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The Structure of Copper(I) Mercury(II) Chloride Selenide

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Abstract

CuHgSeCl is orthorhombic, space group *Pbam*, with $a = 6{\cdot}9444\ (9)$, $b = 12{\cdot}7561\ (19)$, $c = 4{\cdot}2526\ (5)$ Å, $Z = 4$; final $R = 0{\cdot}071$ for 748 unique reflections. The structure is built up of a three-dimensional network of Se—Hg—Se chains in planes $z = 0$, connected to Se_2Cl_2 distorted tetrahedra in which the Cu atoms occupy an off-centred position. Se and Cl atoms form a distorted cubic-centred lattice. The Se—Hg—Se chains are different from the S—Hg—S chains in CuHgSCl.

Introduction

The diagram showing the stability regions of eightfold, sixfold, and fourfold zinc blende and wurtzite coordination (St John & Bloch, 1974) led us to study solid solutions between two binary compounds belonging to different regions; for example, a zinc blende type compound and a rock salt like compound as in CuX(zinc blende)–HgS(cinnabar) solid solutions (X = Cl, Br) (Guillo, Mercey & Deschanvres, 1979).

In the present work we are looking at the CuCl–HgSe system, two compounds belonging to the same stability region of the diagram. Whereas CuBr–HgSe solid solution leads to a CuHgSeBr phase of the same type as the CuHgSCl already obtained, in the CuCl–HgSe solid solution we obtain CuHgSeCl, a compound with a different structure type.

Experimental

CuCl and HgSe were prepared, respectively, by precipitation and by fusion methods. The two binary compounds, in stoichiometric amounts, were intimately mixed, then sealed in an evacuated quartz tube. To avoid dispersed condensations, this tube was placed in the thermal gradient of a horizontal furnace so that products were in the cold zone. The tube was heated for two days at 1073 K and slowly cooled to obtain a red melt with small crystals. The density was determined at 298 K in CCl_4 by the pycnometric method [$d_c = 6{\cdot}67$, $d_m = 6{\cdot}71\ (3)$ Mg m^{-3}, with $Z = 4$]. The small crystal used for the collection of intensities was selected after film studies with a Weissenberg camera. Intensities were measured with a four-circle CAD-4 Enraf–Nonius diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. X-ray photographs showed an orthorhombic lattice with systematic extinctions ($h0l$: $h = 2n + 1$; $0kl$: $k = 2n + 1$) which agree with *Pbam* and *Pba*2. A least-squares treatment with 25 reflections was used to refine the cell parameters. Intensities were measured up to $\theta = 45°$ by the ω–2θ technique with a scan width Δ (°) = $1{\cdot}00 + 0{\cdot}85$ tg θ and a counter slit aperture Ω (mm) = $3{\cdot}00 + 0{\cdot}80$ tg θ. The scan width was adjusted for a measurement limited to 60 s, in order to obtain $\sigma(I)/I = 0{\cdot}018$. Three reference reflections were periodically measured. 748 unique reflections with $I > 3\sigma(I)$ were obtained, corrected for Lorentz and polarization factors, and used to solve and refine the structure. For absorption corrections the shape of the crystal was assumed to be a rectangular parallelepiped limited by the three forms {100}, {010} and {001}, respectively 525, 100 and 45 µm. In fact, the crystal sections were irregular and absorption corrections are approximate [μ_l(Mo $K\alpha$) = $58{\cdot}1$ mm^{-1}].

Structure determination

The heavy-atom method was used to solve the structure. Hg and Se atoms were located from a Patterson function, Cu and Cl from difference maps. Scattering factors were for neutral atoms (Cromer & Waber, 1965) corrected for anomalous scattering (Cromer, 1965). A plot of $\langle w|F_o - F_c|\rangle$ *versus* $\sin\theta/\lambda$ allowed us to obtain a linear weighting scheme. In *Pbam* least-squares refinement converged to $R = 0{\cdot}071$ and $R_w = 0{\cdot}077$.

The four independent atoms were located in the mirrors $m(001)$. The mean quadratic displacements $\bar{u}_{ii}$ of the anisotropic thermal factors were between 0·014 and 0·035 Å^2 but the large value (0·105 Å^2) observed for $\bar{u}_{11}$ of Cu suggested abnormal behaviour of this atom.

