

INORGANIC COMPOUNDS

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Diammonium titanium pentafluoride, (NH₄)₂TiF₅, containing Ti³⁺

MIKE DADACHOV AND LARS ERIKSSON

*Division of Structural Chemistry, Arrhenius Laboratory,
Stockholm University, S-106 91 Stockholm, Sweden. E-mail:
lerik@struc.su.se*

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Abstract

Single crystals of the title compound have been synthesized by low-temperature hydrothermal treatment of titanium isopropoxide in the presence of hydrofluoric acid and ethylenediamine. The compound consists of parallel infinite chains of *trans*-corner-connected TiF₆ octahedra along the *b* axis, separated from each other by NH₄⁺ ions. The Ti atoms lie on inversion centres and the ammonium ions on mirror planes.

Comment

The title compound was prepared during a systematic investigation of synthetic zeolites and mixed framework compounds. Non-oxide compounds with more strongly electronegative ligands than oxygen, *e.g.* fluorine, could radically enhance the catalytic properties of the open-framework compounds. Our synthesis aimed at fulfilling these goals was not successful, but did result in a low-temperature preparation of a new compound of an ammonium salt of titanium pentafluoride containing rare reduced paramagnetic titanium Ti³⁺. The previously reported reduced titanium fluorides BaTiF₅ and CaTiF₅ (Eicher & Greedan, 1984), NaTiF₄ (Omaly *et al.*, 1976), CsTiF₄ (Sabatier *et al.*, 1982) *etc.* were prepared at high temperatures by solid-state synthesis or crystallization from melt under special atmospheric conditions, thus avoiding oxidation of the titanium. However, in the present case, the title compound was prepared starting from Ti⁴⁺ and fully reduced to Ti³⁺ under mild hydrothermal conditions.

The structure of (NH₄)₂TiF₅ consists of infinite one-dimensional chains, of composition (TiF₅)_n, made from corner-sharing TiF₆ octahedra that extend along the [010] direction. The Ti atoms lie on inversion centres and the ammonium ions on mirror planes. Three octahedra of the chain are shown in Fig. 1 and a packing diagram showing the chains along the *b* direction is shown in Fig. 2. The structure is held together by

electrostatic attraction from ammonium ions located in between the chains. All H atoms are involved in hydrogen bonds to the nearest F atoms. The H atoms attached to N1 are involved in three different types of hydrogen bonds, *i.e.* a single acceptor hydrogen bond to F3, a bifurcated hydrogen bond to F2 and a possible trifurcated hydrogen bond to one F1 and two F3. All four H atoms attached to N2 are involved in bifurcated hydrogen bonds. The different hydrogen bonds are probably dynamic in reality. If the N2 ammonium ion were allowed to rotate, one could imagine a hydrogen-bond disorder as some of the hydrogen-bond angles of the mean crystal structure are rather acute. This disorder is, however, not possible to determine with the present data and would require a neutron-diffraction study. The structure of (NH₄)₂TiF₅ is isostructural with (NH₄)₂MnF₅ (Sears & Hoard, 1969).

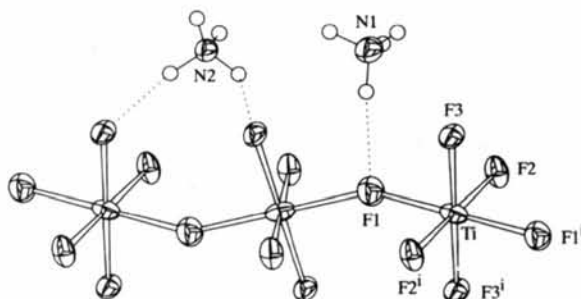


Fig. 1. Part of the chain built from corner-connected TiF₆ octahedra with anisotropic displacement ellipsoids at the 50% probability level [symmetry code: (i) $-x, -y, -z$].

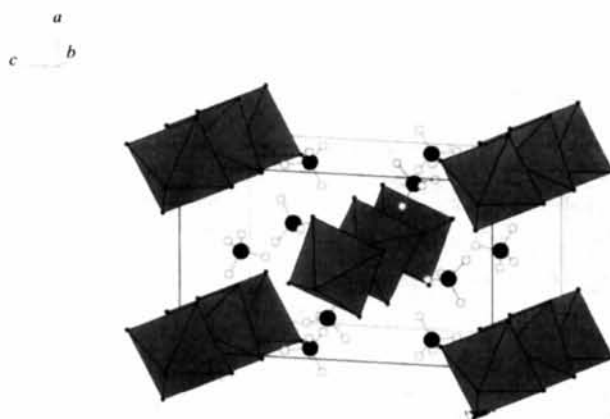


Fig. 2. The chains of corner-connected TiF₆ octahedra along the [010] direction with ammonium ions in between.

