CRYSTAL STRUCTURE OF THE ADDUCT HEXAHYDROXOTELLURIC ACID–DISODIUM ETHYLENEDIAMINETETRAACETATE–WATER (1/1/2)

Ivana CISAROVA, Jana PODLAHOVA and Jaroslav PODLAHA

Department of Inorganic Chemistry,
Charles University, 128 40 Prague 2, The Czech Republic

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The title compound crystallizes in the form of racemic twins of hexagonal symmetry from slightly acidic aqueous solutions containing H_6TeO_6 and Na_2H_2edta in a broad range of molar ratios. The crystals are of excellent quality and high diffraction power, thus enabling the structure determination with a precission not routinely attainable by conventional single crystal X-ray diffraction (R = 0.015 at room temperature). The building units of the structure, held together by a system of hydrogen bonds, are the octahedral $Te(OH)_6$ molecule, the H_2edta^{2-} anion with protonated nitrogens, two water molecules and two sodium cations surrounded by ten oxygens in the $O_4Na(\mu\text{-}O)_2NaO_4$ moiety of irregular geometry.

Hexahydrotelluric acid is known to form a number of solid-state hydrogen-bonded adducts (see[1] for a review) with various inorganic and organic molecules including the natural amino acids glycine[2,3] and sarcosine[4]. In contrast, no such compounds with polyaminepolycarboxylic acids are known. Although ethylenediaminetetraacetic acid, the most popular ligand of this type, does not coordinate tellurium(VI) in any degree which would be of value for analytical purposes[5], it appeared interesting to see whether, *in the solid state*, a hypothetical complex with the isolated TeO_3 group (in analogy to molybdenum(VI) (ref.[6]) and tungsten(VI) (ref.[7]) or, instead, a hydrogen-bonded adduct is formed.

EXPERIMENTAL

Preparation of H_6TeO_6 . Na_2H_2edta . 2 H_2O. The compound crystallizes from aqueous solutions containing the components in the following ranges of conditions: molar ratio H_6TeO_6 : Na_2H_2edta = 2 – 0.3, c_{Te} = 0.03 – 0.7 mol dm^{-3}, pH 5 – 7 (adjusted with NaOH); the components were dissolved by heating to 60 °C and pH was then adjusted with 1 M NaOH. Single crystals with the size of more than 5 mm in diameter can be grown during several weeks from the solution with the composition 0.5 M H_6TeO_6, 0.5 M Na_2H_2edta at pH 5.0. Crystals were isolated by decantation, washing with 30% aqueous ethanol, then ethanol and dried in air at room temperature. Yields varied between 15 and 75% depending on the composition of solution. Content of $edta^{4-}$ calculated: 47.88%; found: 47.8%, by titration with zinc(II) against Xylenol Orange at pH 5.5; an attempted titration at pH 10 against Eriochrome Black T with various divalent metal ions (including those which do not form insoluble

tellurates) gave erratic results indicating, possibly, some degree of Te–edta interaction at this pH. Diagnostic bands of the IR spectrum (Nujol mull, cm^{-1}): 3 200 – 3 350 s, νb (H_2O, TeOH); 1 637 vs, ν_{as} (OCO, zwitterionic); 1 408 s, ν_s (OCO); 1 230 m, 667 s (H_6TeO_6). M.p. 240 – 250 °C (dec.).

