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Co₁₀Ge₃O₁₆

JACQUES BARBIER

*Department of Chemistry, McMaster University,
Hamilton, Ontario, Canada L8S 4M1*

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Abstract

The structure of a new cobalt germanate, Co₁₀Ge₃O₁₆, has been determined using X-ray diffraction data collected on a single crystal grown by slow cooling of a stoichiometric melt at atmospheric pressure. Co₁₀Ge₃O₁₆ is isostructural with (Ni,Mg)₁₀Ge₃O₁₆ and is also structurally related to the mineral aerugite, Ni_{8.5}As₃O₁₆. Its crystal structure is based on a cubic close-packing of O atoms with octahedral (Co and Ge) and tetrahedral (Ge) metal-atom sites. It can be described as an intergrowth of {111} spinel triple layers with {111} rock-salt single layers along the [001]_{hex} direction of the rhombohedral cell.

Comment

The original determination of phase relations in the NiO–MgO–GeO₂ and CoO–MgO–GeO₂ systems (Navrotsky, 1973) showed strong similarities between both systems as well as the existence of unidentified intermediate phases in the Co system. The recent discovery of the compound (Ni,Mg)₁₀Ge₃O₁₆ (Barbier, 1987; Fleet & Barbier, 1988) prompted a re-investigation of the CoO–MgO–GeO₂ system, which is currently in progress. Initial results have indeed confirmed the existence of the phase (Co_{1-x}Mg_x)₁₀Ge₃O₁₆, which, unlike the Ni analog, includes the $x = 0$ end-member, Co₁₀Ge₃O₁₆. This new cobalt germanate melts congruently at temperatures between 1573 and 1673 K, which made it possible to grow single crystals from a stoichiometric melt (sealed in a Pt tube to prevent loss of GeO₂ by evaporation). Although no chemical analysis of the crystals has been carried out, their chemical composition is confirmed by the structure refinement.

The Co₁₀Ge₃O₁₆ structure is based on a 12-layer close-packing of O atoms with a c/a ratio of 4.85, close to the ideal value of $6\sqrt{2}/\sqrt{3} = 4.90$. The Co atoms occupy octahedral sites only, whereas the Ge atoms are found in both octahedral and tetrahedral sites (Table 2). No evidence of mixed Co/Ge site occupancy has been shown by the refinement and the displacement parameters of all atoms are nearly isotropic. The atomic distribution has also been confirmed by bond-valence sum calculations (Brown & Altermatt, 1985), which yielded the following values: O1 1.98 (1), O2 1.84 (1), O3 1.94 (1), O4 1.92 (1), Co1 1.89 (1), Co2 1.90 (1), Co3 1.95 (1), Ge1 4.09 (2) and Ge2 3.70 (4). This last value indicates that the tetrahedral Ge2—O bonds are stretched, as is also observed in the isostructural compound (Ni,Mg)₁₀Ge₃O₁₆ (Fleet & Barbier, 1988) and in Mg₂GeO₄ spinel (Von Dreele, Navrotsky & Bowman, 1977). As shown in Fig. 1, the Co1O₆, Co3O₆ and Ge2O₄ polyhedra make up a spinel-like triple layer, while the Co2O₆ and Ge1O₆ octahedra make up a rock-salt type single layer. Exactly the same spinel–rock salt intergrowth also occurs in (Ni,Mg)₁₀Ge₃O₁₆ (Fleet & Barbier, 1988), while related cation-deficient structures are formed by the arsenate mineral aerugite, Ni_{8.5}As₃O₁₆ (Fleet & Barbier, 1989), its Mg analog (Bless & Kostiner, 1973) and its Co analog (formulated as Co₈As₃O₁₆; Krishnamachari & Calvo, 1970).