Experimental

Single crystals of the title compound were prepared by hydrothermal synthesis. Hydrous titanium oxide was obtained by adding titanium isopropoxide to water with continuous stirring. The hydrous oxide was combined with hydrofluoric acid (40%) and ethylenediamine (EDA) in a TiO₂:HF:EDA:H₂O molar ratio of 1:2:5:80. The mixture obtained was sealed in a 45 ml capacity Teflon-lined autoclave and heated to 473 K for 48 h. After cooling, the autoclave was opened and a mixture of pink needle-shaped rods of the title compound was obtained. Electron paramagnetic resonance data indicated that the compound contains the paramagnetic Ti³⁺. The powder diffraction lines of the title compound resembled those of both (NH₄)₂MnF₅ (Sears & Hoard, 1969) and (NH₄)₂FeF₅ (Fourquet *et al.*, 1989).

Crystal data

(NH ₄) ₂ TiF ₅	Mo K α radiation
$M_r = 178.98$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 950 reflections
<i>Pnma</i>	$\theta = 3.26\text{--}25.93^\circ$
$a = 6.3618(14) \text{ \AA}$	$\mu = 1.626 \text{ mm}^{-1}$
$b = 7.5586(12) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 11.059(2) \text{ \AA}$	Prism
$V = 531.8(2) \text{ \AA}^3$	$0.17 \times 0.13 \times 0.11 \text{ mm}$
$Z = 4$	Pink
$D_x = 2.235 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Stoe IPDS diffractometer	244 reflections with $I \geq 2\sigma(I)$
Area-detector scans	$R_{\text{int}} = 0.102$
Absorption correction: numerical (XRED; Stoe & Cie, 1997a)	$\theta_{\text{max}} = 25.94^\circ$
$T_{\text{min}} = 0.753$, $T_{\text{max}} = 0.817$	$h = 0 \rightarrow 7$
4040 measured reflections	$k = 0 \rightarrow 9$
555 independent reflections	$l = 0 \rightarrow 13$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{\text{max}} = 0.329 \text{ e \AA}^{-3}$
$wR(F^2) = 0.065$	$\Delta\rho_{\text{min}} = -0.365 \text{ e \AA}^{-3}$
$S = 0.737$	Extinction correction: SHELXL97 (Sheldrick, 1997)
555 reflections	Extinction coefficient: 0.0132(17)
46 parameters	Scattering factors from International Tables for Crystallography (Vol. C)
H atoms treated by a mixture of independent and constrained refinement	
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ti	0	0	0	0.0254 (4)
F1	0.0750 (5)	1/4	0.0115 (4)	0.0376 (11)
F2	0.2705 (4)	-0.0484 (3)	-0.0637 (2)	0.0333 (8)
F3	0.1066 (4)	-0.0328 (4)	0.1586 (2)	0.0307 (7)
N1	0.4225 (10)	1/4	0.1953 (5)	0.0362 (18)
N2	0.4917 (10)	3/4	0.1392 (4)	0.0252 (13)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ti—F1	1.9531 (9)	Ti—F3	1.896 (2)
Ti—F2	1.895 (2)		
F2—Ti—F3	89.66 (11)	F2—Ti—F1	89.39 (13)
F2—Ti—F3 ⁱ	90.34 (11)	F3—Ti—F1	88.78 (16)
F2 ⁱ —Ti—F1	90.61 (13)	F3 ⁱ —Ti—F1	91.22 (16)

Symmetry code: (i) $-x, -y, -z$.

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H11...F2 ⁱ	0.90	2.17	2.873 (6)	134
N1—H11...F2 ⁱⁱ	0.90	2.17	2.873 (6)	134
N1—H12...F1	0.90	2.14	3.003 (7)	160
N1—H12...F3	0.90	2.46	2.962 (6)	115
N1—H12...F3 ⁱⁱⁱ	0.90	2.46	2.962 (6)	115
N1—H13...F3 ^{iv}	0.90	2.10	2.924 (5)	152
N1—H13...F2 ⁱ	0.90	2.63	3.310 (5)	132
N2—H21...F3 ^{vi}	0.90	2.20	2.869 (5)	130
N2—H21...F3 ^{vii}	0.90	2.20	2.869 (5)	130
N2—H22...F2 ^{viii}	0.90	2.40	2.841 (5)	110
N2—H22...F2 ^{ix}	0.90	2.40	2.841 (5)	110
N2—H23...F3 ^x	0.90	2.23	2.957 (6)	138
N2—H23...F2 ^{xi}	0.90	2.37	2.957 (6)	134

Symmetry codes: (i) $1-x, \frac{1}{2}+y, -z$; (ii) $1-x, -y, -z$; (iii) $x, -\frac{1}{2}-y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vi) $\frac{1}{2}+x, 1+y, \frac{1}{2}-z$; (vii) $1-x, 1-y, -z$; (viii) $x, \frac{1}{2}-y, z$.

