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Acta Cryst. (1994). **C50**, 336–338

Structure of K₂Co₂(SeO₃)₃

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(Received 27 April 1993; accepted 9 August 1993)

Abstract

The structure of hexagonal dicobalt dipotassium triselenite, K₂Co₂(SeO₃)₃, is composed of CoO₆ octahedra, KO₉ polyhedra and two crystallographically different types of pyramidal SeO₃ groups. Pairs of face-sharing CoO₆ octahedra are linked *via* the SeO₃ groups forming [Co₂(SeO₃)₃]²⁻ layers parallel to (0001), which are connected by the K atoms. This new structure type is closely related to the buetschliite-type compounds K₂M(XO₃)₂ (M = Ca, Mg with X = C, and M = Co, Mn with X = Se).

Comment

Single crystals of K₂Co₂(SeO₃)₃ were obtained as a by-product in experiments aimed at the hydrothermal synthesis of the zemannite-type compound K₂Co₂(SeO₃)₃·2H₂O (Wildner, 1993), starting with appropriate mixtures of Co(OH)₂, K₂CO₃, SeO₂ and H₂O in synthesis (i) (giving both compounds) or Co powder, H₂SeO₃, KOH and H₂O in synthesis (ii) [giving only K₂Co₂(SeO₃)₃] in closed teflon-lined steel vessels at ~493 (5) K (6 d). X-ray intensity data were collected from a crystal obtained by synthesis

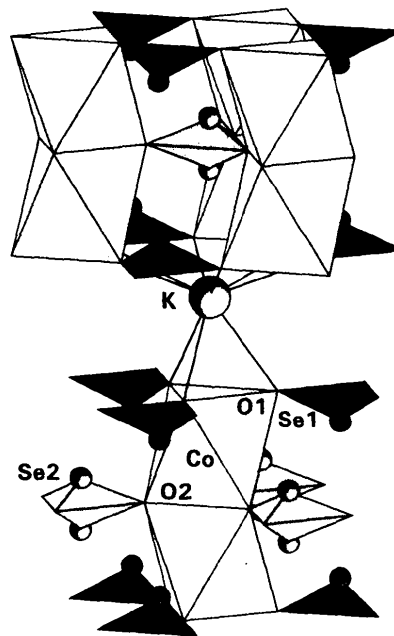


Fig. 1. Projection of the title structure along a direction slightly inclined to [11 $\bar{2}$ 0], showing the environment of the K atom. Only one of the two Se2 positions related by the mirror plane parallel to (0001) is randomly occupied.

(ii) and the structure was solved by interpretation of a three-dimensional Patterson function and a subsequent Fourier synthesis. The atomic arrangement is illustrated in Fig. 1.

All cations occupy sites with 3*m* symmetry. The CoO₆ octahedra share faces *via* the O2 atoms forming Co₂O₉ dimers. The repulsion between two neighbouring Co atoms [Co...Co = 2.957 (1) Å] results in an off-centring of the Co atoms along the threefold axis and in markedly different distances to O1 and O2. The mean Co—O distance (2.123 Å) is in the usual range and correlates with the expectations from the observed bond-length distortion (Wildner, 1992*a*). The CoO₆ octahedra share all their corners with SeO₃ groups, thus forming [Co₂(SeO₃)₃]²⁻ double-octahedral layers parallel to (0001). The Se1 atoms are one-sided pyramidally coordinated to three O1 atoms with usual interatomic bond lengths and angles (Hawthorne, Groat & Ercit, 1987; Fischer & Zemann, 1974); the Se apices and their lone-pair electrons point towards the centre of the layers. The Se2 atoms have an occupancy factor of only 0.5 and are randomly distributed on one of two positions [Se2...Se2' = 1.237 (2) Å] symmetrically related by the mirror planes parallel to (0001) which contain the O2 atoms. The Se2—O2 distances are very short and the pyramids are extremely flattened compared to the average shapes of SeO₃ groups reported in the literature (Se—O = 1.709 Å, O—Se—O = 100.2°; Hawthorne, Groat & Ercit, 1987). This structural feature

might be caused by a dynamic transition of the Se2 atom between the two related positions, thus yielding atomic coordinates which are shifted towards the mirror plane. Anisotropic displacement parameters of the Se2 atom, however, indicate nearly spherical motion and are, therefore, in contradiction to this explanation. Another reason might be the repulsion between electrons of the K atoms and the lone-pair electrons of Se2, which are directed towards the K atoms along the threefold axis; the Se2 and K atoms are separated by only 3.161 (2) Å. An increase in this distance seems to be impeded by the opposing influence of a short K—Co contact of 3.529 (2) Å. The K atoms are nine-coordinated with three shorter and six longer bonds to O1 atoms and connect consecutive $[\text{Co}_2(\text{SeO}_3)_3]^{2-}$ layers. The mean K—O distance (2.906 Å) is in good agreement with crystal chemical expectations.

