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Crystal Structures of Trisammonium Bisperoxotetrafluoroniobate(V) and Analogous Tantalate(V)

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$(NH_4)_3[Nb(O_2)_2F_4]$ (I) and $(NH_4)_3[Ta(O_2)_2F_4]$ (II) are isostructural, and belong to the cubic Fm3m space group with four molecules in the unit cell. The unit cell parameters are a = *9.4442(4) (I) and* a = *9.4512(4) Å (II). The structures were solved by the Patterson method and were refined by the least-squares method to the conventional R factors of 0.036 for 86 reflections (I) and 0.043 for 103 reflections (II) (in both structures having $I \geqslant 2\sigma(I)$). The disordered distributions of fluorine and peroxo oxygens with partially occupied sites are observed. The disordered NH_4^+ tetrahedra appear in the structures.*

The metal atoms exhibit an octahedral coordination with two corners of a polyhedron at the centre of the peroxo bonds. Inter-atomic distances are Nb–F, 1.95(2), Nb–O, 1.94, Ta–F, 1.91(4) and Ta–O, 2.07 Å.

The structures (I, II) are composed of $[M^V(O_2)_2F_4]^{3-}$ octahedra and two symmetrically-independent ammonium cations connected by N–H•••O and N–H•••F hydrogen bonds. These two structures are compared with the structure of $(NH_4)_3[Ti(O_2)F_5]$.

Introduction

Alkaline and ammonium diperoxotetrafluoro niobates and tantalates were prepared by dissolving the metal pentoxide in conc. hydrofluoric acid by adding hydrogen peroxide to the clear solution; the obtained complexes were characterized by analytical data, conductivity measurements (3/1 electrolytes), and infrared spectra [1]. According to the infrared spectra the molecule of crystalline water was assigned [1]. However, X-ray structure determination of the two title compounds has not revealed the presence of water molecules in the unit cells.

The unit cell parameters of the title compounds are isodimensional to those of $(NH_3)_3[ZrF_7]$ [2–5] and $(NH_4)_3[Ti(O_2)F_5]$ [6] (Table I). The lattice constants of potassium analogous to the title com-

TABLE I. Crystallographic Data for Structurally Related Fluoro Complexes of Ti, Zr, Nb, and Ta.

Complex	Unit cell dimension [(25.0 ± 0.5) °C] *a* (Å)	Space group	D_m (g cm^{-3})	D_x (g cm^{-3})	Reference
$K_3[ZrF_7]$	8.951(10)			3.17	[3]
$K_3[Ta(O_2)_2F_4]$	9.046(1)	Fm3m	3.84	3.94	this work
$K_3[Nb(O_2)_2F_4]$	9.058(2)	Fm3m	2.96	3.14	
$(NH_4)_3[Ti(O_2)F_5]$	9.20	Fm3m	1.90	1.93	[6]
	9.2433(6)				this work
$(NH_4)_3[ZrF_7]$	9.353		2.20	2.22	[2]
	9.365(10)	Fm3m			[3]
	9.4172(4)				this work
$(NH_4)_3[Nb(O_2)_2F_4]$	9.4442(4)	Fm3m	2.16	2.27	this work
$(NH_4)_3[Ta(O_2)_2F_4]$	9.4512(4)	Fm3m	2.90	2.96	this work

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pounds are also isodimensional to $K_3[ZrF_7]$ [3]. Considering the space group symmetry, unit cell dimensions, and crystal structure patterns of these compounds, the appropriate classification can be given: potassium and ammonium bisperoxotetrafluoroniobates(V) and tantalates(V) are isotyped, whereas ammonium and potassium heptafluorozirconates(IV) and ammonium peroxopentafluorotitanate(IV) are homeotyped. Close structural relations found in this series are common among fluorides [7, 8].

