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## Synthesis and Structure of Dihydroxo( $\eta^3$ -2,2'-iminodiethoxo)germanium(IV)

BY HUNG-CHEH CHIANG,\* SU-MI LIN AND CHUEN-HER UENG\*

*Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan*

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**Abstract.**  $[\text{Ge}(\text{OH})_2\{\text{HN}(\text{CH}_2\text{CH}_2\text{O})_2\}]$  was prepared from germanium dioxide and 2,2'-iminodiethanol in refluxed  $\text{H}_2\text{O}$  and identified with IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, elemental analysis, and X-ray single-crystal structure determination.  $\text{C}_4\text{H}_{11}\text{GeNO}_4$ ,  $M_r = 209.6$ , monoclinic,  $P2_1/n$ ,  $a = 5.161$  (2),  $b = 12.251$  (4),  $c = 11.266$  (3) Å,  $\beta = 94.87$  (2)°,  $V = 709.8$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.96$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7093$  Å,  $\mu = 4.21$  mm<sup>-1</sup>,  $F(000) = 424$ ,  $T = 298$  K,  $R = 0.039$  for 1096 observed reflections. The title compound has a trigonal bipyramidal structure with the N atom of the tridentate ligand and one of the hydroxo groups in the axial position. The two Ge—O bond lengths for 2,2'-iminodiethoxide are similar, but are significantly different for the two hydroxo groups.

**Introduction.** Germanium complexes are attracting particular interest because of their specific biological activity (Brutkiewicz & Suzuki, 1987). It is also important to examine the expansion of the valence shell of the metal in these compounds beyond the limits permitted by the filled-octet rule. Reports about the structures of germanium complexes reveal that the coordination numbers of the metal are diverse (Breliere, Carre, Corriu & Royo, 1988; Day, Holmes, Sau & Holmes, 1982; Gurkova, Gusev, Sharapov, Alekseev, Gar & Chromova, 1984; Lazraq, Couret, Declercq, Dubourg, Escudie & Riviere-Bandet, 1990; Mizuta, Yoshida & Miyoshi, 1989). Among them, Gurkova *et al.* (1984) reported that the derivative for the triethanolamine has a trigonal bipyramidal structure. The main purpose of this paper is to try to synthesize the title compound from  $\text{GeO}_2$  and diethanolamine and to determine the crystal structure.

**Experimental.** The title compound was prepared as follows: germanium dioxide (0.52 g, 5.0 mmol) was added to an aqueous solution (100 cm<sup>3</sup>) of diethanolamine (2,2'-iminodiethanol) (1.05 g, 10.0 mmol) and the mixture refluxed for 2 h. After removal of the solvent, the crude product was recrystallized from methanol. The final products were colorless needle crystals, m.p. 458 K (dec.); yield 0.902 g (86%) (elemental analysis found: C, 22.54; H, 5.21; N, 6.56; Ge, 34.60%,  $\text{C}_4\text{H}_{11}\text{GeNO}_4$  requires: C, 22.90; H, 5.24; N, 6.68; Ge, 34.61%);  $\nu_{\text{max}}$  at 934 (s) and 821 (s) cm<sup>-1</sup> (Ge—OC), 685 (s) cm<sup>-1</sup> (Ge—N);  $\delta_{\text{H}}$  ( $\text{D}_2\text{O}$ ) 2.95 (4H, t, 2NCH<sub>2</sub>) and 3.77 (4H, t, 2OCH<sub>2</sub>);  $\delta_{\text{C}}$  ( $\text{D}_2\text{O}$ ) 51.8 (2NCH<sub>2</sub>) and 60.8 (2OCH<sub>2</sub>). A crystal, prepared from methanol by evaporation, had dimensions 0.30 × 0.30 × 0.50 mm. CAD-4 diffractometer. Unit cell: 25 reflections,  $2\theta$  range 18.64 to 26.42°.  $\theta/2\theta$  mode with  $\theta$  scan width =  $(0.80 + 0.35\tan\theta)$ °. Mo  $K\alpha$  radiation. Three standard reflections were monitored every 1 h: variation in  $I < 2.0\%$ . 1383 reflections measured ( $2.0 < 2\theta < 50.0^\circ$ ,  $h, k, l: -6$  to 6, 0 to 14, 0 to 13, respectively), giving 1244 unique reflections and 1096 observed with  $I > 2.0\sigma(I)$ . Absorption correction was made according to experimental  $\psi$  rotation (Enraf–Nonius, 1979) (maximum/minimum transmission factors = 0.644/0.982). Structure solved by heavy-atom method. Positions of H atoms were found in a difference Fourier map and were included in the structure factor calculation but not refined. The last least-squares cycle was calculated with 21 atoms, 92 parameters with anisotropic temperature factors for non-H atoms, and 1096 reflections.  $(\Delta/\sigma)_{\text{max}} = 0.001$ . Weighting scheme,  $w = 1/\sigma^2(F_o)$ , with  $\sigma(F_o)$  from counting statistics. Quantity minimized  $\sum w(KF_o - F_c)^2$ . Final  $R$ ,  $wR$  and  $S$  were 0.039, 0.046 and 2.96, respectively. Peaks in the final  $\Delta F$  map were 1.10 to

\* To whom correspondence should be addressed.

