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Anion and cation disorder in $[CN_3H_6]\cdot(TaF_6)$

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Abstract

A new guanidinium fluoride tantalate, $[CN_3H_6]\cdot(TaF_6)$, crystallises at 50 °C from a solution of Ta_2O_5 in 40% aqueous HF and of guanidinium chloride. The structure is rhombohedral, $R\bar{3}m$ space group, with the equivalent hexagonal cell $a_H = 8.647(1)$ Å, $c_H = 8.507(2)$ Å, $Z = 3$ and $R = 0.029$, $R_w = 0.077$ for 312 reflections. The three-dimensional network is built up from parallel $(0001)_H$ layers $_\infty([CN_3H_6]F_6)^{5-}$ between which tantalum atoms are inserted. These tantalum atoms, in 3a sites, adopt an octahedral coordination with $\langle d_{Ta\text{–}F}\rangle = 1.894(7)$ Å. $(TaF_6)^-$ anions are disordered over $(0001)_H$ mirror plane related positions while guanidinium cations are disordered over centrosymmetric positions; site occupancy of fluoride and nitrogen sites is fifty per cent.

Keywords: Hybrid fluoride; Guanidine; Tantalate; X-ray diffraction

1. Introduction

In the search of open structures in fluorides, high valence cations, Zr^{+IV} and Ta^{+V}, were recently examined and associated with amine cations in fluoride solutions [1–3]. Only one 3D open framework was evidenced in a guanidinium zirconate, $(H_3O)\cdot[CN_3H_6]_5\cdot(ZrF_5)_6$ [4], while numerous phases with isolated fluoride polyanions were obtained [5–8]. Then, the study of the Ta_2O_5-guanidine-aqueous HF system was undertaken over large concentration domains of the starting materials at low crystallisation temperatures. One new phase, which exhibits anion and cation disorder, was evidenced; it is reported here.

2. Experimental

Ta_2O_5 powder (1 g) was first dissolved under stirring in 40% aqueous HF (40 ml) at 80 °C during 4–5 h. After cooling to room temperature, guanidinium chloride (0.191 g) was added. Single crystals of $[CN_3H_6]\cdot(TaF_6)$, which are moisture sensitive, were grown by the slow evaporation of the solution at 50 °C over 2 days.

Truncated $(0001)_H$ platelets were selected by optical examination and single crystal diffraction data were obtained on a Siemens AED2 four-circle diffractometer.

3. Structure determination

Crystal data and the conditions of the intensity measurements are reported in Table 1 for $[CN_3H_6]\cdot(TaF_6)$. Absorption effects were corrected by the Gauss method. The structure was determined in the equivalent hexagonal cell by direct methods using SHELXS-86 [9] and refined with SHELXL-97 [10]. The rhombohedral cell parameters are $a_R = 5.742(1)$ Å, $\alpha_R = 97.17(2)°$, $V_R = 183.7(1)$ Å^3.

One heavy atom position was found in 3a special position (0, 0, 0) of $R\bar{3}m$ space group with TREF option of SHELXS-86 and was attributed to Ta. Then, successive refinements and Fourier difference maps allowed to locate F(1), F(2), N in 18h positions with a fifty per cent site occupancy and C in

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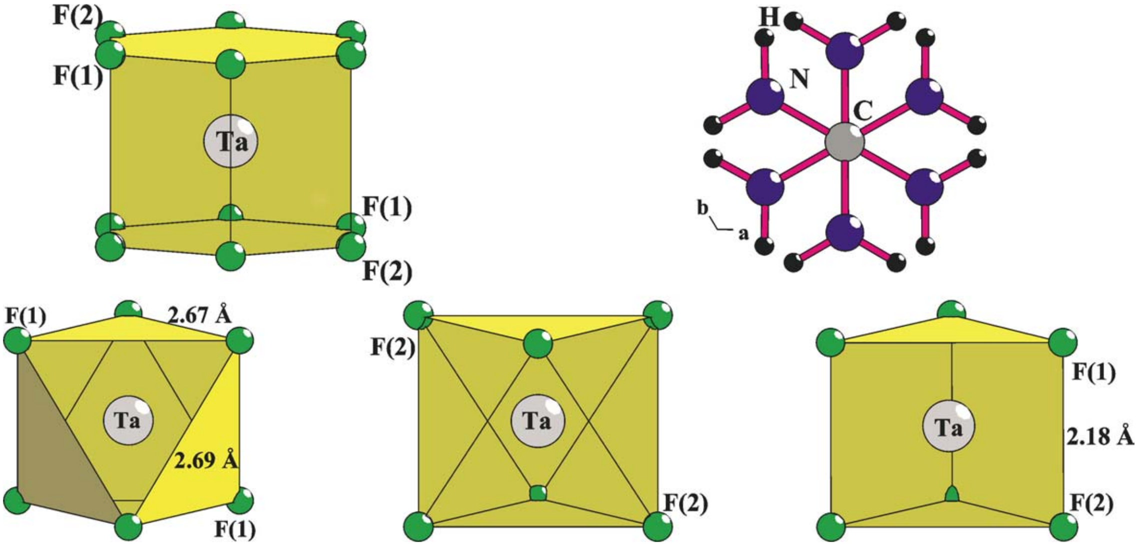

