The Crystal Structure of Potassium Trioxalatogermanate(IV) Monohydrate

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Two independent tris-chelate anions are present in $K_2[Ge(C_2O_4)_3]\cdot H_2O$ with crystallographic symmetry C_2 and approximate symmetry D_3. The Ge–O bond lengths and chelate O–Ge–O angles are all close to their average values of 1.882 Å and 85.6°, respectively. Potassium ions in irregular eight-fold co-ordination link the anions in three dimensions (K–O 2.72—3.04 Å). The crystals are monoclinic, space group $C2/c$, a = 9.918(8), b = 17.53(1), c = 15.41(1) Å, β = 104.2(1)°, Z = 8, and R = 0.068 for 1 555 film data (Cu radiation).

THE structures of a number of salts of trioxalato- complexes of trivalent cations [1-3] and of the complexes $[Zr(C_2O_4)_4]^{4-}$ and $[Sn_2(C_2O_4)_7]^{6-}$ which contain tetravalent central cations [4,5] have previously been determined by X-ray diffraction. However, none of the complexes $[M(C_2O_4)_3]^{2-}$ (M = Si^{IV},[6] Ge^{IV},[6,7] Sn^{IV},[6] and Ti^{IV} [6]) appears to have been the subject of an X-ray study. For this reason, and because relatively little work has been done on chelate complexes of germanium(IV), we have determined the structure of the title compound, $K_2[Ge(C_2O_4)_3]\cdot H_2O$.

EXPERIMENTAL

The complex salt was prepared by the method of Arvedson and Larsen,[7] but was recrystallised by allowing its half-saturated aqueous solution to stand at room temperature in contact with ethanol vapour.

Crystal Data.—$C_6H_2GeK_2O_{13}$, M = 432.9, Monoclinic, a = 9.918(8), b = 17.53(1), c = 15.41(1) Å, β = 104.2(1)°, U = 2 598 Å^3, D_m = 2.20, Z = 8, D_c = 2.21 g cm^{-3}, F(000) = 1 696; Cu-K_α radiation (λ = 1.541 8 Å), μ(Cu-K_α) = 94.8 cm^{-1}. Space group Cc or $C2/c$ from systematic absences, $C2/c$ from structural analysis.

There are discrepancies between these cell dimensions and those reported by Arvedson and Larsen [7] (a = 9.89, b = 17.56, c = 14.95 Å, β = 68°, no space group) which cannot be reconciled by an alternative choice of the c axis. Moreover they reported Z = 6 (whence D_c = 2.02 g cm^{-3}) and D_m = 1.79 g cm^{-3}. Nevertheless our structural determination agrees with the results of their elemental analyses.

The colourless tablet-form crystals appeared to be stable in air but were given a thin coat of cement as a precaution before data were collected. Equi-inclination multi-film Weissenberg photographs of the levels 0—8kl, h0—2l, and hk0—3 were scanned by the S.R.C. Microdensitometer Service, Daresbury Laboratory; 1 555 unique reflections were above background. Absorption corrections were applied during data reduction, based on the distances of indexed bounding faces of the crystal from a common interior point. The ' SHELX '76 ' program [8] was used in these and in all subsequent calculations. The structure was solved in the centrosymmetric space group $C2/c$. A Patterson synthesis did not indicate the positions of the germanium and potassium atoms unambiguously, but these were located by means of the direct-methods TANG routine. The carbon and oxygen atoms were located in subsequent Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at R 0.068 (200 parameters; unit weights for all reflections). A final difference synthesis showed that no water molecules had been overlooked and confirmed the absence of ethanol. Tables of structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22823 (11 pp.).*

RESULTS AND DISCUSSION

Atomic co-ordinates are given in Table 1, and derived distances and angles in Table 2. The crystal structure reveals no surprises. There are two independent tris-chelate complexes (no ' dangling ' ligands), each on a crystal diad axis (Figure). The germanium atoms of adjacent complexes on the same diad axis are separated by 5.2 Å; these complexes differ in orientation about the axis so that outer oxygen atoms avoid one another. The Ge–O bond lengths (1.866—1.892, average 1.882 Å) are close to those in the GeO_6 groups of tetragonal GeO_2 (average 1.88 Å) [9] and to the predicted value of 1.88 Å based on the covalent radii tabulated by Alcock.[10] The C–C and C–O bond lengths are normal. The chelate O–Ge–O angles are all close to 85.6°, the other O–Ge–O angles ranging from 88.0 to 96.9°. The four independent chelate rings are all slightly puckered

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Ge(1)	5 000	1 415(1)	2 500
Ge(2)	5 000	4 388(1)	2 500
K(1)	533(2)	2 799(1)	3 860(2)
K(2)	1 645(3)	882(2)	377(2)
O(1)	4 198(8)	5 178(4)	3 035(5)
O(2)	4 394(9)	6 430(4)	3 246(6)
O(3)	3 932(8)	3 669(4)	2 959(5)
O(4)	1 945(8)	3 011(4)	2 536(6)
O(5)	3 591(8)	4 326(4)	1 438(5)
O(6)	1 600(8)	3 717(5)	853(6)
O(7)	4 083(7)	625(4)	1 755(5)
O(8)	4 044(11)	−652(5)	1 664(7)
O(9)	6 465(8)	1 422(4)	1 915(5)
O(10)	6 954(9)	1 867(5)	670(6)
O(11)	4 140(9)	2 129(5)	1 643(5)
O(12)	4 430(10)	2 684(5)	383(6)
C(1)	4 604(11)	5 861(6)	2 685(7)
C(2)	2 774(11)	3 462(6)	2 385(8)
C(3)	2 590(11)	3 848(6)	1 480(8)
C(4)	4 461(12)	−57(6)	2 040(8)
C(5)	6 227(13)	1 810(7)	1 209(9)
C(6)	4 817(12)	2 271(6)	1 022(8)
Aq(1)	3 744(10)	4 261(6)	4 861(7)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2

