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Strategy for the Synthesis of Di- and Polymer Tartratogermanates with Single-Charge Cations. Crystal Structures of $K_2[Ge_2(OH)_2(\mu\text{-Tart})_2] \cdot 4.5H_2O$ and $(NH_4)_{2n}[Ge_2(\mu\text{-O})(\mu\text{-Tart})_2]_n \cdot n MeCN \cdot nH_2O$

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Abstract—Tartratogermanates of alkaline metals and ammonium are synthesized for the first time using different solvents (water, acetonitrile) and starting reagents (GeO_2 and $GeCl_4$): dimeric $Kat_2[Ge_2(OH)_2(\mu\text{-Tart})_2] \cdot 4.5H_2O$ (H_4Tart is *D*-tartaric acid, Kat = Na (**I**) and K (**II**)) and polymer $(NH_4)_{2n}[Ge_2(\mu\text{-O})(\mu\text{-Tart})_2]_n \cdot nCH_3CN \cdot nH_2O$ (**III**). The complexes are characterized by elemental analysis, IR spectroscopy, and X-ray diffraction analysis. The structure of complex **II** contains binuclear isolated $[Ge_2(OH)_2(\mu\text{-Tart})_2]^{2-}$ complexes. In complex **III**, the oxo ligands join the binuclear fragments into polymer chains.

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INTRODUCTION

It has previously been shown [1] that in the GeO_2–tartaric acid (H_4Tart)–water system in the range of ligand concentrations from 1×10^{-5}–7×10^{-2} mol/L, there is a stable complex acid with the composition Ge : ligand = 1 : 1 for which the acidic dissociation constant was determined: $pK = 4.4 \times 10^{-2}$. Tartratogermanate acid in the solid state was not isolated under these conditions. Therefore, its salts with diantipyrylmethane (Dam) and barium were isolated to determine the structure of the complex anion.

The binuclear complex anion $(HDam)_2[Ge_2(\mu\text{-Tart})_2(OH)_2] \cdot 4H_2O$ includes a trigonal–bipyramidal polyhedron of germanium(IV) with the complexing form $GeOH^{3+}$ [2]. Bis(μ-tartrato)di(μ-hydroxo)digermanate, $\{[Ba(H_2O)_4][Ge_2(\mu\text{-OH})_2(\mu\text{-Tart})_2] \cdot 5H_2O\}_n$ [3], consists of polymer complex anions $\{[Ge_2(\mu\text{-Tart})_2(\mu\text{-OH})_2]^{2-}\}_n$ between which the Ba^{2+} hydrated cations and molecules of water of crystallization are localized. Two completely deprotonated $Tart^{4-}$ ligands perform the tridentate bis(chelate)-bridging function binding two germanium atoms, whose each polyhedron is supplemented to an octahedron by two bridging OH groups to form a polymer chain of complex anions. The data presented show that the structure of the tartrate complexes isolated in the solid state changes substantially, depending on the cation nature.

Further we succeeded to isolate tartratogermanate acid in the crystalline form by the reaction of germanium tetrachloride with *D*-tartaric acid in 85% acetic acid [4].

The purpose of this work is to continue investigations in this direction and to monitor the influence of the single-charge cations (sodium, potassium, and ammonium) and the replacement of the starting reagents (GeO_2, $GeCl_4$) and solvent (water, acetonitrile) on the structure of tartratogermanates formed.

EXPERIMENTAL

Elemental analysis was carried out on a semiautomated C,N,H-analyzer. The contents of germanium, sodium, and potassium were determined by atomic emission spectroscopy with inductively-coupled plasma on an Optima 2000 DV instrument (Perkin-Elmer).

The starting reagents for the synthesis of the complexes were germanium dioxide GeO_2 (99.999%), germanium tetrachloride $GeCl_4$ (99.999%), *D*-tartaric acid $C_4H_6O_6$ (99%), and sodium and potassium hydrocarbonates (high-purity grade) (all Sigma-Aldrich).

