

Tabelle 2. Ausgewählte interatomare Abstände und Winkel

Symmetrieoperation: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iii) $1 + x, y, z$; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (vi) $-\frac{1}{2} + x, y, \frac{1}{2} - z$; (vii) $-x, 1 - y, -z$; (viii) $-1 + x, y, z$; (ix) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (x) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (xi) $\frac{1}{2} - x, -\frac{1}{2} + y, z$; (xii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

(a) Abstände (Å) zu den benachbarten O-Atomen; Standardabweichungen sind 0,003 Å für K—O und V—O, 0,004 Å für Aq—O

K(1)	Aq	2,697	O(2 ⁱ)	2,747	O(1 ⁱⁱ)	2,845
	O(3 ⁱⁱ)	2,922	Aq ^{iv}	2,988	O(4 ⁱⁱⁱ)	3,078
K(2)	O(2 ⁱ)	2,713	O(4 ^v)	2,769	O(4 ⁱⁱ)	2,772
	O(3)	2,943	O(3 ^v)	2,966	O(1 ⁱⁱ)	3,065
	Aq ^{vi}	3,102				
K(3)	O(1 ^{vii})	2,654	Aq ^{viii}	2,778	O(3 ^v)	2,826
	O(1)	2,836	O(2)	2,871	O(2 ^{ix})	3,030
	O(4 ^{ix})	3,056	Aq ^{vi}	3,080		
V	O(2)	1,689	O(1)	1,690	O(4)	1,730
	O(3)	1,735				
Aq	O(4 ^v)	2,570	O(3 ^x)	2,640		

(b) Winkel (°) mit Standardabweichungen in Klammern

O(2)—V—O(1)	109,80 (14)	O(2)—V—O(4)	108,98 (15)
O(2)—V—O(3)	111,05 (15)	O(1)—V—O(4)	109,58 (16)
O(1)—V—O(3)	108,88 (16)	O(4)—V—O(3)	108,52 (14)
O(4 ^v)—Aq—O(3 ^x)	107,19 (14)		

Obwohl sich die H-Atome mit Hilfe einer Differenz-Fouriersynthese nicht lokalisieren ließen, verraten die in Tabelle 2 aufgeführten kurzen Aq—O-Abstände schon das Bestehen der Wasserstoffbrücken zwischen den betreffenden Atomen (Brown, 1976). Die kürzesten O—O-Abstände sind O(1)—O(2) 2,764 (4) Å in einer VO₄-Gruppe und O(4)—O(4^{xiii}) 3,511 (6) Å zwischen zwei verschiedenen VO₄-Gruppen [Symmetrieoperation (xiii): $-x, -y, -z$]. Berechnet man nach

Brown & Wu (1976) für jedes O-Atome die ihm zustehende Valenzsumme der Bindungen, so weisen O(3) und O(4) tatsächlich ein Defizit auf, das durch Wasserstoffbrücken ersetzt werden muß. Für diese O-Atome errechnen sich die Valenzsummen jeweils zu 1,605 und 1,659, während sie für O(1) und O(2) 1,925 bzw. 1,927 betragen.

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Structure of Cobalt Diselenite

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Abstract. CoSe₂O₅, $M_r = 296.8$, orthorhombic, *Pnca*, $a = 6.080$ (1), $b = 6.797$ (1), $c = 10.370$ (2) Å, $V = 428.5$ (1) Å³, $Z = 4$, $D_x = 4.60$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 223.9$ cm⁻¹, $F(000) = 540$, $T = 297$ K, $R = 0.048$ for 544 observed reflections. Isostructural with the Mn and Zn compounds; CoO₆ octahedra link

by sharing edges to form $\alpha\text{-PbO}_2$ -like chains that are linked together by corner-sharing diselenite groups. The stereochemistry of SeO₃ groups is briefly reviewed. The grand mean Se—O distance is 1.709 Å, r.m.s. deviation = 0.010 Å, and the grand mean O—Se—O angle is 100.2°, r.m.s. deviation = 1.3°. Individual bond-length variations can be rationalized using bond-valence theory, and a bond-valence curve for the Se—O bond is derived: $S = (R/1.808)^{-5.2}$.

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Introduction. Structural characterization of selenium oxyanion minerals (Hawthorne, 1984) is often hampered by inadequate material, and an idea of the range of bond geometries expected is useful in assessing the quality of the results of such studies. Consequently examination of the structures of a few simple selenite compounds (Hawthorne, Ercit & Groat, 1986; this study) and a brief survey of observed SeO_3 group stereochemistry seemed warranted.

