

Structures of Zinc Selenite and Copper Selenite

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Abstract. ZnSeO₃, $M_r = 192.3$, orthorhombic, $Pcab$, $a = 6.233$ (1), $b = 7.200$ (2), $c = 11.987$ (3) Å, $V = 537.9$ (3) Å³, $Z = 8$, $D_x = 4.75$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 236.7$ cm⁻¹, $F(000) = 704$, $T = 297$ K, $R = 0.035$ for 608 observed reflections. CuSeO₃, $M_r = 190.5$, orthorhombic, $Pcab$, $a = 5.954$ (1), $b = 7.006$ (1), $c = 12.232$ (2) Å, $V = 510.2$ (1) Å³, $Z = 8$, $D_x = 4.96$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 239.4$ cm⁻¹, $F(000) = 696$, $T = 297$ K, $R = 0.037$ for 675 observed reflections. The cation coordinations are trigonal bipyramidal and trigonal pyramidal for (Zn, Cu) and Se, respectively. The trigonal bipyramids share edges and corners to form a sheet parallel to (011). These sheets are linked along x by the SeO₃ groups that share corners with adjacent sheets to form an open framework.

Introduction. At the start of a study of some selenite minerals (Hawthorne, 1984), we noticed a paucity of data on the stereochemistry of inorganic selenites. Consequently, an examination of a few simple selenite compounds seemed in order before examining some of the more exotic compositions found in the natural state.

Experimental. Crystals of ZnSeO₃ and CuSeO₃ were obtained from Dr J. A. Mandarino, Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, Ontario, Canada. Crystal size: ZnSeO₃ 0.06 × 0.20 × 0.30; CuSeO₃ 0.10 × 0.13 × 0.19 mm; space group and crystal data from precession photographs, unit-cell parameters refined from 25 reflections automatically centred on a Nicolet R3m diffractometer at 297 K.

Data collection for ZnSeO₃(CuSeO₃): 757(772) reflections, $3 < 2\theta < 60^\circ$ hkl , graphite monochromator, Mo $K\alpha$ X-radiation, $\theta/2\theta$ scan, variable scan speed 4–29.3° min⁻¹, scan range $(K\alpha_1 - 1) \rightarrow (K\alpha_2 + 1)^\circ$, background/scan = 0.5, two standard reflections every 48 reflections, variation $\pm 1.9(2.0)\%$, absorption correction by refinement of a thin plate (ellipsoidal) correction from ψ -scan data, minimum transmission 0.056(0.050), maximum transmission 0.576(0.119), Lorentz and polarization corrections, 608(675) observed reflections with $I > 2.5\sigma(I)$.

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Table 1. Atomic parameters and equivalent isotropic temperature factors (Å² × 10⁴)

	x	y	z	U_{eq}
ZnSeO₃				
Zn	0.1353 (2)	0.6076 (1)	0.4045 (1)	105 (2)
Se	0.1119 (1)	0.0445 (1)	0.3575 (1)	82 (2)
O(1)	0.2007 (9)	-0.0343 (8)	0.2328 (5)	138 (16)
O(2)	0.3394 (10)	0.0311 (8)	0.4342 (6)	170 (16)
O(3)	-0.0162 (9)	-0.1517 (7)	0.4071 (5)	110 (15)
CuSeO₃				
Cu	0.1500 (2)	0.5783 (1)	0.4067 (1)	116 (3)
Se	0.1118 (1)	0.0514 (1)	0.3544 (1)	97 (2)
O(1)	0.2050 (9)	-0.0419 (8)	0.2359 (4)	134 (15)
O(2)	0.3534 (9)	0.0425 (8)	0.4305 (4)	125 (14)
O(3)	-0.0263 (9)	-0.1432 (8)	0.4085 (4)	129 (14)

Structure determination and refinement: atomic scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974), all calculations performed with *SHELXTL* (Sheldrick, 1981) on a Nova 4S computer. Structures solved by direct methods using the weighted tangent-formula method. The phase set with the maximum combined figure of merit gave an E map in which the complete structure was apparent. Refinement by full-matrix least squares with anisotropic temperature factors converged to $R = 0.035(0.037)$, $wR = 0.035(0.034)$, $w = 1$, maximum final shift/e.s.d. < 0.05 , mean < 0.01 , maximum height in final difference Fourier map $0.8(0.7) e \text{ \AA}^{-3}$.