The IR absorption spectra (400–4000 cm^{-1}) of the complexes as KBr pellets were recorded on a Frontier spectrometer (PerkinElmer).

Synthesis of $Na_2[Ge_2(OH)_2(\mu\text{-Tart})_2] \cdot 4.5H_2O$ (I). Water (400 mL) was added to a mixture of weighed samples of GeO_2 (1.046 g, 0.01 mol) and H_4Tart (1.5 g,

0.01 mol), and the mixture was refluxed with stirring to the complete dissolution of the reagents and evaporated in a water bath to a volume of 30 mL (~2 h). Then an equimolar amount of $NaHCO_3$ was added to the solution cooled to ambient temperature. A precipitate of compound **I** was formed after an equal volume of ethanol was added to the solution. The yield was 80%.

IR for **I**, ν, cm^{-1}: 3488 ν(OH), 1677 $\nu_{as}(COO^-)$, 1342 $\nu_s(COO^-)$, 1065 ν(C–O), 680 ν(Ge–O), 860 δ(GeOH).

For $C_8H_{15}O_{18.5}Na_2Ge_2$ (**I**)				
anal. calcd. (%):	C, 16.05;	H, 2.51;	Ge, 24.27;	Na, 7.69.
Found (%):	C, 16.00;	H, 2.44;	Ge, 24.20;	Na, 7.67.

Synthesis of $K_2[Ge_2(OH)_2(\mu\text{-Tart})_2] \cdot 4.5H_2O$ (II) was carried out by the same procedure using $KHCO_3$ at the last stage. In a day, complex **II** containing single crystals suitable for X-ray diffraction analysis precipitated from the solution. The yield was 85%.

IR for **II**, ν, cm^{-1}: 3500 ν(OH), 1680 $\nu_{as}(COO^-)$, 1341 $\nu_s(COO^-)$, 1063 ν(C–O), 681 ν(Ge–O), 859 δ(GeOH).

For $C_8H_{15}O_{18.5}K_2Ge_2$ (**II**)				
anal. calcd. (%):	C, 15.23;	H, 2.38;	Ge, 23.04;	K, 12.38.
Found (%):	C, 15.07;	H, 2.26;	Ge, 23.00;	K, 12.25.

Synthesis of $(NH_4)_{2n}[Ge_2(\mu\text{-O})(\mu\text{-Tart})_2]_n \cdot n CH_3CN \cdot nH_2O$ (III). H_4Tart (1.5 g, 0.01 mol) was dissolved in an acetonitrile–water (1 : 1) mixture (50 mL), $GeCl_4$ was added in different molar ratios $GeCl_4 : H_4Tart = 1 : 1$ and 1 : 2, and the solution was brought to pH 3 with ammonium hydroxide and heated (40°C) for 5 min. In 2–3 days, compound **III** containing single crystals suitable for X-ray diffraction analysis with the composition $GeCl_4 : H_4Tart = 1 : 1$ precipitated from the solution. The yield was 75%.

IR for **III**, ν, cm^{-1}: 3422 ν(OH), 1686 $\nu_{as}(COO^-)$, 1348 $\nu_s(COO^-)$, 1070 ν(C–O), 681 ν(Ge–O), 845 ν_{as}(Ge–O–Ge), 491 ν_s(Ge–O–Ge), 3125 $\nu_3(NH_4^+)$, 1401 $\nu_4(NH_4^+)$, 2223 ν(C≡N).

For $C_{10}H_{14}N_3O_{14}Ge_2$ (**III**)				
anal. calcd. (%):	C, 22.00;	H, 2.57;	N, 7.70;	Ge, 26.66.
Found (%):	C, 21.83;	H, 2.38;	N, 7.60;	Ge, 26.54.

