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Synthesis and Structure of Diaquabis(glycolato-*O*,*O*′)germanium(IV)

BY HUNG-CHEH CHIANG,* MEI-HUEY WANG AND CHUEN-HER UENG*

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

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Abstract. Diaquabis(oxoacetato-*O*,*O*′)germanium-(IV), $[Ge(C_2H_2O_3)_2(H_2O)_2]$, was prepared from germanium dioxide and glycolic acid in refluxed H_2O and identified with IR, ^1H NMR, ^{13}C NMR, mass spectrum, elemental analysis, and X-ray single-crystal structure determination. $C_4H_8GeO_8$, M_r = 256.7, monoclinic, $P2_1/n$, a = 4.862 (2), b = 5.952 (2), c = 13.448 (4) Å, β = 95.91 (2)°, V = 387.1 (2) Å^3, Z = 2, D_x = 2.20 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 3.92 mm^{-1}, $F(000)$ = 256, T = 298 K, R = 0.030 for 462 observed reflections. The title compound has a distorted octahedral structure with two aqua groups on the axial position and two bidentate glycolate groups on the equatorial position. The Ge—O bond lengths for the aqua groups are longer than those for the anion ligands.

Introduction. The adduct of germanium dioxide and glycolic acid was first published by Clark (1959) and its approximate composition ratio, Ge–glycolic acid 1:3, was identified mainly by conductimetric, polarimetric and pH measurement. Subsequently, Mikanova & Bartusek (1981) studied the less-stable mononuclear 1:3 chelates of Ge formed by the reaction of Ge^{IV} with glycolic acid in dilute aqueous solution with potentiometric titration. Because Ge complexes are attracting particular interest in their specific biological activity (Brutkiewicz & Suzuki, 1987) and it is important to elucidate the reaction between germanium dioxide and glycolic acid in aqueous solution, the title compound has been synthesized and the crystal structure determination has been undertaken (Chiang, Lin & Ueng, 1992).

* To whom correspondence should be addressed.

Experimental. The IR spectrum was recorded using a potassium bromide pellet and a Jasco Model 700 spectrophotometer. The NMR spectrum was recorded in D_2O solution on a Jeol JNM-EX 400 MHz spectrophotometer. The mass spectrum was obtained using the electron-impact method on a Jeol JMS-D300 instrument. Microanalysis was performed by the National Science Council, Taipei, Taiwan. The title compound was prepared by adding germanium dioxide (0.52 g, 5.0 mmol) to an aqueous solution (100 cm^3) of glycolic acid (1.52 g, 20.0 mmol) and refluxing the acidic mixture (pH = 1.5) for 4 h. After reducing to about 5 ml, the solution was allowed to stand for 2 d, which yielded colourless square crystals which were filtered, washed with water and dried; m.p. 439–440 K (dec); yield 1.08 g (85%). Analysis found: C 18.69, H 2.93%. Analysis calculated for $C_4H_8GeO_8$: C 18.69, H 3.11%. IR ν_{max}: 1678*s* (C=O), 1084*s* and 930*m* (Ge—OC), and 561*m* cm^{-1} (Ge—OH_2). ^1H NMR δ_H (D_2O): 4.22. (2H, *s*, CH_2). ^{13}C NMR δ_C (D_2O): 62.8 (CH_2) and 179.8. (C=O). Mass spectrum *m*/*Z*: 222 ($M - 2H_2O$) and 106 ($M - 2H_2O - 2CH_2CO_2$).

A crystal suitable for X-ray diffraction (CAD-4 diffractometer) was prepared from H_2O by evaporation and had dimensions 0.25 × 0.30 × 0.40 mm. The unit cell was determined using 24 reflections with 2θ 18.76–29.08°. $\theta/2\theta$ scans, with θ scan width of (1.00 + 0.35tanθ)°, and Mo $K\alpha$ radiation were used for data collection. Three standard reflections were monitored every hour and showed variation on I < 2.0%. 507 unique reflections were measured (2.0 < 2θ < 44.9°; h − 5 to 5, k 0 to 6, l 0 to 14; R_{int} = 0.008) of which 462 were observed with $I > 2.0\sigma(I)$. Absorption corrections were made according to

