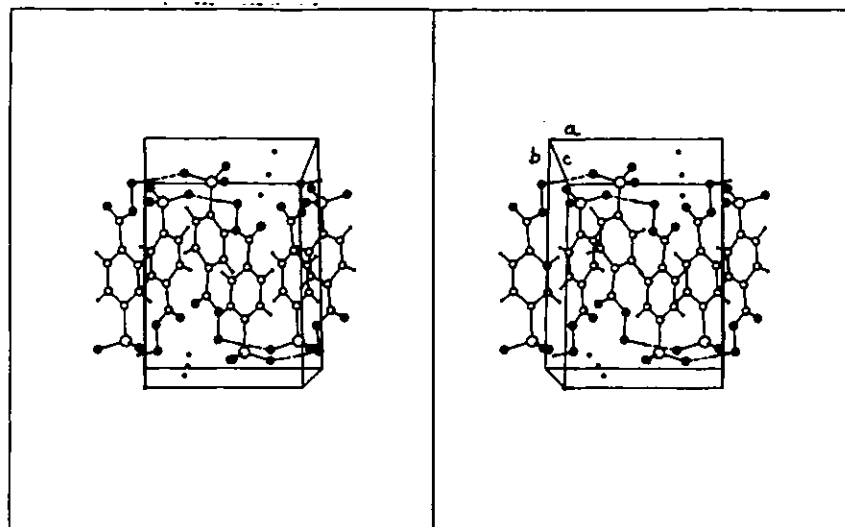


Figure 5-1-2. A stereoscopic view of the potassium 4-sulphonatoperbenzoic acid structure, including the hydrogen bond.

essential part of the reason for the stability of these types of compounds. Of course, in addition, the coordination of oxygen atoms to the potassium atom will also enhance the stability of the compound.

A P P E N D I X A

CRYSTALLOGRAPHIC METHODS

INTRODUCTION.

Single crystal X-ray crystallography is one of the most important techniques used by the research chemist to help elucidate the molecular structure of a compound. Since the early observations¹⁰⁴ of von Laue¹⁰⁵ and Bragg,¹⁰⁶ the technique has become increasingly more widespread due to the advent of computers and the ever increasing sophistication of the software associated with them. This has enabled X-ray crystallography to become more available to chemists in general rather than a skill restricted only to the professional crystallographer. Much literature^{107,108,109,110,111} has been produced on the theory and application of diffraction to crystalline materials, and so in this Appendix, we only intend to give a brief description of structure determination by X-ray diffraction techniques, mentioning the preparation and identification of single crystals and the procedure for data collection and structure determination.

SECTION A-1. PREPARATION OF SINGLE CRYSTALS.

It can not be emphasised too strongly that the preparation of suitable single crystals can be one of the major stumbling blocks for the solution of molecular structure by X-ray crystallography. In this study crystals were prepared by one of the three different methods described.

(a) Crystallisation by evaporation of solvent: This is one of the simplest and most commonly used methods of producing crystals. The procedure is to allow a saturated or nearly saturated solution to stand under conditions where the solvent, usually water in this case, evaporates slowly. It was found that the best conditions for producing crystals of perhydrates, and other hydrogen peroxide based compounds, are to leave a loosely stoppered flask at reduced temperature for several days. This method was very effective for the preparation of crystals of sodium sulphate hemiperhydrate monohydrate.

(b) Crystallisation by vapour diffusion: This method depends on the compound of interest being more soluble in a single solvent, say water, than a mixed solvent, say water/ethanol. The procedure is to dissolve the compound in a single solvent and then allowing the vapour of a second solvent to diffuse slowly into the solution forming a mixed solvent solution. Gradually, as the concentration of the second solvent in the mixture increases, crystallisation may occur often forming relatively large single crystals. This method is also particularly good for many perhydrates as they are often very soluble in water yet insoluble in ethanol or methanol and water mixtures.

(c) Crystallisation directly from reaction mixture: This method relies on the product being slightly soluble in the solvent in which the reaction takes place, so that effectively a supersaturated or near supersaturated solution of the product is formed during the reaction. It is also important that the reactants must be soluble in the reaction solvent so that any excess reactant does not also crystallise. This method does not often produce large crystals. However, single crystals of hexa-aquomagnesium(II)bis(2-carboxylato-monoperbenzoic acid) and tripotassium tris(2-carboxylato-monoperbenzoic acid) monohydrate, which were suitable for further study, were prepared by this method.

SECTION A-2. IDENTIFICATION AND CHOICE OF SUITABLE CRYSTALS.

If a crystal is to be satisfactory for collecting X-ray diffraction data, as well as being of proper size it must possess uniform internal structure, i.e., it must be pure at the molecular, ionic or atomic level and of course must be a single crystal and not twinned. The crystals need not have uniform or well-formed external faces but it should not be fractured, bent or otherwise physically distorted. To check if a crystal is single it should be examined between 'cross' Nicols with a polarising microscope; rotated about an axis normal to the plane of the polariser single crystals cut off the light (appearing dark) in all positions, or they let the light through but cut the light off (appearing uniformly dark—extinguish), once every 90° of rotation. Multiple crystals show themselves by having both light and dark regions at the same time. The ultimate check for a single crystal is to look at the diffraction pattern itself. The pattern observed on an X-ray photograph (oscillation, precession, rotation or Weissenberg photographs) should be made up of single spots, and the pattern should be discernible according to a particular crystal system and space group.

The size of a suitable crystal may vary enormously, but it should be appreciably smaller than the cross-sectional dimensions of the primary X-ray beam of the diffractometer, as all parts of the crystal must be exposed to the same intensity of X-ray radiation. Another factor important in determining the size of the crystal is absorption of X-rays by the crystal; this depends mainly on the type of compound and its atomic composition. Taking all things into consideration the optimum dimensions are in the range 0.1 to 0.5 mm in each direction.

SECTION A-3. BASIC CRYSTALLOGRAPHIC PRINCIPLES.

A single crystal contains groups of atoms packed in such a way that they repeat the atomic arrangement regularly in three dimensions. This regular three-dimensional lattice can be described by the distance between each repeating array of atoms in three different directions (a, b, and c) and the angles between these three vectors (α , β and γ) forming the unit cell. There are 14 Bravais Lattices and when combined with the 32 different point groups there results 230 different space groups, one of which will be able to describe the regular three-dimensional arrangement of atoms which make up the structure.

If a single-crystal is rotated in an X-ray beam, then diffraction maxima arise when the Bragg equation:

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

is satisfied, where d is the interplanar spacing, λ the X-ray wavelength, θ the reflection angle and n an integer. The unit-cell and space group parameters determine the location of particular diffraction maxima in space and the electron density distribution in the crystals determine the intensity of the diffraction maxima, and so if the intensity and relative position in space of each diffraction maxima can be measured (data collection) then an insight into the arrangement of atoms causing the diffraction can be obtained (structure determination).

SECTION A-4. DATA COLLECTION

Throughout this study data collection has been carried out on a Nicolet R3m on-line four-circle diffractometer (figure A-1) at 18°C. Copper radiation (CuK_α radiation, $\lambda = 1.5418\text{\AA}$), monochromated by a highly ordered graphite crystal, was directed to the centre of the circles by means of a collimator. The detector unit was mounted on the

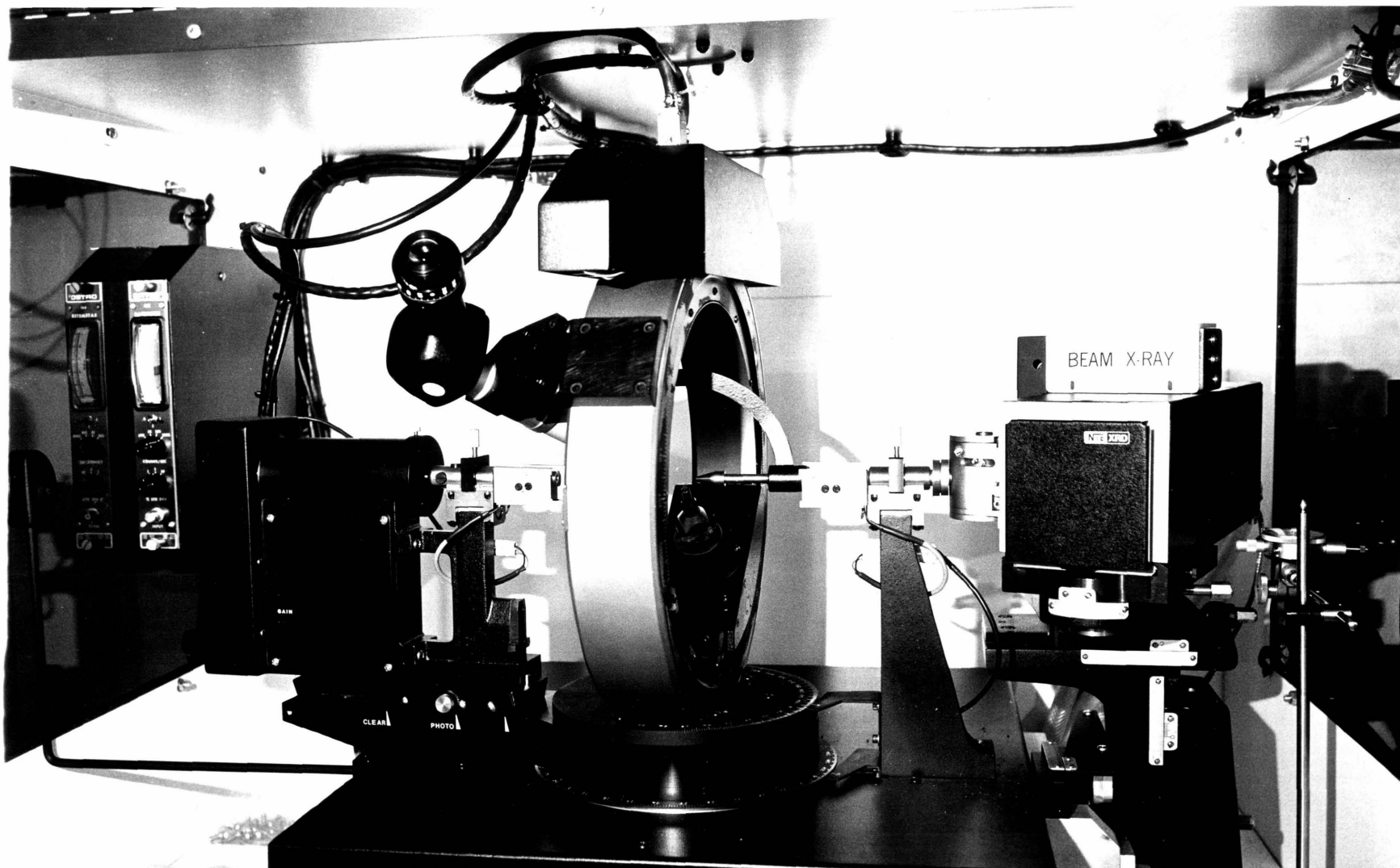


Figure A-1. Nicolet R3m diffractometer showing the graphite monochromator/ X-ray collimator unit, the four circles, the goniometer head with its mounted crystal, and the counting assembly.

2θ circle of the goniometer. The crystal to be studied was mounted with Araldite on a quartz fibre, which was fitted to a 'pip'. The 'pip' is essentially a brass tube about 1.5 cm long and has a cross-sectional diameter of about 0.3 cm with a fine hole running down the length of the pip where the glass fibre is secured, with dental wax. The mounted crystal then had a coat of picture varnish applied to it in order to help prevent decomposition of the crystal while under X-rays. After fitting the 'pip' into a goniometer head, which in turn was fitted to the goniometer, the crystal lay approximately at the centre of the circles. The crystal was then centred by eye using a 40X telemicroscope with cross wires, mounted on the full χ -circle. A polaroid photograph was then taken using a Polaroid camera mounted on the detector. Figure A-2 shows an example of one of the polaroid photographs produced. From figure A-2 it can be seen that each reflection (spot) is matched horizontally and vertically by a mirror image of itself. From the photograph the distances between like reflections were measured, where $2x$ is the horizontal distance in centimeters between pairs of spots and $2y$ is the vertical distance in centimeters between pairs of spots. The $2x$ and $2y$ distances were then entered into the diffractometer control console to be used as a starting point in the search for and centering of reflections, so that the positions of each reflection could be given in terms of the 2θ , ω , ϕ and χ angles. These angles were then used to index the reflections and thence generate the cell dimensions and cell volume. From these indices and angles an orientation matrix was calculated as were the standard deviations of the lattice parameters. The unit cell could now be transformed from the reduced primitive cell to the most likely Bravais lattice, recalculating new lattice parameters and reflection indices. At this point data collection could now be started. However, if required, the cell parameters could be further

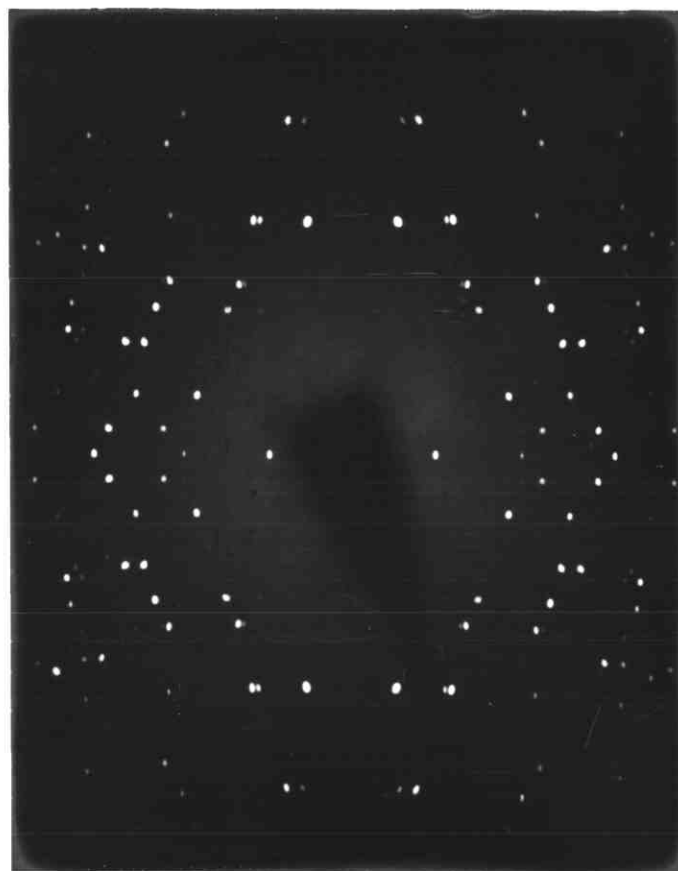


Figure A-2. Typical X-ray polaroid photograph produced prior to data collection for crystal centering.

refined by centering of more higher-angle reflections, whose positions would be calculated given their reflection indices. Before data collection began, a number of relatively strong reflections, usually two, were chosen as reference reflections which could be monitored regularly throughout data collection as standards. The scan range, scan speed, range of indices for reflections to be measured and any other required restrictions were set. Data collection was then started with the reflection indices, angles, scan rates, background intensities, peak intensities, standard deviations, X-ray exposure time and peak profiles being recorded on magnetic tape. When the required amount of data had been collected, the data could then be used for the 'structure determination'. In all cases the ω -scan technique was used for the data collection.

Data Collection for Absorption Correction.

If the crystal is irregular in shape the incident and diffracted rays may have different average path lengths, in the crystal for different reflections. As a result these reflections will suffer to a varying extent from absorption. If the crystal shape cannot be easily described in terms of Miller indices of the faces, the best alternative is to collect the data for a range of particular reflections as the crystal is rotated about the diffraction vector. The resulting fluctuation in peak intensities can be used to give a clue to the absorption effects due to the shape of the crystal. This is done by assuming that the crystal is ellipsoid shaped and by finding the ellipsoid of best fit; i.e., the ellipsoid that would cause the same fluctuations in peak intensities. Using this information the full data set could be empirically corrected to allow for the absorption and would subsequently be used in the structure refinement. The data for the

absorption correction was collected in a similar way to the full data set except that the indices of particular reflections were input as well as the instructions concerning the diffraction vector rotation. Each reflection was usually measured in 36 positions about the diffraction vector (i.e., $0 \rightarrow 360^\circ$ in steps of 10°).

SECTION A-5. STRUCTURE DETERMINATION.

Before we can use the data to solve the structure we first have to solve the "phase problem".¹⁰⁷ This arises because the data, as we have collected it, only gives information on the relative intensities of the diffracted X-rays and says nothing about the phases. There is no general solution to this problem, however, in this study two techniques have proved successful, the 'Heavy Atom' and 'Direct Methods' techniques.

The 'Heavy Atom' technique: In this method the position of the heavy atom (or atoms) in the unit cell is found first, using a Patterson synthesis. The Patterson synthesis produces a map of the vectors between centres of electron density (atoms) in the structure. If the 'heaviest' atoms have significantly greater electron density about them than the other atoms in the structure, the vectors between these 'heavy' atoms dominate the map. From the position of these vector peaks and the symmetry of the crystal space group, the coordinates of the 'heavy atom', relative to the cell axes, may be determined. This information is then used in a calculation of structure factors (F_c) which serve as a source of phases, reasonably close to the true ones. Difference Fourier synthesis maps, which use the difference between the calculated and the observed structure factors, $F_o - F_c$, often show the positions of other atoms, which can then be used to improve the phasing.

The 'Direct Method' technique: Until the development of the so-called 'direct method' structures could in general only be solved by the 'heavy atom' method. This was a problem particularly for organic compounds. The growth of direct methods has in recent years been one of the most important achievements in structural crystallography. It means that structures of organic compounds without heavy-atom and also of inorganic compounds with no obvious 'heavy atom' or with too many heavy atoms can now be solved. In very simple terms 'direct methods' rely on the fact that the phases of certain groups of reflections are related and not random. The use of sophisticated mathematical techniques and fast computers usually allows a sufficient number of phases to be determined to give at least part of the structure. Once this stage is reached, difference Fourier synthesis can be used to reveal the rest of the atomic positions. In general, solutions of centrosymmetric structures, where the phases can only be 0 or 180°, are easier than of non-centrosymmetric structures, where the phase can be anywhere between 0 and 360°.