X-ray diffraction analysis. Experimental data were collected on Enraf Nonius CAD-4 (**II**) and Bruker SMART APEX II (**III**) diffractometers (Center for Collective Use, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences). An absorption correction was applied by the semiempirical method using the MULTISCAN (**II**) [5] and SADABS (**III**) programs [6]. Structures **II** and **III** were determined by a combination of direct methods and Fourier syntheses. The values of site occupancies of the disordered MeCN molecule in structure **III** (0.55 : 0.45) were obtained by the isotropic refinement and were fixed in further calculations. The hydrogen atoms of the water molecules, hydroxo group, and ammonium were partially localized from the difference Fourier syntheses. The aliphatic hydrogen atoms of the $Tart^{4-}$ anion were calculated from geometric concepts.

In [4], we mistakenly ascribed an incorrect structure to the anion in complex tartratogermanate acid (the valid formula is $\{H_3O\}_2[(H_2O)(OH)Ge(\mu\text{-Tart})_2Ge(OH)] \cdot 3H_2O$ (**IV**)) and did not take into account the halved population of two positions of molecules of water of crystallization. The repeated application of absorption correction (MULTISCAN [5]) of the same experimental data made it possible to decrease R_1 from 0.0547 to 0.0364, and the maximum peak in the difference Fourier synthesis decreased from 3.783 to 1.735 $e/Å^3$. The hydrogen atoms of the coordinated hydroxo groups and water molecules in compound **IV** were objectively localized from the difference Fourier synthesis, and the hydrogen atoms of the oxonium cation and crystallization water molecules were revealed partially.

Structures **II**, **III**, and **IV** were refined by the full-matrix anisotropic least-squares method (the C and N atoms of the disordered MeCN molecule were isotropically refined) taking into account hydrogen atoms. All calculations were performed using the SHELXS-97 and SHELXL-97 programs [7].

The main structural data are presented in Table 1. The experimental data for compounds **II**, **III**, and **IV** were deposited with the Cambridge Crystallographic Data Centre (CCDC) (nos. 934646, 934647, and 934759 respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

According to the elemental analysis data, in compounds **I** and **II** the molar ratio germanium : tartrate : Na (K) is 1 : 1 : 1, whereas in compound **III** germanium : tartrate : N = 1 : 1 : 1.5. The IR spectra of complexes **I** and **II** are similar but differ from the spectrum of compound **III**. A common feature is the presence in the IR spectra of complexes **I**–**III** of broad stretching vibration bands ν(OH), indicating the presence of crystallization water molecules, the disappearance (compared to the spectrum of tartaric acid) of the ν(C=O) band, and the appearance of $\nu_{as}(COO)$, $\nu_s(COO)$ characteristic of carboxylate groups. The presence of the ν(C–O) band of the alcoholate type indicates the binding with germanium of both the carboxy and deprotonated alcohol groups of the tartrate ligands. The formation of a bond between germanium and tartaric acid is also indicated by the appearance of

Table 1. Main crystallographic data and the refinement results for structures **II**, **III**, and **IV**

Value	Parameter		
	II	**III**	**IV**
Temperature, K	293	293	173
Radiation; λ, Å	MoK_α; 0.71073	MoK_α; 0.71073	MoK_α; 0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12$	$P2_12_12$
a, Å	11.0304(17)	8.7612(12)	13.4025(12)
b, Å	15.711(2)	14.2158(19)	15.8643(14)
c, Å	11.3252(18)	15.449(2)	8.6813(8)
β, deg	91.57(2)	90	90
V, Å^3	1961.9(5)	1924.1(4)	1845.8(3)
Z	2	4	4
ρ_{calcd}, g/cm^3	2.135	1.883	2.092
μ, mm^{-1}	3.581	3.201	3.362
Crystal sizes, mm	0.35 × 0.3 × 0.25	0.35 × 0.3 × 0.25	0.22 × 0.15 × 0.15
θ, deg	2.59–29.97	2.64–29.00	2.57–26.43
Range of h, k, l	$-2 \le h \le 15$, $0 \le k \le 22$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-19 \le k \le 19$, $-20 \le l \le 20$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-10 \le l \le 10$
Collected reflections	7270	18429	13836
Independent reflections	5887	4931	3791
R_{int}	0.0390	0.0412	0.0326
Reflections with $I > 2\sigma(I)$	4402	4313	3648
Number of refined parameters	551	259	289
Flack parameter	0.014(16)	0.015(15)	0.010(15)
Goodness-of-fit (F^2)	1.147	1.006	1.074
R_1, wR_2 ($I > 2\sigma(I)$)	0.0365, 0.0968	0.0396, 0.1210	0.0364, 0.1111
R_1, wR_2 (all reflections)	0.0719, 0.1394	0.0482, 0.1291	0.0377, 0.1118
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.948, –0.875	0.975, –0.644	1.730, –0.545

