

Table 4. Bond lengths (Å) and valence angles (°) with *e.s.d.'s* in parentheses

O(1)—As(2)	1.743 (4)	O(3)—As(2)	1.738 (4)
O(1)—C(6)	1.466 (6)	O(3)—C(4)	1.481 (6)
C(5)—C(6)	1.538 (8)	C(4)—C(5)	1.520 (8)
C(6)—C(9)	1.490 (10)	C(4)—C(7)	1.510 (8)
C(6)—C(10)	1.523 (8)	C(4)—C(8)	1.530 (10)
As(2)—Cl	2.258 (2)	<C—H>	1.00 (6)
As(2)—O(1)—C(6)	126.3 (4)	As(2)—O(3)—C(4)	123.6 (3)
O(1)—As(2)—Cl	100.9 (2)	O(3)—As(2)—Cl	97.9 (1)
O(1)—C(6)—C(5)	110.4 (5)	O(3)—C(4)—C(5)	109.2 (5)
O(1)—C(6)—C(9)	107.5 (5)	O(3)—C(4)—C(7)	107.1 (5)
O(1)—C(6)—C(10)	105.2 (5)	O(3)—C(4)—C(8)	104.4 (5)
C(5)—C(6)—C(9)	109.7 (6)	C(5)—C(4)—C(7)	117.1 (6)
C(5)—C(6)—C(10)	113.9 (6)	C(5)—C(4)—C(8)	108.6 (5)
C(9)—C(6)—C(10)	109.8 (6)	C(7)—C(4)—C(8)	109.7 (6)
O(1)—As(2)—O(3)	101.1 (2)	<C—C—H>	110 (3)
C(4)—C(5)—C(6)	119.2 (5)	<H—C—H>	108 (5)

form occurs. In this conformation the steric hindrance due to ring substituents is relieved, while an intermediate stabilization *via* the anomeric interaction can remain. Bond lengths and valence angles are given in Table 4. The As—Cl bond is longer than normal [2.258 *vs* 2.161 Å in AsCl₃ and As(CH₃)₂Cl (Sutton, 1965)] in accordance with the anomeric effect. The *n*(O)—σ* (As—Cl) delocalization causes an increase in electron density in the anti-bonding σ* (As—Cl) orbital with a consequent lengthening of the bond and a decrease of the force constant. One also notices that the C—O bonds are longer than those normally encountered in ethers and alcohols (1.43–1.44 Å). The same phenomenon was observed in cyclic sulfites (Petit, 1982) and cyclic phosphates (Van Nuffel, Lenstra & Geise, 1980, 1981, 1982).

Bond angles are found to be normal. The As—O—C angles (123.6 and 126.3°) may seem large, but similar values were observed for P—O—C in 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide (Silver & Rudman, 1972) and in 2α-bromo-5β-bromoethyl-5α-methyl-1,3,2-dioxaphosphorinane 2-oxide

(Beineke, 1969). Again, such values fit in with the anomeric effect, since the delocalization increases the *sp*² character of the O atoms in the ring.

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catena-Poly{copper(I)-di-μ-bromo-copper(I)-2,3:2,4-[bis-μ-(1,4-oxathiane-S:S)]-[di-μ-bromo-dicopper(I)]-3,1:4,1-[bis-μ-(1,4-oxathiane-S:S)]}

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Abstract. (C₄H₈BrCuOS)_n, orthorhombic, *Fdd2*, *a* = 37.91 (2), *b* = 15.11 (1), *c* = 9.95 (1) Å, *V* = 5699.6 Å³, *F*(000) = 3839, *D*_c = 2.31 g cm⁻³, *Z* = 32, 0567-7408/82/123091-03\$01.00

μ(Cu Kα) = 121.7 cm⁻¹. Final *R* = 0.067 for 1302 observed reflexions. The structure contains Cu₂Br₂ rings linked by S-bridging 1,4-oxathiane molecules into © 1982 International Union of Crystallography

infinite chains parallel to the c axis; Cu—Br 2.44–2.52 Å, Cu—S 2.27–2.33 Å. There may be weak Cu...Cu interactions.

Introduction. The polymeric title compound (I) was reported (Walton, 1966) as the major product of the reaction of 1,4-oxathiane (tx) with $CuBr_2$ in ethanol. It occurs as fine, almost colourless needles readily separated under the microscope from the minor product, green $CuBr_2 \cdot 2tx$. The structure has been determined as part of a programme to investigate the roles in which 1,4-oxathiane occurs as a bridging ligand.