Co₁₀Ge₃O₁₆ forms as part of a (Co,Mg)₁₀Ge₃O₁₆ solid solution which exists on the Co-rich side of the CoO–MgO–GeO₂ system together with a

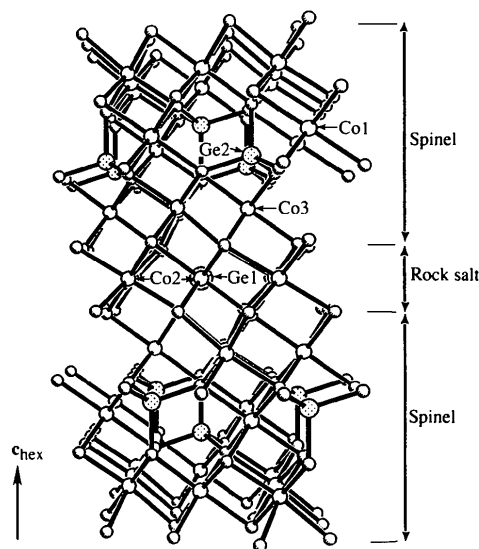


Fig. 1. Perspective view of the Co₁₀Ge₃O₁₆ structure along the [210] direction. The structure consists of an intergrowth of spinel slabs and rock-salt layers along the c_{hex} direction of the rhombohedral unit cell. Large, medium and small circles represent Ge, Co and O atoms, respectively. Note that the Ge atoms occupy tetrahedral sites (Ge2) in the spinel slabs, and octahedral sites (Ge1) in the rock-salt layers.

(Co,Mg)₂GeO₄ spinel phase. On the Mg-rich side, an olivine-type (Mg,Co)₂GeO₄ phase coexists with an (Mg,Co)₁₄Ge₅O₂₄ solid solution isostructural with Mg₁₄Ge₅O₂₄ (Von Dreele, Bless, Kostiner & Hughes, 1970). Another new phase forms at intermediate compositions and its structural characterization, together with the elucidation of its relations to the other phases of the system, is currently in progress.

Experimental

Crystals of the title compound were prepared by melting a pre-reacted stoichiometric powder mixture in a sealed platinum tube, which was then cooled from 1723 to 1523 K at 15 K h⁻¹.

Crystal data

Co ₁₀ Ge ₃ O ₁₆	Ag K α radiation
$M_r = 1063.07$	$\lambda = 0.5608 \text{ \AA}$
Rhombohedral	Cell parameters from 26 reflections
$R3m$	
$a = 5.951 (1) \text{ \AA}$	$\theta = 7.39\text{--}14.90^\circ$
$c = 28.875 (6) \text{ \AA}$	$\mu = 11.04 \text{ mm}^{-1}$
$V = 885.59 \text{ \AA}^3$	Room temperature
$Z = 3$	(001) plate
$D_x = 5.98 \text{ Mg m}^{-3}$	$0.2 \times 0.1 \times 0.01 \text{ mm}$
	Reddish brown

Data collection

Siemens R3m/V diffractometer	$R_{\text{int}} = 0.047$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 35^\circ$
Absorption correction: empirical	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.417, T_{\text{max}} = 0.814$	$k = -1 \rightarrow 12$
2187 measured reflections	$l = -1 \rightarrow 58$
1045 independent reflections	3 standard reflections monitored every 100 reflections
1045 observed reflections	intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 2.1 \text{ e \AA}^{-3}$
$R(F) = 0.058$	$\Delta\rho_{\text{min}} = -1.6 \text{ e \AA}^{-3}$
$wR(F^2) = 0.069$	Extinction correction:
$S = 0.820$	$F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin^2\theta)]^{-1/4}$
1045 reflections	Extinction coefficient:
37 parameters	$\chi = 0.0056 (3)$
$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2]$	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C)
where $P = [\max(F_o^2, 0) + 2F_o^2]/3$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	x	y	z	U_{eq}
Ge1	0	0	0	0.00461 (13)
Ge2	0	0	0.18922 (2)	0.00471 (11)
Co1	0	0	1/2	0.00609 (17)
Co2	1/2	0	0	0.00571 (10)
Co3	0.16336 (4)	$1-x$	0.08551 (2)	0.00559 (8)

O1	0	0	0.12779 (13)	0.0068 (7)
O2	0	0	0.37613 (14)	0.0058 (6)
O3	0.2990 (6)	0.1495 (3)	0.03787 (8)	0.0069 (4)
O4	0.5026 (2)	1.0053 (4)	0.12507 (8)	0.0062 (3)

Table 2. Selected geometric parameters ($\text{\AA}, ^\circ$)

