of Research on Structure of Matter, Chinese Academy of Sciences, and the National Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lang, J.-P., Li, J.-G., Bao, S. & Xin, X.-Q. (1993). *Polyhedron*, **12**, 801–806.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Müller, A., Bögge, H. & Koniger-Ahlborn, E. (1979). *Z. Naturforsch Teil B*, **34**, 1698–1702.

Müller, A., Dartmann, D., Romer, C., Clegg, W. & Sheldrick, G. M. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 1060–1061.

Müller, A., Jaegermann, W. & Hellmann, W. (1983). *J. Mol. Struct.* **100**, 559–570.

Nicholson, J. R., Flood, A. C., Garner, C. D. & Clegg, W. (1983). *J. Chem. Soc. Chem. Commun.* pp. 1179–1180.

Pruss, E. A., Snyder, B. S. & Stacy, A. M. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 256–257.

Stalick, J. K., Siedle, A. R., Mighell, A. D. & Hubbard, C. R. (1979). *J. Am. Chem. Soc.* **101**, 2903–2907.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Bis(1,2-benzenediolato)dimethanolgermanium(IV)

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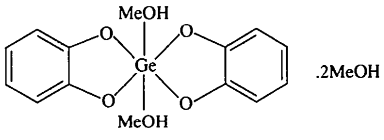
Abstract

$[Ge(C_6H_4O_2)_2(CH_3OH)_2].2CH_3OH$ was prepared from germanium dioxide and catechol in refluxing H_2O followed by refluxing the crude product in methanol; the product was identified by IR, ^1H NMR, ^{13}C NMR and elemental analysis. The complex has a slightly distorted octahedral structure with two methanol ligands in axial positions and two bidentate deprotonated catechols in equatorial positions. The Ge—O bonds involving the methanol groups are longer than the Ge—O bonds involving the catechol ligands.

Comment

Reports concerned with the structures of germanium complexes indicate that the coordination numbers of the central Ge atom are diverse (Yoder & Zukerman, 1967; Sau & Holmes, 1981; Day, Holmes, Sau & Holmes, 1982; Lazraq, Couret, Declercq, Dubourg, Escudie & Riviere-Bandet, 1990; Cereau, Chuit, Corriu & Reye, 1991). Among these, Yoder & Zukerman (1967) reported that the complex $[Ge(C_6H_4O_2)_2(C_5H_5N)_2]$ has an octahedral structure and Sau & Holmes (1981) showed that the complex $[Ge(C_6H_4O_2)_2X]^-$ is square pyramidal. These interesting findings have prompted our investigation of related derivatives with catechol, as a part of a general study of the structures of germanium complexes (Chiang, Lin & Ueng, 1992; Chiang, Wang & Ueng, 1993). Here we report the synthesis and structure of the title compound, (I).



(I)

An *ORTEP* diagram (Johnson, 1965) of the molecular structure is shown in Fig. 1. The complex has a slightly distorted octahedral structure with two methanol molecules in axial positions and two bidentate deprotonated catechol moieties in equatorial positions. The Ge atom lies on a crystallographic inversion centre, as found in $[Ge(H_2O)_2\{OCH(C_6H_5)COO\}_2]$ (Sterling, 1967) and $[Ge(H_2O)_2(OCH_2COO)_2]$ (Chiang, Wang & Ueng, 1993). The 12 *cis* angles around the metal are in the range 89.3 (1)–90.8 (1)° and the dihedral angles between two of the three mutually perpendicular planes are 90.06 (5), 89.25 (5) and 90.50 (5)°. The Ge—O bond lengths for the methanol group are longer than those for the catechol groups owing to the stronger coordination for the aryloxide ligands. The good planarity of the five-membered chelate rings is indicated by the sum of the