Crystal and measurement data. H_6TeO_6 . $Na_2H_2C_{10}H_{12}N_2O_8$. 2 H_2O (601.89), trigonal, space group $P3_1$ (No. 144), a = 8.905(1), c = 21.620(1) Å, V = 1 484.8(2) $Å^3$, Z = 3, D_c = 2.019 g cm^{-3}, D_m = 2.02 g cm^{-3} (flotation in bromoform–benzene), $F(000)$ = 900. A colorless crystal of the dimensions 0.39 × 0.39 × 0.29 mm was measured at 22 °C on a CAD4 diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Absorption was neglected (μ = 1.63 mm^{-1}). The lattice parameters were determined from 25 reflections in the 17 – 20 ° θ-range. Intensities of reflections were measured using the θ – 2θ scan between h <–12,10>, k <0,12>, l <–30,30>, $(\sin\theta/\lambda)_{max}$ = 0.5 $Å^{-1}$. Three standard reflections monitored every 1 h showed 7% intensity decrease during the measurement; the data were corrected appropriately. From 9 070 measured reflections, 5 764 were unique (R_{int} = 0.021) and 5 728 of them were regarded as "observed" using the $I \geq 2\sigma(I)$ criterion.

Data treatment. The structure was solved by the Patterson method (SHELXS86, ref.[8]) and then developed and refined by succesive Fourier series (SHELXL93, ref.[9]). Hydrogen atoms of the methylene groups were placed in the theoretical positions and then refined with the isotropic temperature factors defined as 1.2 fold of the mean isotropic temperature factors of their bonding partners. Hydrogens of telluric acid, water and nitrogen atoms of H_2edta^{2-}, clearly discernible in the difference Fourier map, were refined isotropically. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = (\sigma_F^2 \times |F_o|^2 + (0.0204\ P)^2 + 0.3378\ P)^{-1}$ and $P = (F_o^2 + 2\ F_c^2)/3$. Convergence was achieved at R = 0.015, R_w = 0.040, S = 1.11 with $(\Delta/\sigma)_{max}$ = 0.05; –0.03 for non-H atoms and with the refined coefficient of secondary extinction of 0.0091(3). The final difference electron density map showed no peaks of chemical significance (extreme values of 0.43; –0.89 e $Å^{-3}$ corresponding to "ghosts" near Te). The racemic twin form of the crystal was revealed by calculation of the Flack's enantiomorph parameter[10] which had converged to 0.552(8) and 0.448(8) for $P3_1$ and $P3_2$ group, respectively.

The final positional parameters are given in Table I. Tables of observed and calculated structure factors and of anisotropic displacement parameter in the form of standard CIF files as generated by SHELXL can be obtained from the authors upon request.

RESULTS AND DISCUSSION

The crystal structure (Fig. 1) consists of the chemically independent molecules of telluric acid, dihydrogen ethylenediaminetetraacetate dianions, disodium dications with their coordination environment and water molecules. These units with their closest hydrogen-bonded partners are depicted on Figs 2, 3 and 4; bonding distances and angles within the units are summarized in Table II. The structure is held together by an extensive system of hydrogen bonds summarized in Table III.

There is nothing unusual on the metric parameters of both telluric acid and the H_2edta^{2-} ion. The distortion of the TeO_6 octahedron is very small as demonstrated by the mean values of the O–Te–O angles of 90(2)° and 178.2° which fall into the most populated range within the set of all known $Te(OH)_6$ structures[1]. Likewise, the extended conformation of H_2edta^{2-} with nearly tetrahedral nitrogen atoms (the range of bond angles involving hydrogen is 103 – 109(2)° for N1 and 106 – 110(2)° for N2) is typical for structures containing this anion in the non-complexed form[11–14]; the