Ge1—O3 ⁱ	1.890 (2)	Co1—O4 ^{xiii}	2.118 (2)
Ge1—O3	1.890 (2)	Co1—O4 ^{xiv}	2.118 (2)
Ge1—O3 ⁱⁱ	1.890 (2)	Co2—O2 ^{xv}	2.116 (2)
Ge1—O3 ⁱⁱⁱ	1.890 (2)	Co2—O2 ^{xvi}	2.116 (2)
Ge1—O3 ^{iv}	1.890 (2)	Co2—O3 ⁱⁱ	2.117 (2)
Ge1—O3 ^v	1.890 (2)	Co2—O3 ^{xvii}	2.117 (2)
Ge2—O1	1.774 (4)	Co2—O3 ^{xviii}	2.117 (2)
Ge2—O4 ^{vi}	1.778 (2)	Co2—O3	2.117 (2)
Ge2—O4 ^{vii}	1.778 (2)	Co3—O1 ^{xix}	2.080 (2)
Ge2—O4 ^{viii}	1.778 (2)	Co3—O4	2.089 (2)
Co1—O4 ^{ix}	2.118 (2)	Co3—O4 ^{xx}	2.089 (2)
Co1—O4 ^x	2.118 (2)	Co3—O3 ^{xxi}	2.123 (2)
Co1—O3 ^{xi}	2.118 (2)	Co3—O3 ^{xxix}	2.123 (2)
Co1—O4 ^{xii}	2.118 (2)	Co3—O2 ^{xxii}	2.143 (2)
O3 ⁱ —Ge1—O3 ⁱⁱ	89.86 (10)	O1—Ge2—O4 ^{vii}	108.02 (8)
O3 ⁱ —Ge1—O3 ^{iv}	90.14 (10)	O4 ^{vi} —Ge2—O4 ^{vii}	110.88 (7)
O4 ^{ix} —Co1—O4 ^{xii}	91.03 (9)	O1 ^{xix} —Co3—O4	91.13 (8)
O4 ^{ix} —Co1—O4 ^{xiii}	88.97 (9)	O1 ^{xix} —Co3—O3 ^{xxix}	91.84 (8)
O3 ⁱⁱ —Co2—O2 ^{xv}	90.35 (7)	O3 ^{xxix} —Co3—O4	94.63 (9)
O3 ⁱⁱ —Co2—O2 ^{xvi}	89.65 (7)	O2 ^{xxii} —Co3—O4	88.31 (7)
O3—Co2—O3 ⁱⁱ	78.37 (12)	O2 ^{xxii} —Co3—O3 ^{xxix}	88.79 (8)
O3 ⁱⁱ —Co2—O3 ^{xvii}	101.63 (12)	O3 ^{xxi} —Co3—O3 ^{xxix}	77.89 (12)

Symmetry codes: (i) $-x, -y, -z$; (ii) $y, y - x, -z$; (iii) $x - y, x, -z$; (iv) $-y, -y + x, z$; (v) $-x + y, -x, z$; (vi) $\frac{2}{3} + x - y, x - \frac{2}{3}, \frac{1}{3} - z$; (vii) $\frac{2}{3} - x, \frac{2}{3} - y, \frac{1}{3} - z$; (viii) $y - \frac{2}{3}, -\frac{2}{3} - x + y, \frac{1}{3} - z$; (ix) $\frac{1}{3} + x - y, x - \frac{1}{3}, \frac{2}{3} - z$; (x) $-\frac{1}{3} - x + y, \frac{1}{3} - x, \frac{1}{3} + z$; (xi) $y - \frac{2}{3}, -\frac{1}{3} - x + y, \frac{2}{3} - z$; (xii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (xiii) $\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$; (xiv) $x - \frac{1}{3}, y - \frac{2}{3}, \frac{1}{3} + z$; (xv) $\frac{1}{3} + x, y - \frac{1}{3}, z - \frac{1}{3}$; (xvi) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (xvii) $1 - x, -y, -z$; (xviii) $1 - y, -y + x, z$; (xix) $x, 1 + y, z$; (xx) $1 - y, 1 - y + x, z$; (xxi) $-x + y, 1 - x, z$; (xxii) $\frac{1}{3} + x, \frac{2}{3} + y, z - \frac{1}{3}$.

Data collection: R3m/V Crystallographic Research System (Siemens, 1989). Cell refinement and data reduction: SHELXTL-Plus (Sheldrick, 1991). Structure solution: SHELXS86 (Sheldrick, 1990). Structure refinement: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nickel Bistrifluorostannate(II) Hexahydrate, $[\text{Ni}(\text{H}_2\text{O})_6](\text{SnF}_3)_2$

ISAAC ABRAHAMS

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, England

JOHN D. DONALDSON AND ZAHIDA I. KHAN

Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, England

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Abstract

The structure of the title compound has been solved by single crystal X-ray diffraction. Nickel is present as the hexaaquanickel cation, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, which is balanced in charge by discrete trigonal pyramidal $[\text{SnF}_3]^-$ complex anions in a 1:2 ratio. The non-bonding electron pairs on tin are stereochemically active.

