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Poly[μ_2 -chloro- μ_2 -1,4-oxathiane- κ^2 S:S-copper(I)]Natalya F. Salivon,^a Yaroslav E. Filinchuk^{b,c} and
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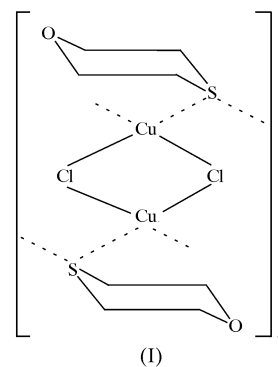
The title complex, $[\text{CuCl}(\text{C}_4\text{H}_8\text{OS})]_n$, contains infinite spiral $(\text{CuS})_n$ chains linked by bridging Cl atoms into layers. The Cl atoms do not form polymeric fragments with Cu^{I} , but combine into isolated centrosymmetric Cu_2Cl_2 units. The compound is non-isomorphous with the Br-containing analogue, which contains Cu_8S_8 rings linked by Br atoms into chains. The O atom of the 1,4-oxathiane molecule does not realize its coordination abilities in the known copper(I)–halide complexes, while in copper(II)–halide complexes, oxathiane is coordinated *via* the S and O atoms. This falls into a pattern of the preferred interactions, *viz.* weak acid (Cu^{I} atom) with weak base (S atom) and harder acid (Cu^{II} atom) with harder base (O atom).

Comment

1,4-Oxathiane (xt) behaves either as a monodentate ligand in mononuclear transition metal complexes (McEwen & Sim, 1967; Barnes *et al.*, 1977; Olmstead *et al.*, 1982) or as a bridging ligand in polymeric complexes (Barnes & Paton, 1982, 1984; Barnes *et al.*, 1983; Boorman *et al.*, 1998; Salivon *et al.*, 2006). In the latter case, it may coordinate to metal atoms *via* both S and O atoms. The copper(I)–halide complexes $[\text{CuX}(\text{xt})]$, where X is Cl, (I), or Br, (II), are known to be non-isomorphous (Barnes *et al.*, 1983). However, the structure was determined only for the bromine-containing compound (II) (Barnes & Paton, 1982), while no suitable crystals were obtained for the chlorine-containing analogue (Barnes *et al.*, 1983). We have succeeded in obtaining (I) in the form of good quality single crystals and report here its crystal structure.

A major factor governing structure formation in complexes (I) and (II) is the competition between the halide and S atoms for the coordination to Cu^{I} . Both structures contain polynuclear $(\text{CuS})_n$ fragments. In (I), the infinite spiral-like $(-\text{Cu}-\text{S}-\text{Cu}'-\text{S}')_n$ chains (Fig. 1) are similar to the $\text{Zn}-\text{S}$ chains running along [100] in the sphalerite structure; the torsion

angles $\text{Cu}-\text{S}-\text{Cu}'-\text{S}'$ [$-72.8(2)^\circ$] and $\text{S}-\text{Cu}'-\text{S}'-\text{Cu}$ [$-67.3(2)^\circ$] in (I) are close to the corresponding angles $\text{Zn}-\text{S}-\text{Zn}'-\text{S}'$ and $\text{S}-\text{Zn}'-\text{S}'-\text{Zn}$ (both -60°) in sphalerite.



The Cl atoms do not form polymeric fragments with Cu^{I} on their own. Instead, they form isolated centrosymmetric Cu_2Cl_2 fragments (Fig. 2a). Hence, at the S:Cl ratio 1:1, the softer base (the S atom) appears to be more competitive in the formation of polymeric structures with a soft acid (Cu^{I} atom) than the harder base (the O atom). The Cl atoms merely bridge the $(\text{CuS})_n$ chains into layers in the (100) plane (Fig. 1). Polymeric $(\text{CuCl})_n$ fragments appear only when the S:Cl ratio is changed in favour of the Cl atoms. For example, polymeric $(\text{Cu}_2\text{Cl}_2)_n$ strips appear in the structure of the $[(\text{CuCl})_3(\text{xt})_2]$ complex, (III) (Salivon *et al.*, 2006). These strips are linked *via* the bridging S atoms into layers in the (010) plane (Fig. 2c). The bromine-containing compound (II) is built in a slightly different manner. The $(\text{CuS})_n$ fragments are represented by isolated eight-membered Cu_4S_4 rings, which are linked *via* Br atoms into infinite chains running along [001] (Fig. 2b).

A significant difference between the two Cu–S bond lengths in complex (I) (Table 1) indicates a pyramidal deformation of the nearly tetrahedral coordination of the Cu^{I} atom. A similar difference between the two Cu–S distances is observed for one of the three Cu atoms in complex (III); in all other cases, this asymmetry is even less noticeable (Olmstead *et al.*, 1982; Barnes & Paton, 1982). The 1,4-oxathiane molecule has a chair conformation in all the known transition metal complexes (Fowler & Griffiths, 1978; Olmstead *et al.*, 1982; Barnes *et al.*, 1983; Buchholz *et al.*, 1996; Boorman *et al.*, 1998).