After having located the position of the first set of atoms the remaining atoms, including hydrogen atoms, can often be located from subsequent difference Fourier synthesis maps, however, it is usually necessary to refine the non-hydrogen atoms anisotropically before the hydrogen atoms can be located. In certain circumstances the hydrogen atoms may be fixed using known parameters, for example the hydrogen atoms attached to the carbon atoms of an aromatic ring.

Further improvement to the refinement can result by applying weighting schemes, extinction corrections and absorption corrections. These improvements are usually used towards the end of refinement of a

structure, usually after any very weak reflections, with say, $3\sigma(I) > (I)$, have been omitted as 'unobserved'. The weighting scheme employed for least-squares and analysis of variance was:

$$\text{weight} = 1/(\sigma^2|F| + |g|F^2)$$

where g is the weighting factor applied, which can also be refined by fitting $(F_o - F_c)^2$ to $(\sigma^2|F| + |g|F^2)/k$, where k is a scale factor which cancels in all calculations. The extinction correction defines a new calculated structure factor (F^*):

$$F^* = F_c / (1 + 0.002x F_c^2 / \sin 2\theta)^{0.25}$$

where x is an empirical isotropic extinction factor. The method is similar to that outlined by Larson.¹¹²

The state of refinement is monitored by the Residual Index or R-factor:

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

The R-factor tends to zero as F_c approaches F_o hence the nearer R gets to zero, the more accurate should be the solution. When the R-factor reaches a steady limit and refinement is terminated, final structure factors, inter-atomic distances and bond angles plus other relevant information can be determined from the atomic coordinates and temperature factors.

Throughout this study calculations have been carried out using SHELXTL,²² a hardware/software combination designed for the determination of crystal structures from X-ray (or neutron) diffraction data. SHELXTL can carry out all the calculations required for structure

determination including data reduction, direct methods and Patterson synthesis, blocked-cascade least-squares refinement, Fourier synthesis, absorption corrections, bond lengths and angle calculations and molecular plotting instructions for the drawing of structures in many different forms, from straightforward single molecules to stereopacking diagrams. The programs used for this study were:-

XTAPE: This program reads the tape on which data were collected and writes data files which can be read by other SHELXTL programs e.g., 'X' and 'XEMP'. This program also scales the data using the standard reference reflections and calculates direction cosines for absorption corrections.

X: This is the master program for data reduction, structure solution and refinement. It uses raw data files prepared by 'XTAPE' and instruction files prepared using the editing program 'XED'.

XEMP: This program carries out an empirical absorption correction based on the data collected for the absorption correction. The program refines six parameters, which define a pseudo-ellipsoid, which are then used to calculate the corrections. This program requires approximate crystal dimensions and the linear absorption coefficient, μ , for the crystal. This program can also carry out an empirical absorption correction for crystals approximating to thin plates rather than ellipsoids.

XP: This program writes a plotfile which can be plotted using subsidiary program 'XPLOT'. The plotfile produced by 'XP' is essentially an instruction file containing the information required to plot molecular diagrams, space-filling models, thermal ellipsoid diagrams and packing diagrams in mono or stereo. The program can also be used to give information on bond lengths, angles, thermal motion analysis, least-squares planes, etc.

XED: This is the interactive text editor, used for creating and updating files for use with program 'X'.

A P P E N D I X B

Physical Measurements

Infrared spectra were measured at 25°C on Perkin Elmer 257, 457, 597 and 325 instruments as Nujol and Voltalef-3S mulls, or as a thin film between CaF₂ plates for aqueous solutions. Occasionally a disc was used; prepared by compressing the compound to be studied with KBr.

Raman spectra were obtained for powdered solids at 25°C on a Spex Ramalog 5 instrument with DPC-2 detector using a krypton-ion laser, usually with 530.9 nm excitation. Raman spectra of solutions were measured using a spinning solution-cell attachment (see Figure A-3) at 25°C. For comparison Raman spectra at 4°C were sometimes measured.

Electron spin resonance spectra were recorded at 25°C on an X-band Varian Associates E-9 spectrometer.

¹³C and ¹¹B nuclear magnetic resonance spectra were measured on a Bruker WM 250 instrument at 20°C. Some spectra were measured at 5°C for comparison. 10 mm n.m.r. tubes containing a deuteriated water insert, for locking purposes, were used for all solutions. ¹³C n.m.r. spectra were measured relative to D.S.S. using the internal reference facility of the instrument. ¹¹B n.m.r. spectra were measured relative to a [B(OH)₄]⁻ reference.

X-ray powder diffraction photographs were taken by Dr. R.S. Osborn of the University of London Intercollegiate X-ray Service, using a Guinier Nonius Mark II camera employing Cu(K_α) radiation.

Microanalyses were performed by the Imperial College Organic Chemistry Department. Samples were analysed for peroxide content (O₂²⁻) by titration in aqueous sulphuric acid solution with 0.02 M

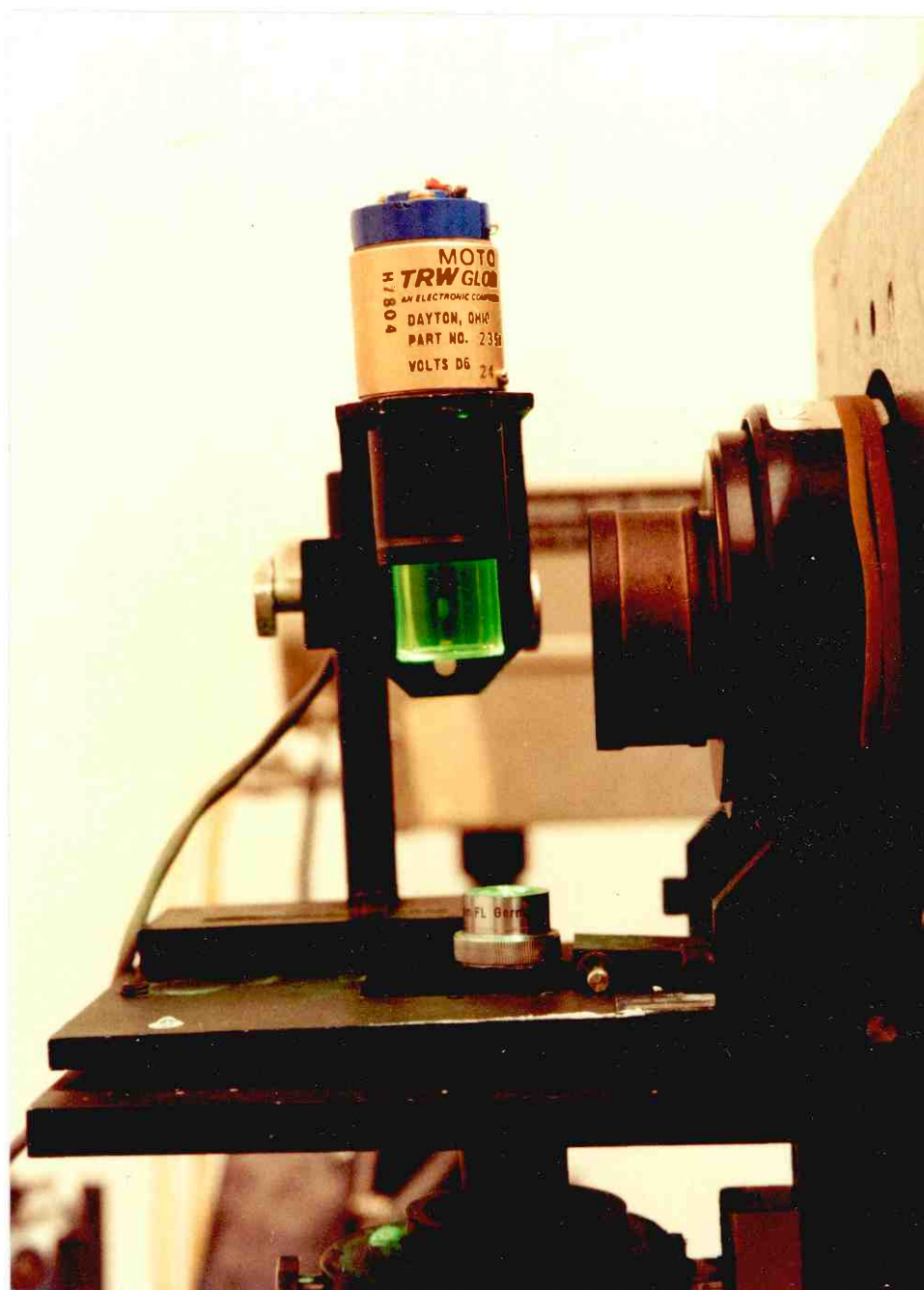


Figure A-3. Raman Spinning solution cell.

potassium permanganate solution. Boron content was found using a Mannitol/HCl back titration technique. Potassium, rubidium and caesium content was found gravimetrically as the tetraphenylborate.

Table A-1. Observed and calculated structure factors for sodium peroxoborate tetrahydrate.

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
1	0	0	23	30	1	3	0	18	19	-3	-4	1	12	11	-3	-1	1	47	50	-2	2	1	99	97
2	0	0	116	118	2	3	0	63	64	-2	-4	1	69	67	-2	-1	1	25	27	-1	2	1	370	379
3	0	0	339	332	3	3	0	134	134	-1	-4	1	83	84	-1	-1	1	146	145	0	2	1	357	354
4	0	0	66	67	4	3	0	11	5	0	-4	1	74	74	0	-1	1	326	326	1	2	1	163	165
5	0	0	19	18	-6	4	0	11	13	1	-4	1	26	28	1	-1	1	64	64	2	2	1	239	238
-6	1	0	86	88	-5	4	0	25	26	2	-4	1	96	96	2	-1	1	291	299	3	2	1	144	147
-5	1	0	85	87	-3	4	0	94	97	3	-4	1	58	60	3	-1	1	171	176	4	2	1	38	38
-4	1	0	26	27	-1	4	0	22	21	4	-4	1	72	76	4	-1	1	24	24	-6	3	1	29	22
-3	1	0	48	55	0	4	0	96	98	5	-4	1	119	121	-6	0	1	24	22	-5	3	1	122	123
-2	1	0	271	268	1	4	0	86	87	6	-4	1	11	15	-5	0	1	215	207	-4	3	1	20	22
-1	1	0	129	130	2	4	0	69	67	-4	-3	1	146	146	-4	0	1	51	50	-3	3	1	29	28
0	1	0	114	120	3	4	0	15	12	-3	-3	1	35	34	-3	0	1	36	41	-2	3	1	59	57
1	1	0	19	26	-5	5	0	176	176	-2	-3	1	83	86	-2	0	1	323	320	-1	3	1	66	67
2	1	0	149	149	-3	5	0	11	4	-1	-3	1	317	321	-1	0	1	22	21	0	3	1	118	116
3	1	0	68	72	-2	5	0	132	135	0	-3	1	146	148	0	0	1	132	135	1	3	1	35	36
4	1	0	39	39	-1	5	0	18	18	1	-3	1	43	45	1	0	1	212	217	2	3	1	149	153
5	1	0	81	77	0	5	0	48	49	2	-3	1	237	244	2	0	1	121	126	3	3	1	71	70
-6	2	0	16	11	1	5	0	127	123	3	-3	1	46	42	3	0	1	237	238	-6	4	1	31	33
-5	2	0	53	56	-4	6	0	73	69	4	-3	1	138	141	4	0	1	32	35	-5	4	1	14	17
-4	2	0	200	206	-3	6	0	47	46	5	-3	1	39	43	5	0	1	64	62	-4	4	1	75	73
-3	2	0	77	77	-2	6	0	60	60	6	-3	1	45	46	-6	1	1	29	30	-3	4	1	52	55
-1	2	0	315	324	-1	6	0	56	57	-5	-2	1	48	45	-5	1	1	58	55	-2	4	1	95	92
0	2	0	101	102	0	6	0	39	37	-4	-2	1	60	58	-4	1	1	72	72	-1	4	1	28	27
1	2	0	58	53	0	-6	1	29	29	-3	-2	1	21	22	-3	1	1	85	89	0	4	1	47	50
2	2	0	165	166	1	-6	1	21	24	-2	-2	1	48	52	-2	1	1	54	55	1	4	1	96	95
3	2	0	48	47	3	-6	1	45	43	-1	-2	1	203	207	-1	1	1	188	186	2	4	1	55	55
4	2	0	62	64	-2	-5	1	11	11	0	-2	1	126	124	0	1	1	301	306	-5	5	1	16	16
-6	3	0	56	55	-1	-5	1	11	2	1	-2	1	119	120	1	1	1	314	310	-4	5	1	106	106
-5	3	0	26	26	0	-5	1	255	259	2	-2	1	154	148	2	1	1	99	107	-3	5	1	49	50
-4	3	0	184	186	1	-5	1	14	2	3	-2	1	163	159	3	1	1	38	37	-2	5	1	176	176
-3	3	0	119	125	2	-5	1	86	85	4	-2	1	41	44	4	1	1	59	58	-1	5	1	100	101
-2	3	0	78	77	3	-5	1	78	80	5	-2	1	16	20	-6	2	1	105	107	0	5	1	20	18
-1	3	0	397	393	4	-5	1	11	10	-5	-1	1	28	27	-5	2	1	162	165	1	5	1	74	72
0	3	0	120	119	5	-5	1	23	27	-4	-1	1	70	66	-3	2	1	186	183	-4	6	1	80	78

Table A-1 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	6	1	11	10	-3	-2	2	81	85	-1	1	2	168	160	-4	5	2	80	77	-5	-2	3	91	92
-1	6	1	41	41	-1	-2	2	129	132	0	1	2	135	142	-3	5	2	15	11	-4	-2	3	47	49
0	-6	2	109	107	0	-2	2	448	441	1	1	2	255	252	-2	5	2	91	95	-3	-2	3	97	98
1	-6	2	23	17	1	-2	2	54	54	2	1	2	131	132	-1	5	2	42	41	-2	-2	3	55	54
2	-6	2	126	127	2	-2	2	286	291	3	1	2	93	98	0	5	2	50	49	0	-2	3	235	225
3	-6	2	101	100	3	-2	2	164	162	4	1	2	47	48	0	-6	3	61	59	1	-2	3	61	60
-2	-5	2	13	3	4	-2	2	79	79	-6	2	2	83	81	1	-6	3	66	67	3	-2	3	51	49
-1	-5	2	13	7	5	-2	2	52	56	-5	2	2	216	216	2	-6	3	84	82	4	-2	3	71	72
0	-5	2	19	20	-5	-1	2	54	53	-4	2	2	57	59	3	-6	3	104	103	5	-2	3	43	39
1	-5	2	49	52	-4	-1	2	142	136	-3	2	2	341	345	4	-6	3	14	13	-5	-1	3	102	99
2	-5	2	61	61	-3	-1	2	134	136	-2	2	2	147	143	-2	-5	3	86	85	-4	-1	3	57	59
3	-5	2	124	123	-2	-1	2	346	353	-1	2	2	30	27	-1	-5	3	36	32	-3	-1	3	37	40
4	-5	2	43	44	-1	-1	2	156	149	0	2	2	118	122	0	-5	3	36	38	-2	-1	3	207	204
5	-5	2	77	76	0	-1	2	44	42	1	2	2	232	234	1	-5	3	81	83	-1	-1	3	194	195
-3	-4	2	37	37	1	-1	2	366	370	2	2	2	53	52	2	-5	3	85	85	0	-1	3	60	59
-2	-4	2	71	71	2	-1	2	279	279	3	2	2	47	48	3	-5	3	24	27	1	-1	3	442	437
-1	-4	2	167	165	3	-1	2	200	201	4	2	2	40	42	4	-5	3	14	10	3	-1	3	90	89
0	-4	2	143	140	4	-1	2	60	64	-6	3	2	58	55	5	-5	3	28	27	4	-1	3	169	175
1	-4	2	46	44	-5	0	2	64	59	-5	3	2	121	124	-3	-4	3	13	5	5	-1	3	82	83
2	-4	2	94	96	-4	0	2	19	13	-4	3	2	99	103	-2	-4	3	11	3	-5	0	3	100	100
4	-4	2	12	15	-3	0	2	112	104	-3	3	2	146	146	-1	-4	3	64	62	-4	0	3	118	118
5	-4	2	54	56	-2	0	2	456	437	-2	3	2	19	20	0	-4	3	119	117	-3	0	3	127	116
-4	-3	2	45	41	-1	0	2	27	23	-1	3	2	16	11	1	-4	3	92	92	-2	0	3	165	150
-3	-3	2	54	54	0	0	2	86	87	0	3	2	136	135	2	-4	3	280	282	-1	0	3	77	67
-2	-3	2	50	52	1	0	2	283	280	3	3	2	46	47	3	-4	3	79	78	0	0	3	42	41
-1	-3	2	243	245	2	0	2	46	47	-6	4	2	26	23	4	-4	3	27	26	1	0	3	88	88
0	-3	2	266	264	3	0	2	78	77	-5	4	2	50	49	5	-4	3	106	104	2	0	3	28	28
1	-3	2	185	186	4	0	2	67	69	-4	4	2	28	25	-3	-3	3	172	176	3	0	3	184	184
2	-3	2	296	301	5	0	2	53	50	-3	4	2	32	33	0	-3	3	20	16	4	0	3	47	44
3	-3	2	98	98	-6	1	2	30	31	-2	4	2	106	106	1	-3	3	116	113	-6	1	3	39	41
4	-3	2	61	61	-5	1	2	55	55	-1	4	2	66	64	2	-3	3	25	26	-5	1	3	64	60
5	-3	2	75	73	-4	1	2	114	113	0	4	2	12	2	3	-3	3	14	16	-4	1	3	67	64
-5	-2	2	85	85	-3	1	2	53	48	1	4	2	121	116	4	-3	3	28	25	-3	1	3	322	317
-4	-2	2	24	21	-2	1	2	29	28	-5	5	2	61	61	5	-3	3	43	44	-2	1	3	40	33