TABLE I

Positional parameters (. 10^4) and equivalent isotropic displacement parameters ($Å^2$. 10^3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{eq}
Te	454.8(1)	5138.1(1)	0	14.3(1)
Na(1)	4302(1)	4504(1)	650(1)	24(1)
Na(2)	6707(1)	5906(1)	−711(1)	25(1)
O(1)	−1935(2)	4476(2)	−48(1)	21(1)
O(2)	−121(2)	3061(2)	−437(1)	30(1)
O(3)	1003(2)	7215(2)	428(1)	31(1)
O(4)	2856(2)	5776(2)	56(1)	19(1)
O(5)	840(2)	6390(2)	−758(1)	28(1)
O(6)	70(2)	4005(2)	785(1)	31(1)
N(1)	5734(2)	1336(2)	−845(1)	15(1)
C(1)	5871(2)	120(2)	−403(1)	17(1)
C(2)	5076(2)	162(2)	216(1)	19(1)
N(2)	5272(2)	−974(2)	686(1)	15(1)
C(11)	6744(2)	1513(2)	−1425(1)	19(1)
C(12)	7153(2)	3186(2)	−1759(1)	19(1)
O(11)	7757(2)	3364(2)	−2296(1)	29(1)
O(12)	6912(2)	4241(2)	−1469(1)	31(1)
C(13)	3895(2)	865(2)	−991(1)	19(1)
C(14)	3326(2)	2009(2)	−645(1)	21(1)
O(13)	4399(2)	3141(2)	−292(1)	24(1)
O(14)	1829(2)	1696(2)	−771(1)	41(1)
C(21)	4301(2)	−984(2)	1251(1)	20(1)
C(22)	4168(2)	−2271(2)	1736(1)	20(1)
O(21)	3786(2)	−1962(2)	2266(1)	26(1)
O(22)	4383(2)	−3501(2)	1583(1)	30(1)
C(23)	7129(2)	−429(2)	822(1)	19(1)
C(24)	7703(2)	−1539(2)	459(1)	20(1)
O(23)	6538(2)	−2820(2)	180(1)	22(1)
O(24)	9270(2)	−1066(2)	481(1)	37(1)
O(31)	1678(2)	2084(2)	974(1)	32(1)
O(32)	−649(2)	−1726(2)	−1127(1)	33(1)
H(C1)A	7079(2)	456(2)	−346(1)	20
H(C1)B	5268(2)	−1048(2)	−570(1)	20
H(C2)A	5638(2)	1345(2)	369(1)	22
H(C2)B	3855(2)	−227(2)	159(1)	22
H(C11)A	6072(2)	527(2)	−1694(1)	22
H(C11)B	7814(2)	1534(2)	−1321(1)	22

TABLE I
(*Continued*)

Atom	*x*	*y*	*z*	U_{eq}
H(C13)A	3124(2)	–338(2)	–881(1)	22
H(C13)B	3789(2)	981(2)	–1433(1)	22
H(C21)A	3142(2)	–1257(2)	1131(1)	23
H(C21)B	4876(2)	169(2)	1430(1)	23
H(C23)A	7263(2)	–546(2)	1262(1)	23
H(C23)B	7863(2)	781(2)	712(1)	23
H(O1)	–2310(41)	4421(40)	291(15)	35(8)
H(O2)	608(50)	2737(44)	–495(16)	45(9)
H(O3)	358(63)	7465(62)	450(21)	78(14)
H(O4)	3196(48)	5879(48)	–233(16)	46(10)
H(O5)	1236(55)	6111(57)	–1004(20)	64(12)
H(O6)	672(47)	3653(45)	785(16)	45(9)
H(N1)	6260(32)	2340(32)	–695(11)	16(5)
H(N2)	4750(36)	–2062(36)	513(12)	27(6)
H(O31)A	917(45)	1016(49)	831(16)	45(9)
H(O31)B	1697(47)	1753(49)	1325(18)	50(10)
H(O32)A	–86(50)	–2292(49)	–986(17)	54(10)
H(O32)B	–103(59)	–646(61)	–1068(20)	75(14)