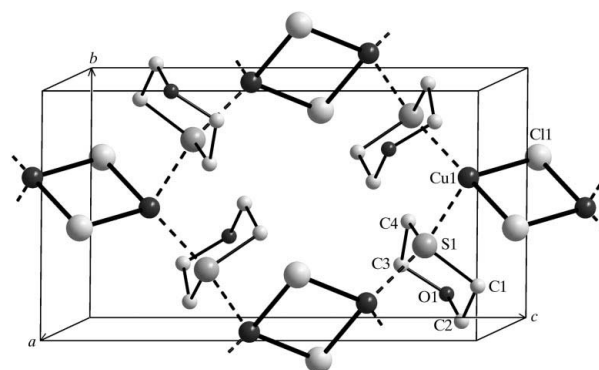


Figure 1

The title compound, as seen in the *bc* projection. Cu–Cl bonds are shown as thick solid lines, while Cu–S bonds are represented as dashed lines.

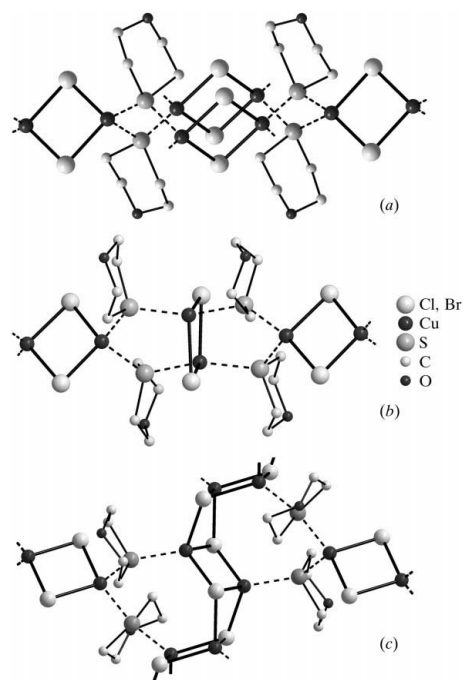


Figure 2
The polymeric structure of complexes (a) [CuCl(xt)], (I), (b) [CuBr(xt)], (II), and (c) [(CuCl₂)₃(xt)₂], (III). Thick and dashed lines are used to highlight the copper-halide fragments.

The O atoms do not realize their coordination abilities in any of the complexes mentioned here. This falls into a pattern of the preferred interaction weak acid (Cu^I atom) with weak base (S atom). On the other hand, the harder base (O atom) may form a hydrogen bond; in (I), a bond with an O...C2 distance of 3.33 (3) Å links the layers into a three-dimensional structure. However, the O atom of the 1,4-oxathiane molecule can also be involved in an interaction with a transition metal. This can be achieved either by an increase of the acid's hardness, as in the Cu^{II} complexes [(CuCl₂)₃(xt)₂] and [CuCl₂(xt)] (Barnes *et al.*, 1983), where oxathiane becomes a bidentate ligand (coordination *via* the S and O atoms), or by an increase of the metal-to-ligand ratio, as in the Ag^I complex [(AgNO₃)₆(xt)] (Barnes & Paton, 1984), where oxathiane behaves as a tetradentate ligand (μ_2 -S and μ_2 -O).

Experimental

CuCl (1 mmol) was added to a solution of 1,4-oxathiane (1 mmol) in benzene (2 ml) at 278 K. The resulting product was mainly composed of light-brown crystals of (I). Detailed examination of some batches revealed also dark-brown plate-like crystals of complex (III) (Salivon *et al.*, 2006).

Crystal data

[CuCl(C ₄ H ₈ OS)]	$Z = 4$
$M_r = 203.17$	$D_x = 1.974 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.5068 (12) \text{ \AA}$	$\mu = 3.79 \text{ mm}^{-1}$
$b = 6.5035 (10) \text{ \AA}$	$T = 293 (1) \text{ K}$
$c = 11.4259 (16) \text{ \AA}$	Prism, light brown
$\beta = 104.572 (15)^\circ$	$0.17 \times 0.09 \times 0.07 \text{ mm}$
$V = 683.71 (17) \text{ \AA}^3$	

Data collection

Stoe IPDS diffractometer	4497 measured reflections
φ oscillation scans	1658 independent reflections
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1999)	892 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.739$, $T_{\max} = 0.859$	$R_{\text{int}} = 0.061$
	$\theta_{\max} = 28.1^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2]$
$wR(F^2) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.77$	$(\Delta/\sigma)_{\max} = 0.044$
1600 reflections	$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
43 parameters	$\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—S1 ⁱ	2.2792 (10)	Cu1—S1	2.4139 (12)
Cu1—Cl1	2.3529 (12)	S1—Cl1	1.815 (4)
Cu1—Cl1 ⁱⁱ	2.3793 (12)	S1—C4	1.831 (5)
S1 ⁱ —Cu1—Cl1	120.71 (4)	Cl1—Cu1—S1	103.67 (4)
S1 ⁱ —Cu1—Cl1 ⁱⁱ	123.01 (5)	Cl1 ⁱⁱ —Cu1—S1	99.15 (4)
Cl1—Cu1—Cl1 ⁱⁱ	96.71 (4)	Cl1—S1—C4	95.9 (2)
S1 ⁱ —Cu1—S1	110.11 (3)	Cu1 ⁱⁱⁱ —S1—Cu1	127.96 (5)

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 1, -z + 2$; (iii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

H atoms were treated using a riding model, with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS Software*; data reduction: *TWIN* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3054). Services for accessing these data are described at the back of the journal.

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