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experimental ψ rotation (maximum and minimum transmission factors 0.604 and 0.999). The structure was solved by the heavy-atom method. Positions of H atoms were found in difference Fourier maps and were included in the structure-factor calculation but not refined. The last least-squares cycle was calculated with 11 atoms, 62 parameters, with anisotropic temperature factors for non-H atoms, and 462 reflections. $(\Delta/\sigma)_{max} = 0.03$. Weighting scheme $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics. The quantity minimized was $\sum w(KF_o - F_c)^2$, giving final $R = 0.030$, $wR = 0.034$ and $S = 1.87$. Peaks in final ΔF map were at 0.48 to -0.37 e Å^{-3}. Secondary-extinction coefficient was 0.24 (3) (length in μm). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computtations were performed using the NRCVAX package (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990) and *ORTEP* (Johnson, 1965) from the Enraf–Nonius (1979) *Structure Determination Package.*

Discussion. There are three characteristic regions of the IR spectrum of the title compound: ν_{max} at 1678 cm^{-1} for the C=O stretching, 1084 and 930 cm^{-1} for the asymmetric and symmetric stretching of Ge—OC and 561 cm^{-1} for the stretching of Ge—OH_2. Thermal gravimetric analysis reveals that 14.0% of weight is lost at 444 K and 59.2% of weight is lost at 621.5 K, corresponding to two H_2O and two CH_2O_2 species, respectively. This data coincides with the mass spectrum data in which there is a fragment at 222 (m/Z), $M - 2H_2O$, and at 106, $M - 2H_2O - 2CH_2CO_2$.

Atomic positional parameters, and selected bond lengths and 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 two glycolate ions, each having the O atom of the alkoxide and one of the O atoms of the carboxylate as donors, and two aqua groups. The coordination around the metal is a slightly distorted octahedron with O atoms of the two bidentate ligands equatorial, and two aqua groups at apices. Owing to an inversion centre at the central Ge atom, the title compound has a typical *trans* structure with the same type of bonding atoms being opposite to each other; the three bond angles of the three mutually perpendicular axes of the octahedron are all 180°. The 12 *cis* angles around the central atom [89.1 (2)–90.9 (2)°] are near those of an ideal octahedron, and the distance between Ge and the equatorial plane is 0.00 Å. Distortion from the ideal octahedral geometry results only from the non-equal bond lengths for the three types of Ge—O bond. From the order of these lengths [Ge—O(4) 1.949 (4), Ge—O(2) 1.866 (4) and Ge—O(1) 1.817 (4) Å], it is obvious that the bond strength for the alkoxide is greater than that for the carboxylate which is in turn greater than that for the aqua group. That the coordination sites of the glycolate bonded to the central Ge atom are the O atom of the alkoxide and one of the O atoms of the carboxylate rather than the two O atoms of the carboxylate, may be attributed to the fact that the complex containing a five-membered ring is more stable than that containing a four-membered ring. The lengths of the C—O bonds, C—C bonds and the C=O bonds and the angles within the five-membered rings are all reasonable. As a whole, the crystalline structure of the title compound is similar to that of germanomandelic acid (Sterling, 1967).

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2)

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

	x	y	z	B_{eq}
Ge	0	½	0	1.32 (3)
O(1)	−0.2162 (7)	0.4836 (7)	0.1022 (3)	1.6 (2)
O(2)	0.1550 (7)	0.7644 (6)	0.0554 (3)	1.6 (1)
O(3)	0.1127 (8)	0.9945 (7)	0.1823 (3)	2.2 (2)
O(4)	0.2871 (7)	0.3239 (7)	0.0761 (3)	2.0 (2)
C(1)	−0.180 (1)	0.674 (1)	0.1654 (4)	2.0 (2)
C(2)	0.045 (1)	0.827 (1)	0.1348 (4)	1.5 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ge—O(1)	1.817 (4)	O(1)—C(1)	1.416 (7)
Ge—O(2)	1.866 (4)	C(1)—C(2)	1.513 (8)
Ge—O(4)	1.949 (1)	C(2)—O(2)	1.298 (7)
		C(2)—O(3)	1.211 (7)
O(1)—Ge—O(1)*	180.0	Ge—O(1)—C(1)	111.4 (3)
O(1)—Ge—O(2)*	89.1 (2)	Ge—O(2)—C(2)	112.7 (3)
O(1)—Ge—O(2)*	90.9 (2)	O(1)—C(1)—C(2)	111.5 (5)
O(1)—Ge—O(4)	90.7 (2)	O(2)—C(2)—C(1)	115.0 (5)
O(1)—Ge—O(4)*	89.3 (2)	O(2)—C(2)—O(3)	123.9 (5)
O(2)—Ge—O(2)*	180.0	C(1)—C(2)—O(3)	121.2 (5)
O(2)—Ge—O(4)	90.4 (2)		
O(2)—Ge—O(4)*	89.6 (2)		
O(4)—Ge—O(4)*	180.0		

* Centrosymmetrically equivalent atom in the same molecule.