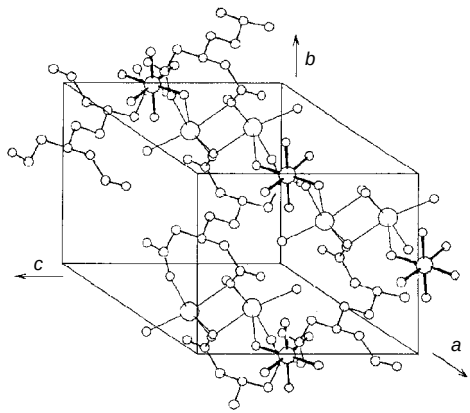

FIG. 1
Crystal packing scheme

TABLE II

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses. Symmetry code: *i*, $x-1, y+1, z$; *ii*, $x, y-1, z$; *iii*, $y-x, z-1/3$; *iv*, $-y, x-y, z+1/3$; *v*, $x, y+1, z$; *vi*, $x+1, y-1, z$; *vii*, $x+1, y, z$; *viii*, $1-y, x-y, z+1/3$; *ix*, $y-x+1, 1-x, z-1/3$; *x*, $x+1, y+1, z$; *xi*, $1-y, x-y+1, z+1/3$; *xii*, $x-1, y, z$

Atoms	Distances	Atoms	Angles	Atoms	Angles
		Telluric acid			
Te–O3	1.901(1)	O3–Te–O2	179.09(7)	O1–Te–O6	90.43(7)
Te–O2	1.905(1)	O3–Te–O1	91.79(6)	O5–Te–O6	176.40(8)
Te–O1	1.906(1)	O2–Te–O1	87.48(6)	O3–Te–O4	88.60(6)
Te–O5	1.914(1)	O3–Te–O5	88.06(8)	O2–Te–O4	92.14(6)
Te–O6	1.916(1)	O2–Te–O5	91.37(7)	O1–Te–O4	179.14(7)
Te–O4	1.923(1)	O1–Te–O5	88.91(6)	O5–Te–O4	91.87(6)
		O3–Te–O6	88.42(8)	O6–Te–O4	88.82(6)
		O2–Te–O6	92.14(8)		
		H_2edta^{2-}			
N1–C1	1.494(2)	C1–N1–C11	110.3(1)	N1–C13–C14	112.7(1)
N1–C11	1.505(2)	C1–N1–C13	113.8(1)	O13–C14–O14	128.0(2)
N1–C13	1.507(2)	C11–N1–C13	111.4(1)	O13–C14–C13	117.5(2)
C1–C2	1.524(2)	N1–C1–C2	109.7(1)	O14–C14–C13	114.5(2)
C2–N2	1.503(2)	N2–C2–C1	111.4(1)	N2–C21–C22	113.4(1)
N2–C21	1.494(2)	C21–N2–C23	112.5(1)	O22–C22–O21	127.5(2)
N2–C23	1.502(2)	C21–N2–C2	107.1(1)	O22–C22–C21	119.5(2)
C11–C12	1.527(2)	C23–N2–C2	113.2(1)	O21–C22–C21	113.0(2)
C12–O12	1.234(2)	N1–C11–C12	109.5(1)	N2–C23–C24	111.0(1)
C12–O11	1.256(2)	O12–C12–O11	126.9(2)	O24–C24–O23	127.5(2)
C13–C14	1.539(2)	O12–C12–C11	117.1(2)	O24–C24–C23	116.2(2)
C14–O13	1.245(2)	O11–C12–C11	116.0(2)	O23–C24–C23	116.3(2)
C14–O14	1.248(2)				
C21–C22	1.515(2)				
C22–O22	1.248(2)				
C22–O21	1.263(2)				
C23–C24	1.537(2)				
C24–O24	1.241(2)				
C24–O23	1.248(2)				
		Na-environment			
Na1–O11(*viii*)	2.288(2)	O11(*viii*)–Na1–O31	111.03(7)	O12–Na2–O23(*v*)	168.24(6)
Na1–O31	2.358(2)	O11(*viii*)–Na1–O13	91.48(6)	O12–Na2–O32(*x*)	86.58(7)
Na1–O13	2.394(2)	O31–Na1–O13	93.42(6)	O23(*v*)–Na2–O32(*x*)	99.10(6)
Na1–O23(*v*)	2.436(2)	O11(*viii*)–Na1–O23(*v*)	83.04(6)	O12–Na2–O21(*ix*)	102.28(6)

