Crystal structure of dipiperazine decafluorodititanate dihydrate, $(C_4H_{12}N_2)_2[Ti_2F_{10}] \cdot 2H_2O$

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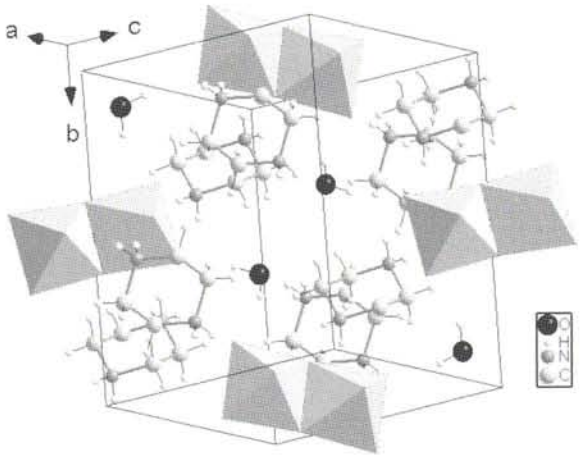

Abstract

$C_4H_{14}F_5N_2OTi$, monoclinic, $P12_1/n1$ (No. 14), $a = 8.655(5)$ Å, $b = 11.269(5)$ Å, $c = 9.224(5)$ Å, $\beta = 97.533(5)°$, $V = 891.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.032$, $wR_{all}(F^2) = 0.092$, $T = 293$ K.

Source of material

$(C_4H_{12}N_2)_2[Ti_2F_{10}] \cdot 2H_2O$ was prepared at room temperature from a water solution of piperazine, titanium isopropoxide (TiPT) and hydrofluoric acid. 0.66 g Titanium isopropoxide was hydrolized in 3.37 ml water, then 0.94 g aqueous HF acid (40%) was added under stirring to dissolve the hydrous titanium oxide. Finally, 0.65 g piperazine was added. Crystals of the title compound with well defined faces were formed in about 24 hours.

Discussion

The crystal structure consists of edge-shared TiF_6 octahedral pairs, diprotonated piperazine cations and crystal water. The fluoro-bridged dimeric anions $[Ti_2F_{10}]$ are isolated from each other. A Jahn-Teller distortion of the octahedrally coordinated titanium introduces some shortening on the Ti—F distances for the bridging F atoms and a significant deviation of their F–Ti–F angles from 90°. The three-dimensional structure is held together via a complicated network of hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colourless, prismatic, size 0.1 × 0.1 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	5.03 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2°$
$2\theta_{max}$:	52.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6713, 1732
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1511
$N(param)_{refined}$:	128
Programs:	SIR97 [1], DIAMOND [2], WinGX [3], SHELXL-97 [4]

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

Atom	Site	x	y	z	U_{iso}
HW(A)	4e	0.604(5)	–0.407(3)	0.312(4)	0.07(1)
HW(B)	4e	0.595(4)	–0.306(3)	0.408(4)	0.07(1)
H(1A)	4e	0.0885	–0.1232	0.4672	0.049(4)
H(1B)	4e	–0.0755	–0.1500	0.4232	0.049
H(4A)	4e	0.1703	–0.4090	0.2997	0.049
H(4B)	4e	0.3333	–0.3796	0.3449	0.049
H(2A)	4e	–0.0360	–0.3474	0.4599	0.039(3)
H(2B)	4e	0.0244	–0.2782	0.6041	0.039
H(3A)	4e	0.2787	–0.2866	0.5502	0.039
H(3B)	4e	0.2118	–0.4162	0.5473	0.039
H(5A)	4e	0.2291	–0.2526	0.1616	0.039
H(5B)	4e	0.2903	–0.1825	0.3050	0.039
H(6A)	4e	0.0417	–0.1162	0.2191	0.039
H(6B)	4e	–0.0234	–0.2462	0.2186	0.039

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)	4e	0.37856(4)	0.02298(3)	0.58303(4)	0.0140(2)	0.0210(2)	0.0217(2)	–0.0004(1)	–0.0002(1)	0.0019(1)
F(1)	4e	0.2164(2)	0.0303(1)	0.4197(1)	0.0191(6)	0.0334(8)	0.0309(7)	–0.0017(5)	–0.0067(5)	0.0025(5)
F(2)	4e	0.5047(2)	0.0189(1)	0.7674(1)	0.0323(8)	0.0380(8)	0.0213(6)	0.0106(6)	–0.0026(5)	–0.0015(5)
F(3)	4e	0.2888(2)	0.1703(1)	0.6444(2)	0.0218(6)	0.0288(7)	0.0462(8)	0.0072(5)	0.0036(5)	–0.0124(6)
F(4)	4e	0.2228(2)	–0.0688(2)	0.6668(2)	0.0379(8)	0.0504(9)	0.0452(9)	–0.0149(7)	0.0200(7)	0.0062(7)

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Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(5)	4*e*	0.4775(2)	–0.1072(1)	0.5126(2)	0.0303(7)	0.0301(7)	0.0406(8)	–0.0018(6)	0.0059(6)	0.0015(6)
OW	4*e*	0.5569(2)	–0.3789(2)	0.3830(2)	0.032(1)	0.040(1)	0.047(1)	–0.0050(8)	0.0174(8)	–0.0064(8)
N(1)	4*e*	0.0221(2)	–0.1772(2)	0.4224(2)	0.0150(8)	0.029(1)	0.042(1)	0.0021(8)	0.0015(7)	–0.0079(8)
N(4)	4*e*	0.2349(2)	–0.3539(2)	0.3449(2)	0.0207(9)	0.028(1)	0.032(1)	–0.0006(8)	0.0031(7)	–0.0089(8)
C(2)	4*e*	0.0410(3)	–0.2908(2)	0.5033(3)	0.025(1)	0.038(1)	0.033(1)	0.002(1)	0.0079(9)	0.001(1)
C(3)	4*e*	0.2024(3)	–0.3398(2)	0.4985(2)	0.027(1)	0.038(1)	0.026(1)	0.006(1)	0.0004(9)	0.0022(9)
C(5)	4*e*	0.2136(3)	–0.2398(2)	0.2627(2)	0.031(1)	0.032(1)	0.025(1)	–0.006(1)	0.0066(9)	–0.0036(9)
C(6)	4*e*	0.0527(3)	–0.1921(2)	0.2689(3)	0.031(1)	0.031(1)	0.031(1)	–0.002(1)	–0.0062(9)	0.0039(9)

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