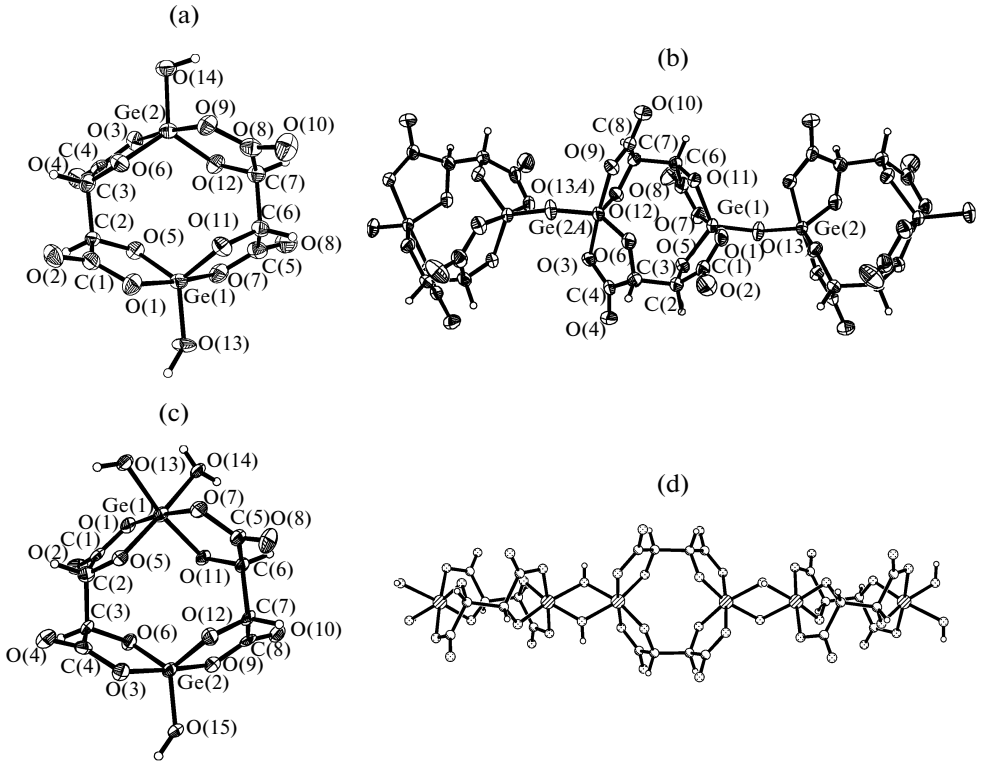

Fig. 1. Structure of the complex anion in compounds (a) **II**, (b) **III**, (c) **IV**, and (d) $\{[Ba(H_2O)_4][Ge_2(\mu\text{-}OH)_2(\mu\text{-}Tart)_2] \cdot 5H_2O\}_n$.

the bands corresponding to the stretching vibrations of the Ge–O bonds in the IR spectra of compounds **I**–**III**.