As (I) is not stable in air on prolonged exposure crystals were mounted in capillaries or else varnished. Weissenberg photographs were taken with $Cu K\alpha$ radiation for the levels $hk(0-9)$ where c is the needle axis and levels $(0-3)$ for a crystal mounted on the ab diagonal. Intensities of 1302 reflexions above background were measured with a computerized microdensitometer (SRC Service, Daresbury Laboratory). Unfortunately, the 20 strongest reflexions proved to be too intense to be measured on any of the films; these intensities were estimated visually and added to the data set along with 495 reflexions not observed above background which were assigned $I = \frac{1}{2}I_{min}$.

All calculations were performed using *SHELX 76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975). Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Preliminary calculations showed that the (uuu) reflexions of the F lattice were systematically less intense than the (ggg) reflexions. For all E maps the data were renormalized to bring some (uuu) reflexions above the limit $E > 1.2$. The E maps were dominated by false symmetry but the sixth map in rank gave the desired pattern of two heavy and four medium weight peaks, interpreted as two Br, two Cu and two S atoms.

At this point only the 1302 measured reflexions were retained and absorption corrections were applied (crystal size $0.20 \times 0.20 \times 0.54$ mm). A Fourier map then revealed all the remaining non-H atoms ($R = 0.25$). Refinement continued by least squares and Fourier methods. As in other 1,4-oxathiane complexes examined recently (Barnes, Blyth & Paton, 1982), the dimensions found for the oxathiane molecules were unsatisfactory, and the refinement stopped at $R = 0.14$. Inclusion of the oxathiane as a restrained group defined by C—S 1.81, C—O 1.45, C—C 1.54 Å with S as the pivot atom allowed refinement to continue to $R = 0.071$ with anisotropic Cu, Br and S and to convergence at $R = 0.067$ with all non-H atoms anisotropic and H atoms included on calculated positions. Two reflexions for which secondary extinction appeared to be severe were excluded from the

final calculation. The weighting scheme used was $w = 72.2342/[\sigma^2(F) + 0.0100F^2]$.*

Discussion. Atomic coordinates for (I) are given in Table 1; bond lengths and angles are in Table 2. The structure consists of Cu_2Br_2 rings alternately normal to the c axis [Cu(1),Br(2),Cu(1)',Br(2)'] and normal to the a axis [Cu(2),Br(1),Cu(3),Br(1)']. These planar rings are linked into chains parallel to the c axis by the S atoms of the oxathiane molecules. S(11) joins Cu(1) to Cu(2) and S(21) joins Cu(1) to Cu(3), so that each Cu atom has approximately tetrahedral geometry (Fig. 1). The O atoms of the oxathiane molecules take no

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38041 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for the non-H atoms with e.s.d.'s in parentheses

For the S, C and O atoms the e.s.d.'s are those of the rigid group refined. The e.s.d.'s of the rotational parameters of the pivot atoms are S(11) 0.0053(x), 0.0051(y), 0.0032(z) and S(21) 0.0055(x), 0.0044(y), 0.0036(z).

	x	y	z	U_{eq}^* (Å ²)
Br(1)	7792 (1)	3611 (1)	-3111 (1)	34 (1)
Br(2)	7192 (1)	1317 (1)	1845 (2)	33 (1)
Cu(1)	7194 (1)	2985 (1)	1924 (6)	34 (1)
Cu(2)	7500	2500	-4502 (7)	31 (1)
Cu(3)	7500	2500	-1622 (7)	33 (1)
S(11)	7072 (1)	3180 (2)	4136 (6)	21 (1)
C(12)	7045 (1)	4309 (2)	4685 (6)	47 (4)
C(13)	6715 (1)	4765 (2)	4102 (6)	32 (4)
O(14)	6409 (1)	4313 (2)	4625 (6)	64 (4)
C(15)	6331 (1)	3451 (2)	4251 (6)	47 (4)
C(16)	6629 (1)	2817 (2)	4564 (6)	45 (4)
S(21)	7078 (1)	3215 (2)	-309 (7)	26 (1)
C(22)	7067 (1)	4356 (2)	-827 (7)	33 (4)
C(23)	6762 (1)	4872 (2)	-326 (7)	57 (4)
O(24)	6423 (1)	4469 (2)	-862 (7)	39 (3)
C(25)	6380 (1)	3580 (2)	-294 (7)	46 (4)
C(26)	6648 (1)	2913 (2)	-881 (7)	33 (4)

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Cu(1)—Br(2)	2.523 (3)	Cu(2)—Br(1)	2.442 (4)
Cu(1)—Br(2)'	2.552 (3)		
Cu(1)—S(11)	2.269 (4)	Cu(3)—Br(1)	2.498 (4)
Cu(1)—S(21)	2.293 (4)	Cu(2)—S(11)	2.350 (4)
Cu(1)...Cu(1)'	2.740 (3)	Cu(3)—S(21)	2.331 (4)
		Cu(2)...Cu(3)	2.865 (4)
Cu(1)—Br(2)—Cu(1)'	65.4 (1)	Cu(2)—Br(1)—Cu(3)	70.9 (1)
Br(2)—Cu(1)—Br(2)'	114.5 (2)	Br(1)—Cu(2)—Br(1)'	110.9 (2)
S(11)—Cu(1)—S(21)	151.8 (2)	Br(1)—Cu(3)—Br(1)'	107.3 (2)
S(11)—Cu(1)—Br(2)	99.1 (2)	S(11)—Cu(2)—Br(1)	109.8 (1)
S(21)—Cu(1)—Br(2)	96.9 (2)	S(21)—Cu(3)—Br(1)	109.0 (1)