Discussion. Fractional coordinates and equivalent isotropic temperature factors of atoms in the asymmetric unit are listed in Table 1 and selected interatomic distances and angles are given in Table 2.† In each structure, the selenite group is trigonal pyramidal with typical distances and angles (e.g. Hawthorne, 1984). The divalent cation is coordinated by five O atoms in a trigonal bipyramidal arrangement with mean apical angles close to 90° and mean meridional angles close to 120° (Table 2).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43035 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Each trigonal bipyramid shares one edge with an adjacent bipyramid to form an edge-sharing ($M_2^2+O_8$) dimer; these edge-sharing dimers seem to be very typical of structures with five-coordinate cations. Each dimer shares four corners with adjacent dimers to form a sheet (Fig. 1) of six-membered bipyramidal rings, the divalent cations lying at the vertices of a (distorted) 6_3 net. These sheets stack along z (Fig. 2), being linked by the SeO_3 groups that share corners with the bipyramidal groups.

High-pressure polymorphs of $ZnSeO_3$ and $CuSeO_3$ were synthesized by Kohn, Inoue, Horie & Akimoto (1976). In these structures, the divalent cation is six-coordinate and the ($M^{2+}O_3$) framework is topologically the same as that of the perovskite structure. The Se takes up an extremely off-centre position in the twelve-coordinate cavity of this structure type to form the usual trigonal pyramidal SeO_3 group.

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

	$ZnSeO_3$	$CuSeO_3$
Se—O(1)	1.691 (6)	1.684 (5)
Se—O(2)	1.693 (6)	1.715 (5)
Se—O(3)	1.728 (6)	1.724 (6)
$\langle Se-O \rangle$	1.704	1.708
O(1)—O(2)	2.607 (9)	2.608 (7)
O(1)—O(3)	2.629 (9)	2.619 (7)
O(2)—O(3)	2.598 (8)	2.622 (7)
$\langle O-O \rangle_{Se}$	2.611	2.616
Se—O(1 ^{vi})	3.267 (6)	3.106 (6)
Se—O(1 ^{vii})	2.839 (6)	2.741 (5)
Se—O(3 ^{viii})	2.986 (6)	3.014 (5)
$\langle Se-O \rangle$	3.012	2.928
O(1)—Se—O(2)	100.8 (3)	100.2 (3)
O(1)—Se—O(3)	100.5 (3)	100.4 (3)
O(2)—Se—O(3)	98.8 (3)	99.4 (3)
$\langle O-Se-O \rangle$	100.0	100.0
$M-O(1^i)$	1.979 (6)	1.964 (5)
$M-O(2^{ii})$	2.016 (7)	2.007 (5)
$M-O(2^{iv})$	2.128 (6)	1.980 (5)
$M-O(3^v)$	1.973 (5)	2.216 (6)
$M-O(3^i)$	2.195 (6)	1.980 (5)
$\langle M-O \rangle$	2.058	2.029
O(1 ⁱ)—O(2 ^{iv})	3.013 (8)	2.920 (7)
O(1 ⁱ)—O(3 ⁱ)	2.778 (8)	2.712 (8)
O(2 ⁱⁱ)—O(2 ^{iv})	2.588 (12)	2.508 (10)
O(2 ⁱⁱⁱ)—O(3 ^v)	3.169 (12)	3.129 (8)
O(2 ⁱⁱⁱ)—O(3 ⁱ)	2.902 (9)	2.858 (7)
O(2 ^{iv})—O(3 ^v)	2.894 (8)	2.900 (8)
$\langle O-O \rangle$	2.890	2.838
O(1 ⁱ)—O(2 ⁱⁱⁱ)	3.618 (10)	3.626 (8)
O(1 ⁱ)—O(3 ^v)	3.496 (11)	3.580 (8)
O(3 ⁱ)—O(3 ^v)	3.423 (9)	3.332 (5)
$\langle O-O \rangle$	3.512	3.512
O(1 ⁱ)— $M-O(2^{iv})$	94.3 (2)	95.5 (2)
O(1 ⁱ)— $M-O(3^i)$	83.2 (2)	86.9 (2)
O(2 ⁱⁱⁱ)— $M-O(2^{iv})$	77.3 (3)	78.0 (2)
O(2 ⁱⁱⁱ)— $M-O(3^v)$	105.2 (3)	95.5 (2)
O(2 ⁱⁱⁱ)— $M-O(3^i)$	87.0 (2)	91.6 (2)
O(2 ^{iv})— $M-O(3^v)$	89.7 (2)	87.3 (2)
$\langle O-M-O \rangle$	89.5	89.1
O(1 ⁱ)— $M-O(2^{iii})$	129.8 (2)	146.0 (2)
O(1 ⁱ)— $M-O(3^v)$	124.4 (3)	117.7 (2)
O(3 ⁱ)— $M-O(3^v)$	110.3 (1)	105.0 (1)
$\langle O-M-O \rangle$	121.5	122.9
O(2 ^{iv})— $M-O(3^i)$	157.4 (2)	164.7 (2)

