Acta Cryst. (1992). C**48**, 410–412

Isotypism of a Selenite with a Carbonate: Structure of the Buetschliite-Type Compound $K_2Co(SeO_3)_2$

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(*Received* 3 *June* 1991; *accepted* 27 *September* 1991)

Abstract. Dipotassium cobalt diselenite, $K_2Co(SeO_3)_2$, $M_r = 391.05$, trigonal, $R\bar{3}m$, $a = 5.516\,(1)$, $c = 18.520\,(5)$ Å, $V = 488.0\,(3)$ Å^3, $Z = 3$, $D_x = 3.992$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 14.64$ mm^{-1}, $F(000) = 543$, $T = 295$ K, $R = 0.024$, $wR = 0.025$ for 295 independent reflections with $F_o > 3\sigma(F_o)$ and 16 refined parameters. $K_2Co(SeO_3)_2$ is isotypic with the mineral buetschliite, $K_2Ca(CO_3)_2$. The structure consists of KO_9 polyhedra (mean K—O distance 2.931 Å), CoO_6 octahedra (Co—O = 2.142 Å) and pyramidal SeO_3 groups (Se—O = 1.692 Å). The directions of non-planarity of the SeO_3 pyramids in the title compound and of the CO_3 groups in buetschliite are the same.

Introduction. As part of a study on the geometry of $Co^{II}O_6$ polyhedra (Wildner, 1990*a*), several Co^{II} compounds were synthesized under hydrothermal conditions and their structures were determined using single-crystal X-ray diffraction methods, among them the selenites $NaCo_2(SeO_3)_2(OH)$, $CoSeO_3.2H_2O$ and $Co_3(SeO_3)_3.H_2O$ (Wildner, 1988, 1990*b*, 1991). Recently, the title compound was synthesized in the system $CoO–K_2O–SeO_2–H_2O$; in spite of the different stereochemical behaviour of Se^{IV} and C^{IV} and the different shapes of the SeO_3 and CO_3 groups, $K_2Co(SeO_3)_2$ proved to be isotypic with the mineral buetschliite, $K_2Ca(CO_3)_2$ (Pabst, 1974; Knobloch, Pertlik & Zemann, 1980; Effenberger & Langhof, 1984) and with the synthetic compound $K_2Mg(CO_3)_2$ (Hesse & Simons, 1982). This seems to be the first example for isotypism of a selenite and a carbonate compound.

Experimental. For preparation of the title compound an equimolar mixture of $Co(OH)_2$ and SeO_2 was inserted into a teflon-lined vessel; a KOH pellet and some drops of water were added. Purple-coloured single crystals up to 0.4 mm were obtained after a heating period of six days at 490 (5) K; observed crystallographic forms are $\{0001\}$ and $\{02\bar{2}3\}$. X-ray investigations were performed on a Stoe AED2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, all calculations were performed with the program system *STRUCSY* (Stoe & Cie, 1984). Crystal dimension: diameter ≃ 0.2 mm; lattice parameters were derived from 32 accurately measured reflections in the range $28 \leq 2\theta \leq 42°$; intensity measurements: $2\theta/\omega$ scan mode, minimum 35 steps per reflection (increased for α_1–α_2 splitting), 0.5 to 1.5 s and 0.03° per step, five steps each side for background measurements; three standard reflections every 120 min (maximum drift ± 3.7%), 1535 measured reflections up to $2\theta = 70°$ (h: $-8\rightarrow 8$, k: $0\rightarrow 8$, l: $-29\rightarrow 29$), 297 unique reflections ($R_{\rm int} = 0.067$); empirical absorption correction using three ψ scans (transmission factors: 0.037 to 0.083) and corrections for Lorentz and polarization effects were applied. Complex neutral atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The Se, Co and K atoms were located by direct methods, the O atoms by subsequent Fourier syntheses. 295 reflections with $F_o > 3\sigma(F_o)$ were used in the least-squares refinement of 16 variables, including the atomic coordinates, anisotropic displacement parameters and an extinction factor (Zachariasen, 1967; $g = 1.1\,(1) \times 10^{-5}$), which gave $R = 0.024$, $wR = 0.025$ $\{w = [\sigma(F_o)]^{-2}\}$, $S = 2.69$; $(\Delta/\sigma)_{\rm max} < 10^{-3}$; electron densities in final difference Fourier synthesis: $(\Delta\rho)_{\rm max} = 0.97$, $(\Delta\rho)_{\rm min} = -1.13$ e Å^{-3}. Table 1* gives the atomic coordinates and the isotropic displacement parameters, Table 2 lists some important interatomic distances and bond angles.