The chemical formula and the cubic Fm3m symmetry of the discussed compounds suggest certain irregularities in their structures. In the structures of ammonium compounds listed in Table I, an incompatibility of the symmetry of NH_4^+ tetrahedron and the symmetry m3m (4b) of the space group Fm3m occupied by the nitrogen atom at (½, ½, ½) is obvious. A heptacoordination appearing in the $(NH_4)_3[ZrF_7]$, $K_3[ZrF_7]$ [3–5], and $(NH_4)_3(Ti(O_2)F_5]$ [6] structures could not be fitted in a regular cubic symmetry. A peroxoligand occurring in the title structures could not be situated in any of the Wyckoff positions in the space group Fm3m. The disordered models of $[ZrF_7]^{3-}$ [3, 6], $[Ti(O_2)F_5]^{3-}$ [6] and nitrogen atoms 3,5 were postulated on the basis of X-ray powder data.

The dynamical disorder of both NH_4^+ tetrahedra and $[ZrF_7]^{3-}$ were confirmed by neutron and X-ray diffractions [5], and ^1H and ^{19}F NMR studies [9, 10]. In order to compare the disordered models of the title structures with the $(NH_4)_3[Ti(O_2)F_5]$ structure, single crystal data of titanium compound (III) were also recorded. The disordered distributions of ammonium, fluorine and peroxo oxygen atoms were observed in these structures.

Experimental

The space group was determined from Weissenberg photographs recorded with CuKα radiation. The diffraction symmetry and extinctions indicated the space group Fm3m and this was confirmed during structure refinement. The precise values of unit cell parameters given in Table I were deduced from zero-layer rotation patterns of single crystals taken in asymmetric (Straumanis) positions, and from the pairs of reflections at high angles chosen from single crystal diffraction patterns taken by a counter diffractometer [11]. The densities were measured at 298 K pycnometrically with decalin. The intensities were collected with the crystals of dimensions 0.021 X 0.021 X 0.021 mm (Nb-compound, μ = 14.3 cm^{-1} MoKα) 0.040 X 0.038 X 0.036 mm (Ta-compound, μ = 129.6 cm^{-1} MoKα) and 0.029 X 0.029 X 0.029 mm (Ti-compound, μ = 11.3 cm^{-1} MoKα) on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-scan mode with graphite monochromated MoKα radiation. In the range $3 < \theta < 32°$ 86 (I), 103 (II), and 83 (III) independent reflections were recorded $[I \geq 2\sigma(I)]$ and used in the calculations. The data were corrected for background, Lorentz and polarization effects.

TABLE II. Final Coordinates ($\times 10^3$) and Occupance Factors.

	x	y	z	
I				
Nb	0	0	0	1
F	207(2)	0	0	0.667
N(1)	¼	¼	¼	1
N(2)	½	½	½	1
O	0	77	190	0.167
II				
Ta	0	0	0	1
F	203(3)	0	0	0.667
N(1)	¼	¼	¼	1
N(2)	½	½	½	1
O	0	77	204	0.167
III				
Ti	0	0	0	1
F	207(1)	0	0	0.333
N(1)	¼	¼	¼	1
N(2)	½	½	½	1
O	0	77	180	0.083

Results and Discussion

Structure Determination and Refinement

The Patterson maps were solved in Fm3m, which showed that the heavy metal atoms (Nb, Ta, Ti) are positioned at site 4(a) and nitrogen atoms at sites 4(b) and 8(c).

Fourier synthesis (I, II, III) based on the coordinates of the heavy metal atoms and the nitrogen atoms revealed positions of fluorine at site 24(e) and peroxo-oxygen at 96(j). Considering the chemical formula and a cubic symmetry of these compounds, certain irregularities in their crystal structures were expected. During data collection the differences in the intensities of symmetry-related reflections, which cannot be attributed to an absorption effect, were observed. The disordered distributions of fluorine and peroxo-oxygen atoms are the consequence of partly occupied sites (Table II).