The IR spectra of complexes **I** and **II** exhibit the δ(GeOH) bands, indicating that the germanium atoms are in the composition of the both compounds in the hydrolyzed form. This spectrum is absent from the IR spectrum of compound **III**, but the bands characteristic of stretching vibrations of the Ge–O–Ge bridging group are observed [8]. Note that the spectrum of compound **III** exhibits two bands corresponding to the ν_3 and ν_4 stretching vibrations of the NH_4^+ tetrahedral ion [9] and the band responsible for the C≡N vibrations of acetonitrile.

Structure **II** is formed of the $[Ge_2(OH)_2(\mu\text{-}Tart)_2]^{2-}$ complex anions (Fig. 1a), cations K^+, water molecules coordinated by the K atoms, and molecules of crystallization water. All the four independent germanium atoms (the structure includes two crystallographically independent anions of the same structure) have the coordination number five (Table 2), and the coordination polyhedron is a trigonal bipyramid with the oxygen atoms of the deprotonated hydroxo groups $Tart^{4-}$ and OH^- ligand in the base and the oxygen atoms of the carboxy groups in the apical positions. The coordination numbers of two K atoms are 7 and 8, and their coordination polyhedra are irregular. The potassium cations are joined by the complex anions into a framework, whose cavities contain the molecules of water of crystallization. The branched network of hydrogen bonds (Table 3) additionally strengthens the framework and includes the crystallization water molecules into it.

In the polymer anion $Ge_2(\mu\text{-}O)(\mu\text{-}Tart)_2]_n^{2n-}$ of structure **III** (Fig. 1b), the fragments similar to the $[Ge_2(OH)_2(\mu\text{-}Tart)_2]^{2-}$ dimers in structure **II** are easily distinguished. The environment of the germanium atom is similar to that observed in structure **II**, taking into account the replacement of the coordinated hydroxo groups by the bridging oxo ligands. The polymer chains of the complex anions parallel to the *y* axis, ammonium cations, and molecules of water of crystallization are joined into a framework, whose cavities contain disordered MeCN molecules.

In the binuclear anion of acid **IV** (Fig. 1c), one of the Ge atoms has the coordination number five and its coordination polyhedron is a trigonal bipyramid (its structure is the same as that in **II**). The second Ge atom has the coordination number 6 and its coordination polyhedron represents an octahedron with the oxygen atoms of the carboxylate groups in the *trans* positions to each other and the O atoms of the hydroxo group and coordinated water molecules in the *trans* positions to the oxygen atoms of the deprotonated hydroxo groups of the $Tart^{4-}$ ligand.

Structure **IV** includes a branched system of hydrogen bonds joining the complex anion, oxonium ions,

Table 2. The Ge–O bond lengths in structures **II**, **III**, and **IV**

Bond	*d*, Å	Bond	*d*, Å
II		**III**	
Ge(1)–O(1)	1.901(6)	Ge(1)–O(1)	1.915(3)
Ge(1)–O(5)	1.767(6)	Ge(1)–O(5)	1.779(3)
Ge(1)–O(7)	1.904(6)	Ge(1)–O(7)	1.910(3)
Ge(1)–O(11)	1.783(6)	Ge(1)–O(11)	1.788(3)
Ge(1)–O(13)	1.754(7)	Ge(1)–O(13)	1.732(3)
Ge(2)–O(3)	1.915(6)	Ge(2)–O(3)	1.917(3)
Ge(2)–O(6)	1.780(6)	Ge(2)–O(6)	1.775(3)
Ge(2)–O(9)	1.908(6)	Ge(2)–O(9)	1.889(3)
Ge(2)–O(12)	1.783(6)	Ge(2)–O(12)	1.771(3)
Ge(2)–O(14)	1.750(7)	Ge(2)–O(13)	1.752(3)
Ge(3)–O(15)	1.911(6)	**IV**	
Ge(3)–O(19)	1.760(7)	Ge(1)–O(1)	1.882(3)
Ge(3)–O(21)	1.928(6)	Ge(1)–O(5)	1.863(4)
Ge(3)–O(25)	1.782(6)	Ge(1)–O(7)	1.878(4)
Ge(3)–O(27)	1.758(5)	Ge(1)–O(11)	1.856(3)
Ge(4)–O(17)	1.890(7)	Ge(1)–O(13)	1.850(3)
Ge(4)–O(20)	1.783(6)	Ge(1)–O(14)	1.926(4)
Ge(4)–O(23)	1.945(6)	Ge(2)–O(3)	1.900(3)
Ge(4)–O(26)	1.773(6)	Ge(2)–O(6)	1.782(4)
Ge(4)–O(28)	1.756(5)	Ge(2)–O(9)	1.895(4)
		Ge(2)–O(12)	1.777(4)
		Ge(2)–O(15)	1.756(3)