Experimental. Crystals of CoSe_2O_5 were obtained from Dr J. A. Mandarino, Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, Ontario, Canada. Crystal size: $0.14 \times 0.18 \times 0.20$ 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: 1043 reflections, $3 < 2\theta < 60^\circ$, h 0–8, k 0–9, l 0–14, graphite monochromator, Mo $K\alpha$ X-radiation, $\theta/2\theta$ scan, variable scan speed $4\text{--}29.3^\circ \text{ min}^{-1}$, scan range $(K\alpha_1 - 1) \rightarrow (K\alpha_2 + 1)^\circ$, background/scan = 0.5, two standard reflections every 48 reflections, variation 1.9%, absorption correction by refinement of a thin plate correction from ψ -scan data with merging R reduced from 0.224 to 0.028, minimum transmission 0.061, maximum transmission 0.127, Lorentz and polarization corrections, 544 observed reflections with $I > 2.5\sigma(I)$.

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. Starting parameters from MnSe_2O_5 (Koskenlinna, Niinistö & Valkonen, 1976), refinement by full-matrix least squares (on F) with anisotropic temperature factors converged to $R = 0.035$, $wR = 0.035$, $w = 1$, maximum final shift/e.s.d. < 0.05 , mean < 0.01 , maximum height in final difference Fourier map $0.7 \text{ e } \text{\AA}^{-3}$.

Discussion. Fractional coordinates and equivalent isotropic temperature factors of atoms in the asymmetric unit are listed in Table 1 and interatomic distances and angles are given in Table 2.* The selenite group is trigonal pyramidal with typical distances and angles [see Table 3 (deposited)]. The O(2) anion bridges between two SeO_3 groups, and $\text{Se}-\text{O}(2)$ is considerably elongated relative to the mean bond length so that the local bond-valence requirements about the O(2) anion are satisfied. The divalent cation is coordinated

by six O atoms in an octahedral arrangement with individual bond angles deviating considerably from 90° .

Table 1. Atomic parameters and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for CoSe_2O_5

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Se	0.0326 (1)	0.13111 (8)	0.3459 (1)	0.89 (2)
Co	$\frac{1}{4}$	0	0.0616 (2)	0.98 (4)
O(1)	0.0483 (8)	0.3398 (6)	0.4336 (7)	1.3 (1)
O(2)	$\frac{1}{4}$	0	0.4296 (9)	1.9 (2)
O(3)	0.1575 (9)	0.1943 (7)	0.2115 (6)	1.6 (2)

Table 2. Interatomic distances ($\text{\AA}$) and angles ($^\circ$) in CoSe_2O_5

Se—O(1)	1.688 (5)	Co—O(1 ^{iv})	2.109 (6) × 2
Se—O(2)	1.815 (5)	Co—O(1 ^{iii,iv})	2.116 (5) × 2
Se—O(3)	1.644 (6)	Co—O(3 ^v)	2.116 (6) × 2
<Se—O>	1.716	<Co—O>	2.114
O(1)—Se—O(2)	96.5 (3)	O(1)—O(2)	2.615 (11)
O(1)—Se—O(3)	102.2 (3)	O(1)—O(3)	2.593 (9)
O(2)—Se—O(3)	101.4 (3)	O(2)—O(3)	2.679 (10)
<O—Se—O>	100.0	<O—O>Se	2.629
O(1 ⁱ)—Co—O(1 ⁱⁱ)	102.1 (3)	O(1 ⁱ)—O(1 ⁱⁱ)	3.280 (10)
O(1 ⁱ)—Co—O(1 ⁱⁱⁱ)	77.4 (2) × 2	O(1 ⁱ)—O(1 ⁱⁱⁱ)	2.642 (9)
O(1 ⁱ)—Co—O(1 ^{iv})	104.3 (2) × 2	O(1 ⁱ)—O(1 ^{iv})	3.336 (11)
O(1 ⁱ)—Co—O(3 ^v)	89.2 (2) × 2	O(1 ⁱ)—O(3 ^v)	2.967 (10)
O(1 ⁱⁱⁱ)—Co—O(3)	83.7 (2) × 2	O(1 ⁱⁱⁱ)—O(3)	2.824 (9)
O(1 ^{iv})—Co—O(3)	94.4 (2) × 2	O(1 ^{iv})—O(3)	3.105 (10)
O(3)—Co—O(3 ^v)	85.4 (3)	O(3)—O(3 ^v)	2.870 (10)
<O—Co—O>	90.5	<O—O>Co	2.992

Se—O(2)—Se^v 122.9 (5)

