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Synthesis and Structure of Cobalt Diselenite, $CoSe_2O_5$

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Abstract. $M_r = 296{\cdot}85$, orthorhombic, *Pnab*, $a = 6{\cdot}075\ (2)$, $b = 10{\cdot}366\ (2)$, $c = 6{\cdot}7911\ (8)$ Å, $V = 427{\cdot}8$ Å^3, $Z = 4$, $D_x = 4{\cdot}61$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 207$ cm^{-1}, $F(000) = 540$, $T = 298\ (5)$ K, $R = 0{\cdot}028$ for 642 observed reflections with $I > 3\sigma(I)$. The phase was synthesized hydrothermally at 473 (5) K. The structure consists of strings of edge-sharing CoO_6 octahedra running parallel to **a**, crosslinked by O—Se—O linkages which may be considered to be part of discrete $Se_2O_5^{2-}$ units. The structure is isomorphous with those of $ZnSe_2O_5$ and $MnSe_2O_5$. Thermogravimetric and X-ray powder diffraction data are also recorded.

Introduction. Previous studies on the cobalt–selenium(IV)–oxygen system have often revealed phases that are isomorphous with other divalent selenite phases. Leider & Gattow (1967*a*) found that $CoSe_2O_5.3H_2O$ was isostructural with the Ni and Zn analogues, and the same workers (Leider & Gattow, 1967*b*) found that $CoSeO_3.2H_2O$ adopted the same structure as the Ni, Zn, Mg, Mn and Cu selenite dihydrates. Kohn, Inone, Horie & Akimoto (1976) used high-pressure methods to synthesize the perovskite-type phases $M^{2+}SeO_3$ (M = Mg, Co, Ni, Cu, Zn). The present paper describes the synthesis and structure of the phase, $CoSe_2O_5$, which is once again isomorphous with the M^{2+} analogues $ZnSe_2O_5$ (Meunier & Bertaud, 1974) and $MnSe_2O_5$ (Koskenhinna, Niinistö & Valkonen, 1976). It contains a discrete $Se_2O_5^{2-}$ unit which was also found by Hawthorn, Groat & Ercit (1987).

Experimental. The title compound was synthesized hydrothermally from the starting materials $CoSO_4.7H_2O$ (BDH analytical grade, 2 g) and excess SeO_2 (Johnson Matthey analytical grade, 5 g) in 15 cm^3 of water. The teflon-lined steel bomb was heated to 473 K for 48 h and cooled to room temperature overnight. An estimated maximum pressure of 3 MPa was achieved. Purple, transparent crystals with dimensions of up to 0·5 mm were recovered from the reaction mixture.

An irregular crystal, dimensions *ca* 0·12 × 0·12 × 0·1 mm, was mounted on an Enraf–Nonius CAD-4 diffractometer. The unit-cell constants were determined and refined from 25 centred high-angle reflections in the range $10 < \theta < 18°$. Data were collected in the ω–2θ scan mode [ω-scan width = $(1{\cdot}00 + 0{\cdot}35\tan\theta)°$, scan speed = 1·3–6·7° min^{-1}] using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) over the range $0 < \theta < 33°$ for $-1 \leq h \leq 9$, $-1 \leq k \leq 15$, $-1 \leq l \leq 10$, $(\sin\theta)/\lambda_{\max} = 0{\cdot}77$ Å^{-1}, with regular checks on reflection intensity (every 100 reflections) and orientation (every hour). Systematic absences ($0kl$: $k + l \neq 2n$, absent; $h0l$: h; $hk0$: k) uniquely defined the space group as *Pnab*. 2080 reflections were measured, of which 642 were used in structure solution and refinement [merging $R = 6{\cdot}98\%$; reflections with $I < 3\sigma(I)$ considered unobserved]. Heavy-atom positions were determined by a super-sharpened Patterson function using the program *SHELXS*86 (Sheldrick, 1986); O-atom positions were located by successive Fourier difference syntheses following refinement of the heavy-atom positions. For the final cycle of full-matrix anisotropic refinement on F, maximum shift/e.s.d. = 0·001, $R = 2{\cdot}79\%$, $wR = 3{\cdot}23\%$ [three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) with coefficients 16(1), −15(2) and 9(2) where the digit in parentheses is the e.s.d.], maximum residual electron density = 0·7 e Å^{-3}. Structure analysis and refinement were carried out using the

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Oxford *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985) on a VAX 11/750 computer. Complex, neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). An isotropic secondary-extinction correction [Larson (1970): refined value = 250 (8)] and empirical absorption correction (correction factors between 1·0–1·4) (*DIFABS*; Walker & Stewart, 1983) were also applied.