and molecules of crystallization water into a framework. Seven positions of oxygen of the oxonium ions and molecules of crystallization water are occupied by five O atoms. One position is disordered (distance O···O 1 Å), and two positions are half-occupied (Fig. 2). We partially localized several positions of hydrogen atoms (50% occupancies were ascribed to some of them), but it is impossible to unambiguously reveal the positions of all H atoms in partially disordered structure **IV** in terms of a routine X-ray diffraction experiment from a crystal of this quality. The distribution of short hydrogen bonds in the structure (Table 3) indicates that the "acidic" protons should easily jump over the oxygen atoms.

The bond lengths in structures **II**, **III**, and **IV** are usual for similar compounds [10].

The X-ray diffraction studies of *D*-tartratogermanate acid and its four salts allow one to confidently conclude about the structure of the complex anion in a solution. In spite of the fact that four types of the anion are present in the five compounds, namely, $[Ge_2(OH)_2(\mu\text{-Tart})_2]^{2-}$ in **II** and $(HDam)_2[Ge_2(\mu\text{-Tart})_2(OH)_2]\cdot 4H_2O$ (Fig. 1a), $[Ge_2(\mu\text{-O})(\mu\text{-Tart})_2]_n^{2n-}$ in **III** (Fig. 1b), $[(H_2O)(OH)Ge(\mu\text{-Tart})_2Ge(OH)]^{2-}$ in **IV** (Fig. 1c), and $[Ge_2(\mu\text{-OH})_2(\mu\text{-Tart})_2]_n^{2n-}$ in $\{[Ba(H_2O)_4][Ge_2(\mu\text{-OH})_2(\mu\text{-Tart})_2]\cdot 5H_2O\}_n$ (Fig. 1d) with different coordination numbers (5 and 6), the dimeric fragment $Ge_2(\mu\text{-Tart})_2$, which is completed by the terminal or bridging oxygen atoms of the oxo and hydroxo ligands or water molecules, can be distinguished in all complexes. In all cases, the oxygen atoms of the carboxy groups are in the *trans* positions to each other and the oxygen atoms of the hydroxo groups of the Tart ligands are unfolded by 30°, which allows the environment of Ge in the $Ge_2(\mu\text{-Tart})_2$ fragment to transit from that characteristic of a trigonal pyramid (the angle in the base is 120°) to the environment typical of an octahedron (90°).

Table 3. Geometric parameters of hydrogen bonds in structures **II**, **III**, and **IV**