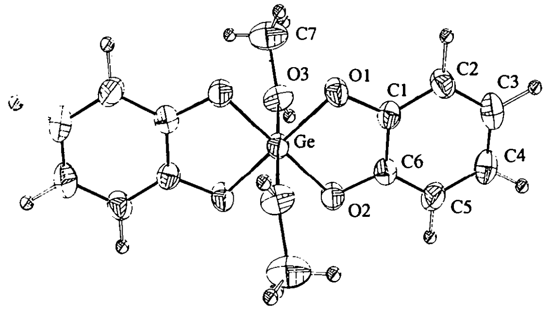


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular structure of $[Ge(C_6H_4O_2)_2(CH_3OH)_2]$. Displacement ellipsoids are shown at the 50% probability level.

five bond angles (539.9°) and the χ^2 value [107.7; χ^2 is defined as $\Sigma\Delta d_i^2/(\sigma x_i^2 + \sigma y_i^2 + \sigma z_i^2)$, where Δd_i^2 is the distance from the least-squares plane and σx_i, σy_i and σz_i are standard deviations of coordinates *x*, *y* and *z*, respectively].

Experimental

The title compound was synthesized as follows. Catechol (1.10 g, 10.0 mmol) was added to an aqueous solution (100 cm^3) of germanium dioxide (0.52 g, 5.0 mmol) and the mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the solid residue, after being washed twice with warm benzene, was refluxed in methanol for 1 h. Then the solvent was removed again and the crude product was recrystallized from methanol. The final product was obtained as colourless plate-like crystals [m.p. 460–461 K (dec.); yield 1.75 g (84%)]. Crystals suitable for X-ray diffraction were prepared from methanol by evaporation. The composition of C, H and Ge found in elemental analysis is 46.67, 5.16 and 18.10%, respectively; $C_{16}H_{24}GeO_8$ requires C 46.09, H 5.76 and Ge 17.41%. The IR spectrum (Jasco 700 spectrophotometer) in the Ge—O stretching region included absorptions at 1246 and 1195 (Ge—OPh), and 667 cm^{-1} (Ge—OCH_3). A solution in CD_3OD showed resonances in the ^1H NMR spectrum (Jeol JNM-EX 400 MHz spectrophotometer, KBr pellet) at δ 6.62–6.79 (8H, *m*, $2C_6H_4$) and 3.38 p.p.m. (6H, *s*, $2OCH_3$), and in the ^{13}C NMR spectrum at δ 150.1, 120.5 and 113.9 ($2C_6H_4$), and 50.6 p.p.m. ($2OCH_3$). Thermogravimetric analysis revealed that 15% of the weight, corresponding to two CH_3OH molecules, is lost at 351 K and 15% of the weight is lost at 438 K, corresponding to another two CH_3OH molecules. These data show that two of the methanol molecules are coordinated to the central Ge atom and are consistent with the observation of the ^1H NMR peak at δ 3.38 p.p.m.

Crystal data

$[Ge(C_6H_4O_2)_2(CH_4O)_2]$.-
$2CH_4O$
$M_r = 416.95$
Orthorhombic
Pbca
$a = 7.5415\ (10)$ Å
$b = 18.3253\ (24)$ Å
$c = 13.382\ (3)$ Å
$V = 1849.4\ (5)$ $Å^3$
$Z = 4$
$D_x = 1.497$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.91–14.2°$
$\mu = 1.67$ mm^{-1}
$T = 298$ K
Plate
0.50 × 0.45 × 0.15 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (*NRCVAX*; Larson *et al.*, 1990)
$T_{min} = 0.802$, $T_{max} = 0.999$
1207 measured reflections
1207 independent reflections

892 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 22.45°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 4%