– 1.39 e Å<sup>-3</sup>. Secondary-extinction coefficient 1.1 (1) (length in μm) (Gabe & Lee, 1981). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computing programs: NRC SDP VAX package (Gabe & Lee, 1981). ORTEP from the Enraf-Nonius (1979) *Structure Determination Package*.

**Discussion.** There are two characteristic regions of the IR spectrum of the title compound,  $\nu_{\max}$  at 934 and 821 cm<sup>-1</sup> for the asymmetric and symmetric stretching of Ge—OC and 685 cm<sup>-1</sup> for the stretching of Ge—N. The chemical shifts of the <sup>1</sup>H NMR spectrum for the NCH<sub>2</sub> and OCH<sub>2</sub> ( $\delta = 2.95$  and 3.77) are further downfield than those of the free ligand (2,2'-iminodiethanol) by 0.38 and 0.25 p.p.m., which may result from the effect of the coordination. Thermal gravimetric analysis reveals that 8.6% of the weight, corresponding to one H<sub>2</sub>O molecule, is lost at 478 K. This phenomenon is consistent with the observation that the hydrolysis of diorganogermanes produces the oxide of general formula (R<sub>2</sub>GeO)<sub>n</sub> (Lesbre, Mazerolles & Satge, 1971).

Atomic positional parameters and selected bond lengths and bond angles of the title compound are listed in Tables 1 and 2 respectively. The molecular structure is shown in Fig. 1.\*

The molecule consists of a central Ge atom bonded to one N and two O atoms of the tridentate ligand and two hydroxo groups. The coordination around the metal is a slightly distorted trigonal bipyramid with O(1), O(2) and O(4) equatorial, and N and O(3) at apices, the three equatorial bond angles being 117.9 (2), 119.1 (2) and 120.2 (2)°, the axial bond angle being 177.9 (3)°. The distance between Ge and the equatorial plane is 0.172 (2) Å. Distortion from the ideal trigonal bipyramidal geometry is largely a result of the formation of the two fused chelate rings formed by the tridentate ligand and the difference between Ge—N and Ge—O (axial) bonds.

The Ge—N length of the title compound [2.134 (4) Å] which is on the short side of the range for Ge complexes (2.09–2.44 Å) (Gurkova *et al.*, 1984) may be the consequence of the strong electron-acceptor effect for the hydroxide group. The equatorial Ge—O(4)H length being significantly shorter than the other two Ge—O lengths [1.762 (4) vs 1.791 (4) and 1.797 (3) Å] may be attributed to the difference between the nature of the hydroxide and

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B <sub>eq</sub>
Ge	0.00293 (9)	0.14709 (4)	0.15760 (5)	1.42 (3)
N	-0.2573 (8)	0.2551 (3)	0.2346 (4)	1.8 (2)
O(1)	0.1873 (7)	0.2690 (3)	0.1369 (3)	2.0 (2)
O(2)	0.0305 (7)	0.0852 (3)	0.3021 (3)	2.4 (2)
O(3)	0.2311 (6)	0.0566 (3)	0.0972 (3)	2.4 (2)
O(4)	-0.2650 (7)	0.1140 (3)	0.0566 (3)	2.2 (2)
C(1)	-0.089 (1)	0.1377 (5)	0.3943 (5)	3.2 (3)
C(2)	-0.322 (1)	0.1995 (5)	0.3463 (5)	3.1 (3)
C(3)	-0.116 (1)	0.3585 (4)	0.2543 (6)	3.1 (3)
C(4)	0.060 (1)	0.3696 (4)	0.1561 (6)	3.3 (3)

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

Ge—N	2.123 (4)	N—C(2)	1.493 (7)
Ge—O(1)	1.797 (3)	N—C(3)	1.469 (7)
Ge—O(2)	1.791 (4)	O(1)—C(4)	1.423 (7)
Ge—O(3)	1.793 (3)	O(2)—C(1)	1.406 (7)
Ge—O(4)	1.762 (4)	C(1)—C(2)	1.484 (9)
		C(3)—C(4)	1.495 (9)
N—Ge—O(1)	84.0 (2)	Ge—N—C(2)	104.7 (3)
N—Ge—O(2)	84.1 (2)	Ge—N—C(3)	106.0 (3)
N—Ge—O(3)	177.9 (2)	C(2)—N—C(3)	114.2 (5)
N—Ge—O(4)	85.3 (2)	Ge—O(1)—C(4)	116.3 (3)
O(1)—Ge—O(2)	117.9 (2)	Ge—O(2)—C(1)	118.1 (3)
O(1)—Ge—O(3)	95.3 (2)	O(2)—C(1)—C(2)	110.9 (5)
O(1)—Ge—O(4)	120.2 (2)	N—C(2)—C(1)	107.9 (4)
O(2)—Ge—O(3)	94.5 (2)	N—C(3)—C(4)	106.9 (4)
O(2)—Ge—O(4)	119.1 (2)	O(1)—C(4)—C(3)	110.6 (5)
O(3)—Ge—O(4)	96.8 (2)		

