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Crystal structure of betainium hexafluorotantalum(IV) dihydrate, $(C_5H_{12}NO_2)_2TaF_6 \cdot 2H_2O$

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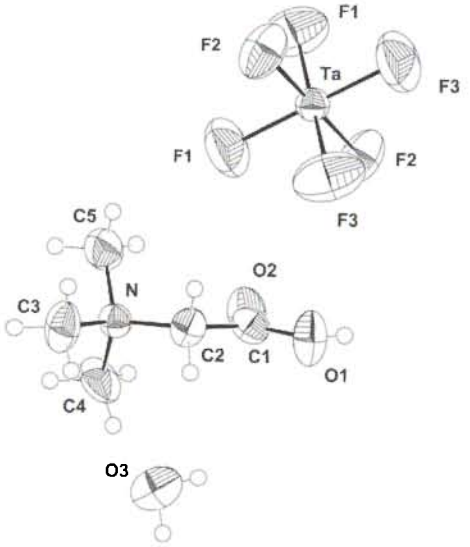

Abstract

$C_{10}H_{28}F_6N_2O_6Ta$, monoclinic, $P12/a1$ (No. 13), a = 12.553(3) Å, b = 6.531(3) Å, c = 12.587(3) Å, β = 110.25(1)°, V = 968.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.030, $wR(F^2)$ = 0.068, T = 293 K.

Source of material

The pure metal was dissolved in concentrated fluoridric acid (40%). Reagent grade betaine (Merck, 99.9% purity) was added to the solution and after a few days of slow evaporation small, transparent crystals were formed, from which a good quality specimen was choosen for X-ray analysis.

The data-collection was performed with the crystal encapsulated in a sealed glass capilary. Betaine is unusualy high sensitive to radiation damage [1] and the intensity of three control reflections measured each 3 h showed a decay which continuously increased attaining a maximum rate of 3.6°h^{-1} by the end of the data collection. A polynomial interpolation was used to correct for this decay in the data reduction. The structure was solved by direct methods. The hydrogen atoms of the cation were placed at calculated positions and refined as riding using the SHELXL-97 [2] defaults: d(O–H) = 0.82 Å, d(C–H) = 0.93 Å. Those of the solvent water molecule could not be located in a difference synthesis and were placed at tentative positions according to the best geometry for hydrogen bonding and refined subject to the restraint d(O–H) = 0.86(2) Å. Examination of the crystal structure with PLATON92 [3] shows that there are no additional solvent-accessible voids in the crystal lattice.