Discussion. The structure of $K_2Co(SeO_3)_2$ is isotypic with buetschliite, $K_2Ca(CO_3)_2$ (Pabst, 1974; Knobloch *et al.*, 1980, Effenberger & Langhof, 1984), and with $K_2Mg(CO_3)_2$ (Hesse & Simons, 1982). The structure is built up from KO_9 polyhedra,

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54654 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/92/030410-03$03.00

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2 × 10^4) *for* $K_2Co(SeO_3)_2$ *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K	0	0	0.19407 (5)	269 (3)
Co	0	0	0	171 (2)
Se	0	0	0.63096 (2)	167 (2)
O	0.16090 (15)	−0.16090 (15)	0.59277 (9)	229 (5)

Table 2. *Selected interatomic bond lengths* (Å) *and angles* (°) *in* $K_2Co(SeO_3)_2$ *with e.s.d.'s in parentheses*

K—O	3.012 (1) (6 ×)			O—O	2.662 (2) (3 ×)
	2.769 (1) (3 ×)				2.853 (2) (6 ×)
					3.764 (3) (6 ×)
Co—O	2.142 (1) (6 ×)	O—Co—O	83.54 (7)	O—O	2.853 (2) (6 ×)
			96.46 (7)		3.195 (3) (6 ×)
Se—O	1.692 (1) (3 ×)	O—Se—O	103.76 (7)	O—O	2.662 (2) (3 ×)

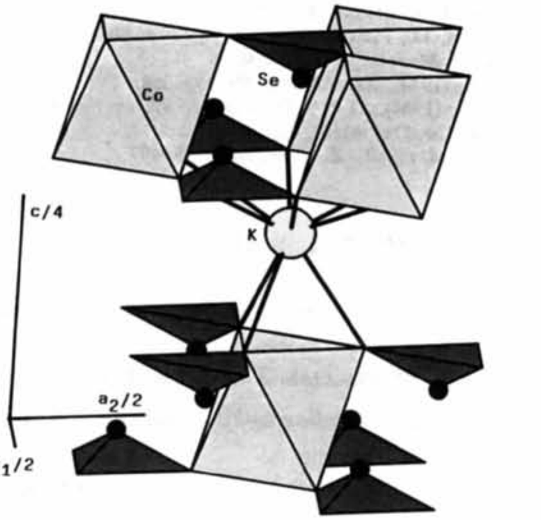

Fig. 1. Projection of the structure of $K_2Co(SeO_3)_2$ along a direction slightly inclined to [10$\bar{1}$0], showing the environment of the K atom.

isolated CoO_6 octahedra and SeO_3 groups, which are characterized by their pyramidal shape and the stereochemical activity of lone-pair electrons. Each CoO_6 octahedron (site symmetry $\bar{3}m$) shares corners with six SeO_3 groups (site symmetry $3m$), forming double layers of O atoms (site symmetry m) parallel to (0001) with the Co and Se atoms in between. The apices of the SeO_3 pyramids point towards the inside of these $[Co(SeO_3)_2]^{2-}$ layers; hence, the direction of non-planarity of the SeO_3 pyramids [the distance Δ of the Se atom from the plane containing the O atoms is 0.707 (2) Å] is the same as for the very slightly non-planar CO_3 groups in buetschliite (Knobloch *et al.*, 1980: $\Delta = 0.038$ Å; Effenberger & Langhof, 1984: $\Delta = 0.014$ Å) and in $K_2Mg(CO_3)_2$ (Hesse & Simons, 1982: $\Delta = 0.014$ Å). A consequence of this arrangement is that the lone-pair electrons of the Se^{IV} atoms are directed towards the K atoms (site symmetry $3m$), which connect consecutive layers (see Fig. 1).