The structure of $\text{K}_2\text{Co}_2(\text{SeO}_3)_3$ is closely related to the structures of buetschliite, $\text{K}_2\text{Ca}(\text{CO}_3)_2$ (Pabst, 1974; Knobloch, Pertlik & Zemann, 1980; Effenberger & Langhof, 1984), and the buetschliite-type compounds $\text{K}_2\text{Mg}(\text{CO}_3)_2$ (Hesse & Simons, 1982), $\text{K}_2\text{Co}(\text{SeO}_3)_2$ (Wildner, 1992b) and $\text{K}_2\text{Mn}(\text{SeO}_3)_2$ (Wildner, 1992c). In $\text{K}_2\text{Co}(\text{SeO}_3)_2$, for example, $[\text{Co}(\text{SeO}_3)_2]^{2-}$ single-octahedral layers (containing unshared CoO_6 octahedra with $\bar{3}m$ point symmetry) are connected by K atoms, analogously to $\text{K}_2\text{Co}_2(\text{SeO}_3)_3$. The absence of Co_2O_9 dimers and, therefore, of repulsion effects between neighbouring Co atoms leads to significantly increased cation-cation distances along the threefold axis in $\text{K}_2\text{Co}(\text{SeO}_3)_2$ [$\text{Co}\cdots\text{K} = 3.594$ Å, $\text{K}\cdots\text{Se}(\equiv\text{Se}2) = 3.240$ Å]. Accordingly, the strong flattening found for the SeO_3 pyramid in $\text{K}_2\text{Co}(\text{SeO}_3)_2$ is still much weaker than that observed for the corresponding polyhedron of Se2 in the title compound. Furthermore, shorter cation-cation contacts in $\text{K}_2\text{Co}_2(\text{SeO}_3)_3$ result in reduced distances between the O-atom levels of consecutive octahedral layers [3.368 Å, as compared to 3.436 Å in $\text{K}_2\text{Co}(\text{SeO}_3)_2$] and in less pronounced differences between shorter and longer K—O bonds [0.117 Å in the title compound, but 0.243 Å in $\text{K}_2\text{Co}(\text{SeO}_3)_2$].

Experimental

Crystal data

$\text{K}_2\text{Co}_2(\text{SeO}_3)_3$
 $M_r = 576.94$
 Hexagonal
 $P6_3/mmc$
 $a = 5.486$ (1) Å
 $c = 17.574$ (3) Å
 $V = 458.1$ (3) Å³
 $Z = 2$
 $D_x = 4.183$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 52 reflections
 $\theta = 15\text{--}22^\circ$
 $\mu = 16.01$ mm⁻¹
 $T = 295$ K
 Forms $\{0001\}$ and $\{0\bar{1}12\}$
 $0.18 \times 0.18 \times 0.12$ mm
 Pink

Data collection

Stoe AED-2 four-circle diffractometer
 $2\theta\text{--}\omega$ scans
 Absorption correction: empirical
 $T_{\min} = 0.05$, $T_{\max} = 0.11$
 4366 measured reflections
 434 independent reflections
 394 observed reflections
 $[F_o > 3\sigma(F_o)]$

$R_{\text{int}} = 0.063$
 $\theta_{\max} = 35^\circ$
 $h = -9 \rightarrow 9$
 $k = 0 \rightarrow 9$
 $l = -28 \rightarrow 28$
 3 standard reflections
 frequency: 120 min
 intensity variation: $\pm 0.6\%$

Refinement

Refinement on F
 $R = 0.038$
 $wR = 0.034$
 $S = 4.12$
 394 reflections
 24 parameters
 $w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.72$ e Å⁻³
 $\Delta\rho_{\min} = -1.09$ e Å⁻³

Extinction correction: Zachariasen (1967)
 Extinction coefficient: $6.8(3) \times 10^{-5}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3}[U_{33} + \frac{2}{3}(U_{11} + U_{22} - U_{12})].^*$$

	x	y	z	U_{eq}
K	1/3	2/3	0.03494 (10)	0.0255 (5)
Co	1/3	2/3	0.66586 (5)	0.0145 (3)
Se1	0	0	0.13913 (3)	0.0129 (2)
Se2†	1/3	2/3	0.21480 (6)	0.0116 (3)
O1	0.1599 (3)	-0.1599 (3)	0.5958 (2)	0.0180 (10)
O2	0.4969 (4)	-0.4969 (4)	1/4	0.0185 (14)

* Fischer & Tillmanns (1988).

† Occupancy factor of 0.5.