Discussion

Betaine (the α-amino-acid trimethyl-glycine) occurs frequently in biological systems where it acts as a transmethylating agent in amino-acid synthesis. It exists as a zwitterion ($CH_3N^+CH_2COO^-$) forming adducts and salts with a variety of acids. Betaine and its derivatives are also well known as chelating agents in metal-carboxylate complexes of several transition metals and lanthanides [4, 5]. The interest in betaine compounds is due to the fact that many of these compounds have interesting physical properties, exhibiting ferroelectric or antiferroelectric ordering at low temperature [6-8] as well as ferroelastic behaviour that drives phase transitions to both commensurate and incommensurate superstructures [9,10]. Many betaine compounds exhibit anomalous temperature dependence of dielectric and elastic properties and a strong anisotropy in their physical properties [11]. The betaine molecule has a large dipole moment but most betaine compounds are centrosymmetric at room temperature and thus polar properties are only observed at low temperature. The geometry of the betainium cation compares well with other structural studies of betaine salts [8, 12]. The difference in the carboxylic C–O bond lengths indicates that the molecule is protonated with the proton attached to O1. The skeleton C1–C2–N–C3 is planar with the C3 and C5 methyl groups lying symmetrically above and below this plane. The carboxylic group is slightly twisted [5(1)°] around the C1–C2 bond. The transition metal atoms are located at the 2e special positions. The anion has almost perfect octahedral geometry within experimental error. The average Ta–F bond length 1.862(3) Å agrees well with the expected value from the ionic radii. The cation is linked to the water molecule via a strong hydrogen bond O1···O3: 2.510 Å. The fluorine atoms do not appear to take part in strong hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	transparent, irregular shape, size 0.22 × 0.32 × 0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	57.60 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω/2θ
$2\theta_{max}$:	49.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1831, 1412
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1172
$N(param)_{refmed}$:	124
Programs:	PLATON [3], SDP [13], DIFABS [14], SHELXS-97 [15], SHELXL-97 [2], ORTEPII [16]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*g*	–0.3011	1.0069	–0.3746	0.111
H(2A)	4*g*	–0.046	0.8447	–0.3162	0.058
H(2B)	4*g*	–0.0655	0.8194	–0.2009	0.058
H(3A)	4*g*	0.1174	0.6569	–0.2484	0.105
H(3B)	4*g*	0.1185	0.4301	–0.2072	0.105
H(3C)	4*g*	0.1025	0.6108	–0.1321	0.105
H(4A)	4*g*	–0.1434	0.4294	–0.4148	0.114
H(4B)	4*g*	–0.0212	0.3342	–0.3731	0.114
H(4C)	4*g*	–0.0416	0.553	–0.4278	0.114
H(5A)	4*g*	–0.0724	0.4803	–0.1239	0.103
H(5B)	4*g*	–0.0534	0.2862	–0.1884	0.103
H(5C)	4*g*	–0.1688	0.4055	–0.2338	0.103
H(31)	4*g*	–0.468(9)	0.98(1)	–0.42(1)	0.108
H(32)	4*g*	–0.429(9)	1.05(2)	–0.491(5)	0.108

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	2*e*	1/4	0.05310(7)	0	0.0453(3)	0.0432(3)	0.0428(3)	0	0.0160(2)	0
N	4*g*	–0.0413(4)	0.5513(9)	–0.2672(5)	0.035(3)	0.043(3)	0.046(3)	–0.002(3)	0.015(2)	0.000(3)
O(1)	4*g*	–0.2325(4)	0.9897(8)	–0.3450(6)	0.049(3)	0.057(4)	0.103(5)	0.011(2)	0.011(3)	0.002(3)
O(2)	4*g*	–0.2793(4)	0.6591(9)	–0.3686(5)	0.038(3)	0.066(3)	0.096(4)	–0.005(3)	0.012(3)	–0.013(3)
C(1)	4*g*	–0.2101(6)	0.793(1)	–0.3356(6)	0.040(4)	0.054(5)	0.054(5)	–0.006(4)	0.019(3)	–0.006(4)
C(2)	4*g*	–0.0853(5)	0.764(1)	–0.2767(7)	0.037(4)	0.044(4)	0.060(5)	–0.007(3)	0.012(3)	0.006(4)
C(3)	4*g*	0.0859(6)	0.563(1)	–0.2084(8)	0.036(4)	0.068(5)	0.095(7)	0.006(4)	0.008(4)	0.013(5)
C(4)	4*g*	–0.0639(8)	0.459(2)	–0.3808(7)	0.079(6)	0.092(6)	0.058(5)	0.022(5)	0.024(4)	–0.026(5)
C(5)	4*g*	–0.0882(7)	0.419(1)	–0.1971(8)	0.074(5)	0.059(6)	0.086(7)	0.008(4)	0.044(5)	0.010(5)
O(3)	4*g*	–0.4373(4)	1.090(1)	–0.4303(5)	0.048(3)	0.087(5)	0.070(4)	0.029(3)	0.008(3)	–0.011(4)
F(1)	4*g*	0.1746(5)	0.255(1)	0.0501(6)	0.123(5)	0.113(5)	0.121(5)	0.042(4)	0.050(4)	–0.029(4)
F(2)	4*g*	0.1350(4)	0.0551(8)	–0.1415(4)	0.091(3)	0.074(3)	0.067(3)	0.000(3)	–0.011(3)	–0.003(3)
F(3)	4*g*	0.1734(6)	–0.150(1)	0.0486(6)	0.145(5)	0.126(5)	0.120(5)	–0.058(5)	0.052(4)	0.025(5)

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