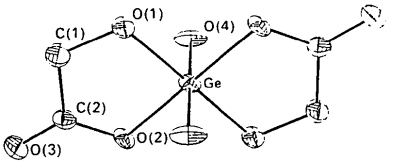

Fig. 1. Molecular structure of the title compound.

* 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 55494 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1003]

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Structure of (+)-(5*R*,6*R*)-5-Chloro-6-methoxy-5,6-dihydro-1-(2′,3′-didehydro-2′,3′-dideoxy-β-D-*glycero*-2-enopentofuranosyl)thymine

BY HELEN BLANCHARD AND MICHAEL N. G. JAMES

Medical Research Council of Canada Group in Protein Structure and Function, Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2H7

AND RAKESH KUMAR, LEONARD I. WIEBE AND EDWARD E. KNAUS

Faculty of Pharmacy and Pharmaceutical Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2N8

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Abstract. $C_{11}H_{15}ClN_2O_5$, $M_r = 290.70$, m.p. 411–412 K, $[\alpha]_D$ (296 K) = 75.44° (c = 0.42% in MeOH), monoclinic, $P2_1$, $a = 9.901$ (5), $b = 12.659$ (10), $c = 10.998$ (5) Å, $\beta = 100.06$ (5)°, $V = 1357.23$ (9) Å^3, $Z = 4$, $D_x = 1.42$ g cm^{-3}, Cu $K\alpha_1$ radiation (Ni filtered), $\lambda = 1.5405$ Å, $\mu = 26.99$ cm^{-1}, $F(000) = 608$, $T = 293$ K, $R = 0.046$, GOF = 2.02, for 1612 unique observed reflections. Two molecules are present in the asymmetric unit. Conformational differences are exemplified by χ values of −154.4 (5) and −124.2 (6)° for molecules A and B, respectively; and further by the exocyclic C(4′)—C(5′) torsion angles γ (molecule A) = 62.2 (7)° and γ (molecule B) = 49.5 (9)°. This analysis establishes the absolute configuration of the two asymmetric C atoms of the derivatized pyrimidine ring as 5*R*,6*R*.

Introduction. Acquired immunodeficiency syndrome (AIDS) is a degenerative disease of the immune and central nervous systems for which there is no known cure. The pyrimidine analogue 2′,3′-didehydro-2′,3′-dideoxythymidine has demonstrated activity against the causative agent, human immunodeficiency virus type-1 (HIV-1) in some patients with AIDS and AIDS-related complex (ARC) during phase 1 clinical trials (Lin, Schinazi & Prusoff, 1987; Mansuri, Starrett, Ghazzouli, Hitchcock, Sterzychi, Brankovan, Lin, August, Prusoff, Sommadossi & Martin, 1989). HIV in the central nervous system (CNS) may replicate more actively than in other tissues, and the CNS may serve as a principal reservoir of the virus in the whole body (Gartner, Markovits, Markovits, Kaplan, Gallo & Popovic, 1986; Koenig, Gendelman, Orenstein, Dal Canto, Pezeshkpour, Yungbluth, Janotta, Aksamit, Martin & Fauci, 1986; Watkins, Dorn, Kelly, Armstrong, Potts, Michaels, Kufta & Dubois-Dalcq, 1990). Thus, the ability of antiretroviral agents to penetrate the CNS may constitute an important feature for treatment of HIV infection. 5-Halo-6-methoxy-5,6-dihydro-1-(2′,3′-didehydro-2′,3′-dideoxy-β-D-*glycero*-2-enopentofuranosyl)thymines could serve as a new class of lipophilic masked prodrugs to 1-(2′,3′-didehydro-2′,3′-dideoxy-β-D-*glycero*-2-enopentofuranosyl)thymines (Duschinsky, Gabriel, Tautz, Nussbaum, Hoffer, Grunberg, Burchenal & Fox, 1967).

We now describe the X-ray analysis of (+)-5-chloro-6-methoxy-5,6-dihydro-1-(2′,3′-didehydro-2′,3′-dideoxy-β-D-*glycero*-2-enopentofuranosyl)thymine that may penetrate the CNS more effectively, for which the absolute configuration of the substituents in the derivatized pyrimidine ring were unknown.

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