Table A-1 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-1	1	3	15	11	-2	-5	4	16	18	-3	-1	4	135	132	-2	3	4	159	162	-2	-2	5	186	180
0	1	3	292	294	-1	-5	4	29	28	-2	-1	4	26	26	-1	3	4	62	64	-1	-2	5	156	158
1	1	3	116	112	1	-5	4	36	39	-1	-1	4	240	239	0	3	4	45	44	0	-2	5	131	129
2	1	3	99	95	2	-5	4	32	31	0	-1	4	133	130	1	3	4	17	15	2	-2	5	136	133
3	1	3	209	210	3	-5	4	101	101	1	-1	4	67	67	-4	4	4	61	62	3	-2	5	151	149
4	1	3	18	18	4	-5	4	46	44	2	-1	4	120	116	-3	4	4	41	42	4	-2	5	26	23
-5	2	3	22	19	-3	-4	4	189	193	3	-1	4	41	42	-2	4	4	72	69	-5	-1	5	26	24
-4	2	3	53	55	0	-4	4	236	235	4	-1	4	27	26	-1	4	4	47	44	-4	-1	5	22	26
-3	2	3	17	22	1	-4	4	66	68	-5	0	4	82	85	0	4	4	19	19	-3	-1	5	46	51
-2	2	3	192	191	2	-4	4	81	83	-4	0	4	29	31	1	-6	5	20	23	-2	-1	5	79	81
0	2	3	251	243	3	-4	4	240	236	-2	0	4	117	113	2	-6	5	28	26	-1	-1	5	184	186
1	2	3	32	35	4	-4	4	29	29	-1	0	4	223	216	-2	-5	5	11	12	0	-1	5	66	69
2	2	3	29	31	5	-4	4	37	33	0	0	4	17	15	-1	-5	5	85	86	1	-1	5	35	35
3	2	3	50	51	-4	-3	4	32	32	1	0	4	83	85	0	-5	5	63	62	2	-1	5	163	163
-6	3	3	36	36	-3	-3	4	23	25	2	0	4	46	44	2	-5	5	16	20	3	-1	5	14	19
-5	3	3	63	64	-2	-3	4	58	58	3	0	4	140	136	3	-5	5	126	127	4	-1	5	24	24
-4	3	3	55	56	-1	-3	4	87	85	4	0	4	54	52	-3	-4	5	34	33	-5	0	5	51	54
-3	3	3	33	33	0	-3	4	213	206	-5	1	4	135	138	-2	-4	5	115	117	-3	0	5	38	36
-2	3	3	99	101	1	-3	4	59	55	-4	1	4	15	10	-1	-4	5	11	8	-2	0	5	62	61
-1	3	3	20	19	2	-3	4	173	175	-3	1	4	131	127	0	-4	5	109	109	-1	0	5	33	30
0	3	3	57	60	4	-3	4	52	50	-2	1	4	339	327	1	-4	5	22	24	0	0	5	40	42
2	3	3	29	31	5	-3	4	69	66	0	1	4	79	83	2	-4	5	63	61	1	0	5	34	32
-5	4	3	57	59	-4	-2	4	44	45	1	1	4	93	94	3	-4	5	31	30	2	0	5	37	37
-4	4	3	187	185	-3	-2	4	75	72	2	1	4	30	31	-4	-3	5	11	12	-5	1	5	56	51
-3	4	3	92	92	-2	-2	4	123	121	-5	2	4	81	79	-3	-3	5	72	75	-4	1	5	126	130
-2	4	3	75	72	-1	-2	4	178	176	-4	2	4	40	42	-2	-3	5	66	67	-2	1	5	121	119
-1	4	3	154	154	0	-2	4	43	47	-3	2	4	45	42	-1	-3	5	26	28	-1	1	5	131	128
0	4	3	103	102	1	-2	4	66	68	-2	2	4	62	59	0	-3	5	30	32	0	1	5	121	125
1	4	3	48	47	2	-2	4	88	86	-1	2	4	97	98	1	-3	5	26	25	1	1	5	145	150
-3	5	3	28	31	3	-2	4	90	91	1	2	4	15	10	2	-3	5	69	65	2	1	5	103	105
-2	5	3	52	53	4	-2	4	51	49	2	2	4	46	45	3	-3	5	165	162	-5	2	5	13	15
-1	5	3	49	50	5	-2	4	41	38	-5	3	4	35	35	4	-3	5	44	44	-4	2	5	31	32
1	-6	4	121	117	-5	-1	4	68	66	-4	3	4	51	51	-4	-2	5	67	67	-3	2	5	28	22
2	-6	4	35	36	-4	-1	4	205	208	-3	3	4	95	94	-3	-2	5	191	191	-2	2	5	220	214

Table A-1 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-1	2	5	40	41	2	-4	6	28	27	-2	-1	6	107	107	0	1	6	56	58	-3	-2	7	70	72
0	2	5	73	71	3	-4	6	54	54	-1	-1	6	32	33	-4	2	6	48	50	0	-2	7	38	38
1	2	5	96	95	-3	-3	6	21	23	0	-1	6	95	96	-3	2	6	31	31	1	-2	7	86	88
-4	3	5	33	33	-2	-3	6	147	146	1	-1	6	13	12	-2	2	6	39	40	-3	-1	7	22	23
-3	3	5	43	42	0	-3	6	72	73	2	-1	6	28	29	-1	2	6	36	35	-2	-1	7	65	63
-2	3	5	139	140	1	-3	6	66	64	3	-1	6	46	41	0	2	6	94	96	-1	-1	7	40	40
0	3	5	56	55	2	-3	6	42	41	-4	0	6	61	62	-3	3	6	54	52	0	-1	7	130	131
-3	4	5	87	89	3	-3	6	27	26	-2	0	6	140	137	-2	3	6	10	9	-3	0	7	54	56
-1	-5	6	53	54	-4	-2	6	31	33	-1	0	6	23	22	-1	-4	7	17	19	-2	0	7	120	124
0	-5	6	24	24	-3	-2	6	56	55	0	0	6	33	35	0	-4	7	95	97	-1	0	7	120	119
1	-5	6	60	59	-2	-2	6	164	169	1	0	6	139	142	1	-4	7	46	48	0	0	7	50	51
2	-5	6	27	25	0	-2	6	123	124	2	0	6	37	38	-2	-3	7	45	47	1	0	7	59	60
-2	-4	6	102	100	1	-2	6	32	26	-4	1	6	54	52	-1	-3	7	29	34	-3	1	7	30	33
-1	-4	6	11	13	2	-2	6	54	58	-3	1	6	14	14	0	-3	7	167	173	-2	1	7	44	43
0	-4	6	49	50	3	-2	6	28	25	-2	1	6	35	36	1	-3	7	29	28	-1	1	7	69	66
1	-4	6	119	117	-3	-1	6	164	167	-1	1	6	50	48	2	-3	7	27	23	0	1	7	72	73

Table A-2. Observed and calculated structure factors for 'MMPP'.

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	106	92	4	4	0	86	87	9	1	1	288	277	0	3	1	302	294	10	0	2	212	203
4	0	0	301	313	7	4	0	64	77	10	1	1	73	68	1	3	1	183	176	-12	1	2	55	54
6	0	0	133	138	8	4	0	201	191	11	1	1	69	59	3	3	1	110	117	-10	1	2	124	127
12	0	0	97	101	2	5	0	51	27	12	1	1	155	153	4	3	1	180	177	-9	1	2	190	189
1	1	0	264	255	-10	0	1	82	69	-11	2	1	163	163	5	3	1	191	198	-8	1	2	192	182
2	1	0	430	441	-8	0	1	167	159	-10	2	1	127	128	7	3	1	56	62	-7	1	2	161	156
3	1	0	309	313	-6	0	1	244	251	-8	2	1	124	125	8	3	1	72	73	-6	1	2	331	322
4	1	0	86	96	-4	0	1	127	123	-7	2	1	238	236	9	3	1	132	140	-5	1	2	182	174
6	1	0	381	379	-2	0	1	206	196	-6	2	1	147	151	-8	4	1	54	21	-4	1	2	1058	1030
7	1	0	311	306	0	0	1	245	210	-5	2	1	59	56	-7	4	1	88	87	-3	1	2	984	969
8	1	0	110	104	2	0	1	591	621	-4	2	1	737	756	-6	4	1	60	74	-2	1	2	739	709
9	1	0	229	212	4	0	1	214	214	-3	2	1	609	607	-5	4	1	139	131	-1	1	2	693	649
10	1	0	59	30	6	0	1	154	164	-2	2	1	126	126	-1	4	1	217	226	0	1	2	79	70
11	1	0	157	138	8	0	1	202	202	-1	2	1	353	332	0	4	1	233	234	1	1	2	217	223
12	1	0	160	156	10	0	1	154	148	0	2	1	165	165	1	4	1	126	125	2	1	2	464	504
0	2	0	291	273	-12	1	1	191	186	1	2	1	246	244	2	4	1	111	109	3	1	2	824	854
1	2	0	62	55	-11	1	1	68	18	3	2	1	549	526	3	4	1	203	205	4	1	2	119	119
2	2	0	500	486	-10	1	1	112	106	4	2	1	51	17	5	4	1	77	67	5	1	2	294	306
4	2	0	392	413	-8	1	1	122	127	5	2	1	57	64	-4	5	1	106	100	6	1	2	66	74
5	2	0	145	154	-7	1	1	313	316	6	2	1	209	219	-2	5	1	76	72	7	1	2	213	213
6	2	0	80	95	-6	1	1	416	411	7	2	1	148	146	-1	5	1	105	91	8	1	2	232	235
7	2	0	251	243	-5	1	1	94	113	8	2	1	142	135	1	5	1	190	193	9	1	2	165	169
8	2	0	140	145	-4	1	1	452	453	9	2	1	176	165	2	5	1	67	39	10	1	2	151	152
11	2	0	183	190	-3	1	1	318	325	10	2	1	322	322	3	5	1	109	102	-10	2	2	292	296
12	2	0	59	17	-2	1	1	840	860	11	2	1	116	118	-10	0	2	177	184	-8	2	2	120	128
1	3	0	175	164	-1	1	1	822	819	-10	3	1	141	135	-8	0	2	192	201	-7	2	2	168	172
2	3	0	403	399	0	1	1	257	258	-9	3	1	148	137	-6	0	2	138	141	-5	2	2	283	287
3	3	0	390	381	1	1	1	245	259	-8	3	1	69	49	-4	0	2	380	380	-4	2	2	212	216
4	3	0	174	179	2	1	1	359	369	-6	3	1	72	60	-2	0	2	754	719	-1	2	2	50	44
6	3	0	74	78	3	1	1	274	269	-5	3	1	123	137	0	0	2	401	422	1	2	2	399	401
7	3	0	76	80	5	1	1	116	111	-4	3	1	67	76	2	0	2	136	131	2	2	2	365	370
9	3	0	160	168	6	1	1	305	290	-3	3	1	170	173	4	0	2	131	124	3	2	2	365	354
2	4	0	135	135	7	1	1	319	323	-2	3	1	163	160	6	0	2	930	947	4	2	2	294	302
3	4	0	227	221	8	1	1	314	307	-1	3	1	80	74	8	0	2	293	292	5	2	2	226	229

Table A-2 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	2	2	219	227	2	5	2	124	117	-9	2	3	199	196	-7	4	3	172	185	4	1	4	503	506
8	2	2	176	183	3	5	2	161	156	-8	2	3	89	96	-6	4	3	210	215	5	1	4	264	292
10	2	2	67	62	-12	0	3	95	111	-7	2	3	149	141	-4	4	3	76	71	6	1	4	190	185
11	2	2	204	202	-10	0	3	114	107	-5	2	3	541	540	-2	4	3	279	257	7	1	4	148	147
-10	3	2	75	61	-8	0	3	57	74	-4	2	3	81	84	-1	4	3	73	64	8	1	4	144	144
-8	3	2	71	83	-6	0	3	65	59	-3	2	3	180	175	0	4	3	70	70	9	1	4	224	221
-6	3	2	257	278	-4	0	3	622	606	-2	2	3	126	123	1	4	3	254	253	10	1	4	120	133
-5	3	2	234	240	-2	0	3	526	509	-1	2	3	169	181	3	4	3	78	91	11	1	4	85	82
-4	3	2	165	168	0	0	3	942	976	0	2	3	145	134	4	4	3	54	28	12	1	4	60	46
-3	3	2	242	238	2	0	3	580	637	1	2	3	434	429	5	4	3	163	167	-11	2	4	159	169
-1	3	2	303	289	4	0	3	637	656	2	2	3	509	506	6	4	3	204	208	-10	2	4	72	73
0	3	2	108	103	6	0	3	89	93	4	2	3	151	161	-1	5	3	76	67	-9	2	4	178	186
2	3	2	271	262	8	0	3	464	452	5	2	3	59	71	2	5	3	222	230	-8	2	4	270	275
3	3	2	52	49	10	0	3	109	116	6	2	3	164	166	-12	0	4	70	78	-6	2	4	357	358
4	3	2	134	140	12	0	3	155	139	7	2	3	158	164	-8	0	4	55	45	-5	2	4	261	255
5	3	2	223	223	-12	1	3	70	66	8	2	3	82	74	-6	0	4	208	208	-4	2	4	201	196
6	3	2	111	110	-11	1	3	155	157	9	2	3	105	98	0	0	4	285	298	-2	2	4	268	266
7	3	2	141	144	-9	1	3	77	67	11	2	3	105	104	2	0	4	396	423	-1	2	4	88	70
8	3	2	292	295	-8	1	3	170	171	-7	3	3	177	186	4	0	4	813	840	0	2	4	220	207
-7	4	2	104	95	-7	1	3	97	88	-5	3	3	366	376	8	0	4	116	121	1	2	4	157	165
-6	4	2	93	105	-4	1	3	99	92	-4	3	3	157	168	12	0	4	157	141	2	2	4	609	618
-5	4	2	103	106	-3	1	3	358	347	-3	3	3	300	310	-12	1	4	74	82	3	2	4	279	280
-4	4	2	195	202	-2	1	3	276	274	-1	3	3	479	459	-11	1	4	114	122	4	2	4	406	422
-3	4	2	98	114	-1	1	3	389	368	0	3	3	152	149	-9	1	4	167	175	5	2	4	73	78
-1	4	2	186	176	0	1	3	404	399	1	3	3	337	335	-7	1	4	265	247	6	2	4	195	202
0	4	2	210	207	1	1	3	266	274	2	3	3	171	172	-6	1	4	166	163	8	2	4	92	96
1	4	2	160	155	2	1	3	321	333	3	3	3	151	139	-5	1	4	180	178	10	2	4	161	150
2	4	2	95	90	3	1	3	125	128	5	3	3	322	317	-4	1	4	258	247	11	2	4	62	54
3	4	2	56	64	4	1	3	550	563	6	3	3	192	196	-2	1	4	1347	1249	-6	3	4	85	93
4	4	2	90	77	5	1	3	187	195	7	3	3	331	335	-1	1	4	266	237	-5	3	4	183	182
6	4	2	88	88	9	1	3	192	183	8	3	3	54	36	0	1	4	231	231	-3	3	4	253	252
7	4	2	98	112	10	1	3	63	42	9	3	3	109	113	1	1	4	173	171	-1	3	4	134	119
-4	5	2	58	44	-11	2	3	76	93	10	3	3	91	115	2	1	4	89	94	0	3	4	64	70
-2	5	2	97	98	-10	2	3	157	153	-8	4	3	129	133	3	1	4	416	430	2	3	4	78	63

Table A-2 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	3	4	89	99	-5	1	5	389	371	-2	3	5	188	192	-8	1	6	105	102	8	2	6	89	86
5	3	4	227	230	-4	1	5	63	20	0	3	5	144	143	-7	1	6	68	79	9	2	6	385	356
6	3	4	120	120	-3	1	5	546	510	1	3	5	119	123	-6	1	6	115	96	10	2	6	85	70
7	3	4	82	72	-2	1	5	176	158	2	3	5	66	60	-4	1	6	126	131	-8	3	6	103	103
9	3	4	78	73	-1	1	5	55	52	3	3	5	238	255	-3	1	6	312	301	-7	3	6	85	84
10	3	4	55	35	0	1	5	208	181	4	3	5	117	120	-2	1	6	314	302	-6	3	6	171	187
-6	4	4	89	87	1	1	5	528	564	5	3	5	89	98	-1	1	6	191	184	-5	3	6	264	268
-4	4	4	81	83	3	1	5	64	50	6	3	5	60	56	0	1	6	856	830	-4	3	6	109	104
-2	4	4	326	319	4	1	5	223	234	7	3	5	260	253	1	1	6	242	249	-3	3	6	336	326
-1	4	4	180	178	5	1	5	194	217	8	3	5	261	252	2	1	6	142	146	-2	3	6	312	311
0	4	4	112	117	6	1	5	205	195	9	3	5	220	210	3	1	6	90	95	0	3	6	91	96
1	4	4	319	321	8	1	5	173	165	-6	4	5	55	54	4	1	6	305	311	1	3	6	181	191
2	4	4	124	123	10	1	5	122	127	-5	4	5	60	72	5	1	6	177	187	3	3	6	133	144
4	4	4	51	9	-11	2	5	58	27	-4	4	5	135	136	6	1	6	185	183	4	3	6	63	39
5	4	4	172	170	-9	2	5	193	192	-2	4	5	110	116	8	1	6	81	63	5	3	6	84	83
0	5	4	55	48	-6	2	5	162	166	-1	4	5	437	413	9	1	6	59	62	7	3	6	128	125
1	5	4	328	338	-5	2	5	247	240	0	4	5	254	236	11	1	6	153	138	8	3	6	68	54
2	5	4	158	153	-4	2	5	340	331	4	4	5	239	247	-10	2	6	84	84	9	3	6	71	46
-12	0	5	259	275	-3	2	5	576	554	6	4	5	104	102	-9	2	6	61	49	-6	4	6	57	62
-10	0	5	62	83	-2	2	5	128	133	7	4	5	92	88	-8	2	6	119	114	-4	4	6	126	131
-8	0	5	390	392	-1	2	5	130	120	-1	5	5	81	77	-7	2	6	115	117	-3	4	6	91	99
-6	0	5	281	297	0	2	5	75	80	0	5	5	88	106	-6	2	6	143	145	-2	4	6	124	129
-4	0	5	215	195	1	2	5	131	135	-10	0	6	112	104	-5	2	6	398	379	-1	4	6	113	117
-2	0	5	215	216	3	2	5	57	65	-8	0	6	354	367	-4	2	6	172	165	0	4	6	56	43
0	0	5	257	247	4	2	5	550	557	-6	0	6	809	841	-3	2	6	98	92	1	4	6	96	112
6	0	5	285	280	7	2	5	134	138	-4	0	6	138	131	-2	2	6	362	345	2	4	6	116	123
8	0	5	315	314	8	2	5	157	160	-2	0	6	800	752	-1	2	6	108	107	4	4	6	86	69
12	0	5	234	229	10	2	5	141	132	0	0	6	269	279	0	2	6	377	363	5	4	6	66	58
-12	1	5	57	57	11	2	5	49	27	2	0	6	433	435	1	2	6	187	198	6	4	6	235	225
-11	1	5	105	105	-9	3	5	56	51	4	0	6	164	175	2	2	6	285	297	-10	0	7	113	116
-10	1	5	73	86	-8	3	5	102	115	6	0	6	139	142	3	2	6	111	117	-6	0	7	523	539
-9	1	5	196	194	-7	3	5	91	95	8	0	6	158	153	4	2	6	149	153	-4	0	7	102	104
-7	1	5	53	14	-6	3	5	203	200	-10	1	6	116	124	5	2	6	127	127	-2	0	7	124	115
-6	1	5	298	293	-3	3	5	411	412	-9	1	6	119	116	6	2	6	93	96	0	0	7	177	158