The peroxo-oxygen atom was located in a difference Fourier synthesis and its coordinates were not refined. One of three equivalent trans positioned peroxo pairs is chosen. The structures were refined by full-matrix least-squares, minimizing $\Sigma w(|F_o| - |F_c|)^2$. Weights were assigned as $w = w_1 \cdot w_2$ where $w_1 = 1$ for $|F_o| \leq 50$ and $50/|F_o|$ for $|F_o| > 50$

TABLE III. Anisotropic Thermal Parameters ($\times 10^2$).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I						
Nb	2.76(4)	2.76(4)	2.76(4)	0	0	0
F	2.52(6)	23(1)	23(1)	0	0	0
N(1)	4.9(2)	4.9(2)	4.9(2)	0	0	0
N(2)	4.8(4)	4.8(4)	4.8(4)	0	0	0
O	2.3(5)	18(2)	7(2)	0	0	−5(1)
II						
Ta	1.65(3)	1.65(3)	1.65(3)	0	0	0
F	2(1)	17(2)	17(2)	0	0	0
N(1)	3.4(3)	3.4(3)	3.4(3)	0	0	0
N(2)	3.4(3)	3.4(3)	3.4(3)	0	0	0
O	2.1(8)	8(2)	3(2)	0	0	−2(2)
III						
Ti	2.10(9)	2.10(9)	2.10(9)	0	0	0
F	1.8(5)	14.7(9)	14.7(9)	0	0	0
N(1)	4.9(3)	4.9(3)	4.9(3)	0	0	0
N(2)	5.7(5)	5.7(5)	5.7(5)	0	0	0
O	0.4(8)	22(4)	3(3)	0	0	−2(3)

(compound I); $w_1 = 1$ for $|F_o| \leqslant 120$ and $120/|F_o|$ for $|F_o| > 120$ (compound II); $w_1 = 1$ for $|F_o| \leqslant 30$ and $30/|F_o|$ for $|F_o| > 30$ (compound III); $w_2 = 1$ for $\sin\theta \geqslant 0.30$ and $\sin\theta/0.30$ for $\sin\theta < 0.30$ for the structures I, II, III. The final difference Fourier syntheses indicate no significant residuals which can locate hydrogen atoms. The final $R = 0.036$ and $R_w = 0.042$(I), $R = 0.043$ and $R_w = 0.053$(II), $R = 0.051$ and $R_w = 0.063$(III).

The scattering factors given by Cromer and Mann [12] were used. The anomalous-dispersion corrections were included for Nb, Ta, and Ti [13].

Calculations were carried out on a Univac 1110 Computer at the Computing Centre in Zagreb with the X-RAY System [14]. Final atomic coordinates and anisotropic thermal parameters are listed in Tables II and III.

Description and Discussion of the Structures

Metal coordination

The Nb and Ta atoms are coordinated by four symmetrically-related F atoms and two peroxo groups. The coordination polyhedra are octahedra with two of the corners in the middle of the peroxo bonds (Fig. 1a). The metal–fluorine and metal–peroxo-oxygen distances are:Nb–F, 1.95(2), Ta–F, 1.91(4), Nb–O, 1.94, and Ta–O, 2.07 Å. The $(NH_4)_3[Ti(O_2)F_5]$ complex also exhibits an octahedral coordination with a corner of a polyhedron in the middle of a peroxo bond. The bond distances are Ti–F, 1.91(1) and Ti–O, 1.82 Å. However, the coordination polyhedron around titanium can be described as a pentagonal bipyramid [6] accepting the peroxo group as a bidentate ligand. In this case an analogy with the heptacoordination appearing in $[ZrF_7]^{3-}$ species can be seen [3, 6].