Table 2. Selected geometric parameters (Å, °)

K—O1	2.828 (2)	3×	O1—O1	2.631 (3)	3×
K—O1	2.945 (1)	6×	O1—O1	2.855 (3)	6×
			O1—O1	3.695 (5)	6×
Co—O1	2.057 (2)	3×	O1—O1	2.885 (3)	3×
Co—O2	2.188 (1)	3×	O2—O2	2.794 (5)	3×
			O1—O2	3.162 (3)	6×
Se1—O1	1.699 (1)	3×	O1—O2	3.631 (3)	3×
Se2—O2	1.673 (2)	3×	O2—O2	2.692 (5)	3×
O1—Co—O1	87.9 (1)	3×	O1—Se1—O1	101.5 (1)	3×
O2—Co—O2	79.3 (1)	3×	O2—Se2—O2	107.1 (2)	3×
O1—Co—O2	96.3 (1)	6×			
O1—Co—O2	174.2 (4)	3×			

The Se2 atoms have an occupancy factor of 0.5 and are randomly distributed on position 4(f) of space group $P6_3/mmc$. Preliminary X-ray investigations included long-time-exposed rotation and Weissenberg photographs, which showed no indications of superlattice reflections. Programs used were *STRUCSY* (Stoe & Cie, 1984) and *ATOMS* (Dowty, 1991).

The author thanks Professor E. Tillmanns and Dr H. Effenberger for helpful comments.

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71571 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1067]

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Acta Cryst. (1994). **C50**, 338–340

Structure of CePdAl

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(Received 15 May 1993; accepted 16 July 1993)

Abstract

The cerium palladium aluminide, CePdAl, was found to crystallize with a hexagonal ZrNiAl-type structure, which is an ordered Fe₂P-type derivative.

Comment

The structure determination of CePdAl was carried out as part of an investigation of LnTX compounds (Ln = rare-earth element, T = transition-metal element, X = B-group element). The structure of CePdAl was found to crystallize in the ZrNiAl-type

structure found, for example, in CeNiAl and HoNiAl (Dwight, Mueller, Conner, Downey & Knott, 1968), CeNiGa (Yarmolyuk, Gryn & Gladyshevskii, 1979), and ScRuSi and ScTGe (T = Ru, Rh, Pd or Os) (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982).

The sample was synthesized by arc melting the constituent elements under purified Ar in a water-cooled copper hearth. Traces of a second phase were detectable on the Guinier powder photograph taken with Cu K α radiation. All crystals found in the crushed ingot were intergrown or twinned. The best crystal, which showed only slight twinning, was used for the data collection.

The structure consists of strongly distorted hexagonal close packing (ABAB) of Ce and Al atoms with all the Ce atoms in the A layers, all the Al atoms in the B layers, and with one third of the Pd atoms inserted in the A layers and two thirds [Pd in 2(d)] inserted in the B layers. Thus, each Pd atom in a 1(a) site is located at the centre of a trigonal prism of Al atoms [at a distance of 2.685 (6) Å] and has three Ce neighbours in the equatorial plane at 3.038 (2) Å. Pd in 2(d), on the other hand, is at the centre of a similar polyhedron formed by six Ce atoms at 3.025 (1) Å and three Al atoms at 2.859 (6) Å. The nonequivalence of the 1(a) and 2(d) sites was discussed by Rundqvist & Jellinek (1959), who predicted that ternary phases would exist with an ordered Fe₂P-type structure (their unit cell is shifted by $z = \frac{1}{2}$). The Al atom is surrounded by a tetragonal pyramid of five Pd atoms, while the Ce atom is surrounded by a tetrahedron of four Pd atoms. The structure of CePdAl is a further example which obeys the rule, demonstrated by Hovestreydt *et al.* (1982) in the

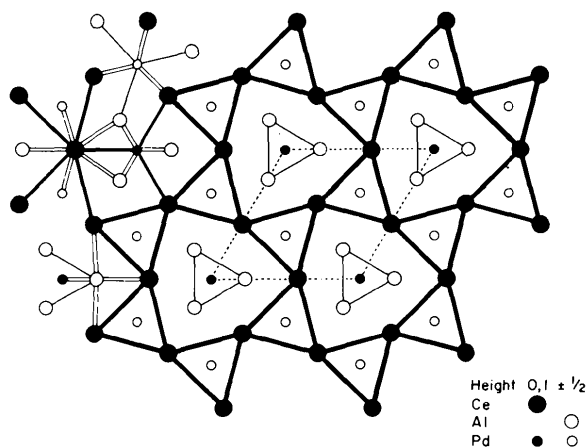


Fig. 1. The ZrNiAl-type structure of CePdAl projected onto the basal plane; the hexagonal unit cell is indicated by dashed lines, the trigonal prisms around the Pd atoms are shown in the main part and on the left-hand side the bonds are indicated for each kind of atom.