TABLE II
(*Continued*)

Atoms	Distances	Atoms	Angles	Atoms	Angles
		Na-environment			
Na1–O4	2.460(2)	O31–Na1–O23(*v*)	165.92(6)	O23(*v*)–Na2–O21(*ix*)	85.75(6)
Na1–O22(*v*)	2.665(2)	O13–Na1–O23(*v*)	85.51(5)	O32(*x*)–Na2–O21(*ix*)	108.61(7)
Na2–O12	2.277(2)	O11(*viii*)–Na1–O4	155.06(7)	O12–Na2–O13	84.99(6)
Na2–O23(*v*)	2.279(2)	O31–Na1–O4	93.91(6)	O23(*v*)–Na2–O13	87.48(5)
Na2–O32(*x*)	2.415(2)	O13–Na1–O4	87.05(5)	O32(*x*)–Na2–O13	166.70(7)
Na2–O21(*ix*)	2.459(2)	O23(*v*)–Na1–O4	72.02(5)	O21(*ix*)–Na2–O13	83.27(6)
Na2–O13	2.460(2)	O11(*viii*)–Na1–O22(*v*)	91.67(6)	O12–Na2–O1(*vii*)	82.45(6)
Na2–O1(*vii*)	2.585(2)	O31–Na1–O22(*v*)	93.94(6)	O23(*v*)–Na2–O1(*vii*)	86.52(5)
		O13–Na1–O22(*v*)	170.36(6)	O32(*x*)–Na2–O1(*vii*)	98.31(6)
		O23(*v*)–Na1–O22(*v*)	85.83(5)	O21(*ix*)–Na2–O1(*vii*)	152.84(6)
		O4–Na1–O22(*v*)	86.25(5)	O13–Na2–O1(*vii*)	70.41(5)

orientation of acetates is, of course, strongly influenced by the hydrogen bonds in which their carboxyls participate.

The immediate environment of two closely separated (3.484(3) Å) sodium counterions is composed of ten oxygen atoms originating, at each sodium, from of one tellurate, three carboxylates and one water molecule, and completed by two bridging carboxylate oxygens. This irregular moiety looks rather unusual but is not unprecedented[15–21].

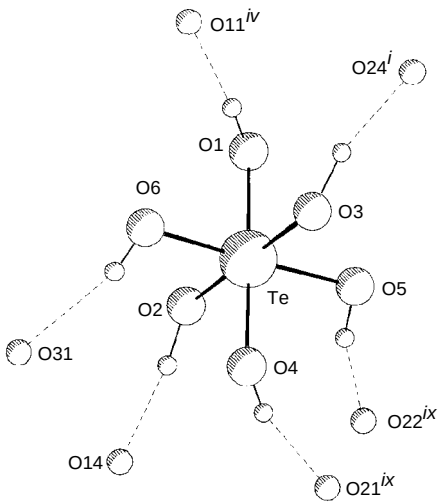

FIG. 2
H_6TeO_6 molecule with hydrogen bonds

TABLE III

Hydrogen bond distances (Å) and angles (°) with estimated standard deviations in parentheses. For symmetry code, see Table II