Some structural features found in $K_2Co(SeO_3)_2$ indicate a repulsion between the lone-pair electrons of the Se atoms and electrons of the K atoms: the SeO_3 pyramids are clearly flattened [O—Se—O = 103.76 (7)°] and Se—O bonds are somewhat short [Se—O = 1.692 (1) Å] as compared to data reported in the literature [*e.g.* Hawthorne, Groat & Ercit (1987) give 100.2° and 1.709 Å as mean values]. In addition, with regard to buetschliite the K atom is shifted towards the following $[Co(SeO_3)_2]^{2-}$ sheet. As a consequence the [6 + 3] coordination in buetschliite and in $K_2Mg(CO_3)_2$ changes to a [3 + 6] coordination in $K_2Co(SeO_3)_2$; the mean K—O distance is increased from 2.801 Å in $K_2Mg(CO_3)_2$ and 2.878 Å in $K_2Ca(CO_3)_2$ to 2.931 Å in the title compound, the distance between the oxygen levels of neighbouring layers is extended to 3.436 Å (in buetschliite it is only 3.178 Å). Nevertheless, the ellipsoid of thermal motion of the K atom is compressed parallel to [0001], whereas in the isotypic carbonates it is clearly elongated in this direction. Also this fact indicates repulsion by lone-pair electrons of the Se^{IV} atom in $K_2Co(SeO_3)_2$.

The unusual flattening of the SeO_3 groups mentioned above is somewhat compensated by the elongation of the CoO_6 polyhedra along the $\bar{3}$ axis: the Co—O distance is 2.142 (1) Å, which is rather long as compared with usual mean Co—O bond lengths (2.111 Å or, considering the bond length distortion $\Delta_{oct} = 0$, only 2.103 Å are expected as the mean Co—O distance; Wildner, 1990*a*). The bond angle distortion ($\sigma^2_{oct} = 45.5$) is significantly larger than found for the $M^{II}O_6$ polyhedra in the isotypic carbonates ($\sigma^2_{oct} = 20.1$ and 1.6 for the CaO_6 and MgO_6 polyhedron, respectively).

Recently single crystals of the isotypic compound $K_2Mn(SeO_3)_2$ were obtained by hydrothermal synthesis. Results of the structure determination of this new compound are published in Wildner (1992).

The author thanks Professor J. Zemann, Dr H. Effenberger and Professor F. Pertlik for many discussions and helpful comments.

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Acta Cryst. (1992). **C48**, 412–413

Synthesis and Structure of Cobalt Diselenite, $CoSe_2O_5$

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(*Received* 25 *August* 1989; *accepted* 16 *January* 1990)

Abstract. M_r = 296·85, orthorhombic, *Pnab*, *a* = 6·075 (2), *b* = 10·366 (2), *c* = 6·7911 (8) Å, *V* = 427·8 Å^3, *Z* = 4, D_x = 4·61 g cm^{-3}, λ(Mo *Kα*) = 0·71069 Å, μ = 207 cm^{-1}, *F*(000) = 540, *T* = 298 (5) K, *R* = 0·028 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 = (1·00 + 0·35tanθ)°, scan speed = 1·3–6·7° min^{-1}] using graphite-monochromated Mo *Kα* radiation (λ = 0·71069 Å) over the range $0 < \theta < 33°$ for $-1 \leq h \leq 9$, $-1 \leq k \leq 15$, $-1 \leq l \leq 10$, $(\sin\theta)/\lambda_{\max}$ = 0·77 Å^{-1}, with regular checks on reflection intensity (every 100 reflections) and orientation (every hour). Systematic absences (0*kl*: $k + l \neq 2n$, absent; *h*0*l*: *h*; *hk*0: *k*) uniquely defined the space group as *Pnab*. 2080 reflections were measured, of which 642 were used in structure solution and refinement [merging *R* = 6·98%; 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* = 2·79%, *wR* = 3·23% [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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0108-2701/92/030412-02$03.00