Table A-2 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	7	442	466	5	2	7	170	188	4	0	8	231	251	9	2	8	181	163	1	1	9	286	309
4	0	7	69	72	6	2	7	72	84	6	0	8	377	390	-8	3	8	172	193	3	1	9	171	185
8	0	7	274	265	7	2	7	110	121	8	0	8	198	198	-7	3	8	277	288	4	1	9	64	70
10	0	7	107	96	8	2	7	115	119	10	0	8	117	112	-6	3	8	70	42	5	1	9	127	138
-10	1	7	105	93	9	2	7	68	70	-10	1	8	197	218	-4	3	8	210	221	6	1	9	56	16
-9	1	7	215	218	10	2	7	202	186	-7	1	8	125	115	-1	3	8	209	204	8	1	9	247	240
-7	1	7	310	316	-7	3	7	224	235	-6	1	8	198	209	2	3	8	144	156	-7	2	9	256	260
-5	1	7	178	172	-6	3	7	137	141	-5	1	8	152	142	3	3	8	89	110	-6	2	9	113	115
-4	1	7	119	120	-5	3	7	84	80	-4	1	8	66	50	5	3	8	242	250	-5	2	9	269	264
-3	1	7	421	400	-4	3	7	251	258	-3	1	8	295	280	7	3	8	127	125	-4	2	9	165	158
-2	1	7	304	286	-3	3	7	198	193	-2	1	8	329	298	8	3	8	63	32	-3	2	9	60	35
-1	1	7	295	264	-2	3	7	62	56	-1	1	8	92	84	-5	4	8	77	72	-2	2	9	193	180
0	1	7	146	136	-1	3	7	61	48	0	1	8	390	367	-2	4	8	114	95	-1	2	9	91	77
2	1	7	111	118	0	3	7	158	148	1	1	8	382	396	-1	4	8	178	177	0	2	9	130	135
3	1	7	141	144	1	3	7	88	95	2	1	8	264	279	0	4	8	167	162	1	2	9	53	42
4	1	7	54	44	3	3	7	92	91	3	1	8	262	275	1	4	8	55	49	2	2	9	77	92
5	1	7	94	85	7	3	7	115	107	5	1	8	85	83	-8	0	9	89	97	3	2	9	51	54
7	1	7	365	354	8	3	7	76	69	6	1	8	231	231	-6	0	9	158	155	9	2	9	140	131
8	1	7	169	166	-6	4	7	103	121	7	1	8	70	64	-4	0	9	102	104	-7	3	9	194	188
10	1	7	61	34	-2	4	7	150	153	9	1	8	113	112	-2	0	9	94	102	-3	3	9	402	392
11	1	7	115	115	-1	4	7	89	82	10	1	8	75	67	0	0	9	527	530	-2	3	9	234	224
-10	2	7	154	167	0	4	7	80	86	-8	2	8	85	79	2	0	9	231	232	-1	3	9	92	84
-9	2	7	88	98	1	4	7	66	67	-6	2	8	64	70	4	0	9	221	218	0	3	9	100	83
-7	2	7	79	78	3	4	7	53	53	-5	2	8	54	59	6	0	9	388	386	1	3	9	133	142
-6	2	7	259	242	4	4	7	75	70	-4	2	8	110	98	-10	1	9	70	76	2	3	9	237	247
-4	2	7	94	84	5	4	7	376	385	-3	2	8	64	39	-9	1	9	112	115	5	3	9	64	63
-3	2	7	92	85	6	4	7	158	158	-1	2	8	219	201	-7	1	9	75	82	7	3	9	51	45
-2	2	7	58	65	-10	0	8	204	211	0	2	8	54	50	-6	1	9	137	154	-3	4	9	52	50
-1	2	7	225	211	-8	0	8	239	254	1	2	8	280	281	-5	1	9	98	88	-1	4	9	184	171
0	2	7	80	86	-6	0	8	54	46	2	2	8	82	82	-4	1	9	93	80	2	4	9	63	46
1	2	7	100	104	-4	0	8	252	248	3	2	8	146	140	-3	1	9	128	119	-8	0	10	105	125
2	2	7	380	387	-2	0	8	172	169	4	2	8	212	223	-2	1	9	139	132	-2	0	10	646	584
3	2	7	194	196	0	0	8	236	231	5	2	8	172	179	-1	1	9	220	215	0	0	10	287	296
4	2	7	288	298	2	0	8	444	460	8	2	8	82	91	0	1	9	83	90	4	0	10	280	286

Table A-2 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	0	10	115	113	-2	3	10	110	91	-3	2	11	249	245	-2	1	12	58	58	-2	1	13	171	165
8	0	10	212	206	-1	3	10	179	168	-2	2	11	102	99	-1	1	12	221	200	0	1	13	82	71
-7	1	10	184	185	3	3	10	139	148	0	2	11	113	111	0	1	12	70	75	1	1	13	77	72
-6	1	10	66	55	6	3	10	56	38	1	2	11	59	70	2	1	12	136	155	2	1	13	266	259
-5	1	10	131	128	-8	0	11	193	196	2	2	11	112	115	3	1	12	155	159	3	1	13	119	120
-3	1	10	83	81	-4	0	11	72	88	3	2	11	146	139	4	1	12	132	132	5	1	13	114	122
-2	1	10	79	71	-2	0	11	90	82	5	2	11	59	53	-5	2	12	80	83	-4	2	13	136	133
-1	1	10	203	192	4	0	11	335	337	7	2	11	59	60	-4	2	12	102	102	-3	2	13	164	177
0	1	10	246	226	6	0	11	412	424	-4	3	11	153	147	-3	2	12	165	156	-2	2	13	179	174
1	1	10	48	26	8	0	11	120	102	-3	3	11	65	65	-2	2	12	200	194	-1	2	13	95	78
2	1	10	196	197	-8	1	11	81	82	0	3	11	63	50	-1	2	12	121	108	0	2	13	101	97
4	1	10	116	120	-7	1	11	110	117	1	3	11	131	128	1	2	12	61	62	1	2	13	144	148
5	1	10	111	112	-4	1	11	116	120	2	3	11	82	83	2	2	12	186	198	3	2	13	53	50
6	1	10	71	68	-3	1	11	138	141	3	3	11	239	250	3	2	12	110	120	-4	0	14	72	68
7	1	10	227	233	-1	1	11	300	277	4	3	11	97	110	4	2	12	66	69	-2	0	14	79	79
8	1	10	114	96	0	1	11	161	159	-4	0	12	139	136	-1	3	12	87	94	0	0	14	201	187
9	1	10	83	62	1	1	11	55	36	-2	0	12	277	265	1	3	12	83	77	2	0	14	97	93
-8	2	10	109	108	2	1	11	152	165	0	0	12	77	65	2	3	12	71	86	4	0	14	114	111
-5	2	10	156	150	3	1	11	68	64	2	0	12	192	204	-6	0	13	99	88	-3	1	14	91	89
-4	2	10	474	482	4	1	11	109	94	4	0	12	352	364	-4	0	13	139	134	-2	1	14	62	53
-2	2	10	136	125	5	1	11	70	63	6	0	12	58	73	2	0	13	206	210	-1	1	14	128	117
0	2	10	118	118	6	1	11	279	265	-7	1	12	135	145	4	0	13	126	125	0	1	14	92	82
1	2	10	81	81	-6	2	11	126	127	-6	1	12	153	158	6	0	13	127	132	1	1	14	278	292
3	2	10	59	51	-5	2	11	260	263	-5	1	12	277	280	-4	1	13	60	50	2	1	14	164	156
4	2	10	49	14	-4	2	11	163	165	-3	1	12	60	53	-3	1	13	117	125	3	1	14	97	111
-4	3	10	161	163																				

Table A-3. Observed and calculated structure factor for KMPP.

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	0	0	121	141	-4	4	0	330	327	3	7	0	219	218	3	11	0	79	77	1	-9	1	111	129
2	0	0	803	769	-3	4	0	122	126	4	7	0	247	247	-2	12	0	174	184	2	-9	1	484	492
3	0	0	371	360	-2	4	0	272	278	-5	8	0	60	53	-1	12	0	115	109	3	-9	1	150	146
4	0	0	317	301	-1	4	0	47	37	-4	8	0	205	215	0	12	0	69	62	4	-9	1	98	105
5	0	0	276	276	0	4	0	825	781	-3	8	0	176	182	2	12	0	133	124	-4	-8	1	303	306
-5	1	0	214	213	1	4	0	134	126	-1	8	0	69	50	-1	13	0	50	28	-3	-8	1	225	236
-4	1	0	216	224	3	4	0	431	435	0	8	0	84	97	-1-13	1	65	75	0	-8	1	186	184	
-3	1	0	496	505	4	4	0	217	215	1	8	0	426	421	0-13	1	71	57	1	-8	1	159	155	
-2	1	0	601	595	5	4	0	334	312	2	8	0	197	195	2-13	1	127	136	2	-8	1	91	97	
-1	1	0	60	90	-5	5	0	362	329	3	8	0	236	252	-3-12	1	71	79	3	-8	1	214	220	
0	1	0	400	418	-4	5	0	240	238	5	8	0	75	75	-2-12	1	102	97	4	-8	1	187	181	
1	1	0	355	363	-3	5	0	108	96	-5	9	0	134	126	-1-12	1	65	45	5	-8	1	225	224	
2	1	0	393	398	-1	5	0	1033	971	-4	9	0	111	95	0-12	1	131	121	-5	-7	1	60	79	
3	1	0	271	263	0	5	0	274	277	-3	9	0	373	373	1-12	1	76	80	-4	-7	1	177	179	
4	1	0	512	510	1	5	0	349	368	-2	9	0	378	378	2-12	1	74	89	-3	-7	1	206	208	
-5	2	0	208	195	3	5	0	317	322	-1	9	0	321	311	3-12	1	159	168	-2	-7	1	87	82	
-4	2	0	96	92	4	5	0	75	83	0	9	0	108	107	4-12	1	243	248	-1	-7	1	212	192	
-3	2	0	225	238	5	5	0	136	131	1	9	0	230	230	-4-11	1	50	26	0	-7	1	542	533	
-2	2	0	1198	1173	-5	6	0	149	136	2	9	0	363	358	-2-11	1	151	163	1	-7	1	84	77	
-1	2	0	225	204	-4	6	0	73	78	4	9	0	96	93	-1-11	1	52	35	2	-7	1	57	40	
0	2	0	545	541	-2	6	0	459	445	-3	10	0	87	83	0-11	1	144	160	4	-7	1	75	67	
1	2	0	178	193	0	6	0	136	146	-1	10	0	282	287	1-11	1	123	125	5	-7	1	98	90	
2	2	0	484	487	1	6	0	352	346	0	10	0	222	212	3-11	1	152	151	-4	-6	1	117	122	
3	2	0	232	217	2	6	0	144	144	1	10	0	109	108	4-11	1	117	127	-3	-6	1	122	115	
5	2	0	512	483	3	6	0	70	73	2	10	0	227	226	5-11	1	130	139	-1	-6	1	340	352	
-5	3	0	215	213	4	6	0	338	345	3	10	0	55	46	-4-10	1	177	178	0	-6	1	160	160	
-4	3	0	222	224	5	6	0	150	165	4	10	0	62	82	-2-10	1	307	309	1	-6	1	523	515	
-3	3	0	129	134	-5	7	0	295	283	-5	11	0	54	48	-1-10	1	149	156	2	-6	1	229	238	
-2	3	0	1137	1140	-4	7	0	185	175	-3	11	0	111	107	1-10	1	53	63	3	-6	1	140	144	
-1	3	0	516	514	-3	7	0	216	222	-2	11	0	110	119	2-10	1	477	480	4	-6	1	281	272	
0	3	0	490	499	-2	7	0	257	268	-1	11	0	65	46	3-10	1	68	57	5	-6	1	65	61	
1	3	0	259	282	-1	7	0	236	237	0	11	0	179	152	-3	-9	1	135	130	-5	-5	1	324	308
2	3	0	591	625	1	7	0	199	208	1	11	0	75	66	-1	-9	1	201	201	-4	-5	1	238	229
-5	4	0	156	150	2	7	0	184	192	2	11	0	87	94	0	-9	1	82	82	-3	-5	1	782	770

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	-5	1	500	505	4	-2	1	44	33	-4	2	1	885	826	-4	6	1	351	335	5	9	1	64	56
-1	-5	1	653	630	5	-2	1	238	236	-3	2	1	147	152	-3	6	1	241	245	-3	10	1	115	108
0	-5	1	473	444	-5	-1	1	242	230	-2	2	1	364	374	-2	6	1	174	181	-2	10	1	68	63
2	-5	1	225	231	-4	-1	1	581	572	-1	2	1	566	558	-1	6	1	507	493	0	10	1	302	361
3	-5	1	198	195	-3	-1	1	62	58	2	2	1	343	362	0	6	1	149	155	4	10	1	171	170
4	-5	1	196	105	-2	-1	1	293	305	3	2	1	270	259	1	6	1	570	572	-4	11	1	58	67
5	-5	1	306	298	-1	-1	1	255	270	4	2	1	130	133	4	6	1	252	257	-2	11	1	92	98
5	-4	1	427	390	0	-1	1	1231	1198	-4	3	1	476	447	-4	7	1	195	200	-1	11	1	113	103
-3	-4	1	435	412	1	-1	1	263	262	-2	3	1	222	235	-3	7	1	227	230	0	11	1	76	73
-2	-4	1	441	456	3	-1	1	226	229	-1	3	1	831	813	-2	7	1	214	208	1	11	1	72	88
-1	-4	1	55	82	4	-1	1	591	577	0	3	1	280	294	-1	7	1	448	442	2	11	1	225	225
0	-4	1	415	428	5	-1	1	119	103	1	3	1	129	130	0	7	1	114	102	3	11	1	59	38
1	-4	1	1663	1610	-5	0	1	204	182	3	3	1	379	361	1	7	1	471	475	-2	12	1	197	197
2	-4	1	129	139	-4	0	1	89	83	4	3	1	374	371	3	7	1	137	134	-1	12	1	56	58
3	-4	1	267	250	-3	0	1	384	384	-5	4	1	150	136	4	7	1	106	114	0	12	1	141	145
4	-4	1	207	210	-2	0	1	174	183	-3	4	1	404	403	5	7	1	177	177	-1-13	2	57	57	
5	-4	1	57	56	-1	0	1	176	199	-2	4	1	116	111	-5	8	1	163	140	0-13	2	256	255	
-5	-3	1	199	197	0	0	1	510	562	-1	4	1	657	631	-4	8	1	166	160	3-13	2	110	117	
-3	-3	1	587	556	1	0	1	210	216	0	4	1	377	388	-3	8	1	341	336	-1-12	2	112	104	
-2	-3	1	584	565	2	0	1	78	68	1	4	1	963	988	-2	8	1	170	168	0-12	2	120	127	
-1	-3	1	244	257	3	0	1	67	52	3	4	1	67	59	-1	8	1	157	162	4-12	2	123	116	
0	-3	1	403	381	4	0	1	524	525	4	4	1	97	92	0	8	1	115	119	-2-11	2	258	250	
1	-3	1	140	157	5	0	1	65	73	5	4	1	167	175	1	8	1	166	173	-1-11	2	70	71	
2	-3	1	1022	992	-5	1	1	273	275	-4	5	1	61	71	2	8	1	359	357	0-11	2	77	69	
4	-3	1	298	293	-4	1	1	44	32	-3	5	1	68	67	5	8	1	58	53	1-11	2	201	191	
5	-3	1	74	66	-3	1	1	280	291	-2	5	1	411	403	-5	9	1	99	102	2-11	2	223	215	
-5	-2	1	216	199	-2	1	1	1362	1323	-1	5	1	571	554	-4	9	1	268	264	3-11	2	131	136	
-4	-2	1	274	280	-1	1	1	161	181	0	5	1	113	111	-3	9	1	192	192	4-11	2	76	71	
-3	-2	1	571	560	0	1	1	498	554	1	5	1	250	268	-2	9	1	68	61	-4-10	2	52	55	
-1	-2	1	517	560	1	1	1	76	86	2	5	1	441	454	-1	9	1	163	171	-2-10	2	128	128	
0	-2	1	260	255	2	1	1	1028	1010	3	5	1	251	268	1	9	1	90	83	-1-10	2	107	111	
1	-2	1	361	355	4	1	1	224	213	4	5	1	213	214	2	9	1	213	211	0-10	2	89	71	
2	-2	1	925	937	5	1	1	126	118	5	5	1	171	176	3	9	1	200	202	2-10	2	265	264	
3	-2	1	139	139	-5	2	1	70	66	-5	6	1	287	279	4	9	1	134	137	3-10	2	107	103	

