

served in the coordination polyhedra about Li(Na) atoms at the  $M(5)$  position. This position in nambulite has eight near O atoms, whereas in Li-hydrorhodonite the position is shifted to one side so that it has six near O atoms; the coordination polyhedra are essentially octahedral (Fig. 2). The  $M(5)$ —O distances in the two minerals are compared in Table 2.

Other bond lengths for Li-hydrorhodonite are listed in Table 3.

The close structural relationship between these two minerals and babingtonite appears somewhat puzzling since the number of cations in the latter is different from the numbers in the former two. Fig. 1(a) and (b) shows that the babingtonite structure is, in principle, derivable from the nambulite (or Li-hydrorhodonite) structure by removing the  $M(5)$  atoms; the babingtonite structure can thus be regarded as a cation-deficient structure of the nambulite type. It is to be noted that the Ca(2) position in the babingtonite structure, which corresponds to  $M(4)$  in Li-hydrorhodonite, is occupied by the larger Ca, increasing the size of the polyhedron; the polyhedron shares an edge with the adjacent polyhedron which is related to the former by inversion (Fig. 1b).

Silicate chains of Li-hydrorhodonite are attached to octahedral bands in a way that is typical of pyroxenoids of the  $p$ - $p$  (pectolite-pyroxene) series (Takéuchi, 1976; Takéuchi & Koto, 1977); the triplet of tetrahedra Si(1), Si(5), Si(4) is not attached to the same octahedron as in wollastonite, which belongs to the other series of pyroxenoids. For pyroxenoids of the  $p$ - $p$  series, Takéuchi, Kudoh & Yamanaka (1976) pointed out that octahedra like  $M(2)$ , whose location relative to the silicate chain corresponds to that of  $M(1)$  in pectolite, is better able to accommodate relatively larger cations. This means, in turn, that the Mg atoms which

are smaller than the major cations, Mn, in the present structure are expected to be located in octahedral positions other than  $M(2)$ . Our result, that Mg is located at  $M(3)$ , is fully in accord with the view given by Takéuchi *et al.* (1976).

The short distance of 2.464 (8) Å between O(1) and O(11) strongly suggests the existence of a hydrogen-bonded system. An account is given in a paper published elsewhere (Takéuchi & Koto, 1977) of the hydrogen-bonded systems of pyroxenoids in the pectolite-pyroxene series in general.

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## Polymeric Copper(II) Chloride–1,4-Dioxan (3:2)

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**Abstract.**  $C_8H_{16}Cl_6Cu_3O_4$ , monoclinic,  $C2/m$ ,  $a = 7.880$  (6),  $b = 12.045$  (14),  $c = 9.208$  (13) Å,  $\beta = 106.45$  (2)°,  $Z = 2$ ,  $D_x = 2.30$ ,  $D_m = 2.29$  (1) g cm<sup>-3</sup>;  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 128$  cm<sup>-1</sup>. Zigzag  $(\text{CuCl}_2)_\infty$  chains lie along **c**. Each Cu atom is also bonded to two O atoms of dioxan molecules, which cross-link the chains in the *ac* plane.

**Introduction.** Slow recrystallization from acetonitrile usually gave clumps of fine needles, but larger prisms were occasionally formed. The latter were mostly split, but a data set adequate for resolving the structure was obtained from two crystals sealed in capillaries. Equi-inclination Weissenberg photographs of the levels 0–5*kl* and *h0*–5*l* were scanned by a microdensitometer

(SRC service, Rutherford Laboratory). The systematic absences indicated the space groups  $C2$ ,  $Cm$  or  $C2/m$ . Absorption corrections were applied. The structure was solved by the heavy-atom method. Parallel refinement in space groups  $C2$  and  $Cm$  indicated that the space group was probably  $C2/m$ . The final conventional  $R$  in  $C2/m$ , following full-matrix least-squares refinement, was 0.098 (Cu and Cl anisotropic, 39 parameters, 470 independent reflexions above background), with H atoms included at calculated positions ( $d_{C-H} = 1.07 \text{ \AA}$ ,  $U_H = 1.5 U_C$ ). The final positional parameters are given in Table 1, and interatomic distances and angles in Table 2. Further refinement in space groups  $C2$  (66 parameters) and  $Cm$  (72 parameters) converged in both cases at  $R = 0.092$ .\* Although the decrease in  $R$  is statistically significant at the 5% level (*International Tables for X-ray Crystallography*, 1974), the standard deviations in both positional and thermal parameters were considerably larger than in  $C2/m$  and the bond

\* A list of structure factors and a table of thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32266 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0	0	0
Cu(2)	-850 (4)	0	3109 (3)
Cl(1)	-1217 (6)	1307 (3)	1221 (4)
Cl(2)	0	1307 (4)	5000
O(1)	2407 (22)	0	2348 (17)
O(2)	6175 (21)	0	3097 (16)
C(1)	3419 (22)	977 (13)	2942 (16)
C(2)	5161 (24)	1006 (14)	2517 (17)

