Crystal structure of dipyridine oxonium undecafluorodititanate hydrate, $(C_5H_6N)_2(H_3O)[Ti_2F_{11}] \cdot H_2O$

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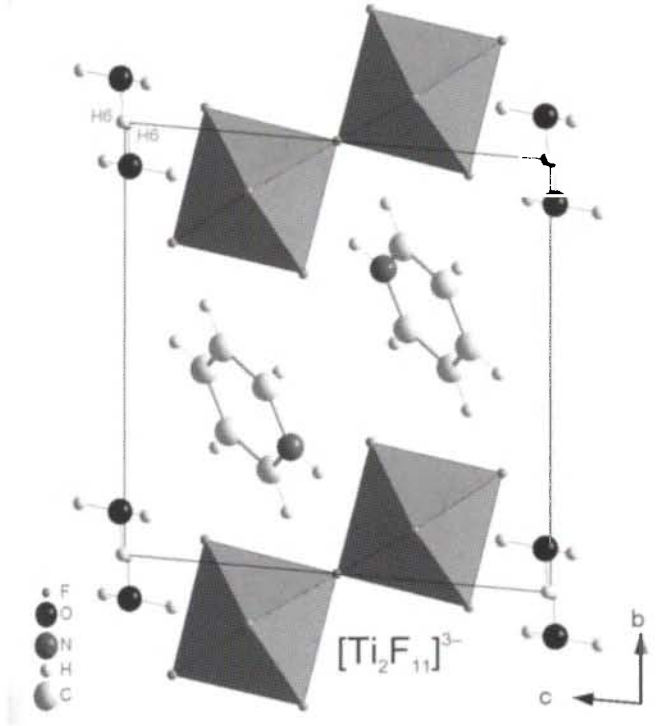
Received January 22, 2001, revised version May 28, 2001, CCDC-No. 1267/605



Abstract

$C_{10}H_{17}F_{11}N_2O_2Ti_2$, triclinic, $P\bar{1}$ (No. 2), a = 6.684(5) Å, b = 8.215(5) Å, c = 8.345(5) Å, α = 84.733(5)°, β = 85.250(5)°, γ = 86.692(5)°, V = 454.1 Å^3, Z = 1, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.091, T = 293 K.

Source of material

$(C_5H_6N)_2(H_3O)[Ti_2F_{11}] \cdot H_2O$ was prepared at room temperature from a water solution of pyridine (pyr), titanium isopropoxide (TiPT), and hydrofluoric acid. 0.6985 g TiPT was hydrolyzed in 3.3781 g water and hydrous titanium oxide was obtained. Then, 0.9444 g aqueous hydrofluoric acid (40%) was added under stirring to dissolve the hydrous titanium oxide. Finally, 0.1700 g pyridine was added. Composition of initial solution was following TiPT:HF:H_2O:pyr = 1:7.6:88:0.8. Needle shaped prismatic crystals of $(C_5H_6N)_2(H_3O)[Ti_2F_{11}] \cdot H_2O$ were formed in about 15 days.

Experimental details

One of the hydrogen atoms (H6) of the oxonium/water molecules has an occupancy of 0.50 (i.e. only one of the two H atoms near the origin is present). This means that there are one oxonium and one water molecule in the unit cell.

Discussion

The structure of dipyridine oxonium undecafluorodititanate hydrate $(C_5H_6N)_2(H_3O)[Ti_2F_{11}] \cdot H_2O$ consists of vertex connected octahedral pairs, $[Ti_2F_{11}]^{3-}$, separated from each other by charge compensating protonated pyridinium and oxonium cations. The hydrogens of pyridinium nitrogen and oxonium/water oxygen participate in hydrogen bonding with the fluorine atoms of titanium octahedra and oxygen atoms of oxonium/water. Thus, a three-dimensional network of diortho Ti-F octahedra, pyridinium and oxonium/water is formed.

Table 1. Data collection and handling.

Crystal:	colourless prismmatic needles, size 0.04 × 0.02 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	9.95 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 111 exposures, $\Delta\phi$ =1.8°
$2\theta_{max}$:	51.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3473, 1616
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1273
$N(param)_{refined}$:	136
Programs:	SIR97 [1], SHELXL-97 [2], WinGX [3], DIAMOND [4]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	2*i*		1.165	0.2326	0.5424	0.101
H(1A)	2*i*		0.7409	0.5033	0.8787	0.076
H(2)	2*i*		1.273	0.4546	0.6356	0.082
H(3)	2*i*		0.6517	0.2678	0.7836	0.075
H(4)	2*i*		0.8627	0.1342	0.6163	0.077
H(5)	2*i*		1.0582	0.595	0.8071	0.083
H(6)	2*i*	0.50	1.058(7)	0.001(5)	1.007(7)	0.04(2)
H(7)	2*i*		1.167(5)	0.111(4)	1.113(3)	0.07(1)
H(8)	2*i*		1.252(4)	0.095(5)	0.948(4)	0.09(1)