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

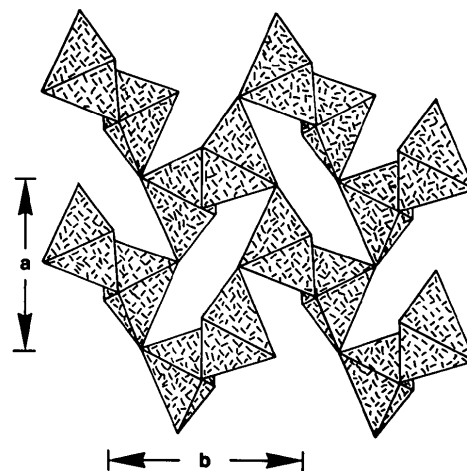


Fig. 1. The $(ZnO_3)_\infty$ sheet in the structure of $ZnSeO_3$.

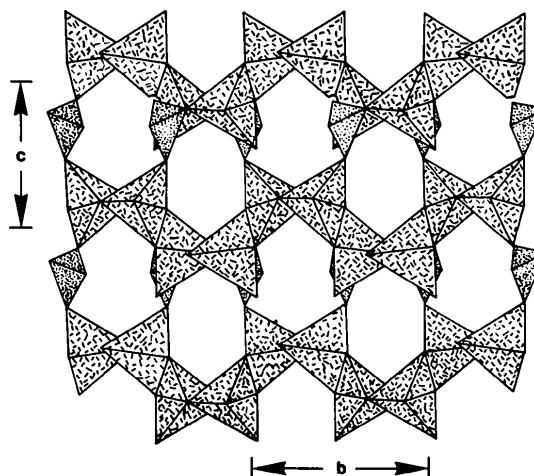


Fig. 2. The structure of $ZnSeO_3$; infinite sheets of (ZnO_3) trigonal bipyramids are linked by (SeO_3) trigonal pyramids to form a three-dimensional framework.

Thus there is no apparent relationship between the two structure types, although the higher pressure phases have much lower molar volumes as expected.