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Cu(1)—Cl(1)	2.296 (3)	Cu(2)—O(2) <sup>i</sup>	2.341 (17)
Cu(1)—O(1)	2.436 (15)	O(1)—C(1)	1.440 (18)
Cu(2)—Cl(1)	2.302 (4)	O(2)—C(2)	1.466 (19)
Cu(2)—Cl(2)	2.302 (4)	C(1)—C(2)	1.531 (22)
Cu(2)—O(1)	2.846 (19)		
Cl(1)—Cu(1)—Cl(1) <sup>ii</sup>	93.7 (2)	Cu(2)—Cl(2)—Cu(2) <sup>iii</sup>	93.7 (2)
Cl(1)—Cu(1)—O(1)	83.7 (3)	C(1)—O(1)—C(1) <sup>iv</sup>	109.6 (14)
Cl(1)—Cu(2)—Cl(2)	92.9 (2)	C(2)—O(2)—C(2) <sup>iv</sup>	111.5 (14)
Cl(2)—Cu(2)—Cl(2) <sup>iv</sup>	86.3 (2)	O(1)—C(1)—C(2)	111.2 (13)
Cl(1)—Cu(2)—O(2) <sup>i</sup>	95.1 (3)	O(2)—C(2)—C(1)	108.9 (13)
Cu(1)—Cl(1)—Cu(2)	85.5 (2)		

Distances between non-bonded atoms

C(1)⋯Cl(1) <sup>v</sup>	3.68 (2)	C(1)⋯Cl(2) <sup>v</sup>	3.81 (2)
C(2)⋯Cl(1) <sup>v</sup>	3.51 (2)	C(2)⋯Cl(2) <sup>v</sup>	3.99 (2)

Symmetry code: (i)  $-1 + x, y, z$ ; (ii)  $-x, y, -z$ ; (iii)  $-x, y, 1 - z$ ; (iv)  $x, -y, z$ ; (v)  $\frac{1}{2} + x, \frac{1}{2} - y, z$ .

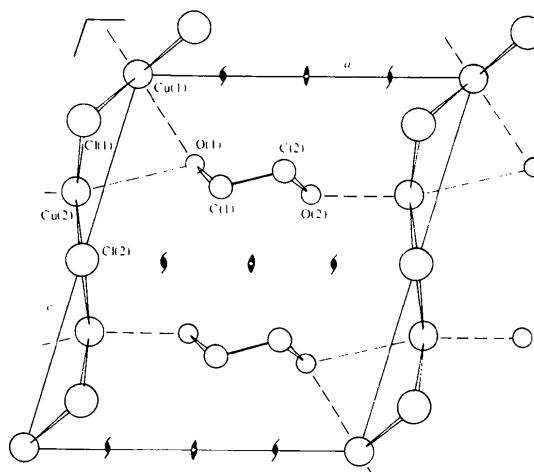


Fig. 1. The  $b$  axis projection of part of one layer. The cell is  $C$  centred.

lengths, particularly in the dioxan ring, less acceptable on chemical grounds. G. M. Sheldrick's *SHELX-76* system was used in all calculations.

**Discussion.** Barnes (1969) predicted that the structure of  $\text{Cu}_3\text{Cl}_6(\text{C}_4\text{H}_8\text{O}_2)_2$  would resemble that of, e.g.,  $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$  (Willett & Rundle, 1964) with planar  $\text{Cu}_3\text{Cl}_6$  groups linked by long Cu—Cl—Cu bridges, and with some terminal Cu—Cl bonds as suggested by the IR spectrum (Fowles, Rice & Walton, 1968). Instead, ribbon-like  $(\text{CuCl}_2)_\infty$  chains lying along  $c$  are cross-linked in the  $ac$  plane by dioxan molecules *via* long Cu—O bonds (Fig. 1). Only weak contacts occur between the resultant layers. The cross-linking is the apparent cause of the pleating of the chains at atoms of the type Cl(1) [in contrast to the chains in  $\text{CuCl}_2$  itself (Wells, 1947)] and results in Cu⋯Cu distances of 3.120 (3) and 3.358 (3)  $\text{\AA}$  alternately. The latter distance is similar to those in, e.g.,  $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$  (3.35  $\text{\AA}$ ),  $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$  (3.29, 3.30  $\text{\AA}$ ; Willett & Rundle, 1964) and  $\text{Cu}_3\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 2\text{C}_4\text{H}_8\text{SO}_2$  (3.33  $\text{\AA}$ ; Swank & Willett, 1974). The Cu atoms differ in their coordination geometry (Fig. 1). Cu(1) lies on an inversion centre in a *trans*-elongated  $\text{Cl}_4\text{O}_2$  octahedron. In contrast, Cu(2) is displaced 0.19  $\text{\AA}$  from the  $\text{Cl}_4$  plane towards one O atom in a similar grouping. The dimensions of the dioxan molecule, and its chair conformation, are normal. The bridging role of dioxan had been inferred earlier from the Raman spectrum (Fowles, Rice & Walton, 1970).