Distances						Angle
X–H		Y...H		X...Y		X–H–Y
O1–HO1	0.80(3)	O11(*iv*)–HO1	1.86(4)	O1–O11(*iv*)	2.653(3)	173(3)
O2–HO2	0.84(5)	O14–HO2	1.85(5)	O2–O14	2.669(3)	166(3)
O3–HO3	0.71(6)	O24(*i*)–HO3	1.98(6)	O3–O24(*i*)	2.664(3)	161(4)
O4–HO4	0.68(4)	O21(*ix*)–HO4	1.99(4)	O4–O21(*ix*)	2.667(3)	179(4)
O5–HO5	0.75(5)	O22(*ix*)–HO5	1.94(5)	O5–O22(*ix*)	2.673(3)	169(4)
O6–HO6	0.74(5)	O31–HO6	2.04(4)	O6–O31	2.755(3)	160(3)
O31–HO31A	0.90(4)[a]	O24(*xii*)–H31A	1.86(4)	O31–O24(*xii*)	2.755(2)	174(3)
O31–HO31B	0.82(4)	O32(*iv*)–H31B	2.00(4)	O31–O32(*iv*)	2.818(3)	176(3)
O32–HO32A	0.92(5)[b]	O5(*ii*)–H32A	1.81(5)	O32–O5(*ii*)	2.727(3)	174(3)
O32–HO32B	0.84(5)	O14–H32B	2.03(5)	O32–O14	2.833(2)	158(4)
N1–HN1	0.84(3)	O1(*vii*)–HN1	2.26(3)	N1–O1(*vii*)	3.048(3)	157(2)
N2–HN2	0.92(3)	O4(*ii*)–HN2	2.07(3)	N2–O4(*ii*)	2.938(2)	157(2)

[a] H31A–O31–H31B 94(3). [b] H32A–O32–H32B 114(3).

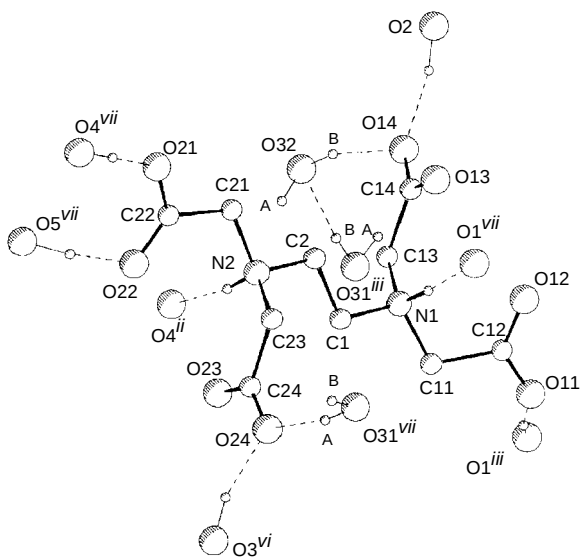

FIG. 3

H_2edta^{2-} ion with hydrogen bonds

All O- and N-bonded hydrogen atoms participate on hydrogen bonding of the simple X–H…Y type. As a consequence of the high quality of experimental data, no ambiguities were encountered in distinguishing proton donors from proton acceptors, a problem which otherwise tends to be notorious for structures of this kind determined by X-ray diffraction. The acidobasic forms of the adduct partners are therefore certain: as could be expected, the protons of telluric acid and the N-bonded protons of the H_2edta^{2-} zwitterion are donated to oxygen atoms of carboxylate groups and, in one case, to the oxygen atom of the water molecule. The resulting environment of the water oxygens is somewhat more complicated. Besides being coordinated to sodium cations and hydrogen-bonded through their hydrogen atoms, the water oxygens function also as the acceptors of one proton either from telluric acid (O31) or from the second water molecule (O32), which results in linking of the Na_2O_{10} units through one hydrogen bond into a unidimensional chain. The immediate environment of both water oxygens is thus composed of three hydrogens and one sodium in a roughly tetrahedral arrangement.

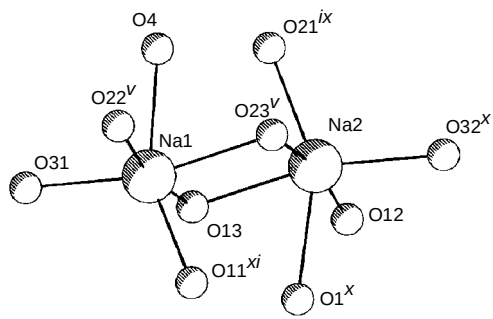

FIG. 4
Environment of sodium cations

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