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

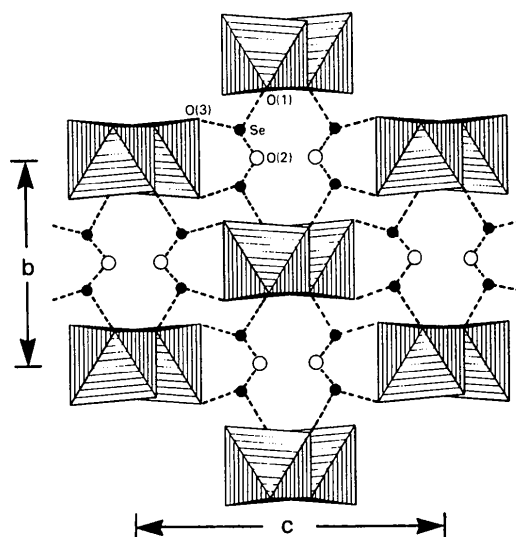


Fig. 1. The structure of CoSe_2O_5 projected along x ; octahedral chains are line-shaded.

* Lists of structure factors and anisotropic thermal parameters and Table 3 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44196 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Octahedra link together by sharing edges to form α - PbO_2 -like chains (Wells, 1985) that run parallel to x . Two SeO_3 groups link by sharing a corner to form an Se_2O_5 group, and the octahedral chains share corners with the Se_2O_5 groups to complete the structure. This is illustrated in Fig. 1, which shows the staggered octahedral chains viewed end-on and forming a centred array, with the Se_2O_5 groups linking the chains along both y and z .

Table 3 summarizes bond lengths and angles in selenite groups from fairly precisely determined inorganic crystal structures. The grand mean Se—O distance is 1.709 Å with a root-mean-square deviation of 0.010 Å, and the grand mean O—Se—O angle is 100.2° with a root-mean-square deviation of 1.3° .

There is significant variation of individual Se—O distances in the structures listed in Table 3. In previous work, this has been tacitly assumed to be in accord with bond-strength arguments. H-atom positions have been assigned on qualitative considerations of relative bond lengths, and Valkonen & Leskelä (1978) have reviewed Se—O and Se—OH distances in acid selenites, showing that Se—O and Se—OH distances cluster around 1.66 and 1.75 Å respectively. In order to put such arguments on a more quantitative basis, we have derived bond-valence curve parameters for the Se—O bond using selected data from Table 3 and fitting them to a curve of the general form $S = (R/R_0)^{-N}$ (Brown, 1981);

the relevant parameters are $R_0 = 1.808$ and $N = 5.2$. This curve should help in deciphering hydrogen-bonding schemes, particularly in the more hydrated of the selenium oxyalts.

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Structure of Cadmium Dimagnesium Hexabromide Dodecahydrate, $\text{CdMg}_2\text{Br}_6 \cdot 12\text{H}_2\text{O}$

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Abstract. $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CdBr}_6]$, $M_r = 856.66$, rhombohedral, hexagonal setting, $R\bar{3}$ {Hall symbol $R\bar{3}$ [Hall (1981). *Acta Cryst.* **A37**, 517–525]}, $a = 10.371$ (2), $c = 17.761$ (2) Å, $V = 1654.4$ Å³, $Z = 3$, $D_x = 2.58$ Mg m^{−3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 11.66$ mm^{−1}, $F(000) = 1206$, room temperature, $R = 0.036$ ($wR = 0.029$) for 1120 reflections. The sample was prepared from a saturated aqueous solution of MgBr_2 and CdBr_2 in a molar ratio of 2:1. The structure, which is the same as $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CaCl}_6]$, consists of two $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ (av. Mg—O = 2.055 Å) and one

CdBr_6^{4-} (Cd—Br = 2.788 Å) octahedral complexes linked by hydrogen bonds.

Introduction. Balarew, Duhlev & Panaiotov (1982) first reported the existence of the double salt $\text{CdMg}_2\text{Br}_6 \cdot 12\text{H}_2\text{O}$ in the system CdBr_2 – MgBr_2 – H_2O at 298 K. This compound was subsequently predicted (Duhlev, 1984; Duhlev & Balarew, 1987) to possess a structure $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CdBr}_6]$ similar to $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CaCl}_6]$ (Leclaire, Borel & Monier, 1980; Clark, Evans & Erd, 1980), $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CdCl}_6]$ (Lédésert & Monier, 1981), and $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{CdCl}_6]$ (Leclaire & Borel, 1982), where in each case the harder ligand, H_2O , is bonded to the harder cation and the softer one, the

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