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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}
Ti(1)	2*i*	0.54540(7)	0.14094(6)	0.29716(5)	0.0288(3)	0.0372(3)	0.0287(2)	–0.0089(2)	0.0025(2)	–0.0032(2)
F(1)	2*i*	0.2652(3)	0.1354(3)	0.2916(2)	0.033(1)	0.085(1)	0.0566(9)	–0.0052(8)	–0.0089(7)	–0.013(1)
F(2)	2*i*	0.8107(3)	0.1169(3)	0.3195(3)	0.031(1)	0.077(1)	0.110(2)	–0.0071(9)	–0.0052(9)	–0.035(1)
F(3)	2*i*	0.5104(3)	0.3118(2)	0.4209(2)	0.058(1)	0.051(1)	0.083(1)	–0.0092(8)	0.0047(9)	–0.032(1)
F(4)	2*i*	0.5663(3)	–0.0514(2)	0.1909(2)	0.055(1)	0.061(1)	0.056(1)	–0.0174(9)	0.0110(8)	–0.0290(9)
F(5)	1*f*	1/2	0	1/2	0.090(2)	0.067(2)	0.033(1)	–0.009(1)	–0.001(1)	0.016(1)
F(6)	2*i*	0.5681(4)	0.2678(3)	0.1131(2)	0.113(2)	0.081(2)	0.056(1)	–0.006(1)	0.024(1)	0.031(1)
O	2*i*	1.1251(3)	0.1009(3)	1.0115(2)	0.044(1)	0.065(2)	0.041(1)	–0.004(1)	–0.0026(8)	–0.012(1)
N(1)	2*i*	1.0855(6)	0.2844(5)	0.6089(4)	0.112(3)	0.075(3)	0.055(2)	0.036(2)	0.018(2)	0.001(2)
C(1)	2*i*	0.8308(6)	0.4462(5)	0.8105(4)	0.075(3)	0.055(2)	0.054(2)	0.017(2)	0.014(2)	–0.005(2)
C(2)	2*i*	1.1449(6)	0.4183(5)	0.6657(5)	0.048(2)	0.072(3)	0.080(2)	–0.014(2)	0.001(2)	0.019(2)
C(3)	2*i*	0.7780(5)	0.3075(5)	0.7528(4)	0.042(2)	0.073(2)	0.072(2)	–0.019(2)	–0.013(2)	0.018(2)
C(4)	2*i*	0.9015(7)	0.2292(4)	0.6550(4)	0.098(3)	0.047(2)	0.054(2)	–0.017(2)	–0.024(2)	–0.010(2)
C(5)	2*i*	1.0183(7)	0.5010(4)	0.7670(5)	0.099(3)	0.040(2)	0.071(2)	–0.023(2)	–0.016(2)	–0.004(2)

Acknowledgments. This work has been supported by the Swedish Natural Science Research Council (NFR). X. D. Zou is a Research Fellow of the Royal Swedish Academy of Sciences supported by a grant from the Knut and Alice Wallenberg Foundation.

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Crystal structure of dipiperazine decafluorodialuminium dihydrate, $(C_4H_{12}N_2)_2[Al_2F_{10}] \cdot 2H_2O$

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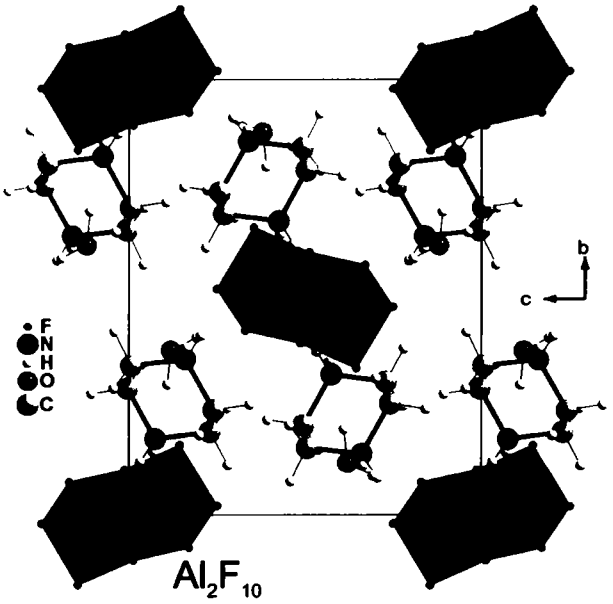
Received March 5, 2001, CCDC-No. 1267/628



Abstract

$C_4H_{14}AlF_5N_2O$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.510(5)$ Å, $b = 11.084(5)$ Å, $c = 9.224(5)$ Å, $\beta = 97.059(5)°$, $V = 863.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.025$, $wR_{ref}(F^2) = 0.067$, $T = 293$ K.

Source of material

$(C_4H_{12}N_2)_2[Al_2F_{10}] \cdot 2H_2O$ was hydrothermally prepared from a water solution of piperazine (pipz), titanium isopropoxide (TiPT), AlF_3 and hydrofluoric acid. 0.5308 g TiPT was hydrolyzed in 3.3854 g water and hydrous titanium oxide was obtained. Then 1.2429 g aqueous hydrofluoric acid (40%) was added under stirring to dissolve the hydrous titanium oxide. Finally, 0.412 g pipearzine and 0.185 g AlF_3 were added. The composition of the initial solution was the following: $TiPT:AlF_3:HF:H_2O$:pipz = 1:1:13:120:2. Then, this solution was put into an autoclave and kept at 458 K. Prismatic crystals of the title compound were formed in about 12 days.