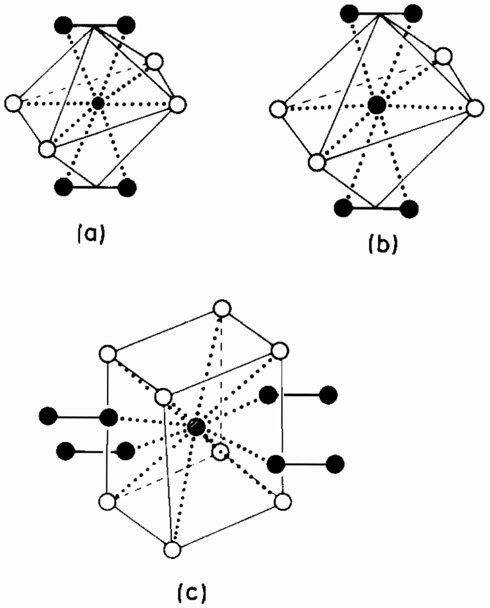

Fig. 1. a) Coordination polyhedron around Nb (and Ta). Open circles represent F atoms and black, large ones peroxo oxygen. b) Octahedral environment around ammonium cation of N(2) (dashed circle) located at m3m. c) Surroundings of ammonium cation of N(1) (dashed circle) positioned at $\bar{4}3$ m.

Bond lengths of the peroxo groups in these complexes 1.45(I), 1.45(II) and 1.42(III) are in agreement with literature data [15].

Ammonium environment

Two symmetrically independent nitrogen atoms exhibit different environments (Fig. 1b and c). The N(1) atom at $\bar{4}3$m (8c) is surrounded by eight F atoms disposed at corners of a quadrilateral prism and four oxygen atoms from four peroxo groups. The N(1)···F contacts (I, II, III) are lager than 3.30 Å, excluding the possibility of N–H···F hydrogen bonds. The corners of the NH_4 tetrahedron are oriented so as to meet the symmetry requirements of $\bar{4}3$ m site [N(1) towards the O atom]. Thus, each N(1) atom is involved in four N–H···O hydrogen bonds [2.92(I), 2.90(II), 2.88(III) Å]. The disordered distribution of F and peroxo-groups might cause the re-orientation of NH_4^+ tetrahedra. An octahedral arrangement of hydrogen electron density around N at (¼, ¼, ¼) in the structure of $(NH_4)_3$-$[ZrF_7]$ [5] suggests disordered NH_4 tetrahedra.

The ammonium cation of N(2) at m3m (4b) is in octahedral environment of four F atoms and two peroxo groups (Fig. 1b). Interatomic contacts of N(2)···F, 2.76(2)(I), 2.82(4)(II), 2.71(1)(III), and

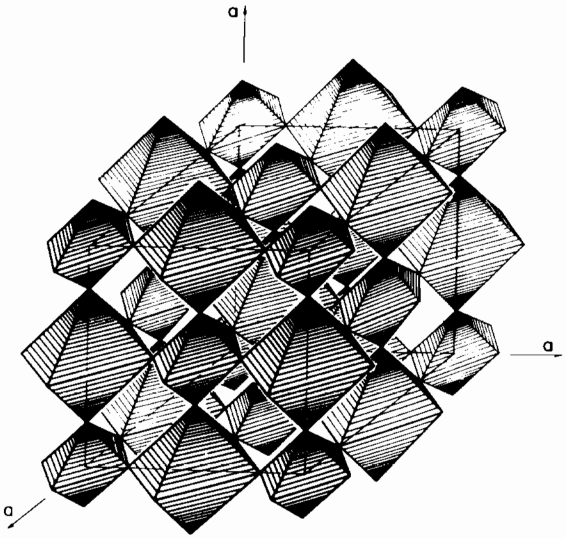

Fig. 2. Molecular packing of octahedra around metal atom and ammonium of N(2). The N(1) tetrahedra are fitted in the holes between octahedra.

N(2)···O, 3.01(1), 2.88(II), 3.03(III) suggest formation of trifurcated hydrogen bonds.

Molecular packing

The crystal structures are composed of $[M^VF_4(O_2)_2]$ octahedra (Fig. 1a). These octahedra share corners with octahedral neighbours around ammonium of N(2), forming an infinite three-dimensional arrangement (Fig. 2). The holes appearing between these octahedra are occupied by the N(1) tetrahedra.

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