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Bis[2,2'-biphenyldiyl(dimethylarsine)]diiodonickel(II)

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Abstract. $[\text{Ni}\{\text{As}_2(\text{CH}_3)_4(\text{C}_{12}\text{H}_8)\}_2\text{I}_2]$, $M_r = 1036.83$, triclinic, $P\bar{1}$, $a = 10.074$ (3), $b = 11.562$ (4), $c = 18.372$ (5) Å, $\alpha = 111.96$ (2), $\beta = 116.07$ (3), $\gamma = 90.95$ (2)°, $U = 1740$ (1) Å³, $Z = 2$, $D_m(\text{floatation}) = 1.92$, $D_x = 1.98$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 6.01$ mm⁻¹, $F(000) = 996$, $T = 125$ K, final $R = 0.0371$ for 3479 independent reflections [$I > 2.5\sigma(I)$]. The Ni^{II} atom has a tetragonally distorted octahedral configuration with the I⁻ ligands occupying the axial positions. The diarsine ligands and the Ni atom form two seven-membered chelate rings. The average Ni–I and Ni–As bond lengths are 2.751 and 2.515 Å, respectively. There are no significant intermolecular interactions.

Introduction. The diarsine 2,2'-bis(dimethylarsino)biphenyl (dmab) has been used to prepare a series of compounds of the type $\text{Ni}(\text{dmab})_2\text{X}_2$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) (Allen, Ashford, Hogarth & Mann, 1977). These compounds are unusual in that they are Ni–diarsine complexes which are not only pseudo-octahedral but also paramagnetic and they contain a seven-membered chelate ring. The structure of the chloro derivative has already been reported (Allen, Kennedy & Nowell, 1980). However, of greater interest is the iodo derivative because for many years the structure of the diamagnetic compound diiodo[*o*-phenylenebis(dimethylarsine)]nickel(II), $[\text{Ni}(\text{diars})\text{I}_2]$ (Stephenson, 1964), has been used as a paradigm despite the long Ni–I bond distance of 3.215 (2) Å. The present study was undertaken as the necessary first step in a detailed analysis of the metal–ligand interactions in these iodo–diarsine complexes using the bonding-orientated angular-overlap model.

Experimental. Crystals grown from butanol as yellow-green rhombs, dimensions 0.30 × 0.18 × 0.08 mm. Preliminary oscillation and Weissenberg photography (Cu $K\alpha$) indicated triclinic system. Space group $P\bar{1}$ chosen and confirmed by success of refinement. Data collected on Nicolet $P\bar{3}$ diffractometer, Mo $K\alpha$ radiation (graphite monochromator) at 125 K; cell dimensions from angular measurement of 25 strong reflections in range $20 < 2\theta < 30^\circ$. 4711 reflections in range $h, k, l: \pm 10, \pm 12, 19$ ($2\theta_{\text{max}} = 47^\circ$) collected using $\theta/2\theta$ scans. 3 standard reflections (700, 080, 009) showed <4% intensity variation. Lp corrections and analytical absorption correction applied; transmission factors 0.621–0.323. Data averaged to give 4566 unique reflections ($R_{\text{int}} = 0.021$) of which 3479 considered observed [$I > 2.5\sigma(I)$]. Surprisingly, the chloro and iodo derivatives are isomorphous. The cell given for the iodo derivative conforms to a type II reduced cell and is related to that reported by Allen *et al.* by the transformation matrix $s_{ij} = \bar{1}\bar{1}\bar{1}/010/100$ (*International Tables for X-ray Crystallography*, 1969). Starting coordinates taken from chloro derivative and refined, with all non-H atoms anisotropic, by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, using SHELX76 (Sheldrick, 1976). H atoms included in calculated positions (C–H = 1.08 Å) with fixed isotropic temperature factors. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974), weighting scheme $w = 0.9854/[\sigma^2(F_o) + 0.0017|F_o|^2]$. Final $R = 0.0371$, $wR = 0.0402$. $(\Delta/\sigma)_{\text{max}} = 0.024$. Final difference map showed a number of residual peaks around heavy atoms (all peaks <1.2 e Å⁻³ and <1.2 Å from heavy atoms); peak heights no higher than those earlier