Discussion

The crystal structure consists of edge-shared AlF_6 octahedral pairs, diprotonated piperazine cations and crystal water. The fluoro-bridged dimeric anions $[Al_2F_{10}]$ are isolated from each other. The three-dimensional structure is held together via a complicated network of hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.3 × 0.016 × 0.016 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	2.84 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 133 exposures $\Delta\phi = 1.5°$
$2\theta_{max}$:	51.86°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6587, 1593
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1383
$N(param)_{refined}$:	128
Programs:	SIR97 [1], SHELXL-97 [2], WinGX [3], DIAMOND [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	–0.1663	–0.4140	0.2049	0.045(2)
H(1B)	4e	–0.3328	–0.3853	0.1634	0.045
H(2A)	4e	–0.0954	–0.1225	0.0321	0.045
H(2B)	4e	0.0731	–0.1462	0.0700	0.045
HW(1)	4e	0.388(3)	–0.409(2)	0.191(2)	0.064(6)
HW(2)	4e	0.404(2)	–0.302(2)	0.110(2)	0.060(6)
H(1C)	4e	–0.2245	–0.2550	0.3434	0.040(2)
H(1D)	4e	–0.2910	–0.1849	0.2010	0.040
H(2C)	4e	–0.2837	–0.2922	–0.0444	0.040
H(2D)	4e	–0.2121	–0.4228	–0.0416	0.040
H(3A)	4e	–0.0378	–0.1154	0.2806	0.040
H(3B)	4e	0.0298	–0.2471	0.2775	0.040
H(4A)	4e	0.0384	–0.3485	0.0372	0.040
H(4B)	4e	–0.0289	–0.2801	–0.1063	0.040

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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}
Al(1)	4*e*	0.12853(4)	–0.52324(3)	0.40917(3)	0.0146(2)	0.0180(2)	0.0220(2)	0.0006(1)	0.0028(1)	0.0010(1)
F(1)	4*e*	–0.01130(9)	–0.52036(7)	0.24960(7)	0.0299(5)	0.0320(4)	0.0220(4)	0.0078(3)	–0.0018(3)	–0.0008(3)
F(2)	4*e*	0.01888(8)	–0.39571(6)	0.48770(7)	0.0200(4)	0.0161(3)	0.0262(3)	–0.0010(2)	0.0043(3)	0.0015(2)
F(3)	4*e*	0.20737(9)	–0.66176(7)	0.35459(8)	0.0233(5)	0.0266(4)	0.0419(4)	0.0063(3)	0.0044(3)	–0.0086(3)
F(4)	4*e*	0.27190(8)	–0.52488(6)	0.56907(8)	0.0194(4)	0.0313(4)	0.0311(4)	–0.0014(3)	–0.0045(3)	0.0015(3)
F(5)	4*e*	0.2574(1)	–0.42443(8)	0.32972(9)	0.0368(5)	0.0398(5)	0.0415(5)	–0.0108(3)	0.0175(4)	0.0056(4)
N(1)	4*e*	–0.2333(1)	–0.35858(9)	0.1608(1)	0.0231(6)	0.0248(6)	0.0349(6)	0.0000(4)	0.0030(4)	0.0085(4)
N(2)	4*e*	–0.0246(1)	–0.17591(9)	0.0748(1)	0.0176(6)	0.0259(6)	0.0428(6)	–0.0016(4)	0.0017(4)	0.0059(5)
OW	4*e*	0.4365(1)	–0.3793(1)	0.1198(1)	0.0342(7)	0.0380(6)	0.0517(7)	0.0044(5)	0.0189(5)	0.0053(5)
C(1)	4*e*	–0.2114(2)	–0.2422(1)	0.2416(1)	0.0341(8)	0.0302(7)	0.0286(6)	0.0083(5)	0.0078(5)	0.0026(5)
C(2)	4*e*	–0.2036(2)	–0.3447(1)	0.0062(1)	0.0313(8)	0.0342(7)	0.0268(6)	–0.0051(5)	–0.0032(5)	0.0002(5)
C(3)	4*e*	–0.0496(2)	–0.1924(1)	0.2304(1)	0.0338(8)	0.0280(7)	0.0323(7)	0.0027(5)	–0.0056(5)	–0.0051(5)
C(4)	4*e*	–0.0425(2)	–0.2925(1)	–0.0045(1)	0.0295(8)	0.0375(8)	0.0296(6)	–0.0003(6)	0.0068(5)	–0.0028(5)

Acknowledgments. This work has been supported by the Swedish Natural Science Research Council (NFR). X. D. Zou is a Research Fellow of the Royal Swedish Academy of Sciences supported by a grant from the Knut and Alice Wallenberg Foundation.

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