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Acta Cryst. (1995). C**51**, 1258–1260

Sodium Bis(2,3-dimethylbutane-2,3-diolato)hydroxogermanate(IV)–Methanol (1/3)

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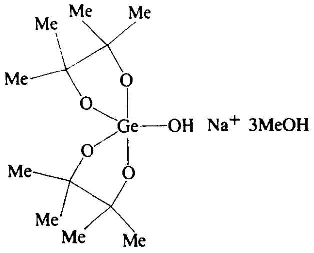
(*Received* 17 *November* 1994; *accepted* 29 *October* 1994)

Abstract

Na[Ge(OH)(C$_6$H$_{12}$O$_2$)$_2$].3CH$_3$OH has been prepared from germanium dioxide, pinacol (2,3-dimethyl-2,3-butanediol) and methanol and characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy and by elemental analysis. Diffraction analysis reveals that the Ge atom has trigonal bipyramidal coordination geometry, with one O atom of each bidentate ligand and the hydroxo group in equatorial positions; the other two O atoms of the bidentate ligands are in axial sites. The Ge—OH bond length [1.769 (2) Å] is significantly shorter than the other two equatorial Ge—O bonds [1.796 (2) and 1.806 (2) Å] which in turn are shorter than the axial Ge—O bonds [1.866 (3) and 1.870 (3) Å].

Comment

The coordination number displayed by germanium in its complexes varies from 4 to 6 (Mehrotra & Chandra, 1963; Yoder & Zukerman, 1967; Sau & Holmes, 1981; Day, Holmes, Sau & Holmes, 1982; Gurkova *et al.*, 1984; Sau, Holmes, Day & Holmes, 1986; Eujen, Brauer & Wilke, 1986; Breliere, Carre, Corriu & Royo, 1988; Mizuta, Yoshida & Miyoshi, 1989; Lazraq *et al.*, 1990; Cereau, Chuit, Corriu & Reye, 1991). We have described previously the syntheses and crystal structures of two tetrahedral germanium complexes (Chen, Chiang & Ueng, 1993), a trigonal bipyramidal complex (Chiang, Lin & Ueng, 1992) and four octahedral complexes (Chiang, Wang & Ueng, 1993; Chiang, Yang & Ueng, 1994; Chiang, Hwang & Ueng, 1995). In a continuation of these studies, the title complex, (I), was synthesized and its crystal structure determined.



(I)

The complex contains a central Ge atom bonded to a hydroxo group and to the four O atoms of two deprotonated pinacol ligands. The coordination around the metal is distorted trigonal bipyramidal with the hydroxo group and one O atom of each pinacolate in equatorial positions; the remaining two pinacolate O atoms occupy axial positions. The deviation of the Ge atom from the equatorial plane is 0.022 (1) Å. The O(1)—Ge—O(4) angle is 173.5 (1)°, the angles in the equatorial plane are 115.6 (1), 120.6 (1) and 123.8 (1)° and the six O$_a$—Ge—O$_e$ (a = axial, e = equatorial) angles are in the range 87.4 (1)–95.9 (1)°. The Ge—O(5) bond is significantly shorter than Ge—O(2) and Ge—O(3), which in turn are shorter than Ge—O(1) and Ge—O(4). This variation is expected since the coordinating ability of the hydroxo group is greater than that of the alkoxide, and equatorial Ge—O bonds are usually stronger than axial Ge—O bonds (Chiang, Lin & Ueng, 1992).

The coordination around the Na$^+$ cation is also distorted trigonal bipyramidal, with the hydroxo group and two methanol O atoms equatorial and a further two methanol O atoms axial. The deviation of the Na atom from the equatorial plane is –0.182 (3) Å. The O$_a$—Na—O$_a$ angle is 168.5 (1)°, the angles in the equatorial plane are 98.3 (1), 116.4 (1) and 143.3 (1)° and the six O$_a$—Na—O$_e$ angles are in the range 82.6 (1)–105.8 (1)°. It is obvious that the distortion of the coordination polyhedron around the Na atom from an ideal trigonal bipyramid is larger than for that around the Ge atom. In addition to the hydroxo group [O(5)] which bridges the

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Ge and Na atoms, the structure also contains a bridging methanol group [O(7)] which links to two Na^+ cations [Na$\cdots$O(7) = 2.359 (3), O(7)$\cdots$Na^i = 2.478 (3) Å].