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-4	-9	2	316	320	0	-6	2	817	749	-5	-2	2	68	61	0	1	2	646	675	-4	5	2	269	250
-3	-9	2	81	81	1	-6	2	357	337	-4	-2	2	237	230	1	1	2	165	151	-3	5	2	308	316
-2	-9	2	177	179	2	-6	2	414	402	-3	-2	2	61	65	2	1	2	321	333	-2	5	2	128	230
-1	-9	2	69	82	3	-6	2	159	161	-2	-2	2	457	436	3	1	2	77	84	0	5	2	110	109
0	-9	2	339	341	4	-6	2	54	31	-1	-2	2	75	68	4	1	2	352	337	2	5	2	256	248
1	-9	2	349	344	-5	-5	2	150	136	0	-2	2	106	114	5	1	2	78	87	5	5	2	87	75
2	-9	2	125	126	-3	-5	2	211	213	1	-2	2	637	674	-5	2	2	79	64	-4	6	2	211	216
3	-9	2	112	120	-2	-5	2	63	60	2	-2	2	806	864	-4	2	2	1424	1366	-2	6	2	114	100
4	-9	2	242	244	-1	-5	2	66	87	3	-2	2	89	87	-3	2	2	237	235	-1	6	2	248	252
5	-9	2	124	110	0	-5	2	354	357	4	-2	2	616	603	-2	2	2	238	253	0	6	2	160	170
-5	-8	2	125	126	1	-5	2	875	876	5	-2	2	165	156	-1	2	2	283	268	1	6	2	280	299
-4	-8	2	277	281	2	-5	2	375	376	-5	-1	2	117	124	0	2	2	220	195	2	6	2	59	49
-3	-8	2	242	255	3	-5	2	358	359	-4	-1	2	191	193	1	2	2	68	45	4	6	2	153	150
-1	-8	2	124	121	4	-5	2	399	391	-3	-1	2	353	370	2	2	2	348	385	5	6	2	287	285
0	-8	2	50	32	5	-5	2	269	268	-2	-1	2	1000	981	4	2	2	343	339	-5	7	2	164	148
1	-8	2	81	80	-5	-4	2	138	114	-1	-1	2	215	229	-4	3	2	220	219	-4	7	2	212	208
2	-8	2	100	100	-4	-4	2	52	48	0	-1	2	435	502	-3	3	2	289	301	-3	7	2	70	80
4	-8	2	171	161	-3	-4	2	282	269	1	-1	2	123	123	-2	3	2	408	406	-2	7	2	142	152
5	-8	2	92	107	-2	-4	2	808	778	2	-1	2	808	817	-1	3	2	420	417	-1	7	2	249	242
-4	-7	2	63	69	-1	-4	2	274	287	3	-1	2	376	387	0	3	2	583	579	0	7	2	377	361
-3	-7	2	193	192	0	-4	2	118	104	4	-1	2	256	255	1	3	2	321	354	1	7	2	291	296
-2	-7	2	299	300	1	-4	2	233	238	-4	0	2	382	360	2	3	2	80	85	2	7	2	124	130
-1	-7	2	119	119	2	-4	2	506	512	-3	0	2	261	267	3	3	2	69	62	3	7	2	95	96
0	-7	2	148	127	3	-4	2	242	240	-2	0	2	1684	1648	4	3	2	336	341	4	7	2	78	87
1	-7	2	84	79	4	-4	2	91	81	-1	0	2	464	448	5	3	2	159	156	-5	8	2	58	68
2	-7	2	209	218	5	-4	2	137	125	1	0	2	240	238	-5	4	2	96	87	-4	8	2	103	97
3	-7	2	47	24	-4	-3	2	207	205	2	0	2	772	798	-4	4	2	224	222	-1	8	2	139	132
4	-7	2	76	66	-3	-3	2	779	748	3	0	2	83	97	-3	4	2	346	345	0	8	2	246	228
5	-7	2	164	153	-2	-3	2	487	490	4	0	2	322	302	-2	4	2	649	646	1	8	2	262	247
-5	-6	2	245	237	-1	-3	2	733	731	-5	1	2	71	72	-1	4	2	993	981	2	8	2	59	68
-4	-6	2	76	62	0	-3	2	385	355	-4	1	2	707	657	1	4	2	1031	1093	3	8	2	292	292
-3	-6	2	106	110	1	-3	2	253	267	-3	1	2	273	271	2	4	2	415	435	5	8	2	81	71
-2	-6	2	355	356	2	-3	2	71	65	-2	1	2	174	162	3	4	2	529	548	-5	9	2	57	62
-1	-6	2	446	466	3	-3	2	790	794	-1	1	2	109	100	5	4	2	108	102	-4	9	2	89	95

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	9	2	161	151	4-11	3	150	156	3	-7	3	43	34	-1	-3	3	101	110	-2	1	3	64	75	
-2	9	2	54	39	5-11	3	121	114	4	-7	3	314	316	1	-3	3	529	534	-1	1	3	376	377	
-1	9	2	100	109	-4-10	3	250	274	5	-7	3	53	46	2	-3	3	598	598	0	1	3	368	385	
0	9	2	506	493	-2-10	3	100	84	5	-6	3	79	60	4	-3	3	317	321	2	1	3	646	678	
4	9	2	225	221	0-10	3	510	506	-4	-6	3	148	150	-5	-2	3	74	76	3	1	3	107	107	
-5	10	2	61	71	1-10	3	395	388	-2	-6	3	159	163	-4	-2	3	71	62	4	1	3	341	352	
-3	10	2	58	45	2-10	3	90	84	-1	-6	3	371	404	-3	-2	3	1154	1110	-5	2	3	55	59	
2	10	2	145	149	3-10	3	174	171	0	-6	3	403	389	-2	-2	3	206	206	-4	2	3	307	284	
-1	10	2	214	216	4-10	3	113	115	1	-6	3	472	459	-1	-2	3	519	525	-3	2	3	164	163	
0	10	2	87	83	-5	-9	3	101	104	2	-6	3	267	251	0	-2	3	244	269	-2	2	3	486	501
1	10	2	152	147	-4	-9	3	115	126	3	-6	3	373	372	1	-2	3	962	942	-1	2	3	242	244
3	10	2	97	95	-3	-9	3	76	89	4	-6	3	66	74	2	-2	3	164	167	0	2	3	723	692
-2	11	2	153	164	-2	-9	3	76	88	5	-6	3	277	268	3	-2	3	718	705	4	2	3	412	406
1	11	2	70	69	-1	-9	3	318	319	-5	-5	3	274	243	5	-2	3	320	310	5	2	3	97	89
2	11	2	179	181	0	-9	3	227	213	-4	-5	3	204	201	-3	-1	3	111	108	-4	3	3	159	151
-2	12	2	98	80	1	-9	3	104	103	-3	-5	3	123	123	-2	-1	3	1011	1025	-2	3	3	663	661
0	12	2	89	81	2	-9	3	153	150	-1	-5	3	151	173	-1	-1	3	159	170	-1	3	3	266	289
-1-13	3	120	123	4	-9	3	307	306	0	-5	3	337	319	0	-1	3	433	476	0	3	3	164	155	
0-13	3	141	144	-4	-8	3	78	65	1	-5	3	290	295	1	-1	3	679	681	1	3	3	179	195	
1-13	3	92	96	-2	-8	3	404	421	2	-5	3	131	142	2	-1	3	1103	1115	2	3	3	724	780	
2-13	3	102	97	0	-8	3	262	261	3	-5	3	335	335	3	-1	3	334	316	3	3	3	226	233	
4-13	3	111	120	1	-8	3	84	84	4	-5	3	219	220	4	-1	3	145	144	5	3	3	103	98	
-2-12	3	172	173	2	-8	3	219	217	-4	-4	3	147	134	5	-1	3	347	333	-5	4	3	115	114	
-1-12	3	54	57	3	-8	3	142	154	-3	-4	3	519	509	-5	0	3	133	131	-4	4	3	56	40	
0-12	3	101	107	4	-8	3	91	94	-2	-4	3	652	659	-4	0	3	73	80	-3	4	3	51	64	
1-12	3	238	249	5	-8	3	244	241	-1	-4	3	418	425	-3	0	3	151	136	-2	4	3	278	266	
2-12	3	184	183	-5	-7	3	239	223	0	-4	3	404	423	-2	0	3	626	604	-1	4	3	195	198	
3-12	3	110	114	-4	-7	3	203	197	1	-4	3	90	96	0	0	3	281	296	0	4	3	288	281	
-4-11	3	97	106	-3	-7	3	68	48	3	-4	3	508	522	1	0	3	447	451	1	4	3	152	145	
-2-11	3	151	135	-2	-7	3	642	652	4	-4	3	92	89	2	0	3	536	555	2	4	3	435	454	
-1-11	3	151	149	-1	-7	3	137	147	-5	-3	3	114	96	3	0	3	113	106	3	4	3	123	122	
0-11	3	149	139	0	-7	3	582	558	-4	-3	3	99	99	-5	1	3	152	139	4	4	3	244	248	
1-11	3	264	258	1	-7	3	349	361	-3	-3	3	189	192	-4	1	3	222	207	5	4	3	60	68	
2-11	3	205	209	2	-7	3	395	391	-2	-3	3	348	328	-3	1	3	415	425	-3	5	3	257	253	

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	5	3	118	124	4	9	3	104	105	-2-10	4	83	88	-4	-6	4	62	44	2	-3	4	759	776	
-1	5	3	240	210	-2	10	3	132	136	-1-10	4	114	112	-3	-6	4	59	72	3	-3	4	936	928	
0	5	3	633	589	-1	10	3	186	181	0-10	4	322	308	-2	-6	4	238	239	4	-3	4	62	70	
1	5	3	255	273	0	10	3	58	68	1-10	4	216	209	-1	-6	4	385	394	-5	-2	4	96	100	
2	5	3	109	93	2	10	3	83	75	2-10	4	65	57	0	-6	4	786	748	-4	-2	4	334	309	
3	5	3	70	65	-3	11	3	104	98	3-10	4	104	116	1	-6	4	418	411	-3	-2	4	156	151	
4	5	3	269	273	-2	11	3	103	106	4-10	4	246	250	2	-6	4	469	466	-2	-2	4	442	459	
5	5	3	201	200	-1	11	3	71	72	-2	-9	4	371	387	3	-6	4	109	106	-1	-2	4	774	759
-5	6	3	212	194	0	11	3	189	182	-1	-9	4	84	85	4	-6	4	536	535	0	-2	4	72	93
-4	6	3	151	131	0-14	4		155	155	0	-9	4	121	119	-5	-5	4	107	127	1	-2	4	288	266
-3	6	3	277	280	1-14	4		186	190	1	-9	4	139	138	-4	-5	4	163	153	2	-2	4	891	913
0	6	3	442	428	2-14	4		97	97	2	-9	4	271	291	-3	-5	4	109	110	3	-2	4	330	324
1	6	3	363	368	-2-13	4		129	139	3	-9	4	140	148	-2	-5	4	327	350	4	-2	4	170	171
2	6	3	84	89	0-13	4		91	84	4	-9	4	90	88	-1	-5	4	487	503	5	-2	4	255	250
4	6	3	229	226	1-13	4		63	62	5	-9	4	85	90	0	-5	4	373	323	-5	-1	4	179	173
-5	7	3	80	80	2-13	4		204	203	-5	-8	4	81	74	1	-5	4	559	551	-4	-1	4	136	146
-2	7	3	124	112	3-13	4		77	81	-4	-8	4	161	153	2	-5	4	290	283	-3	-1	4	236	222
-1	7	3	187	181	4-13	4		68	51	-3	-8	4	187	196	3	-5	4	538	546	-1	-1	4	1082	1028
0	7	3	290	280	-3-12	4		133	147	-2	-8	4	483	479	4	-5	4	247	258	0	-1	4	546	576
1	7	3	188	186	-2-12	4		116	111	-1	-8	4	52	48	5	-5	4	104	103	1	-1	4	1107	1070
3	7	3	123	130	-1-12	4		202	190	0	-8	4	63	74	-5	-4	4	78	82	2	-1	4	187	197
5	7	3	119	124	1-12	4		233	223	1	-8	4	174	182	-4	-4	4	369	372	3	-1	4	114	100
-5	8	3	193	201	2-12	4		157	156	2	-8	4	288	292	-3	-4	4	364	364	4	-1	4	116	116
-3	8	3	231	231	5-12	4		99	97	3	-8	4	156	166	-2	-4	4	231	208	5	-1	4	67	83
0	8	3	430	428	-4-11	4		123	128	4	-8	4	50	16	-1	-4	4	289	298	-5	0	4	204	199
1	8	3	142	141	-2-11	4		168	175	5	-8	4	62	35	0	-4	4	61	51	-4	0	4	305	294
2	8	3	281	293	-1-11	4		509	514	-4	-7	4	268	269	2	-4	4	358	354	-3	0	4	307	316
4	8	3	56	59	0-11	4		404	391	-1	-7	4	193	197	4	-4	4	213	219	-2	0	4	247	247
-4	9	3	56	64	1-11	4		204	188	0	-7	4	190	195	5	-4	4	81	65	-1	0	4	292	275
-3	9	3	117	124	2-11	4		133	132	1	-7	4	69	75	-4	-3	4	101	97	0	0	4	769	719
-1	9	3	214	208	3-11	4		138	140	2	-7	4	251	252	-3	-3	4	150	142	1	0	4	798	781
0	9	3	92	71	4-11	4		63	69	3	-7	4	245	241	-2	-3	4	156	151	2	0	4	282	283
1	9	3	87	83	5-11	4		119	120	5	-7	4	266	264	-1	-3	4	407	389	3	0	4	239	229
3	9	3	174	171	-3-10	4		176	169	-5	-6	4	50	16	1	-3	4	517	532	4	0	4	510	520

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
5	0	4	91	88	-5	5	4	216	215	-1	8	4	156	146	1-11	5	109	105	-4	-7	5	183	162	
-5	1	4	242	233	-4	5	4	123	103	0	8	4	274	256	2-11	5	66	69	-3	-7	5	108	99	
-3	1	4	208	195	-3	5	4	91	103	1	8	4	170	166	3-11	5	65	70	-2	-7	5	117	113	
-2	1	4	406	403	-2	5	4	90	93	2	8	4	71	52	4-11	5	267	263	-1	-7	5	297	306	
-1	1	4	780	817	-1	5	4	174	151	3	8	4	211	196	5-11	5	80	83	0	-7	5	984	951	
0	1	4	155	166	0	5	4	297	277	4	8	4	92	82	-4-10	5	161	163	1	-7	5	88	90	
1	1	4	383	405	1	5	4	120	137	-4	9	4	84	91	-3-10	5	385	390	2	-7	5	294	297	
2	1	4	219	238	2	5	4	159	169	-3	9	4	132	149	-2-10	5	291	300	3	-7	5	43	41	
4	1	4	346	350	3	5	4	188	223	-2	9	4	92	103	-1-10	5	280	293	4	-7	5	586	584	
5	1	4	68	64	4	5	4	468	488	-1	9	4	262	249	0-10	5	108	83	5	-7	5	103	102	
-5	2	4	66	58	5	5	4	120	105	1	9	4	51	53	1-10	5	124	131	-5	-6	5	156	162	
-4	2	4	113	111	-5	6	4	65	84	2	9	4	213	203	2-10	5	295	297	-2	-6	5	273	286	
-3	2	4	393	380	-4	6	4	60	17	-4	10	4	89	93	3-10	5	197	200	-1	-6	5	402	405	
-2	2	4	611	589	-3	6	4	131	124	-3	10	4	60	62	4-10	5	70	64	0	-6	5	123	103	
-1	2	4	403	406	-2	6	4	198	206	-2	10	4	149	142	-5	-9	5	236	229	1	-6	5	476	470
0	2	4	130	116	0	6	4	57	61	-1	10	4	178	176	-4	-9	5	153	172	2	-6	5	282	289
1	2	4	279	301	1	6	4	59	51	1	10	4	120	111	-3	-9	5	241	239	3	-6	5	250	249
2	2	4	765	817	3	6	4	155	159	0-14	5	74	79	-2	-9	5	324	323	4	-6	5	274	282	
3	2	4	76	81	4	6	4	179	197	1-14	5	94	88	0	-9	5	213	205	-5	-5	5	63	67	
4	2	4	95	89	5	6	4	122	122	2-14	5	80	81	1	-9	5	132	132	-4	-5	5	193	201	
-2	3	4	134	145	-5	7	4	72	77	-1-13	5	50	59	2	-9	5	469	478	-3	-5	5	246	260	
-1	3	4	92	95	-4	7	4	139	146	0-13	5	130	128	3	-9	5	120	122	-2	-5	5	169	157	
0	3	4	243	239	-3	7	4	87	90	1-13	5	156	153	-5	-8	5	78	57	-1	-5	5	320	319	
2	3	4	468	506	-2	7	4	64	70	2-13	5	270	262	-4	-8	5	216	203	0	-5	5	745	751	
4	3	4	95	101	-1	7	4	67	64	3-13	5	53	40	-3	-8	5	241	232	1	-5	5	181	176	
-4	4	4	231	222	0	7	4	169	161	-4-12	5	77	94	-2	-8	5	236	252	2	-5	5	276	279	
-3	4	4	88	94	1	7	4	276	281	0-12	5	189	194	-1	-8	5	63	63	3	-5	5	115	126	
-2	4	4	346	354	2	7	4	302	306	2-12	5	144	148	0	-8	5	372	351	4	-5	5	361	352	
-1	4	4	77	81	3	7	4	133	156	3-12	5	109	116	1	-8	5	91	94	5	-5	5	70	77	
0	4	4	578	516	4	7	4	70	64	4-12	5	207	214	2	-8	5	72	57	-5	-4	5	70	52	
1	4	4	280	270	5	7	4	129	134	5-12	5	94	102	3	-8	5	195	193	-4	-4	5	387	367	
3	4	4	95	99	-4	8	4	154	154	-2-11	5	166	173	4	-8	5	273	274	-3	-4	5	136	122	
4	4	4	259	261	-3	8	4	57	72	-1-11	5	160	160	5	-8	5	59	53	-2	-4	5	397	395	
5	4	4	88	86	-2	8	4	88	86	0-11	5	396	378	-5	-7	5	210	205	-1	-4	5	433	415	