Comment

The title compound is one of a series of complex tin(II) fluorides involving first-row transition metals of the general formula $M(\text{SnF}_3)_2 \cdot 6\text{H}_2\text{O}$ (Donaldson & Oteng, 1969). The crystal structure of the title compound represents the first of a nickel tin(II) fluoride.

The structure of the title compound contains the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cation which is balanced in charge by two $[\text{SnF}_3]^-$ complex anions. Unlike many complex tin(II) fluorides, the structure of the title compound contains isolated $[\text{SnF}_3]^-$ anions. This is in contrast to the network structures adopted by other complex stannous fluorides such as $\text{Cs}_2\text{Sn}_6\text{Br}_3\text{F}_{11}$ (Abrahams, Donaldson & Grimes, 1992), SnBrF_5 (Donaldson, Laughlin & Puxley, 1977; Vilminot, Granier & Cot, 1978) and Sn_4OF_6 (Abrahams, Clark, Donaldson, Khan & Southern, 1994), which show one-, two- and three-dimensional polymeric bridging structures, respectively. The non-bonding electron pairs on the Sn atoms, in common with most stannous fluorides,

show strong stereochemical activity with no evidence for direct Sn—Sn interaction.

The Sn—F bond lengths of 2.040 (3)–2.057 (6) Å are comparable with those of other systems that have isolated $[\text{SnF}_3]^-$ anions, e.g. 2.08 Å in NH_4SnF_3 (Bergerhoff & Namgung, 1978) and 2.053–2.096 Å in $\text{N}_2\text{H}_6(\text{SnF}_3)_2$ (Kaučič, Leban, Gašperšič-Škander, Ganter & Rahten, 1988). The structure of the cobalt analogue has been determined (Maury & Gleizes, 1980) and is isostructural with the title structure, with similar Sn—F bond lengths of 2.049–2.052 Å.

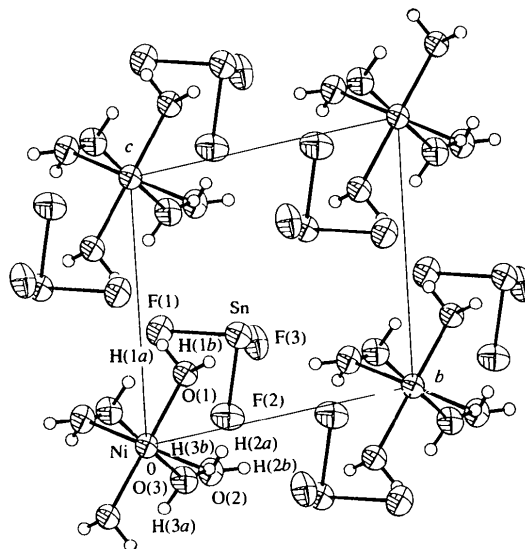


Fig. 1. Unit-cell projection of $[\text{Ni}(\text{H}_2\text{O})_6](\text{SnF}_3)_2$. Atomic displacement ellipsoids are drawn at the 50% level.

Experimental

$[\text{Ni}(\text{H}_2\text{O})_6](\text{SnF}_3)_2$ was prepared by dissolving appropriate molar quantities of NiF_2 and SnF_2 in a minimum amount of boiling water. After slow cooling, pale green triclinic prisms were formed which were collected and dried *in vacuo* over silica gel.

Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6](\text{SnF}_3)_2$
 $M_r = 518.19$
 Triclinic
 $P\bar{1}$
 $a = 6.799$ (20) Å
 $b = 6.938$ (7) Å
 $c = 7.011$ (5) Å
 $\alpha = 77.51$ (7)°
 $\beta = 72.59$ (10)°
 $\gamma = 78.50$ (13)°
 $V = 304.9$ (10) Å³
 $Z = 1$
 $D_x = 2.822$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 14.142$ – 17.764 °
 $\mu = 5.675$ mm⁻¹
 $T = 291$ (2) K
 Triclinic prism
 $0.22 \times 0.20 \times 0.15$ mm
 Pale green