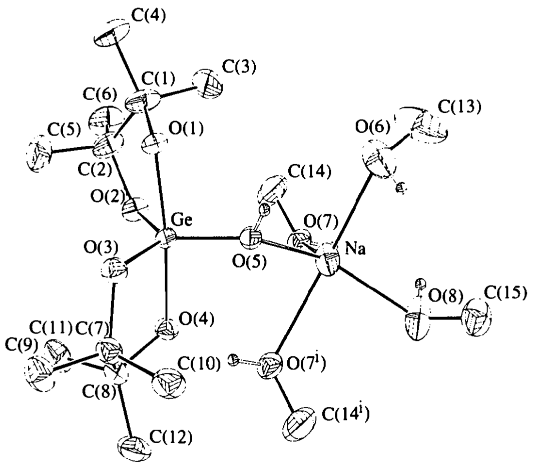

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular structure of the title compound. H atoms, except those of hydroxyl groups, are omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The compound was synthesized as follows. Aqueous sodium hydroxide solution (1 M, 10 cm^3) was added dropwise with stirring to a warm aqueous solution (40 cm^3) of germanium dioxide (0.52 g, 5.0 mmol). Then, pinacol (1.18 g, 10.0 mmol) was added and the mixture was heated under reflux for 3 h. The solvent was removed under reduced pressure, the white solid residue was dissolved in methanol (75 cm^3) and the mixture was heated under reflux for a further hour. It was then cooled to room temperature and the precipitate was filtered and washed twice with ether (30 cm^3). Recrystallization from methanol gave colourless plate-shaped crystals [m.p. 618–619 K (dec.); yield 1.85 g (84%)]. Analysis: found C 40.87, H 8.32, Ge 16.61, Na 5.34%; $Na(GeC_{12}H_{25}O_5).3CH_3OH$ requires C 40.85, H 8.40, Ge 16.48, Na 5.22%. The IR spectrum (Jasco 700 spectrophotometer) in the Ge—O stretching region included absorptions at 963 *s* and 800 *s* cm^{-1} (Ge—OC) and 717 *s* cm^{-1} (Ge—OH) (KBr pellet). Solutions in CD_3OD showed resonances in the ^1H NMR spectrum (Jeol JNM-EX 400 MHz spectrophotometer) at δ 1.10–1.20 (24H, 8 CH_3) and in the ^{13}C NMR spectrum at δ 74.9 (2 OC), 75.8 (2 OC), 25.1 (4 CH_3) and 26.1 (4 CH_3). The splitting of the methyl signals in the ^1H NMR and ^{13}C NMR spectra is due to the different sites (axial or equatorial) occupied by adjacent O atoms in the coordination sphere of germanium. Thermogravimetric analysis shows a weight loss of 21.8% at 701 K, corresponding to the removal of three methanol molecules. Crystals suitable for diffraction analysis were obtained from aqueous solution. The crystal density D_m was measured by flotation in CH_2Cl_2/C_2H_5OH.

Crystal data

$Na[Ge(OH)(C_6H_{12}O_2)_2].$-
$3CH_3OH$
$M_r = 441.03$
Triclinic
$P\bar{1}$
$a = 10.235 (5)$ Å
$b = 10.249 (8)$ Å
$c = 11.810 (3)$ Å
$\alpha = 86.88 (4)°$
$\beta = 80.46 (3)°$
$\gamma = 66.59 (6)°$
$V = 1121 (1)$ Å^3
$Z = 2$
$D_x = 1.307$ Mg m^{-3}
$D_m = 1.3$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.12–13.11°$
$\mu = 1.40$ mm^{-1}
$T = 218$ K
Plate
0.50 × 0.45 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*NRCVAX*; Larsen *et al.*, 1990)
$T_{min} = 0.949$, $T_{max} = 1.000$
2927 measured reflections
2917 independent reflections

2646 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 22.5°$
$h = -9 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections frequency: 120 min intensity decay: 3%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.039$
$S = 2.59$
2646 reflections
227 parameters
H-atom positions taken from ΔF map and not refined
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.012$

$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: extinction (*NRCVAX*; Larson *et al.*, 1990)
Extinction coefficient: 2.1 (5) μm
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ge	0.93310 (4)	0.17596 (4)	0.16909 (3)	2.47 (2)
O(1)	1.0425 (2)	−0.0187 (2)	0.1446 (2)	3.0 (1)
O(2)	1.0806 (2)	0.1841 (2)	0.2298 (2)	3.4 (1)
O(3)	0.7906 (2)	0.1338 (2)	0.2503 (2)	3.3 (1)
O(4)	0.8222 (2)	0.3657 (2)	0.2114 (2)	3.3 (1)
O(5)	0.9318 (2)	0.2198 (2)	0.0222 (2)	3.2 (1)
C(1)	1.1884 (4)	−0.0536 (4)	0.1590 (4)	4.9 (2)
C(2)	1.1847 (4)	0.0467 (4)	0.2508 (4)	4.8 (2)
C(3)	1.2711 (4)	−0.0181 (5)	0.0434 (4)	5.6 (2)
C(4)	1.2589 (4)	−0.2089 (4)	0.1796 (4)	5.4 (2)
C(5)	1.1261 (5)	−0.0034 (6)	0.3703 (4)	7.2 (3)
C(6)	1.3230 (5)	0.0580 (5)	0.2614 (5)	6.4 (3)
C(7)	0.6618 (4)	0.2563 (4)	0.2875 (3)	3.6 (2)
C(8)	0.7126 (4)	0.3773 (4)	0.3074 (3)	3.8 (2)
C(9)	0.5828 (4)	0.2176 (5)	0.3954 (4)	5.2 (2)
C(10)	0.5695 (4)	0.2931 (5)	0.1926 (4)	5.1 (2)
C(11)	0.7785 (4)	0.3567 (5)	0.4166 (3)	5.0 (2)
C(12)	0.5937 (5)	0.5237 (4)	0.3081 (4)	5.8 (2)
C(13)	1.2131 (8)	0.1819 (6)	−0.3229 (7)	11.7 (5)
C(14)	1.3053 (5)	0.3645 (6)	−0.0178 (5)	7.9 (3)
C(15)	0.8698 (5)	0.5367 (5)	−0.3414 (4)	6.2 (3)
O(6)	1.1147 (4)	0.1913 (3)	−0.2319 (3)	7.3 (2)