Table A-3 (continued)

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
1	-4	5	571	566	-4	0	5	180	166	-2	4	5	283	291	-2	9	5	158	165	0	-9	6	233	221
2	-4	5	299	310	-2	0	5	284	293	0	4	5	286	271	-1	9	5	68	48	1	-9	6	238	243
3	-4	5	555	547	-1	0	5	887	966	3	4	5	75	77	1	9	5	240	236	2	-9	6	97	99
4	-4	5	101	105	0	0	5	406	360	4	4	5	210	218	-2	10	5	149	175	3	-9	6	89	97
5	-4	5	202	197	1	0	5	716	709	5	4	5	67	55	-1	-14	6	103	103	4	-9	6	182	180
-5	-3	5	204	191	2	0	5	144	140	-2	5	5	562	606	1	-14	6	63	68	-5	-8	6	123	112
-4	-3	5	345	326	3	0	5	284	301	-1	5	5	55	66	0	-13	6	216	199	-4	-8	6	321	294
-3	-3	5	237	230	4	0	5	244	258	0	5	5	400	380	1	-13	6	58	40	-3	-8	6	51	52
-2	-3	5	255	249	5	0	5	154	148	2	5	5	174	165	2	-13	6	193	204	-1	-8	6	114	125
-1	-3	5	185	176	-5	1	5	143	125	3	5	5	286	296	4	-13	6	89	94	0	-8	6	391	389
0	-3	5	453	496	-3	1	5	56	74	4	5	5	187	198	-4	-12	6	83	114	1	-8	6	146	134
1	-3	5	182	168	-2	1	5	374	378	5	5	5	82	91	-3	-12	6	193	194	4	-8	6	410	413
2	-3	5	374	364	-1	1	5	578	598	-4	6	5	137	142	-1	-12	6	382	371	5	-8	6	53	13
3	-3	5	301	308	1	1	5	846	859	-3	6	5	157	170	1	-12	6	146	141	-5	-7	6	224	198
4	-3	5	56	50	2	1	5	372	383	-2	6	5	289	298	2	-12	6	95	83	-3	-7	6	164	170
-5	-2	5	262	245	3	1	5	157	166	-1	6	5	192	200	3	-12	6	72	82	-2	-7	6	73	74
-4	-2	5	233	236	4	1	5	154	155	0	6	5	157	160	4	-12	6	285	290	0	-7	6	357	352
-3	-2	5	472	456	5	1	5	131	140	2	6	5	55	37	-3	-11	6	213	221	1	-7	6	299	290
-2	-2	5	335	348	-2	2	5	351	394	3	6	5	67	56	-2	-11	6	325	335	3	-7	6	224	229
-1	-2	5	573	574	-1	2	5	114	123	4	6	5	170	173	1	-11	6	70	51	4	-7	6	156	148
0	-2	5	190	193	0	2	5	485	439	-4	7	5	212	227	3	-11	6	86	94	-5	-6	6	65	80
1	-2	5	260	259	1	2	5	157	145	-3	7	5	134	135	4	-11	6	146	150	-3	-6	6	260	260
2	-2	5	478	461	2	2	5	409	437	0	7	5	359	355	5	-11	6	95	100	-2	-6	6	58	40
3	-2	5	624	631	4	2	5	55	47	1	7	5	91	94	-4	-10	6	48	17	-1	-6	6	260	271
5	-2	5	442	428	-5	3	5	110	98	2	7	5	106	116	-3	-10	6	304	294	0	-6	6	410	365
-5	-1	5	120	113	-4	3	5	270	264	3	7	5	308	309	-1	-10	6	72	84	1	-6	6	63	53
-4	-1	5	258	236	-2	3	5	309	324	4	7	5	72	74	1	-10	6	161	167	2	-6	6	152	158
-3	-1	5	151	141	-1	3	5	77	85	-4	8	5	228	225	2	-10	6	423	430	3	-6	6	55	55
0	-1	5	740	747	0	3	5	378	330	-3	8	5	234	230	3	-10	6	151	153	5	-6	6	58	55
1	-1	5	533	513	2	3	5	68	60	-1	8	5	147	142	-5	-9	6	279	280	-4	-5	6	457	429
3	-1	5	192	195	4	3	5	76	64	0	8	5	106	110	-4	-9	6	334	317	-2	-5	6	118	127
4	-1	5	220	228	5	3	5	82	74	1	8	5	179	176	-3	-9	6	118	124	-1	-5	6	476	457
5	-1	5	71	77	-4	4	5	87	77	2	8	5	136	138	-2	-9	6	228	236	0	-5	6	239	249
-5	0	5	326	289	-3	4	5	54	31	3	8	5	104	100	-1	-9	6	150	157	1	-5	6	578	561

Table A-3 (continued)

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
2	-5	6	179	179	-4	-1	6	220	207	1	2	6	232	225	1	6	6	75	64	5	-12	7	126	133
3	-5	6	166	177	-3	-1	6	173	172	2	2	6	169	172	3	6	6	234	233	-4	-11	7	101	108
4	-5	6	106	114	-2	-1	6	313	332	3	2	6	62	67	4	6	6	60	70	-3	-11	7	98	92
5	-5	6	265	277	-1	-1	6	878	925	4	2	6	213	240	-4	7	6	148	149	-2	-11	7	217	225
-5	-4	6	281	271	0	-1	6	248	272	-5	3	6	230	236	-2	7	6	75	85	1	-11	7	255	244
4	-4	6	325	303	1	-1	6	203	173	-4	3	6	77	74	-1	7	6	263	256	2	-11	7	237	227
-3	-4	6	148	149	2	-1	6	108	107	-3	3	6	212	225	0	7	6	468	432	3	-11	7	111	110
-2	-4	6	589	552	3	-1	6	130	109	-2	3	6	49	44	2	7	6	102	101	-4	-10	7	173	186
-1	-4	6	107	115	4	-1	6	217	232	-1	3	6	319	318	4	7	6	126	141	-2	-10	7	105	100
0	-4	6	639	676	5	-1	6	154	157	0	3	6	414	363	-3	8	6	61	77	0	-10	7	222	211
1	-4	6	224	213	-5	0	6	311	287	1	3	6	91	83	-1	8	6	79	79	1	-10	7	84	86
2	-4	6	53	64	-4	0	6	72	69	2	3	6	60	72	0	8	6	135	111	4	-10	7	132	131
3	-4	6	165	167	-3	0	6	104	100	3	3	6	88	93	1	8	6	157	158	-5	-9	7	107	117
4	-4	6	88	89	-2	0	6	216	227	4	3	6	263	286	2	8	6	95	94	-4	-9	7	301	295
5	-4	6	166	160	-1	0	6	51	27	-2	4	6	642	674	3	8	6	152	160	-2	-9	7	138	128
-5	-3	6	142	133	0	0	6	94	100	-1	4	6	139	137	-3	9	6	139	141	-1	-9	7	97	96
-4	-3	6	138	141	1	0	6	349	341	0	4	6	407	364	-2	9	6	132	147	0	-9	7	181	197
-3	-3	6	434	409	2	0	6	406	418	1	4	6	90	88	-1	9	6	208	221	1	-9	7	46	39
-1	-3	6	604	609	3	0	6	204	208	2	4	6	377	377	0	-14	7	133	136	3	-9	7	83	82
0	-3	6	430	429	5	0	6	57	76	3	4	6	117	131	1	-14	7	45	48	4	-9	7	166	183
1	-3	6	160	180	-5	1	6	195	196	4	4	6	443	462	2	-14	7	104	110	-4	-8	7	208	202
2	-3	6	251	241	-4	1	6	370	366	5	4	6	56	43	-1	-13	7	211	214	-3	-8	7	268	277
5	-3	6	348	342	-3	1	6	218	234	-3	5	6	68	50	0	-13	7	215	215	-2	-8	7	279	277
-5	-2	6	101	82	-2	1	6	226	247	-2	5	6	351	364	1	-13	7	176	167	-1	-8	7	129	126
-3	-2	6	51	48	0	1	6	143	139	-1	5	6	196	200	2	-13	7	166	156	0	-8	7	94	97
-2	-2	6	482	492	1	1	6	95	63	0	5	6	179	165	3	-13	7	169	173	2	-8	7	273	277
-1	-2	6	91	108	2	1	6	329	357	1	5	6	103	97	4	-13	7	104	113	4	-8	7	152	152
0	-2	6	395	400	3	1	6	94	93	2	5	6	494	497	-3	-12	7	165	177	5	-8	7	195	198
1	-2	6	371	361	4	1	6	123	132	4	5	6	70	60	-2	-12	7	127	116	-5	-7	7	85	99
2	-2	6	69	70	-4	2	6	249	253	5	5	6	69	62	-1	-12	7	135	131	-4	-7	7	64	72
3	-2	6	891	888	-3	2	6	137	126	-4	6	6	118	115	0	-12	7	103	100	-2	-7	7	318	314
4	-2	6	182	177	-2	2	6	195	203	-3	6	6	124	134	1	-12	7	116	100	-1	-7	7	113	105
5	-2	6	176	182	-1	2	6	167	172	-2	6	6	125	136	2	-12	7	84	96	2	-7	7	174	172
-5	-1	6	81	60	0	2	6	609	538	0	6	6	199	195	4	-12	7	58	47	3	-7	7	58	56

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
5	-7	7	72	86	0	-3	7	493	495	1	1	7	137	135	-4	6	7	84	69	-1	-11	8	59	46
-5	-6	7	115	111	1	-3	7	209	197	4	1	7	369	406	-3	6	7	55	55	0	-11	8	127	120
-4	-6	7	457	439	2	-3	7	137	143	5	1	7	89	103	-1	6	7	50	29	1	-11	8	71	69
-3	-6	7	64	59	3	-3	7	245	236	-5	2	7	117	138	0	6	7	162	156	3	-11	8	122	124
-2	-6	7	174	167	5	-3	7	161	164	-4	2	7	146	154	1	6	7	63	78	5	-11	8	105	92
-1	-6	7	65	75	-5	-2	7	137	127	-3	2	7	206	223	2	6	7	55	37	-5	-10	8	153	160
0	-6	7	543	551	-4	-2	7	65	56	-2	2	7	72	65	3	6	7	108	128	-3	-10	8	157	164
1	-6	7	260	268	-1	-2	7	239	267	-1	2	7	85	75	4	6	7	184	168	-2	-10	8	201	196
3	-6	7	85	79	0	-2	7	516	536	0	2	7	361	317	-4	7	7	142	129	-1	-10	8	121	109
5	-6	7	72	90	1	-2	7	357	343	1	2	7	207	201	-3	7	7	56	25	0	-10	8	227	232
-5	-5	7	94	85	2	-2	7	322	321	3	2	7	217	229	-1	7	7	176	177	1	-10	8	100	98
4	-5	7	355	349	3	-2	7	275	289	4	2	7	537	505	0	7	7	163	151	4	-10	8	83	85
-3	-5	7	99	77	4	-2	7	202	219	5	2	7	69	71	1	7	7	75	76	5	-10	8	50	38
-2	-5	7	201	195	5	-2	7	155	156	-3	3	7	84	100	2	7	7	179	193	-4	-9	8	92	101
0	-5	7	807	816	-5	-1	7	255	235	-2	3	7	251	273	3	7	7	51	60	-2	-9	8	254	259
1	-5	7	92	86	-4	-1	7	67	59	-1	3	7	149	160	-1	8	7	159	148	1	-9	8	188	186
2	-5	7	195	198	-3	-1	7	117	108	0	3	7	447	397	0	8	7	62	73	2	-9	8	316	326
3	-5	7	100	100	-2	-1	7	362	376	1	3	7	72	65	1	8	7	135	137	3	-9	8	130	132
4	-5	7	122	122	-1	-1	7	322	318	2	3	7	175	180	-1	-14	8	121	126	5	-9	8	70	72
5	-5	7	120	103	0	-1	7	224	226	3	3	7	95	94	0	-14	8	110	111	-5	-8	8	74	70
-5	-4	7	104	99	1	-1	7	332	291	5	3	7	92	116	1	-14	8	115	108	-3	-8	8	130	141
-4	-4	7	71	94	4	-1	7	187	191	-4	4	7	77	79	2	-14	8	81	70	-2	-8	8	402	391
-3	-4	7	212	210	5	-1	7	232	238	-3	4	7	132	158	0	-13	8	195	185	-1	-8	8	156	147
-2	-4	7	362	349	-5	0	7	174	186	-2	4	7	285	311	1	-13	8	91	101	1	-8	8	177	172
-1	-4	7	216	228	-4	0	7	273	274	-1	4	7	79	68	2	-13	8	201	208	2	-8	8	419	420
0	-4	7	288	290	-3	0	7	203	222	0	4	7	151	137	3	-13	8	160	169	3	-8	8	54	67
1	-4	7	370	370	-2	0	7	265	300	2	4	7	526	520	-3	-12	8	71	84	4	-8	8	123	128
4	-4	7	167	152	-1	0	7	598	607	3	4	7	101	94	-2	-12	8	49	28	5	-8	8	51	31
5	-4	7	190	198	1	0	7	580	552	4	4	7	182	192	1	-12	8	95	100	-5	-7	8	161	149
-5	-3	7	215	213	2	0	7	229	238	-4	5	7	164	159	2	-12	8	208	204	-4	-7	8	100	93
-4	-3	7	300	294	5	0	7	189	191	-2	5	7	81	55	3	-12	8	103	106	-3	-7	8	93	77
-3	-3	7	213	215	-4	1	7	196	226	-1	5	7	103	112	-4	-11	8	109	102	-2	-7	8	94	91
-2	-3	7	417	416	-1	1	7	170	176	0	5	7	88	87	-3	-11	8	68	68	0	-7	8	285	288
-1	-3	7	305	313	0	1	7	513	458	2	5	7	484	483	-2	-11	8	159	161	1	-7	8	72	68

Table A-3 (continued)

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
3	-7	8	173	167	1	-3	8	338	304	-2	1	8	98	96	1	5	8	74	61	-2-10	9	214	220	
5	-7	8	203	195	2	-3	8	266	263	-1	1	8	69	70	2	5	8	110	113	0-10	9	181	173	
-4	-6	8	204	213	3	-3	8	371	359	0	1	8	231	196	3	5	8	52	20	1-10	9	285	269	
-3	-6	8	66	41	4	-3	8	94	104	1	1	8	480	440	4	5	8	105	193	2-10	9	322	333	
-2	-6	8	64	53	5	-3	8	89	87	2	1	8	87	87	-4	6	8	85	91	3-10	9	219	223	
0	-6	8	632	634	-4	-2	8	106	104	4	1	8	161	163	-3	6	8	113	103	4-10	9	64	69	
1	-6	8	189	177	-3	-2	8	61	64	5	1	8	83	97	-2	6	8	141	139	-4	-9	9	56	40
2	-6	8	228	225	-1	-2	8	160	177	-3	2	8	69	83	0	6	8	227	204	-3	-9	9	71	82
3	-6	8	71	59	0	-2	8	90	89	-2	2	8	86	87	2	6	8	227	231	-2	-9	9	413	402
4	-6	8	342	340	1	-2	8	108	90	-1	2	8	142	139	3	6	8	62	58	-1	-9	9	216	212
5	-6	8	110	122	2	-2	8	68	36	0	2	8	222	196	-3	7	8	67	79	1	-9	9	86	74
-4	-5	8	98	79	3	-2	8	141	149	2	2	8	59	38	-2	7	8	232	231	2	-9	9	346	356
-3	-5	8	266	283	4	-2	8	203	199	3	2	8	94	94	0	7	8	61	61	4	-9	9	98	95
-2	-5	8	288	295	5	-2	8	190	197	4	2	8	164	170	1	7	8	81	70	5	-9	9	54	60
0	-5	8	147	143	-5	-1	8	176	181	5	2	8	66	78	0-14	9	130	122	-3	-8	9	92	78	
1	-5	8	136	126	-4	-1	8	174	171	-5	3	8	83	78	1-14	9	113	119	-1	-8	9	64	48	
2	-5	8	126	121	-3	-1	8	229	248	-4	3	8	125	131	-1-13	9	64	68	0	-8	9	252	257	
3	-5	8	217	231	-1	-1	8	180	201	-3	3	8	147	162	0-13	9	130	132	1	-8	9	137	124	
4	-5	8	295	296	0	-1	8	144	137	-2	3	8	107	113	1-13	9	76	59	2	-8	9	82	86	
5	-5	8	201	214	1	-1	8	624	574	0	3	8	58	48	3-13	9	79	81	3	-8	9	152	158	
-5	-4	8	105	97	2	-1	8	153	171	3	3	8	104	107	-1-12	9	129	110	4	-8	9	191	187	
-4	-4	8	63	67	3	-1	8	153	150	4	3	8	152	166	0-12	9	83	75	5	-8	9	163	172	
-3	-4	8	87	93	4	-1	8	173	180	-4	4	8	286	320	1-12	9	51	51	-4	-7	9	158	164	
-2	-4	8	176	175	5	-1	8	179	187	-3	4	8	110	102	3-12	9	124	126	-3	-7	9	53	23	
-1	-4	8	176	178	-4	0	8	108	118	-2	4	8	52	51	-4-11	9	149	154	-1	-7	9	80	87	
1	-4	8	80	77	-2	0	8	160	166	0	4	8	355	317	-3-11	9	85	88	0	-7	9	209	216	
2	-4	8	790	782	-1	0	8	290	288	1	4	8	159	165	-2-11	9	156	163	1	-7	9	62	57	
3	-4	8	212	218	0	0	8	332	292	2	4	8	112	89	-1-11	9	182	165	2	-7	9	161	156	
4	-4	8	65	62	1	0	8	168	151	3	4	8	110	107	0-11	9	115	106	4	-7	9	362	368	
5	-4	8	91	82	2	0	8	98	91	4	4	8	112	114	1-11	9	124	117	5	-7	9	129	126	
-5	-3	8	107	137	4	0	8	281	307	-5	5	8	95	103	2-11	9	144	152	-5	-6	9	54	47	
-3	-3	8	70	85	5	0	8	132	148	-3	5	8	51	23	3-11	9	78	72	-3	-6	9	69	51	
-2	-3	8	55	28	-5	1	8	79	86	-2	5	8	65	72	4-11	9	66	57	-2	-6	9	423	409	
0	-3	8	171	167	-4	1	8	211	225	0	5	8	177	180	-3-10	9	130	130	-1	-6	9	124	126	