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Final atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.*

Structure description

The Hg atoms are octahedrally coordinated by four Cl atoms, two at 3·105 and two at 3·270 Å, and by two Se atoms in the same plane as the Hg at 2·477 and 2·486 Å. The structure consists of columns of octahedra sharing (SeClCl) faces running along the [100] direction and connected by groups of distorted tetrahedra (Figs. 1 and 2). However, this description involves a large distortion of the octahedra, which is a reason for looking for another description of the structure. Considering the great ability of the Hg atom to form chains with chalcogen atoms we can describe the structure as Se—Hg—Se chains running in the mean direction [100]; in these chains the Hg—Se distances are 2·477 and 2·486 Å, similar to those observed in $Hg_3Se_2Cl_2$, 2·51 Å (Puff & Küster, 1962), and the angles Se—Hg^{ii}—Se^{ii} and Hg—Se—Hg^{ii} are respectively 171·31 and 89·14°.

Table 1. *Positional and thermal parameters, with e.s.d.'s in parentheses*

	Pbam	*x*	*y*	*z*	B_{eq} (Å^2)
Hg	4(*g*)	0·10824 (18)	0·26060 (7)	0	2·10
Se	4(*g*)	0·3394 (4)	0·1118 (2)	0	1·47
Cu	4(*h*)	0·2445 (12)	0·0461 (3)	0·5	4·40
Cl	4(*h*)	0·3545 (10)	0·3767 (4)	0·5	1·94

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry-code superscripts

4(*g*)	None	$x, \quad y, 0$	4(*h*)	None	$x, \quad y, \frac{1}{2}$
	(i)	$\bar{x}, \quad \bar{y}, 0$		(i)	$\bar{x}, \quad \bar{y}, \frac{1}{2}$
	(ii)	$\frac{1}{2}+x, \frac{1}{2}-y, 0$		(ii)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}$
	(iii)	$\frac{1}{2}-x, \frac{1}{2}+y, 0$		(iii)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}$

(*a*)*	Se—Hg^{ii}	2·477 (2)	(*f*)	Cu^{ii}—Cl^{i}	2·268 (7)
(*b*)	Se^{ii}—Hg^{ii}	2·486 (3)	(*g*)	Cu^{ii}—Cl	2·882 (10)
(*c*)	Se^{ii}—Cu^{ii}	2·379 (3)	(*h*)	Cu^{ii}—Cu^{iii}	3·594 (11)
(*d*)	Hg—Cl	3·105 (5)	(*i*)	Cl^{i}—Cl	3·738 (8)
(*e*)	Hg^{ii}—Cl	3·270 (5)	(*j*)	Cl—Se^{ii}	3·985 (6)

Hg—Se—Hg^{ii}	89·14 (6)	Se^{ii}—Cu^{ii}—Se^{ii}	126·74 (18)
Se—Hg^{ii}—Se^{ii}	171·31 (7)	Se^{ii}—Cu^{ii}—Cl^{i}	114·82 (20)
Cl—Cu^{ii}—Cl^{i}	92·33 (18)	Se^{ii}—Cu^{ii}—Cl	98·05 (16)
Cu^{ii}—Cl^{i}—Cu^{iii}	87·67 (18)		

* See Fig. 1.

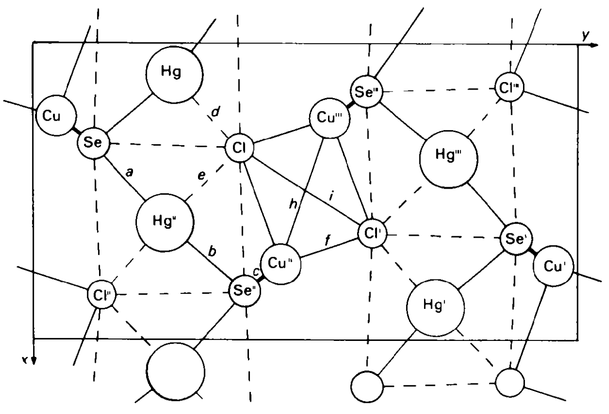

Fig. 1. CuHgSeCl structure projected on to the (001) plane.

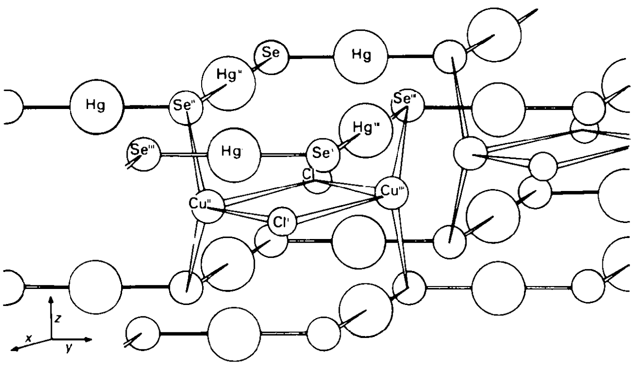

Fig. 2. Perspective view of the CuHgSeCl structure, showing the spatial arrangement of the atoms.