Bond distances and angles with estimated standard deviations in parentheses

(*a*) Interatomic distances/Å

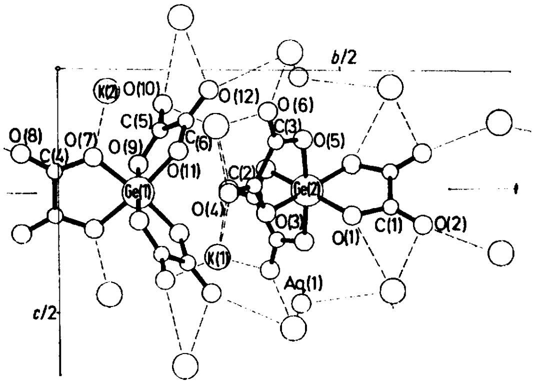
Ge(1)–O(7)	1.885(7)	C(5)–C(6)	1.580(17)
Ge(1)–O(9)	1.888(8)	C(6)–O(11)	1.320(16)
Ge(1)–O(11)	1.866(8)	C(6)–O(12)	1.207(14)
Ge(2)–O(1)	1.885(8)	K(1)–O(2^{II})	2.722(9)
Ge(2)–O(3)	1.892(8)	K(1)–O(4)	2.768(10)
Ge(2)–O(5)	1.877(7)	K(1)–O(4^{III})	2.865(10)
C(1)–O(1)	1.310(13)	K(1)–O(6^{III})	2.779(9)
C(1)–O(2)	1.202(14)	K(1)–O(8^{IV})	2.893(10)
C(1)–C(1^{I})	1.521(25)	K(1)–O(10^{I})	2.919(10)
C(2)–O(3)	1.317(12)	K(1)–O(10^{V})	2.861(9)
C(2)–O(4)	1.204(14)	K(1)–O(12^{V})	2.948(10)
C(2)–C(3)	1.521(16)	K(2)–O(1^{VI})	3.037(10)
C(3)–O(5)	1.312(14)	K(2)–O(2^{VI})	2.751(8)
C(3)–O(6)	1.219(13)	K(2)–O(5^{VII})	2.773(8)
C(4)–O(7)	1.297(13)	K(2)–O(6^{VII})	2.955(9)
C(4)–O(8)	1.216(14)	K(2)–O(7)	2.836(7)
C(4)–C(4^{I})	1.551(22)	K(2)–O(12^{VII})	2.866(8)
C(5)–O(9)	1.254(15)	K(2)–Aq(1^{VI})	2.879(8)
C(5)–O(10)	1.231(18)	K(2)–Aq(1^{VIII})	2.802(7)

(*b*) Interbond angles/°

O(7)–Ge(1)–O(7^{I})	85.3(4)	O(3)–Ge(2)–O(5^{I})	90.2(4)
O(7)–Ge(1)–O(9)	91.5(3)	Ge(2)–O(1)–C(1)	113.7(8)
O(7)–Ge(1)–O(9^{I})	89.0(4)	Ge(2)–O(3)–C(2)	114.1(7)
O(7)–Ge(1)–O(11)	89.6(3)	Ge(2)–O(5)–C(3)	113.8(7)
O(9)–Ge(1)–O(11)	85.9(4)	Ge(1)–O(7)–C(4)	114.5(6)
O(9)–Ge(1)–O(11^{I})	93.6(3)	Ge(1)–O(9)–C(5)	114.5(8)
O(11)–Ge(1)–O(11^{I})	95.9(3)	Ge(1)–O(11)–C(6)	114.5(7)
O(1)–Ge(2)–O(1^{I})	85.3(5)	O(1)–C(1)–O(2)	124.3(1.2)
O(1)–Ge(2)–O(3)	89.5(3)	O(3)–C(2)–O(4)	125.1(1.0)
O(1)–Ge(2)–O(5)	96.9(3)	O(5)–C(3)–O(6)	123.6(1.1)
O(1)–Ge(2)–O(5^{I})	88.0(4)	O(7)–C(4)–O(8)	126.4(1.0)
O(3)–Ge(2)–O(3^{I})	90.8(4)	O(9)–C(5)–O(10)	127.8(1.2)
O(3)–Ge(2)–O(5)	85.5(3)	O(11)–C(6)–O(12)	126.0(1.1)

Symmetry code: I, $1 - x, y, \frac{1}{2} - z$; II, $\frac{1}{2} - x, -\frac{1}{2} + y, z$; III, $-x, y, \frac{1}{2} - z$; IV, $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; V, $-\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$; VI, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; VII, $\frac{1}{2} - x, \frac{1}{2} - y, -z$; VIII, $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

[maximum deviation from mean plane 0.07 Å, C(1)] as a result of slight twists of the ligands about their C–C bonds; one ring [Ge(1), O(9), O(11), C(5), C(6)] has the envelope and the others the twist conformation. The anions are linked in three dimensions by bonding of potassium to all outer oxygen atoms and to the three inner atoms O(1), O(5), and O(7). The potassium ions are in irregular eight-co-ordination. Unlike one cation in $K_3[Rh(C_2O_4)_3]\cdot4.5H_2O$ [3] they do not penetrate the anions, no potassium being bonded to more than one inner oxygen in any anion. The lattice water molecule, Aq(1), is too far from any anion oxygen atom (over 3.0 Å) for effective hydrogen bonding and its main function seems to be to complete the co-ordination sphere of K(2).



The two independent anions in $K_2[Ge(C_2O_4)_3]\cdot H_2O$ (*a* axis projection) with attached cations

[0/173 *Received*, 30*th January*, 1980]

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