Table A-3 (continued)

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
0	-6	9	165	169	5	-2	9	102	122	-3	3	9	120	130	1	-11	10	163	152	-5	-6	10	72	57
1	-6	9	107	94	-4	-1	9	133	161	-2	3	9	105	106	2	-11	10	123	120	-4	-6	10	67	67
2	-6	9	175	173	-3	-1	9	159	168	0	3	9	400	360	3	-11	10	187	197	-3	-6	10	84	85
3	-6	9	220	213	-2	-1	9	182	199	2	3	9	205	186	4	-11	10	87	76	-2	-6	10	383	360
5	-6	9	137	141	-1	-1	9	137	142	3	3	9	252	239	-4	-10	10	65	69	0	-6	10	133	133
-3	-5	9	71	94	0	-1	9	109	95	4	3	9	64	58	-3	-10	10	128	118	1	-6	10	241	222
-2	-5	9	267	276	1	-1	9	90	93	-4	4	9	76	87	-2	-10	10	267	253	2	-6	10	454	450
-1	-5	9	209	211	2	-1	9	229	227	-3	4	9	133	142	-1	-10	10	231	221	3	-6	10	136	138
2	-5	9	638	620	3	-1	9	112	115	-1	4	9	205	217	0	-10	10	62	55	4	-6	10	106	94
-4	-4	9	171	174	4	-1	9	135	142	0	4	9	400	434	1	-10	10	114	107	5	-6	10	75	67
-3	-4	9	137	133	5	-1	9	59	70	2	4	9	100	102	2	-10	10	303	294	-4	-5	10	212	200
-2	-4	9	125	117	-5	0	9	93	110	4	4	9	152	147	4	-10	10	115	107	-3	-5	10	157	155
-1	-4	9	112	123	-4	0	9	240	246	-2	5	9	85	86	5	-10	10	79	100	-1	-5	10	63	64
0	-4	9	74	61	-3	0	9	332	344	-1	5	9	136	144	-4	-9	10	91	88	0	-5	10	117	121
2	-4	9	68	72	-2	0	9	95	106	0	5	9	62	61	-3	-9	10	204	200	1	-5	10	162	163
3	-4	9	121	112	-1	0	9	144	153	-2	5	9	178	170	-1	-9	10	115	121	2	-5	10	162	165
4	-4	9	368	368	0	0	9	205	167	3	5	9	67	70	0	-9	10	162	168	4	-5	10	94	99
5	-4	9	86	93	1	0	9	355	333	-2	6	9	166	167	2	-9	10	159	160	5	-5	10	163	169
-4	-3	9	297	285	2	0	9	66	63	-1	6	9	68	66	3	-9	10	68	86	-4	-4	10	168	170
-1	-3	9	280	306	3	0	9	119	122	-2	-13	10	84	91	4	-9	10	103	100	-3	-4	10	153	155
0	-3	9	55	31	0	1	9	425	390	-1	-13	10	70	61	-5	-8	10	57	72	-2	-4	10	242	247
1	-3	9	65	57	1	1	9	61	68	0	-13	10	85	81	-3	-8	10	141	128	-1	-4	10	285	300
2	-3	9	180	176	2	1	9	132	124	2	-13	10	79	83	0	-8	10	215	223	0	-4	10	452	428
4	-3	9	139	139	3	1	9	81	76	3	-13	10	122	122	2	-8	10	147	142	1	-4	10	222	198
5	-3	9	107	106	5	1	9	122	133	-3	-12	10	75	76	3	-8	10	102	115	2	-4	10	89	84
-5	-2	9	71	85	-5	2	9	185	177	-2	-12	10	136	129	4	-8	10	380	381	3	-4	10	123	140
-4	-2	9	120	111	-4	2	9	166	191	-1	-12	10	241	226	5	-8	10	252	263	4	-4	10	116	123
-3	-2	9	209	223	-3	2	9	254	268	0	-12	10	212	216	-3	-7	10	212	201	5	-4	10	82	86
-2	-2	9	202	219	0	2	9	231	216	1	-12	10	144	139	-2	-7	10	253	251	-3	-3	10	160	152
0	-2	9	181	189	1	2	9	318	303	2	-12	10	97	99	-1	-7	10	159	167	-2	-3	10	296	306
1	-2	9	407	362	2	2	9	245	238	4	-12	10	148	147	1	-7	10	80	68	0	-3	10	155	163
2	-2	9	275	261	3	2	9	214	210	-4	-11	10	84	100	3	-7	10	436	442	1	-3	10	172	157
3	-2	9	245	245	5	2	9	90	91	-2	-11	10	127	130	4	-7	10	81	88	2	-3	10	79	82
4	-2	9	149	159	-4	3	9	202	220	-1	-11	10	56	72	5	-7	10	239	241	3	-3	10	231	226

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	-3	10	272	270	3	2	10	138	137	0	-9	11	106	115	2	-5	11	93	106	-1	0	11	216	204
4	-2	10	63	74	4	2	10	56	71	2	-9	11	109	118	4	-5	11	250	265	0	0	11	231	199
-2	-2	10	482	517	-4	3	10	52	66	3	-9	11	162	173	-5	-4	11	130	133	1	0	11	134	121
-1	-2	10	105	105	-3	3	10	111	115	4	-9	11	143	142	-4	-4	11	75	78	3	0	11	203	211
2	-2	10	273	271	-1	3	10	67	43	5	-9	11	120	134	-2	-4	11	199	201	4	0	11	114	114
3	-2	10	222	237	0	3	10	168	154	-3	-8	11	82	72	-1	-4	11	127	129	-5	1	11	54	47
5	-2	10	84	67	3	3	10	146	138	-2	-8	11	64	57	0	-4	11	242	245	-3	1	11	82	66
-4	-1	10	73	49	-2	4	10	167	170	-1	-8	11	221	236	1	-4	11	196	187	0	1	11	68	52
-3	-1	10	325	330	2	4	10	196	191	2	-8	11	162	157	3	-4	11	103	112	3	1	11	131	124
2	-1	10	161	175	-1	5	10	236	235	4	-8	11	73	77	4	-4	11	213	203	4	1	11	102	106
-1	-1	10	331	333	0	5	10	109	103	5	-8	11	58	59	-2	-3	11	188	204	-4	2	11	49	47
0	-1	10	87	74	-1	-13	11	87	100	-5	-7	11	88	83	-1	-3	11	191	183	-3	2	11	82	65
1	-1	10	225	221	0	-13	11	112	103	-4	-7	11	103	113	1	-3	11	127	103	-2	2	11	89	91
1	-1	10	173	173	1	-13	11	68	65	-2	-7	11	137	127	2	-3	11	216	207	-1	2	11	196	209
3	-1	10	164	167	-1	-12	11	134	141	0	-7	11	71	65	3	-3	11	136	131	1	2	11	146	136
4	-1	10	74	56	0	-12	11	201	194	1	-7	11	176	175	4	-3	11	233	253	2	2	11	126	123
-5	0	10	64	49	2	-12	11	84	88	2	-7	11	264	266	5	-3	11	68	61	3	2	11	114	117
-3	0	10	70	78	-3	-11	11	59	67	3	-7	11	242	245	-5	-2	11	78	80	-2	3	11	262	268
0	0	10	205	180	-2	-11	11	98	93	4	-7	11	102	105	-4	-2	11	70	61	-1	3	11	64	58
1	0	10	217	195	-1	-11	11	130	142	5	-7	11	72	67	-3	-2	11	57	22	0	3	11	58	55
2	0	10	261	250	0	-11	11	239	257	-4	-6	11	279	288	-2	-2	11	196	204	1	3	11	142	138
3	0	10	209	216	1	-11	11	128	116	-3	-6	11	60	44	-1	-2	11	340	342	2	3	11	117	130
5	0	10	79	74	2	-11	11	179	186	-2	-6	11	128	113	0	-2	11	196	179	-2	4	11	99	110
-4	1	10	120	144	4	-11	11	95	99	0	-6	11	337	323	1	-2	11	233	222	-1	4	11	239	245
-3	1	10	157	173	-4	-10	11	110	118	1	-6	11	431	386	2	-2	11	216	202	0	4	11	61	30
-2	1	10	84	86	-3	-10	11	93	101	2	-6	11	190	187	3	-2	11	177	180	1	4	11	55	60
-1	1	10	185	182	-1	-10	11	80	103	3	-6	11	293	311	-3	-1	11	120	103	0	-12	12	188	188
0	1	10	329	294	0	-10	11	66	56	4	-6	11	117	120	0	-1	11	125	128	1	-12	12	103	107
1	1	10	89	90	1	-10	11	107	100	-5	-5	11	79	79	1	-1	11	135	133	2	-12	12	77	83
2	1	10	235	237	2	-10	11	127	122	-4	-5	11	84	80	2	-1	11	211	199	0	-11	12	127	126
3	1	10	156	162	3	-10	11	102	112	-2	-5	11	121	126	3	-1	11	109	104	1	-11	12	203	198
0	2	10	218	193	4	-10	11	103	87	-1	-5	11	163	172	4	-1	11	217	221	2	-11	12	60	67
1	2	10	141	130	-3	-9	11	199	209	0	-5	11	408	393	5	-1	11	57	63	3	-11	12	91	98
2	2	10	64	42	-2	-9	11	155	167	1	-5	11	217	206	-2	0	11	191	204	-3	-10	12	128	134

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	-10	12	102	110	-2	-5	12	113	102	3	-1	12	123	131	-2	-8	13	79	87	-4	-3	13	181	177
0	-10	12	93	88	-1	-5	12	271	273	4	-1	12	123	124	-1	-8	13	165	170	-1	-3	13	81	86
1	-10	12	96	84	0	-5	12	142	140	-3	0	12	64	57	0	-8	13	106	126	0	-3	13	172	152
4	-10	12	110	108	1	-5	12	130	124	-2	0	12	55	51	1	-8	13	224	209	1	-3	13	58	49
-4	-9	12	53	54	2	-5	12	159	158	-1	0	12	56	63	3	-8	13	162	168	-3	-2	13	78	91
-2	-9	12	146	142	3	-5	12	63	60	1	0	12	95	92	4	-8	13	109	120	-2	-2	13	94	106
-1	-9	12	74	77	4	-5	12	102	92	3	0	12	76	72	-3	-7	13	88	83	-1	-2	13	207	203
2	-9	12	146	143	5	-5	12	62	61	-3	1	12	135	145	-2	-7	13	104	193	2	-2	13	175	187
4	-9	12	101	102	-3	-4	12	140	153	-2	1	12	153	168	-1	-7	13	135	136	3	-2	13	69	65
-3	-8	12	52	52	-2	-4	12	153	168	-1	1	12	149	152	0	-7	13	137	175	-2	-1	13	178	174
-2	-8	12	225	234	0	-4	12	67	44	0	1	12	85	89	1	-7	13	134	119	0	-1	13	175	180
-1	-8	12	105	118	2	-4	12	202	190	1	1	12	70	44	2	-7	13	68	93	1	-1	13	109	97
0	-8	12	140	131	3	-4	12	74	61	2	1	12	82	79	4	-7	13	178	176	2	-1	13	203	202
1	-8	12	272	246	4	-4	12	161	157	-3	2	12	60	91	-2	-6	13	203	220	-3	0	13	120	127
2	-8	12	252	247	-4	-3	12	94	95	-2	2	12	149	160	-1	-6	13	78	85	-2	0	13	105	120
3	-8	12	260	279	-3	-3	12	139	157	-1	2	12	122	133	0	-6	13	102	84	0	0	13	109	111
-4	-7	12	240	240	-2	-3	12	95	90	1	2	12	133	132	1	-6	13	107	94	2	0	13	94	83
-1	-7	12	88	101	0	-3	12	79	55	-1	3	12	50	63	2	-6	13	160	169	0	1	13	207	188
0	-7	12	80	84	1	-3	12	76	74	0	3	12	64	56	3	-6	13	90	73	-1	-10	14	178	188
1	-7	12	214	213	2	-3	12	234	239	0	-11	13	89	94	4	-6	13	52	48	0	-10	14	89	93
2	-7	12	102	99	3	-3	12	67	58	1	-11	13	109	106	-2	-5	13	125	144	1	-10	14	53	15
3	-7	12	64	59	4	-3	12	72	82	2	-11	13	146	155	-1	-5	13	156	164	-2	-9	14	104	98
4	-7	12	107	122	-5	-2	12	94	123	-2	-10	13	79	88	0	-5	13	230	219	-1	-9	14	57	40
5	-7	12	110	114	-4	-2	12	167	199	-1	-10	13	60	69	1	-5	13	121	109	0	-9	14	189	184
-5	-6	12	84	76	-3	-2	12	166	149	0	-10	13	101	96	2	-5	13	137	123	1	-9	14	155	155
-4	-6	12	168	165	-1	-2	12	66	68	1	-10	13	126	124	3	-5	13	64	43	0	-8	14	187	167
-2	-6	12	119	139	0	-2	12	167	168	3	-10	13	71	69	4	-5	13	51	59	2	-8	14	73	75
-1	-6	12	153	139	2	-2	12	151	162	-3	-9	13	88	100	-4	-4	13	105	121	-2	-7	14	111	110
0	-6	12	330	321	4	-2	12	86	83	-2	-9	13	148	165	-3	-4	13	76	68	-1	-7	14	48	27
1	-6	12	412	395	-3	-1	12	70	52	-1	-9	13	98	114	-2	-4	13	144	146	0	-7	14	93	92
2	-6	12	123	112	-2	-1	12	87	104	0	-9	13	155	148	0	-4	13	152	131	1	-7	14	132	121
4	-6	12	252	262	-1	-1	12	201	197	1	-9	13	73	76	1	-4	13	182	168	2	-7	14	61	73
5	-6	12	114	115	0	-1	12	123	121	3	-9	13	128	139	2	-4	13	90	83	3	-7	14	111	110
-4	-5	12	79	75	1	-1	12	73	87	-3	-8	13	161	163	4	-4	13	69	83	-3	-6	14	127	139

Table A-3 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	-6	14	83	86	0	-5	14	225	207	2	-4	14	151	144	1	-3	14	58	56	0	-1	14	52	43
1	-6	14	155	156	1	-5	14	173	160	-2	-3	14	77	82	-2	-2	14	235	228	-1	-6	15	92	90
2	-6	14	96	95	-3	-4	14	125	140	-1	-3	14	78	69	0	-2	14	114	118	0	-6	15	174	163
-3	-5	14	99	116	0	-4	14	231	218	0	-3	14	87	71	-1	-1	14	67	65	0	-5	15	199	193
-1	-5	14	63	64																				

Table A-4. Observed and calculated structure factors for sodium sulphate hemiperhydrate monohydrate.