Two chains related by the **c** translation are connected by a distorted tetrahedron built up from two Se atoms belonging to two different chains and two Cl atoms at $z = 0·5$. In this tetrahedron the Cu atom is in a very off-centred position. Two of the above tetrahedra, sharing a Cl—Cl edge, connect the Se—Hg—Se—chains running in the same plane. This is different from CuHgSCl in which two tetrahedra are built up only from chains with a **c** translation. The Se ($z = 0$) atom is in nearly tetrahedral coordination with two Hg atoms ($z = 0$) and two Cu atoms ($z = 0·5$).

Discussion

The coordination and thermal factor of the Cu atom led us to consider this atom more closely. Cu^{I} readily adopts a tetrahedral coordination and it was reasonable to locate it at the centre of the previously described Se_2Cl_2 tetrahedron. But, as can be seen in Fig. 3, the distance between the centres of Cl—Cl edge-sharing tetrahedra is too short (1·85 Å) for two Cu atoms, and, as can be seen on difference maps, the Cu atom is located in a very off-centred position to give a Cu—Cu distance of 3·594 Å. The Cu atom (for example, Cu^{ii})

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35416 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

has been drawn near to a plane of two Se atoms (for example, Se^{ii}, $z = 0$ and $z = 1$) and one Cl atom (for example, Cl^{i}) giving a nearly planar triangular coordination with $Cu^{ii}-Se^{ii} = 2{\cdot}379$ and $Cu^{ii}-Cl^{i} = 2{\cdot}268$ Å. This coordination type has already been found for Cu^{I} compounds: $Cu_xV_4O_{11}$ (Galy & Lavaud, 1971), $Cu_4Bi_5S_{10}$ (Mariolacos, Kupčík, Ohmasa & Miehe, 1975), $Bi_2Cu_3S_4Cl$ (Lewis & Kupčík, 1974) and $CuPbBi_3S_6$ (Mumme, 1975).

The anisotropic temperature coefficients β_{ij} of the Cu atom define an ellipsoid, the major axis of which is directed towards the Cl atom located at 2·882 Å (Fig. 3). The large value observed in this direction seems to indicate an oscillation of the Cu atom between two positions, the first of triangular and the second of tetrahedral coordination. The latter is irregular due to the Cu–Cu distance which must be large enough, and to the Se atoms which have to be in tetrahedral coordination. Refinement giving 50% occupancy to both Cu atomic positions converged but R did not show a significant change. The nearest Cu atoms are separated by 3·594 Å; this separation is greater than in $CsCu_2Cl_3$, 3·098 Å (Brink, Binnendijk & van de Linde, 1954), in which Cu atoms are also located in tetrahedra sharing a Cl–Cl edge. The Se atom has a distorted tetrahedral coordination with two Hg atoms ($z = 0$) at 2·477 and 2·486 Å and two Cu atoms ($z = 0{\cdot}5$) at 2·379 Å.

The geometry of the Se–Hg–Se chains is different from that of the S–Hg–S chains in CuHgSCl. If the angles Hg–M–Hg in the chains are denoted by α, with the sign shown on Fig. 4, the present chain may be described as of the $+-+-$ type, while the chains in CuHgSCl are of the $++--$ type. These chains are like those in HgO and $H(OHg)_4Br$ (Aurivillius, 1967) and in Hg_2O_2NaI (Aurivillius, 1960). CuHgSCl and CuHgSeCl structures have different geometrical features. In CuHgSCl, constraints seem to be more important than in CuHgSeCl; in CuHgSCl, eight S atoms belonging to two different chains build up the cubic-centred packing of S and Cl atoms; in CuHgSeCl the eight Se atoms building up the cubic-centred packing belong to four different chains, reducing constraints in the structure.

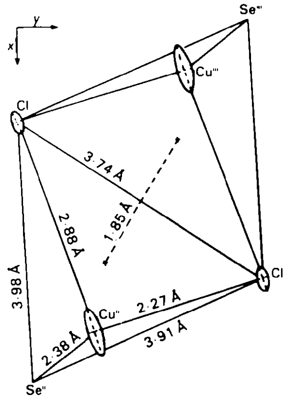

Fig. 3. Coordination and thermal ellipsoids of the Cu and Cl atoms.

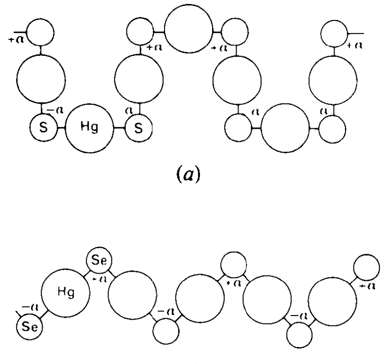

Fig. 4. Chains formed by the Hg and chalcogenide atoms in CuHgSCl and CuHgSeCl. (*a*) Infinite S–Hg–S chains in CuHgSCl. (*b*) Infinite Se–Hg–Se chains in CuHgSeCl.