Bond D–H···A	Distance, Å			Angle DHA, deg	Coordinates of atom A
	D–H	H···A	D···A		
			II		
O(13)–H(1)···O(32)	0.91	1.86	2.729(9)	159	$-x, y-1/2, -z+1$
O(14)–H(2)···O(35)	0.95	1.87	2.727(10)	149	$-x+1, y+1/2, -z$
O(27)–H(3)···O(36)	0.87	1.97	2.775(11)	154	$x, y, z-1$
O(28)–H(4)···O(32)	0.84	1.97	2.745(10)	153	$-x, y-1/2, -z+1$
O(29)–H(5)···O(37)	0.96	2.03	2.971(17)	170	$-x, y+1/2, -z-1$
O(29)–H(6)···O(24)	1.02	1.94	2.956(13)	173	$-x, y+1/2, -z$
O(30)–H(7)···O(8)	1.06	2.02	3.069(15)	170	$x-1, y, z$
O(30)–H(7)···O(7)	1.06	2.53	3.326(13)	131	$x-1, y, z$
O(31)–H(9)···O(10)	0.85	2.07	2.744(11)	136	$-x+1, y-1/2, -z+1$
O(31)–H(10)···O(21)	0.94	2.21	2.830(11)	123	$-x+1, y-1/2, -z$
O(31)–H(10)···O(37)	0.94	2.48	3.103(19)	124	$x, y, z+1$
O(33)–H(13)···O(1)	0.80	2.36	3.039(10)	142	$-x, y+1/2, -z+1$
O(33)–H(13)···O(2)	0.80	2.42	3.113(11)	144	$-x, y+1/2, -z+1$
O(33)–H(14)···O(30)	0.97	1.96	2.866(16)	155	$-x, y+1/2, -z+1$
O(34)–H(15)···O(1)	1.04	2.18	3.151(13)	155	$x+1, y, z$
O(34)–H(16)···O(18)	0.87	1.92	2.725(12)	154	$x+1, y, z+1$
O(35)–H(17)···O(33)	0.89	1.95	2.799(12)	159	$-x+1, y-1/2, -z$
O(36)–H(19)···O(30)	0.72	2.17	2.784(14)	143	$x+1, y, z$
O(36)–H(20)···O(31)	0.95	2.07	2.819(12)	135	
O(37)–H(21)···O(16)	1.04	1.88	2.878(14)	159	
O(37)–H(22)···O(35)	0.80	2.30	2.879(15)	130	$-x+1, y-1/2, -z-1$
			III		
N(2)–H(1)···O(8)	0.79	2.13	2.896(6)	163	$-x-1/2, -y+1, z+1/2$
N(2)–H(2)···O(11)	1.01	1.93	2.926(6)	166	
N(2)–H(3)···O(4)	0.75	2.20	2.921(5)	162	$-x, y+1/2, -z+1/2$
N(2)–H(4)···O(2)	0.99	2.09	2.952(6)	145	$x-1, y, z$
N(3)–H(5)···O(12)	0.90	2.32	2.918(7)	124	$-x+1/2, -y+1, z+1/2$
N(3)–H(5)···O(3)	0.90	2.35	3.136(8)	146	$-x+1/2, -y+1, z+1/2$
N(3)–H(6)···O(8)	0.95	1.96	2.898(8)	169	$-x, y+1/2, -z+1/2$
N(3)–H(7)···O(14)	1.05	1.98	2.778(13)	130	
N(3)–H(8)···O(14)	0.95	1.77	2.696(12)	163	$x+1/2, -y+3/2, -z+1$
O(14)–H(9)···O(5)	0.97	2.01	2.978(8)	174	$-x+1/2, -y+1, z+1/2$
O(14)–H(10)···O(2)	0.88	1.85	2.718(8)	170	
			IV		
O(13)–H(1)···O(10)	0.85	1.96	2.792(6)	165	$x-1/2, -y+1/2, -z+1$
O(14)–H(2)···O(15)	0.84	1.89	2.637(5)	147	$-x+1/2, y+1/2, -z+1$
O(14)–H(3)···O(4)	0.78	1.83	2.608(5)	176	$x+1/2, -y+1/2, -z+1$
O(15)–H(4)···O(18)	0.87	2.00	2.809(5)	153	$-x, -y, z-1$
O(16)–H(5)···O(5)	0.89	1.61	2.501(5)	175	
O(16)–H(6)···O(11)	1.10	1.49	2.555(5)	161	$x-1/2, -y+1/2, -z+1$
O(16)–H(71)···O(211)	0.90	1.63	2.501(9)	161	$x-1/2, -y+1/2, -z+1$
O(16)–H(72)···O(20)	0.51	2.02	2.468(9)	146	
O(17)–H(8)···O(13)	1.11	1.44	2.505(7)	159	
O(17)–H(9)···O(19)	0.85	1.65	2.438(10)	152	$-x, -y+1, z+1$
O(17)–H(101)···O(211)	1.02	1.67	2.684(10)	171	$x-1/2, -y+1/2, -z+1$
O(17)–H(101)···O(212)	1.02	1.63	2.527(10)	144	$x-1/2, -y+1/2, -z+1$
O(18)–H(11)···O(8)	0.96	1.95	2.850(6)	156	
O(18)···O(20)			2.989(9)		
O(18)···O(211)			2.608(9)		$x-1/2, -y+1/2, -z+1$
O(19)···O(2)			2.716(8)		
O(19)···O(15)			2.880(9)		$-x+1/2, y+1/2, -z$
O(20)–H(15)···O(12)	0.90	1.90	2.795(9)	173	$-x, -y, z$
O(20)···O(20)			2.566(16)		$-x, -y, z$
O(211)···O(6)			2.818(8)		
O(212)···O(4)			2.675(9)		$x+1/2, -y+1/2, -z$
O(212)···O(6)			2.594(9)		