Refinement

Refinement on *F*
$R = 0.035$
$wR = 0.039$
$S = 2.36$
892 reflections
116 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.25$ e $Å^{-3}$
$\Delta\rho_{min} = -0.35$ e $Å^{-3}$
Extinction correction: secondary
Extinction coefficient: 1.8 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	*y*	*z*	B_{eq}
Ge	0	0	0	2.30 (3)
O(1)	0.1129 (4)	−0.0179 (2)	−0.1203 (2)	2.8 (2)
O(2)	0.0359 (4)	−0.0949 (2)	0.0358 (2)	2.7 (1)
O(3)	0.2320 (4)	0.0259 (2)	0.0621 (3)	3.2 (3)
O(4)	0.3857 (6)	−0.0473 (2)	0.1980 (3)	5.1 (2)
C(1)	0.1741 (6)	−0.0883 (2)	−0.1210 (4)	2.5 (2)
C(2)	0.2726 (7)	−0.1175 (2)	−0.1972 (4)	3.0 (2)
C(3)	0.3282 (7)	−0.1897 (3)	−0.1910 (4)	3.8 (3)
C(4)	0.2847 (7)	−0.2309 (2)	−0.1081 (4)	3.7 (3)
C(5)	0.1854 (7)	−0.2015 (2)	−0.0304 (4)	3.1 (3)
C(6)	0.1302 (6)	−0.1298 (3)	−0.0370 (4)	2.5 (2)
C(7)	0.3482 (8)	0.0818 (3)	0.0277 (4)	4.9 (3)
C(8)	0.3889 (9)	−0.1220 (3)	0.2052 (4)	5.0 (3)

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

O(1*a*), O(2*a*) and O(3*a*) are the centrosymmetric equivalents of O(1), O(2) and O(3), respectively.

Ge—O(1)	1.850 (3)	C(1)—C(2)	1.370 (7)
Ge—O(2)	1.823 (3)	C(1)—C(6)	1.398 (7)
Ge—O(3)	1.994 (3)	C(2)—C(3)	1.391 (7)
O(1)—C(1)	1.370 (5)	C(3)—C(4)	1.381 (8)
O(2)—C(6)	1.366 (6)	C(4)—C(5)	1.391 (7)
O(3)—C(7)	1.425 (6)	C(5)—C(6)	1.380 (6)
O(1)—Ge—O(2)	89.5 (1)	O(1)—C(1)—C(6)	115.3 (4)
O(1)—Ge—O(2)*a*)	90.5 (1)	C(2)—C(1)—C(6)	121.0 (4)
O(1)—Ge—O(3)	90.1 (1)	C(1)—C(2)—C(3)	119.4 (5)
O(1)—Ge—O(3*a*)	90.0 (1)	C(2)—C(3)—C(4)	119.8 (5)
O(2)—Ge—O(3)	89.3 (1)	C(3)—C(4)—C(5)	121.4 (4)
O(2)—Ge—O(3*a*)	90.8 (1)	C(4)—C(5)—C(6)	118.9 (4)
Ge—O(1)—C(1)	109.2 (3)	O(2)—C(6)—C(1)	116.2 (4)
Ge—O(2)—C(6)	109.7 (3)	O(2)—C(6)—C(5)	123.9 (4)
Ge—O(3)—C(7)	125.1 (3)	C(1)—C(6)—C(5)	119.9 (4)
O(1)—C(1)—C(2)	123.8 (4)		

Crystallographic computations were performed using the *NRCVAX* package (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cereau, G., Chuit, C., Corrius, R. J. P. & Reye, C. (1991). *Organometallics*, **10**, 1510–1515.
Chiang, H.-C., Lin, S.-M. & Ueng, C.-H. (1992). *Acta Cryst.* C**48**, 991–993.
Chiang, H.-C., Wang, M.-H. & Ueng, C.-H. (1993). *Acta Cryst.* C**49**, 244–246.
Day, R. O., Holmes, J. M., Sau, A. C. & Holmes, R. R. (1982). *Inorg. Chem.* **21**, 281–286.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Larson, A. C., Lee, F. L., Le Page, Y., Webster, M., Charland, J.-P. & Gabe, E. J. (1990). *NRCVAX Crystal Structure System*. Chemistry Division, NRC, Ottawa, Canada.
Lazraq, Z. M., Couret, C., Declercq, J.-P., Dubourg, A., Escudie, J. & Reviere-Bandet, M. (1990). *Organometallics*, **9**, 845–848.
Sau, A. C. & Holmes, R. R. (1981). *Inorg. Chem.* **20**, 4129–4135.
Sterling, C. (1967). *J. Inorg. Nucl. Chem.* **29**, 1211–1215.
Yoder, C. M. S. & Zukerman, J. J. (1967). *Inorg. Chem.* **6**, 163–164.