Fig. 1. View of the disordered environment of tantalum (top left) or carbon (top right) atoms in $[CN_3H_6]\cdot(TaF_6)$; possible orientations of the resulting $(TaF_6)^-$ octahedra (bottom left and center) and representation of one possible orientation of a triangular $(TaF_6)^-$ prism (bottom right).

Table 1
Crystallographic data of $[CN_3H_6]\cdot(TaF_6)$

Molar weight ($g\cdot mol^{-1}$)	355.02
Crystal size (mm^3)	$0.19 \times 0.19 \times 0.09$
Crystal system, space group	Rhombohedral, $R\bar{3}m$
a_H (Å)	8.647(1)
c_H (Å)	8.507(2)
V (Å^3), Z	550.9(3), 3
ρ_{calc} ($g\cdot cm^{-3}$)	3.21
Temperature (K)	298
Four circle diffractometer	Siemens AED2
Monochromator	graphite
2θ range (°)	2–70
Reflections measured/unique/used ($I > 2\sigma(I)$)	1080/316/312
(hkl) limits (two centric independent sets in $\bar{3}$)	$\lvert h\rvert \leqslant 13$; $\lvert k\rvert \leqslant 13$; $\lvert l\rvert \leqslant 13$
R_{int}	0.056
Scan mode	$\omega - 2\theta$
Absorption correction, A_{min}, A_{max}	Gaussian, 0.137, 0.299
Parameters refined (on F^2)	22
$^a R/^b R_w$	0.029/0.077
Goodness of fit	1.13
Weighting scheme ($p = [F_0^2 + 2F_c^2]/3$)	$1/[\sigma^2(F_0^2 + (0.0515p)^2 + 0.38P]$
Residues of Fourier difference ($e\,Å^{-3}$)	1.2, −1.5

[a] $R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$; [b] $R_w = \sum[w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
Atomic coordinates, site occupancy and equivalent atomic displacement parameters in $[CN_3H_6]\cdot(TaF_6)$

Atom	Site	τ	x	y	z	B_{eq} (Å^2)
Ta	3a	1	0	0	0	2.25(1)
F(1)	18h	1/2	0.1030(5)	$-x$	0.1292(8)	4.2(1)
F(2)	18h	1/2	$x(F(1))$	$-x$	$-z(F(1))$	B(F(1))
C	3b	1	0	0	1/2	2.3(1)
N	18h	1/2	0.0884(8)	$-x$	0.492(2)	3.5(2)

Table 3
Anisotropic displacement parameters in $[CN_3H_6]\cdot(TaF_6)$

Atom	$U_{11} = U_{22}$	U_{33}	$U_{23} = -U_{13}$	U_{12}
Ta	0.0187(2)	0.0480(3)	0	$U_{11}/2$
F(1), F(2)	0.048(3)	0.073(4)	−0.006(14)	0.032(3)
C	0.025(3)	0.038(5)	0	$U_{11}/2$
N	0.037(4)	0.065(6)	0.002(2)	0.025(5)

Table 4
Selected inter-atomic distances (Å) and angles (°) in $[CN_3H_6]\cdot(TaF_6)$

6 × Ta–F(1,2)	1.894(7)	3 × C–N	1.33(1)
		2 × N···F(1)	3.02(1)
		2 × N···F(2)	3.21(1)
		1 × N···F(1)	3.09(2)
		1 × N···F(1)	3.23(2)
6 × F(1,2)–F(1,2)	2.67(1)		
6 × F(1,2)–F(1,2)	2.69(2)	3 × N–C–N	119.0(4)

3b ($R = 0.15$). These atoms were differentiated from bond distance considerations. It was recognised here that a disorder affected the fluorine and nitrogen atom positions: the F(1)–F(2) distance was very short (2.18 Å) and it was found that F(1) and F(2) positions were related by a mirror plane at $z = 0$ (Fig. 1). Similarly, two CN_3 groups were found to be related by a symmetry centre located on carbon atom. Consequently, the atomic coordinates of F(1) and F(2) were constrained, $x_{F(1)} = x_{F(2)}$, $z_{F(1)} = -z_{F(2)}$ (Table 2), together with their anisotropic thermal motion parameters (Table 3). Hydrogen atom position was found from a difference Fourier map but was not included in the refinement.

The non-centrosymmetric R3m and R32 space groups were tested. The preceding disorder was maintained and