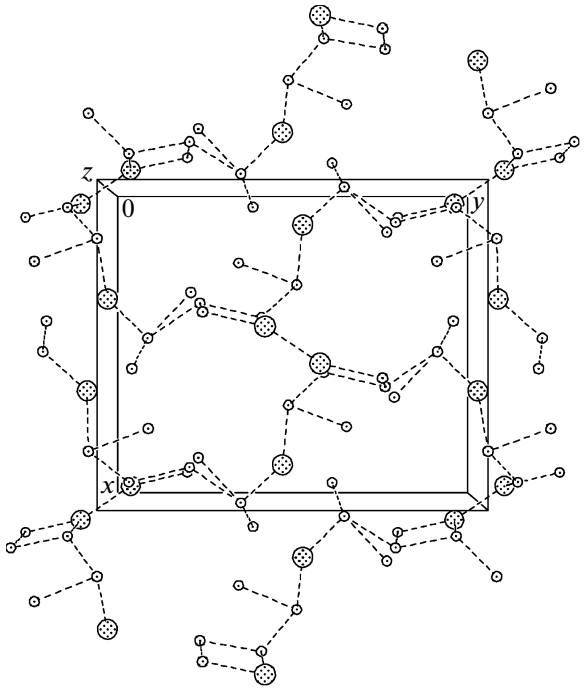

Fig. 2. Packing of the oxygen atoms of oxonium and molecules of water of crystallization in structure **IV** (large circles designate positions with partial occupancy).

The formation of dimers $A_2(\mu\text{-Tart})_2$ (A is an arbitrary element) is characteristic of germanium and other elements as well. The CCDC (version 5.34, February 2013 [11]) contains 307 compounds containing oxocarboxylate cycles formed by coordinated Tart, and 115 of them include dimeric fragments $A_2(\mu\text{-Tart})_2$.

Since coordination compounds **II**, **III**, $(HDam)_2[Ge_2(\mu\text{-Tart})_2(OH)_2] \cdot 4H_2O$, and $\{[Ba(H_2O)_4][Ge_2(\mu\text{-OH})_2(\mu\text{-Tart})_2] \cdot 5H_2O\}_n$ were synthesized by stages (at the first stage, the complex salt was obtained by the reaction of GeO_2 or $GeCl_4$ with *D*-tartaric acid, and then the cation was added to the reaction mixture), we may assert that a solution of *D*-tartratogermanate acid contains equilibrated $Ge_2(H_xO)_y(\mu\text{-Tart})_2$ anions (x, $y = 1, 2$) and the nature of the cation determines the form of the isolated anion. The best confirmation of this assertion is the structure of acid **IV**.

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