Discussion. The structure provides a further example of a discrete oxygen-bridged diselenite group. Fractional atomic coordinates and isotropic thermal parameters are given in Table 1 and salient bond distance/angle data in Table 2.* Co is surrounded by a fairly regular octahedron of O atoms, and the CoO_6 groups form infinite edge-sharing zigzag chains along [100]. The bridging O is O(3), which is also linked to Se. Se is threefold coordinated by O(1), O(2) and O(3), with the stereochemically active lone pair presumably filling the fourth apex of a tetrahedron. O(1) is twofold coordinated by Se and Co, whilst O(2) bridges the Se atoms in the $Se_2O_5^{2-}$ unit. The structure of the $Se_2O_5^{2-}$ unit is very similar to that found in the isostructural Zn and Mn compounds. The crystal structure of $CoSe_2O_5$ is illustrated in Fig. 1. Thermogravimetric measurements carried out on a DuPont 9900 system in air with a heating rate of 10 K min^{-1} show that cobalt diselenite decomposes by losing SeO_2 at about 773 K (observed weight loss = 38%, calculated weight loss = 38%) to result in $CoSeO_3$, which loses a further SeO_2 at 898 K (observed loss = 74%, calculated = 75%), forming CoO as the final decomposition product. The intermediate product was found to be amorphous by powder X-ray measurements. A similar decomposition behaviour was also observed for manganese(II) diselenite, $MnSe_2O_5$ (Koskenhinna, Niinistö & Valkonen, 1976).

X-ray powder data were recorded on a Scintag automated θ–θ diffractometer with Cu $K\alpha$ radiation (λ = 1·54059 Å) at 298 (5) K. The pattern was indexed on the basis of the single-crystal lattice parameters and refined cell constants of a = 6·071 (1), b = 10·361 (2) and c = 6·787 (2) Å were obtained using Scintag least-squares routines.

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Table 1. *Final atomic coordinates with e.s.d.'s and equivalent isotropic thermal coefficients for* $CoSe_2O_5$

$$U_{eq} = (\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j)/3\ \text{Å}^2.$$

	Wyckoff site	x	y	z	U_{eq}
Co	4(*c*)	1/4	−0·06122 (7)	0	0·0053
Se	8(*d*)	0·03241 (6)	0·15411 (3)	0·63098 (5)	0·0048
O(1)	8(*d*)	0·6587 (5)	0·2090 (3)	0·8052 (4)	0·0090
O(2)	4(*c*)	3/4	0·9302 (4)	1/2	0·0091
O(3)	8(*d*)	0·5480 (5)	0·9337 (3)	0·8402 (4)	0·0078

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

Co—O(1)	2·099 (3) × 2	Se—O(1)	1·670 (3)
Co—O(3)	2·105 (3) × 2	Se—O(2)	1·817 (2)
Co—O(3)′	2·111 (3) × 2	Se—O(3)	1·690 (3)
O(1)—Co—O(1)	86·2 (2)	O(3)—Co—O(3)	102·2 (2)
O(1)—Co—O(3)	94·6 (2)	O(1)—Se—O(2)	101·7 (2)
O(1)—Co—O(3)	88·8 (2)	O(1)—Se—O(3)	102·3 (2)
O(1)—Co—O(3)	83·3 (2)	O(2)—Se—O(3)	96·4 (2)
O(3)—Co—O(3)	77·4 (2)	Se—O(2)—Se	122·5 (3)
O(3)—Co—O(3)	104·5 (2)		

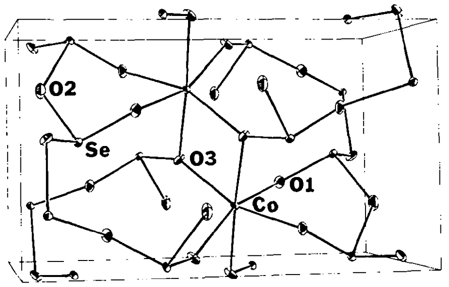

Fig. 1. The crystal structure of $CoSe_2O_5$ viewed down [001] showing the atom-labelling scheme.

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* Lists of structure factors, anisotropic thermal parameters powder diffraction data and thermogravimetric data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54314 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.