Electrical measurements

The large thermal amplitude of the Cu atom led us to study the possibility of ionic conductivity. To obtain the disc used in the apparatus the powder of CuHgSeCl was pressed under isostatic pressure (350 MPa) and annealed under vacuum. Gold electrodes were then sputtered on to the disc. With the Cole & Cole (1941) method electrical measurements were made under an argon pressure. The frequency used was between 20×10^{-3} and 100 kHz at temperatures between 293 and 473 K. The intensity and phase displacement of the signal were measured with a lock-in Tekelec TE 9700 amplifier.

The activation energy and ionic conductivity observed at 298 K are respectively 0·92 eV and $1{\cdot}53 \times 10^{-10}$ $(\Omega\,\mathrm{mm})^{-1}$, indicating that, despite the large thermal amplitude of the Cu atom, this atom cannot move in the structure.

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The Structure of Cesium Hydrogensulfite

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Abstract

The structure of the hydrogensulfite ion has been determined for the first time in $CsHSO_3$ which crystallizes in space group $R3m$ with $a = 4{\cdot}6721\,(7)$ Å, $\alpha = 85{\cdot}31\,(1)°$, $Z = 1$. The absolute configuration of the structure was refined to $R = 0{\cdot}014$ for 506 independent reflections. The S atom has tetrahedral coordination, with three pyramidal S—O bonds and an S—H bond in the fourth direction. The S—O distance is 1·454 (2) Å and the O—S—O angle 113·1 (2)°. The bond distance is similar to that in the SO_4^{2-} ion, while it differs markedly from that in the SO_3^{2-} ion. The Cs^+ ion is nine-coordinated with Cs—O distances of 3·231 (4)–3·249 (4) Å.

Introduction

The existence of crystalline hydrogensulfites has long been a subject of controversy. Foerster, Brosche & Norberg-Scholtz (1924) proposed that the crystalline bisulfites of sodium and potassium were not hydrogensulfites but pyrosulfites of composition $Na_2S_2O_5$ and $K_2S_2O_5$. Simon & Schmidt (1960) reported the synthesis of solid hydrogensulfites, $RbHSO_3$ and $CsHSO_3$, and Beck (1959) reported the existence of a salt of composition $K_2S_2O_5.4KHSO_3$. Maylor, Gill & Goodall (1972) described the preparation of three compounds: NR_3HSO_3, with R = ethyl, *n*-butyl and *n*-amyl. The existence of NH_4HSO_3 has also been reported (Hisatune & Heicklen, 1975). The conclusion that these compounds really contained the HSO_3^- ion was based on evidence from IR and Raman spectroscopy. The existence of $CsHSO_3$ and $RbHSO_3$ was disputed by Schmidt & Wirwoll (1960) who argued that the failure of $CsHSO_3$ and $RbHSO_3$ to react with S_2Cl_2 in anhydrous tetrahydrofuran forming HCl and $M_2S_4O_6$ ($2MHSO_3 + S_2Cl_2 \rightarrow 2HCl + M_2S_4O_6$) showed that these salts did not contain hydrogensulfite ions but were pyrosulfites. However, a recent spectroscopic investigation (Meyer, Peter & Shaskey-Rosenlund, 1979) provides ample evidence for the existence of the HSO_3^- ion.

The structure of the HSO_3^- ion has also been a matter of discussion. The proton may be connected either to an O atom, $HO—SO_2^-$, or to the S atom, HSO_3^-. IR and Raman studies of solid salts and solutions have indicated the form HSO_3^- rather than $HO—SO_2^-$ (Simon & Schmidt, 1960; Hisatune & Heicklen, 1975; Meyer *et al.*, 1979). However, some authors believe that the two forms exist in equilibrium in aqueous solution (Simon & Kriegsmann, 1956; Golding, 1960).

The present study of $CsHSO_3$ is the first crystallographic structure determination of a compound containing the HSO_3^- ion.

Experimental

Crystals of $CsHSO_3$ were prepared by dissolving 2·0 g of dry Cs_2CO_3 in 4·0 ml H_2O under N_2. The reaction vessel was then held at 313 K, while SO_2(g) was passed through the solution to saturation, CO_2(g) being evolved. The clear yellow liquid was then cooled slowly under SO_2(g). At 301 K colorless crystals formed; most were irregular in shape, but some were well formed, flat, trigonal pyramids with the corners of the basal plane truncated. Dry crystals are stable in air.

A few crystals were ground in an agate mortar and the IR spectrum (Table 1) was recorded with the Nujol mull technique. The spectrum agrees well with that published by Simon & Schmidt (1960), who assigned

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