O(7)	1.1706 (3)	0.4473 (3)	−0.0507 (2)	4.3 (1)
O(8)	0.9112 (4)	0.5491 (3)	−0.2403 (3)	6.7 (2)
Na	0.9929 (2)	0.3781 (2)	−0.0998 (1)	4.60 (9)

Table 2. *Selected geometric parameters* (Å, °)

Ge—O(1)	1.870 (3)	Na···O(7^{i})	2.478 (3)
Ge—O(2)	1.806 (2)	O(1)—C(1)	1.428 (4)
Ge—O(3)	1.796 (2)	O(2)—C(2)	1.427 (4)
Ge—O(4)	1.866 (3)	O(3)—C(7)	1.435 (4)
Ge—O(5)	1.769 (2)	O(4)—C(8)	1.430 (4)
O(5)···Na	2.313 (3)	C(13)—O(6)	1.324 (8)
O(6)···Na	2.332 (4)	C(14)—O(7)	1.408 (5)
O(7)···Na	2.359 (3)	C(15)—O(8)	1.359 (6)
O(8)···Na	2.347 (4)		
O(1)—Ge—O(2)	87.6 (1)	C(13)—O(6)···Na	128.9 (3)
O(1)—Ge—O(3)	88.9 (1)	C(14)—O(7)···Na	130.2 (3)
O(1)—Ge—O(4)	173.5 (1)	C(14)—O(7)···Na^{i}	112.5 (3)
O(1)—Ge—O(5)	95.9 (1)	Na···O(7)···Na^{i}	95.7 (1)
O(2)—Ge—O(3)	123.8 (1)	C(15)—O(8)···Na	129.8 (3)
O(2)—Ge—O(4)	90.0 (1)	O(5)···Na···O(6)	87.9 (1)
O(2)—Ge—O(5)	115.6 (1)	O(5)···Na···O(7)	116.4 (1)
O(3)—Ge—O(4)	87.4 (1)	O(5)···Na···O(7^{i})	82.6 (1)
O(3)—Ge—O(5)	120.6 (1)	O(5)···Na···O(8)	143.3 (1)
O(4)—Ge—O(5)	90.6 (1)	O(6)···Na···O(7)	105.8 (1)
Ge—O(1)—C(1)	110.6 (2)	O(6)···Na···O(7^{i})	168.5 (1)
Ge—O(2)—C(2)	112.8 (2)	O(6)···Na···O(8)	94.2 (1)
Ge—O(3)—C(7)	113.8 (2)	O(7)···Na···O(7^{i})	84.3 (1)
Ge—O(4)—C(8)	111.3 (2)	O(7)···Na···O(8)	98.3 (1)
Ge—O(5)···Na	136.3 (1)	O(7^{i})···Na···O(8)	89.5 (1)

Symmetry code: (i) $2 - x, 1 - y, -z$.

The computer programs used were those of the *NRCVAX* package (Larson *et al.*, 1990).

The authors thank the National Science Council (NSC81-0208-M-003-07 and NSC81-0208-M003-14) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1260–1263

Two Transition-Metal Antimony Ethoxides: $M_2Sb_4(OEt)_{16}$; M = Ni or Mn

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(*Received* 17 *December* 1993; *accepted* 16 *January* 1995)

Abstract

Two new metal alkoxides, nickel antimony ethoxide, $Ni_2Sb_4(OEt)_{16}$, and manganese antimony ethoxide, $Mn_2Sb_4(OEt)_{16}$, have been investigated by means of single-crystal X-ray diffraction. These two transition-metal ethoxides are isostructural with $Mg_2Sb_4(OEt)_{16}$. The major structural differences between the three compounds result mainly from the different sizes of the nickel, manganese and magnesium ions. The fourfold coordination around the Sb atoms and the sixfold coordination around the other metal ions, as well as the conformations of the ethoxide groups, are similar in all three compounds.

Comment

Metal alkoxides have become important precursors in the sol–gel route for preparation of, for example, thin oxide layers and oxide materials with special physical properties (Bradley, Mehrotra & Gaur, 1978). Extended knowledge of the molecular structures of metal alkoxides is of importance to provide the basis for understanding various physical and chemical properties, including the gelling process. The present study describes the synthesis and structural characterization of two new transition-metal antimony ethoxides with formulae $Ni_2Sb_4(OEt)_{16}$, (I), and $Mn_2Sb_4(OEt)_{16}$, (II). The

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