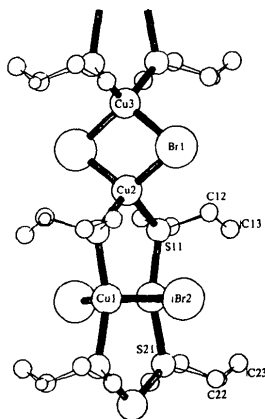


Fig. 1. The title compound viewed normal to the bc plane.

part in complex formation. The two oxathiane molecules are approximately eclipsed when viewed down the c axis. There are approximate local centres of inversion at the centres of the Cu_2Br_2 rings.

The dimensions of the Cu_2Br_2 rings are appreciably different. For the ring $Cu(1), Br(2), Cu(1'), Br(2')$ the average $CuBr$ distance is 2.537 \AA and the average $Cu-S$ distance is 2.281 \AA . The angles about the Cu atom range from 96.9 to 151.8° . $S(11)$ and $S(21)$ both use axial lone pairs for bonding to Cu^I . In the ring $Cu(2), Br(1), Cu(3), Br(1')$ the average $Cu-Br$ distance is 2.470 \AA and the average $Cu-S$ distance 2.340 \AA . The angles about the Cu atoms all lie between 107.3 and 110.9° . The S atoms use equatorial lone pairs for binding to $Cu(2)$ and $Cu(3)$. The $Cu-S$ distances in tetrahedral CuX_4^+ (Barnes *et al.*, 1982) range from 2.279 to 2.370 \AA with no correlation between bond

length and the choice of axial or equatorial directions at the S atoms.

There does not appear to be a close analogue to the structure of (I). $CuBr(Et_2P.PEt_2)$ (Hartung, 1970) contains chains made up of Cu_2Br_2 and Cu_2P_4 rings but with only a single orientation for the Cu_2Br_2 rings.

$Cu-Cu$ bonds have been postulated in several structures containing Cu_2X_2 rings, typically $Cu-Cu$ 2.60 \AA in $[CuI(AsEt_3)]_4$ (Mann, Purdie & Wells, 1936). However, the Cu_2Cl_2 ring in cyclooctadienyl $CuCl$ (Van der Hende & Baird, 1963) has $Cu \cdots Cu$ 2.944 \AA and $CuBr(Et_2P.PEt_2)$ has $Cu \cdots Cu$ 3.49 \AA with $Cu-Br$ 2.55 \AA . In (I) the $Cu \cdots Cu$ distances 2.740 (3) and 2.865 (4) \AA and the very acute $Cu-Br-Cu$ angles 65.4 and 70.9° suggest some $Cu \cdots Cu$ interaction.

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Aqua(3,7-diaza-2,7-nonadiene-2,8-dicarboxylato- O,O',N,N')copper(II)

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Abstract. $C_9H_{14}CuN_2O_5$, monoclinic, $P2_1/n$, $a = 7.178$ (4), $b = 14.425$ (11), $c = 11.147$ (9) \AA , $\beta = 106.25$ (5) $^\circ$, $Z = 4$, $V = 1108.1$ (8) \AA^3 , $D_m = 1.76$, $D_c = 1.76 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 2.06 \text{ mm}^{-1}$. The structure was refined to $R = 0.035$ for 2114 observed reflections. The structure consists of discrete five-coordinate square-pyramidal neutral complexes. The tetradentate ligand is bonded in a square plane about Cu with $Cu-N = 1.984$ (3) and 1.972 (3) \AA and $Cu-O = 1.958$ (3) and 1.953 (3) \AA . The apical position is occupied by a water O atom at a distance of 2.310 (3) \AA .

Introduction. The title compound was first prepared by Nakahara, Yamamoto & Matsumoto (1964) in connection with their studies on the stability of fused five- and six-membered rings in metal chelates. The blue needle-shaped crystals were prepared from 1,3-propanediamine, pyruvic acid and freshly precipitated $Cu(OH)_2$ and recrystallized from water (Nakahara *et al.*, 1964). Systematic absences of the type $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicated space group $P2_1/n$. The crystal chosen for data collection had dimensions $0.40 \times 0.08 \times 0.05 \text{ mm}$. Cell constants were calculated from angular settings of 16 reflections measured on a