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## 2-Phenyl-1,3-dithian-5-one

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**Abstract.**  $C_{10}S_2O_2H_{10}$ ,  $M_r = 210.3$ , monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 14.258$  (5),  $b = 5.217$  (3),  $c = 15.374$  (5) Å,  $\beta = 117.92$  (6)°,  $R = 0.046$ . The carbonyl group is more puckered than in cyclohexanones.

**Introduction.** The structure of 2-phenyl-1,3-dithian-5-one (PTO)\* has been determined by X-ray diffraction in order to determine the deformation of the ring caused by substitution of the ring C atoms by S.

The reflexion data were collected by a Philips PW 1100 X-ray diffractometer with graphite-mono-

chromated Cu  $K\alpha$  radiation. The structure factors of 1731 independent reflexions were obtained within  $\theta = 3 \sim 78^\circ$ . The structure was solved by the three-

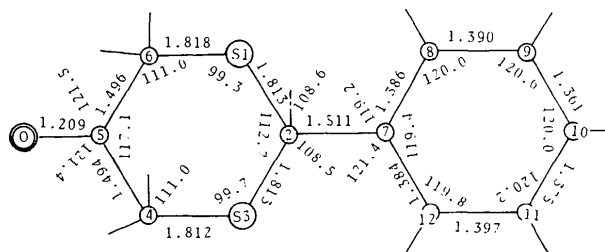


Fig. 1. Bond lengths and bond angles in PTO.

Table 1. *Positional* ( $\times 10^4$  for S, O and C and  $\times 10^3$  for H atoms) and *thermal* ( $\times 10^4$  for S, O and C) parameters

The form of the anisotropic temperature factor is:  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$ .

	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O	813 (2)	1460 (5)	-2251 (2)	93 (2)	780 (15)	63 (1)	-32 (4)	32 (1)	-88 (4)
S(1)	1141 (1)	1647 (2)	212 (0)	57 (0)	432 (3)	43 (0)	-31 (1)	17 (0)	20 (1)
S(3)	2858 (1)	4337 (2)	-64 (1)	60 (0)	759 (5)	44 (0)	-68 (1)	20 (0)	11 (1)
C(2)	2129 (2)	4174 (5)	635 (2)	58 (2)	350 (11)	41 (1)	-8 (4)	19 (1)	0 (3)
C(4)	1773 (3)	4985 (7)	-1277 (2)	81 (2)	615 (17)	46 (2)	-59 (5)	21 (2)	24 (4)
C(5)	954 (2)	2919 (6)	-1589 (2)	59 (2)	469 (14)	40 (1)	1 (4)	14 (1)	3 (4)
C(6)	319 (2)	2727 (6)	-1045 (2)	57 (2)	521 (15)	43 (1)	-18 (4)	15 (1)	9 (4)
C(7)	2909 (2)	3684 (5)	1701 (2)	50 (2)	391 (12)	41 (1)	-9 (4)	18 (1)	0 (3)
C(8)	2921 (2)	5317 (7)	2417 (2)	74 (2)	506 (15)	51 (2)	21 (5)	21 (2)	-27 (4)
C(9)	3634 (3)	4899 (8)	3402 (2)	96 (3)	730 (21)	46 (2)	9 (6)	21 (2)	-35 (5)
C(10)	4337 (2)	2922 (8)	3672 (2)	71 (2)	701 (20)	45 (2)	-6 (5)	12 (2)	19 (5)
C(11)	4329 (3)	1274 (8)	2970 (2)	71 (2)	632 (19)	67 (2)	53 (5)	18 (2)	42 (5)
C(12)	3607 (2)	1638 (7)	1977 (2)	75 (2)	499 (15)	52 (2)	36 (5)	23 (2)	9 (4)

	x	y	z	B		x	y	z	B
H(1)	174 (2)	588 (6)	55 (2)	6 (1)	H(6)	240 (3)	683 (7)	221 (2)	7 (1)
H(2)	149 (3)	657 (6)	-125 (2)	6 (1)	H(7)	362 (3)	612 (8)	392 (3)	9 (1)
H(3)	211 (3)	510 (8)	-171 (3)	8 (1)	H(8)	487 (3)	255 (8)	435 (3)	8 (1)
H(4)	1 (2)	444 (6)	-103 (2)	5 (1)	H(9)	483 (3)	-12 (8)	311 (3)	8 (1)
H(5)	-27 (2)	149 (6)	-133 (2)	5 (1)	H(10)	363 (3)	43 (8)	148 (3)	9 (1)

\* The crystals were prepared by Dr Jochims, University of Konstanz, West Germany.