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	0	0	3254	3293	2	8	2	871	835	3	3	5	2552	2564	1	7	7	262	268	6	2	10	367	355
2	2	0	2950	3065	1	1	3	950	920	5	3	5	462	477	3	7	7	839	802	0	4	10	357	371
6	2	0	1963	1907	3	1	3	476	522	7	3	5	440	424	0	0	8	1077	1098	2	4	10	2154	2144
0	4	0	609	542	5	1	3	368	359	1	5	5	380	374	4	0	8	835	863	4	4	10	704	711
4	4	0	1640	1667	7	1	3	629	605	3	5	5	469	438	0	2	8	588	600	6	4	10	377	377
2	6	0	1978	1876	1	3	3	556	485	5	5	5	833	822	2	2	8	659	627	0	6	10	148	144
0	8	0	274	279	3	3	3	848	809	1	7	5	1265	1258	4	2	8	391	405	2	6	10	720	716
1	1	1	1542	1504	5	3	3	665	676	3	7	5	401	387	6	2	8	968	960	4	6	10	1056	1091
3	1	1	851	864	7	3	3	145	147	2	0	6	4353	4143	0	4	8	506	545	0	8	10	138	141
5	1	1	1650	1669	1	5	3	847	813	6	0	6	1489	1507	2	4	8	726	670	2	8	10	272	276
7	1	1	1260	1218	3	5	3	554	568	0	2	6	2492	2451	4	4	8	1104	1140	1	1	11	1814	1844
1	3	1	1914	1955	5	5	3	222	211	2	2	6	1182	1115	6	4	8	589	602	3	1	11	436	422
3	3	1	871	889	1	7	3	1048	1009	4	2	6	1787	1833	0	6	8	330	322	5	1	11	511	507
5	3	1	1209	1252	3	7	3	410	417	6	2	6	518	519	2	6	8	1544	1540	7	1	11	272	261
7	3	1	211	217	0	0	4	660	679	0	4	6	1455	1469	4	6	8	633	616	1	3	11	1904	1890
1	5	1	1175	1156	4	0	4	1952	2001	2	4	6	1138	1088	0	8	8	897	975	3	3	11	186	188
3	5	1	2010	1940	0	2	4	333	299	4	4	6	555	532	2	8	8	522	506	5	3	11	547	527
5	5	1	288	277	2	2	4	1063	1122	6	4	6	1040	1052	1	1	9	2908	2928	1	5	11	726	726
1	7	1	677	675	4	2	4	1309	1292	0	6	6	895	912	3	1	9	299	303	3	5	11	810	819
3	7	1	1221	1151	6	2	4	562	549	2	6	6	339	327	5	1	9	1075	1120	5	5	11	736	738
2	0	2	1686	1724	0	4	4	1433	1511	4	6	6	630	602	7	1	9	450	430	1	7	11	857	880
6	0	2	970	970	2	4	4	1335	1313	0	8	6	872	930	1	3	9	316	328	3	7	11	1435	1382
0	2	2	1660	1666	4	4	4	642	614	2	8	6	647	608	3	3	9	622	630	0	0	12	165	169
2	2	2	1649	1608	6	4	4	165	167	1	1	7	2020	1959	5	3	9	778	760	4	0	12	750	774
4	2	2	119	112	0	6	4	1154	1149	3	1	7	277	288	1	5	9	257	232	0	2	12	2209	2077
6	2	2	319	320	2	6	4	122	120	5	1	7	1163	1171	3	5	9	1331	1295	2	2	12	1504	1508
0	4	2	350	333	4	6	4	533	539	7	1	7	420	404	5	5	9	569	573	4	2	12	615	558
2	4	2	602	594	0	8	4	801	809	1	3	7	2179	2062	1	7	9	955	978	6	2	12	324	323
4	4	2	612	632	2	8	4	624	612	3	3	7	1285	1313	3	7	9	1313	1285	0	4	12	436	443
6	4	2	311	301	1	1	5	798	749	5	3	7	267	262	2	0	10	1122	1082	2	4	12	470	496
0	6	2	605	625	3	1	5	2468	2545	7	3	7	624	661	6	0	10	2242	2198	4	4	12	590	581
2	6	2	904	871	5	1	5	608	600	1	5	7	1672	1641	0	2	10	2396	2426	6	4	12	281	270
4	6	2	1162	1135	7	1	5	630	610	3	5	7	844	811	2	2	10	923	947	0	6	12	270	262
0	8	2	594	569	1	3	5	2726	2553	5	5	7	1148	1176	4	2	10	857	899	2	6	12	541	544

Table A-4 (continued)

H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC	H	K	L	10FD	10FC
4	6	12	162	152	3	3	15	1511	1572	2	2	18	375	369	3	5	21	1102	1115	4	2	26	1220	1245
0	8	12	29	23	5	3	15	1206	1256	4	2	18	688	702	2	0	22	1492	1512	0	4	26	1016	1008
2	8	12	389	398	1	5	15	1294	1346	0	4	18	276	282	6	0	22	728	745	0	6	26	216	212
1	1	13	596	603	3	5	15	1110	1119	2	4	18	753	767	0	2	22	1648	1625	1	1	27	370	384
3	1	13	377	374	5	5	15	280	272	4	4	18	199	190	2	2	22	563	554	3	1	27	551	530
5	1	13	50	52	1	7	15	1196	1252	0	6	18	110	104	4	2	22	1126	1216	5	1	27	468	461
7	1	13	169	166	3	7	15	579	584	2	6	18	401	415	0	4	22	421	431	1	3	27	739	717
1	3	13	985	995	0	0	16	898	986	4	6	18	690	682	2	4	22	1343	1317	3	3	27	932	916
3	3	13	724	705	4	0	16	1680	1715	1	1	19	2122	2098	4	4	22	542	539	0	0	28	310	321
5	3	13	628	643	0	2	16	238	237	3	1	19	291	294	0	6	22	256	260	4	0	28	858	854
1	5	13	90	92	2	2	16	1960	2012	5	1	19	1148	1196	2	6	22	442	448	0	2	28	529	475
3	5	13	232	221	4	2	16	1013	1026	1	3	19	1416	1415	1	1	23	540	531	2	2	28	356	363
5	5	13	525	529	6	2	16	1137	1162	3	3	19	729	754	3	1	23	546	541	4	2	28	98	103
1	7	13	531	550	0	4	16	2418	2420	5	3	19	728	726	5	1	23	777	811	0	4	28	309	294
3	7	13	223	212	2	4	16	422	432	1	5	19	234	232	1	3	23	578	573	2	4	28	404	420
2	0	14	2154	2114	4	4	16	1670	1664	3	5	19	1409	1444	3	3	23	1066	1102	1	1	29	292	267
6	0	14	165	162	0	6	16	592	622	1	7	19	326	336	5	3	23	300	305	3	1	29	823	846
0	2	14	54	59	2	6	16	698	695	4	0	20	1139	1117	3	5	23	430	424	1	3	29	190	183
2	2	14	1396	1467	4	6	16	153	149	0	2	20	1139	1176	1	7	23	280	288	3	3	29	217	208
4	2	14	441	460	0	8	16	230	232	2	2	20	605	618	4	0	24	812	826	2	0	30	1148	1153
6	2	14	588	598	1	1	17	1238	1246	4	2	20	374	401	0	2	24	1198	1228	0	2	30	139	137
0	4	14	1429	1421	3	1	17	230	225	0	4	20	684	659	2	2	24	1265	1242	2	2	30	782	757
2	4	14	1390	1418	5	1	17	467	469	2	4	20	1227	1298	4	2	24	877	921	0	4	30	702	709
4	4	14	494	492	1	3	17	562	546	4	4	20	577	562	0	4	24	710	709	2	4	30	99	88
6	4	14	653	655	3	3	17	761	808	0	6	20	689	677	2	4	24	1167	1162	1	1	31	1033	947
0	6	14	188	182	5	3	17	809	843	2	6	20	462	482	1	1	25	837	823	3	1	31	1079	1038
2	6	14	140	134	1	5	17	612	627	4	6	20	865	868	3	1	25	1205	1246	1	3	31	1148	1121
4	6	14	507	486	3	5	17	632	641	1	1	21	530	543	5	1	25	783	777	0	2	32	1212	1177
0	8	14	1063	1125	5	5	17	568	579	3	1	21	554	574	1	3	25	1684	1710	2	2	32	1111	1086
2	8	14	608	656	1	7	17	780	807	5	1	21	305	313	3	3	25	1398	1453	2	4	32	167	167
1	1	15	1064	1124	3	7	17	596	595	1	3	21	235	237	3	5	25	338	345	1	1	33	649	626
3	1	15	1484	1524	2	0	18	472	474	3	3	21	476	501	2	0	26	1760	1712	3	1	33	167	167
5	1	15	262	249	6	0	18	1075	1106	5	3	21	733	750	0	2	26	2118	2012	1	3	33	880	880
1	3	15	712	714	0	2	18	1091	1074	1	5	21	1132	1134	2	2	26	752	751	2	0	34	422	417

Table A-4 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	2	34	234	234	1	1	35	773	721	0	0	36	54	49	0	2	36	34	29	1	1	37	179	179
2	2	34	556	556																				

Table A-5. Observed and calculated structure factors for potassium-4-sulphonato-perbenzoic acid

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	215	210	5	5	0	208	217	3	1	1	93	97	2	6	1	340	342	5	1	2	55	46
4	0	0	463	454	6	5	0	121	128	4	1	1	365	364	3	6	1	74	66	6	1	2	63	51
6	0	0	500	506	7	5	0	261	269	5	1	1	115	114	4	6	1	76	82	7	1	2	246	234
8	0	0	285	270	0	6	0	98	97	6	1	1	162	160	5	6	1	137	136	8	1	2	90	94
2	1	0	249	239	2	6	0	205	209	7	1	1	129	128	6	6	1	52	65	0	2	2	663	666
3	1	0	273	269	3	6	0	172	172	8	1	1	86	75	7	6	1	51	74	1	2	2	859	822
4	1	0	397	385	4	6	0	388	405	1	2	1	414	419	1	7	1	138	133	2	2	2	220	220
5	1	0	93	90	5	6	0	156	156	2	2	1	345	338	2	7	1	379	377	3	2	2	354	339
6	1	0	404	409	7	6	0	234	240	3	2	1	54	55	3	7	1	75	78	4	2	2	79	79
8	1	0	190	194	2	7	0	317	320	4	2	1	120	123	4	7	1	164	172	5	2	2	83	85
1	2	0	129	135	3	7	0	83	88	5	2	1	248	253	5	7	1	62	65	6	2	2	275	266
2	2	0	409	399	4	7	0	450	458	7	2	1	161	167	6	7	1	165	171	7	2	2	327	329
3	2	0	552	563	5	7	0	133	136	8	2	1	101	86	1	8	1	74	58	8	2	2	97	100
4	2	0	509	524	6	7	0	68	68	1	3	1	517	533	2	8	1	145	146	0	3	2	864	892
5	2	0	216	219	0	8	0	107	106	2	3	1	343	338	3	8	1	216	218	1	3	2	641	648
6	2	0	70	73	1	8	0	200	195	3	3	1	283	288	4	8	1	157	168	2	3	2	184	187
7	2	0	50	59	2	8	0	439	438	4	3	1	309	306	5	8	1	191	194	3	3	2	378	388
8	2	0	119	114	3	8	0	220	220	5	3	1	128	126	1	9	1	109	112	5	3	2	388	386
1	3	0	153	158	4	8	0	127	129	6	3	1	128	135	2	9	1	101	95	6	3	2	250	259
2	3	0	628	649	5	8	0	317	328	7	3	1	73	72	3	9	1	84	91	7	3	2	198	193
3	3	0	403	431	0	9	0	200	210	8	3	1	91	72	4	9	1	98	94	0	4	2	589	615
4	3	0	294	298	1	9	0	140	145	1	4	1	58	47	5	9	1	59	24	1	4	2	591	597
5	3	0	107	103	2	9	0	133	119	2	4	1	268	288	1	10	1	87	84	2	4	2	201	201
6	3	0	57	63	4	9	0	93	95	3	4	1	147	156	2	10	1	187	201	3	4	2	507	528
7	3	0	191	191	1	10	0	177	160	4	4	1	212	215	1	11	1	70	64	4	4	2	94	85
2	4	0	356	365	2	10	0	126	133	5	4	1	52	34	0	0	2	1442	1367	5	4	2	272	275
3	4	0	402	421	0	11	0	140	115	6	4	1	136	138	2	0	2	1403	1349	6	4	2	149	147
4	4	0	46	61	1	11	0	136	120	7	4	1	44	62	4	0	2	794	781	7	4	2	163	163
5	4	0	216	230	2	0	1	1808	1742	1	5	1	367	370	6	0	2	54	25	0	5	2	427	416
6	4	0	55	54	4	0	1	632	601	2	5	1	400	412	0	1	2	417	406	1	5	2	188	192
7	4	0	190	167	6	0	1	94	90	3	5	1	86	93	1	1	2	588	543	2	5	2	216	222
2	5	0	51	46	8	0	1	74	54	4	5	1	185	186	2	1	2	557	544	3	5	2	506	529
3	5	0	110	116	1	1	1	317	290	5	5	1	151	152	3	1	2	275	262	4	5	2	127	136
4	5	0	182	188	2	1	1	178	180	1	6	1	67	83	4	1	2	367	359	5	5	2	264	276

Table A-5 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
7	5	2	50	31	3	1	3	296	286	6	6	3	82	74	5	2	4	249	239	5	7	4	88	80
0	6	2	446	461	4	1	3	191	189	1	7	3	103	119	6	2	4	83	81	0	8	4	178	173
1	6	2	110	119	5	1	3	187	180	2	7	3	327	328	7	2	4	80	90	1	8	4	200	190
2	6	2	173	174	6	1	3	155	154	3	7	3	102	117	0	3	4	193	197	2	8	4	174	167
3	6	2	198	205	7	1	3	122	122	4	7	3	166	169	1	3	4	415	405	3	8	4	127	132
4	6	2	115	116	1	2	3	232	221	5	7	3	50	55	2	3	4	91	93	4	8	4	219	227
5	6	2	243	239	2	2	3	237	237	6	7	3	136	143	3	3	4	277	282	0	9	4	394	370
6	6	2	120	124	3	2	3	311	307	1	8	3	171	166	4	3	4	323	319	1	9	4	80	65
0	7	2	599	590	4	2	3	171	178	2	8	3	141	135	5	3	4	238	232	3	9	4	111	109
1	7	2	48	43	5	2	3	232	241	3	8	3	205	196	0	4	4	138	139	0	10	4	282	263
2	7	2	72	85	7	2	3	110	94	4	8	3	57	70	1	4	4	289	297	1	10	4	129	127
3	7	2	108	115	1	3	3	250	230	5	8	3	64	79	2	4	4	207	211	2	0	5	328	334
4	7	2	119	122	2	3	3	320	327	1	9	3	118	109	3	4	4	144	147	4	0	5	216	214
5	7	2	121	126	3	3	3	85	76	2	9	3	159	159	4	4	4	233	224	6	0	5	384	381
6	7	2	262	280	4	3	3	70	74	3	9	3	72	59	5	4	4	205	208	1	1	5	96	102
0	8	2	542	516	5	3	3	195	203	4	9	3	98	105	6	4	4	136	142	2	1	5	199	194
1	8	2	173	170	6	3	3	123	128	2	10	3	173	182	7	4	4	118	114	3	1	5	201	205
2	8	2	169	176	1	4	3	134	130	0	0	4	816	838	0	5	4	145	143	5	1	5	246	256
3	8	2	165	156	2	4	3	162	167	2	0	4	364	355	1	5	4	423	438	6	1	5	180	170
4	8	2	177	176	3	4	3	124	117	4	0	4	389	393	2	5	4	160	159	7	1	5	118	108
5	8	2	141	148	5	4	3	71	59	6	0	4	497	480	3	5	4	70	88	1	2	5	151	142
0	9	2	170	160	6	4	3	180	180	0	1	4	743	747	4	5	4	141	136	2	2	5	204	195
2	9	2	364	356	1	5	3	167	168	1	1	4	91	99	5	5	4	103	108	3	2	5	174	173
3	9	2	168	156	2	5	3	100	101	2	1	4	766	741	6	5	4	125	133	4	2	5	67	75
4	9	2	190	198	3	5	3	164	166	3	1	4	89	92	1	6	4	368	371	5	2	5	167	163
2	10	2	219	205	4	5	3	136	140	4	1	4	248	245	2	6	4	350	355	1	3	5	236	236
3	10	2	138	123	5	5	3	197	196	5	1	4	266	256	3	6	4	197	199	2	3	5	250	250
0	11	2	80	72	6	5	3	172	182	6	1	4	328	318	4	6	4	238	249	3	3	5	106	119
2	0	3	626	623	7	5	3	64	56	7	1	4	158	152	5	6	4	71	73	4	3	5	75	88
4	0	3	604	593	1	6	3	60	73	0	2	4	113	108	0	7	4	193	182	5	3	5	134	127
6	0	3	429	423	2	6	3	268	264	1	2	4	107	103	1	7	4	235	237	6	3	5	110	113
8	0	3	88	89	3	6	3	186	192	2	2	4	500	500	2	7	4	303	289	1	4	5	125	117
1	1	3	147	141	4	6	3	153	152	3	2	4	173	175	3	7	4	277	271	2	4	5	126	139
2	1	3	158	152	5	6	3	136	135	4	2	4	317	314	4	7	4	346	358	3	4	5	87	76

Table A-5 (continued)

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	4	5	97	84	6	0	6	63	71	0	5	6	161	150	1	2	7	159	163	4	1	8	81	71
6	4	5	176	167	0	1	6	101	93	1	5	6	79	81	2	2	7	74	91	0	2	8	82	76
1	5	5	94	95	1	1	6	228	230	2	5	6	63	37	3	2	7	64	93	1	2	8	88	84
2	5	5	67	79	2	1	6	327	328	3	5	6	306	294	5	2	7	119	106	2	2	8	184	185
3	5	5	140	133	3	1	6	118	132	4	5	6	77	81	1	3	7	117	119	3	2	8	229	231
5	5	5	172	166	4	1	6	337	337	5	5	6	175	191	2	3	7	189	186	4	2	8	158	161
6	5	5	122	130	6	1	6	70	59	0	6	6	167	160	4	3	7	85	88	0	3	8	119	116
1	6	5	99	77	0	2	6	400	423	2	6	6	77	55	5	3	7	63	45	1	3	8	71	63
2	6	5	142	129	1	2	6	353	349	3	6	6	259	264	2	4	7	157	152	2	3	8	111	118
3	6	5	113	109	2	2	6	137	136	4	6	6	47	52	4	4	7	135	140	3	3	8	168	176
4	6	5	101	98	4	2	6	117	111	0	7	6	514	491	1	5	7	105	107	4	3	8	129	122
5	6	5	154	159	5	2	6	185	180	1	7	6	158	146	2	5	7	62	78	0	4	8	198	200
1	7	5	128	125	6	2	6	149	145	2	7	6	70	77	3	5	7	85	82	1	4	8	137	138
2	7	5	309	314	0	3	6	368	379	3	7	6	65	62	4	5	7	65	63	2	4	8	91	103
3	7	5	67	90	1	3	6	423	446	0	8	6	239	233	1	6	7	156	157	3	4	8	121	118
4	7	5	97	100	2	3	6	64	62	1	8	6	130	128	2	6	7	62	56	0	5	8	120	126
1	8	5	212	211	3	3	6	226	221	2	8	6	132	143	1	7	7	68	48	1	5	8	210	211
2	8	5	89	97	4	3	6	66	62	2	0	7	246	239	2	7	7	201	198	2	5	8	52	46
3	8	5	78	78	5	3	6	172	167	4	0	7	109	96	0	0	8	400	406	1	6	8	216	219
4	8	5	45	57	6	3	6	133	134	1	1	7	151	157	2	0	8	172	177	2	0	9	84	63
1	9	5	77	73	0	4	6	183	183	2	1	7	194	191	4	0	8	97	99	1	1	9	138	147
2	9	5	140	140	1	4	6	189	194	3	1	7	118	142	0	1	8	422	431	2	1	9	139	142
0	0	6	203	209	3	4	6	206	202	4	1	7	183	180	1	1	8	116	123	1	2	9	89	108
2	0	6	159	161	4	4	6	116	128	5	1	7	155	146	3	1	8	167	155	1	3	9	54	40
4	0	6	417	403	5	4	6	149	144															

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