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The Intercalation Compound 1,4-Benzenediammonium Tetrachlorocadmate(II)

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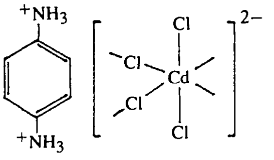
Abstract

Crystals of 1,4-benzenediammonium tetrachlorocadmate(II), $(C_6H_{10}N_2)[CdCl_4]$, contain two-dimensional anionic sheets in which each $CdCl_6$ octahedron shares four corners with adjacent octahedra {*i.e. catena*-poly[1,4-benzenediammonium dichlorocadmium-di-μ-chloro(2−)]}. Layers of organic diammonium cations are intercalated between the metal–halogen sheets.

Comment

Chemists have become increasingly involved in the synthesis and characterization of various low-dimensional solid-state chain or layer compounds because of their unusual physical properties, *e.g.* superconductivity. About twenty years ago many layer perovskites of general formulae $(C_nH_{2n+1}NH_3)_2MCl_4$ and $(NH_3C_nH_{2n}NH_3)MCl_4$ (M = Cd, Cu, Fe, Mn, Pt, Pd) were investigated in view of their interesting thermal and magnetic properties (Arend & Huber, 1978; Needham & Willett, 1984). The structures of these compounds are very similar to those of Langmuir–Blodgett films. In this paper, we report the crystal structure of such a compound, (I).



(I)

From Fig. 1 it can be seen that the title compound consists of two basic species: the $CdCl_6$ polyhedron and the *p*-phenylene cation. In the $CdCl_6$ layers (Fig. 2*a*), each Cd atom occupies the centre of a distorted but exactly centrosymmetric octahedron formed by four symmetry-related and almost coplanar Cl(1) atoms linking adjacent octahedra plus two axial Cl(2) ligands. In the $CdCl_6$ layers the bridging Cd—Cl(1)—Cd bond angles are 153.61 (4)°; the Cd atoms of the four closest octahedra and their associated bridging Cl^- ions form a pseudo-tetragonal arrangement which extends in two dimensions to form the $CdCl_4$ sheet (Fig. 2*b*). The axial Cl(2) ligands protrude above and below the sheets. *p*-Phenylene diammonium cations are trapped between two adjacent $CdCl_6$ layers and lie in the cavities formed by eight $CdCl_6$ octahedra (four octahedra form the base and four form the top of the cavity). The axial Cl(2) ligands protrude from the $CdCl_4$ sheets and thereby hinder the diffusion of the *p*-phenylene cations out of the cavities.

As can be seen from Fig. 2(*b*), in each *p*-phenylenediammonium layer adjacent aromatic rings are almost exactly normal to one another (dihedral angle 88.2°).

The structure of this layer perovskite is stabilized by N—H···Cl hydrogen bonds from both ends of the *p*-phenylenediammonium cations, which hold adjacent $CdCl_6$ layers together. They are arranged so that one hydrogen bond [N—H···Cl(1) 3.254 (6) Å] involves the corner-sharing Cl(1) atom whereas the other two from each —NH_3 group [N—H···Cl(2) 3.155 (6) and 3.210 (5) Å] are directed towards the axial Cl atoms of the $CdCl_6$ octahedra.

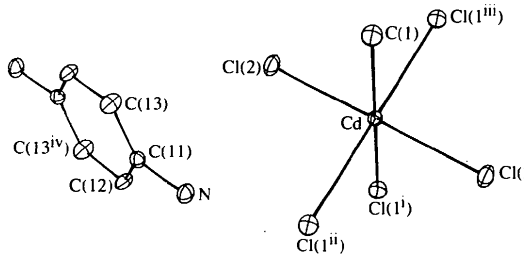


Fig. 1. The numbering of the atoms of the title compound with 30% probability displacement ellipsoids. H atoms are omitted for clarity.

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