The large *R* value is connected with the fact that there were a large number of weak reflections contributing to it, however, this did not hinder the successful structure analysis. Furthermore, R_{int} had a value of 0.0410 when computed only from significant reflections [$I > 3\sigma(I)$], indicating that the high R_{int} is mainly due to the large set of weak reflections. The low value of *S* is most probably due to a slight erroneous estimation of the weights of the large number of weak reflections present in the data set. The structure was first solved by direct methods (Sheldrick, 1990) in *Pna2*₁ (No. 33) as we encountered problems with the direct-methods solution in *Pnma* (No. 62). The *Pna2*₁ model was converted to *Pnma* and found to be isostructural with the model of (NH₄)₂MnF₅ (Sears & Hoard, 1969). Both the *Pna2*₁ and *Pnma* models converged easily, the difference being that the *Pnma* model was better behaved in the least-squares process. The H atoms of the ammonium ions were located from difference Fourier maps and the interatomic distances between hydrogen and nitrogen were restrained in the refinement to a value of 0.90 (2) \AA . Simultaneously, the distance between all four H atoms of each ammonium ion were restrained to a value of 1.47 (2) \AA , giving a regular tetrahedral shape to the ammonium ions. The positions of the H atoms were fixed in the final refinement cycles to get a better data/parameter ratio. This procedure did not affect any other parameters.

Data collection: EXPOSE (Stoe & Cie, 1997b). Cell refinement: CELL (Stoe & Cie, 1997b). Data reduction: INTEGRATE (Stoe & Cie, 1997b). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: DIAMOND (Bergerhoff, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1262). Services for accessing these data are described at the back of the journal.

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Silver-ion conduction pathways in $\text{Ag}_5\text{IP}_2\text{O}_7$

STEFAN ADAMS AND ANDREA PREUSSER

Mineralogisch-Kristallographisches Institut, Universität Göttingen, Goldschmidtstraße 1, D-37077 Göttingen, Germany. E-mail: sadams@gwdg.de

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Abstract

Pentasilver iododiphosphate, $\text{Ag}_5\text{IP}_2\text{O}_7$, is the compound with the lowest AgI content in the pseudo-binary system $\text{AgI}-\text{Ag}_4\text{P}_2\text{O}_7$. The X-ray single-crystal structure determination establishes that the coordination spheres of all the silver ions contain both oxide and iodide anions. Silver-ion conduction pathways in this solid electrolyte are modelled by the bond-valence technique.

Comment

In the course of our structural investigation of crystalline analogues of the ion-conducting silver iodide silver oxyacid salt glasses (Adams, 1996, 1999; Adams & Maier, 1998), we synthesized the compound $\text{Ag}_5\text{IP}_2\text{O}_7$, which was first described by Takahashi *et al.* (1972).

From the assumption that only silver ions coordinated by iodide should contribute to the silver-ion conductivity, these authors had postulated a segregation of $\text{AgI}-\text{Ag}_4\text{P}_2\text{O}_7$, yielding a network of AgI-like regions even for the glassy state. Our crystal structure determination rules out this hypothesis and reveals that all silver ions are coordinated by both diphosphate and iodide anions in crystalline $\text{Ag}_5\text{IP}_2\text{O}_7$. Furthermore, it is demonstrated that the diphosphate unit is completely ordered at room temperature (Fig. 1), whereas the diphosphate groups in the only other structurally characterized silver iododiphosphate, the AgI-rich superionic $\text{Ag}_{16}\text{I}_{12}\text{P}_2\text{O}_7$, are rotationally disordered among six positions according to the room-temperature structure analysis by Garrett *et al.* (1982).

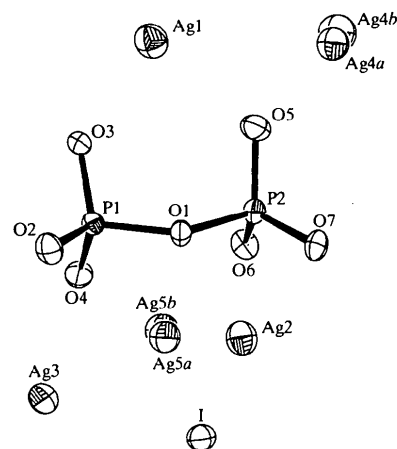


Fig. 1. An ORTEP III (Burnett & Johnson, 1996) plot of the asymmetric unit of the title compound with 50% probability displacement ellipsoids.

$\text{Ag}_5\text{IP}_2\text{O}_7$ is a moderate silver-ion conductor with an activation energy of 0.28 eV and a room temperature conductivity of about $3 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$. An analysis of the Ag bond-valence distribution throughout the unit cell of $\text{Ag}_5\text{IP}_2\text{O}_7$ suggests that long-range Ag migration pathways [modelled in Fig. 2(a) by the infinite bond-valence isosurface with the minimum Ag valence sum mismatch $\Delta V = 0.23$] involve all Ag sites. The Ag^+ conduction occurs preferably within layers extending perpendicular to the *c* axis. A detailed discussion on the modelling of ion-conduction pathways by bond-valence maps introduced by Garrett *et al.* (1982) will be published elsewhere (Adams, 1999). The basic features of the conduction-pathway model for $\text{Ag}_5\text{IP}_2\text{O}_7$ are thus in full accordance with our earlier findings for $\text{Ag}_8\text{L}_4\text{V}_2\text{O}_7$ (Adams *et al.*, 1996). The local hopping processes with the lowest activation energies should be jumps from the Ag4 or Ag2 sites to an interstitial site between these fully occupied sites (Fig. 2b).