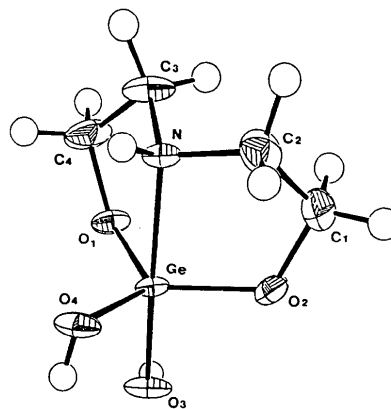


Fig. 1. Molecular structure of dihydroxo(η<sup>3</sup>-2,2'-iminodiethoxy)germanium(IV).

the alkoxide ligands. That the axial Ge—O(3)H length is longer than that of the equatorial one may be a result of the greater steric hindrance for the axial hydroxide (three 90° electron-pair repulsions vs two).

The lengths of the C—O, C—C and C—N bonds are all reasonable and there is no intermolecular contact of structural significance in the title compound.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54778 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0538]

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## Structure of *cis*-Diaquabis(hexafluoroacetylacetonato)nickel(II)

BY RICHARD R. ROMERO, FRANCISCO CERVANTES-LEE AND LEIGH CHRISTOPHER PORTER\*

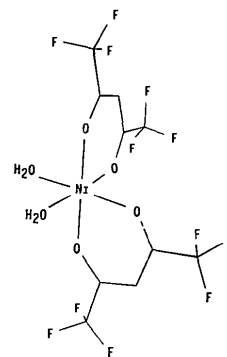
*Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, USA*

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**Abstract.**  $C_{10}H_6F_{12}NiO_6$ ,  $M_r = 508.9$ , monoclinic,  $C2/c$ ,  $a = 21.195$  (5),  $b = 8.247$  (2),  $c = 9.741$  (2) Å,  $\beta = 95.91$  (2)°,  $V = 1693.6$  (7) Å<sup>3</sup>,  $D_x = 1.996$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu = 1.298$  mm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $F(000) = 1000$ ,  $T = 298$  K,  $R = 0.0369$  and  $wR = 0.0645$  for 157 variable parameters ( $S = 0.59$ ) and 1112 reflections with  $F > 0\sigma(F)$ . The Ni atom possesses an octahedral geometry and forms bonds to the O atoms of two chelating  $F_6\text{acac}$  ligands that occupy both axial and equatorial positions [Ni—O(1) 2.026 (3) Å; Ni—O(2) 2.027 (2) Å]. The two molecules of water are coordinated in a *cis* configuration [Ni—O(3) 2.054 (3) Å] and the structure possesses  $C_2$  point group symmetry.

**Introduction.** The ability of the fluorinated derivatives of acetylacetonone to form stable chelating bis adducts with many of the transition-metal elements is well established (Joshi & Pathak, 1977). In most instances stable monomeric adducts containing equatorial acac ligands are obtained. Notable exceptions include the anhydrous bis(acetylacetonato)  $Co^{II}$ ,  $Ni^{II}$  and  $Zn^{II}$  complexes which possess oligomeric structures with bridging acac groups. The structures of the *trans*-diaquabis(acetylacetonato) complexes of both  $Co^{II}$  and  $Ni^{II}$  have been previously described (Bullen, 1959; Montgomery & Lingafelter, 1964) and the preparation of *trans*- $Ni(F_6\text{acac})_2(H_2O)_2$  has been

reported (Pecsock, Reynolds, Fackler, Lin & Pradilla-Sorzano, 1974). In this paper we describe the crystal structure of the previously unreported *cis*- $Ni(F_6\text{acac})_2(H_2O)_2$  isomer.



**Experimental.** Crystals of the title compound were obtained in good yield following the crystallization of a product obtained by reacting one equivalent of the di(*tert*-butyl) nitroxyl free radical with one equivalent of anhydrous bis( $F_6\text{acac}$ ) $Ni^{II}$ . Crystallization from a toluene/petroleum ether solution led to the formation of numerous well formed, multifaceted, green crystals with a trigonal prismatic habit. A regularly shaped crystal of approximate dimensions  $0.30 \times 0.40 \times 0.60$  mm was mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry suggested on the basis of inter-

\* To whom correspondence should be addressed.