The Disordered Structure of Ammonium Pentafluoroperoxotitanate(IV), $(NH_4)_3[TiF_5(O_2)]$

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Ammonium pentafluoroperoxotitanate(IV) has a disordered structure at room temperature for which a possible model is suggested. This model is based on single crystal X-ray diffraction data collected by the integrating Weissenberg film method. The crystals are cubic, space group $Fm3m$, with $a = 9.231(5)$ Å, $V = 787(1)$ Å^3 and $Z = 4$. Least squares refinement of the structural parameters yielded a final R-value of 0.058, based on 68 independent reflexions. The average distance between titanium and the ligand atoms is 1.94(2) Å. The data are consistent with a statistically oriented pentagonal bipyramidal complex anion, and three ammonium ions, one of which is also statistically oriented.

The structure of $(NH_4)_3[TiF_5(O_2)]$ has been studied as part of an investigation on transition metal peroxo complexes. From powder data,[1] Peyronel suggested that the structure was disordered and could be described in a similar way as that used by Hampson and Pauling [2] for $(NH_4)_3[ZrF_7]$, i.e. with $[TiF_5(O_2)]^{3-}$ as a capped octahedron. Since the space group is $Fm3m$ it is evident that an ordered structure is impossible. The model proposed by Peyronel is, however, not the only possible one. In fact, a transition metal peroxo complex with mono-capped octahedral symmetry is highly unlikely in view of existing knowledge concerning the structures of such compounds. Instead, a pentagonal bipyramidal arrangement of ligand atoms seems more natural. In a re-investigation [3] of $(NH_4)_3[ZrF_7]$, the $[ZrF_7]^{3-}$ ion has been shown to have a pentagonal bipyramidal configuration. The present investigation was undertaken in order to elucidate the structure of the $[TiF_5(O_2)]^{3-}$ ion.

EXPERIMENTAL

The compound was prepared according to Piccini,[4] whose method gave small, pale yellow octahedral crystals. The intensity data were collected with an integrating Weissenberg camera using CuKα radiation. A total of 68 independent reflexions were recorded by the multiple film method. The intensities of the reflexions were estimated visually and corrected for Lorentz and polarization effects but not for absorption and extinction.

A powder photograph of the substance, taken with CuKα$_1$ radiation in a Guinier camera with lead nitrate as internal standard, was used to determine the cell dimensions accurately. Observed and calculated d-values are given in Table 1. All calculations were performed at the Göteborg Universities' Computing Centre using an IBM 360/65 computer and a set of crystallographic programs in use at Göteborg. The atomic scattering factors used in the calculation of structure factors were taken from Cromer and Waber.[5]

Table 1. Observed lines in the powder photograph of $(NH_4)_3[TiF_5(O_2)]$ at room temperature registered with CuKα radiation, using lead nitrate ($a = 7.8566$ Å) as internal standard.

d_o	d_c	$h\ k\ l$	I_o
5.334	5.325	1 1 1	vs
4.618	4.611	2 0 0	s
3.261	3.261	2 2 0	s
2.6635	2.6625	2 2 2	vw
2.3064	2.3059	4 0 0	s
2.0607	2.0624	4 2 0	w
1.8824	1.8828	4 2 2	m
1.7762	1.7751	{5 1 1 / 3 3 3	m
1.6298	1.6305	4 4 0	w
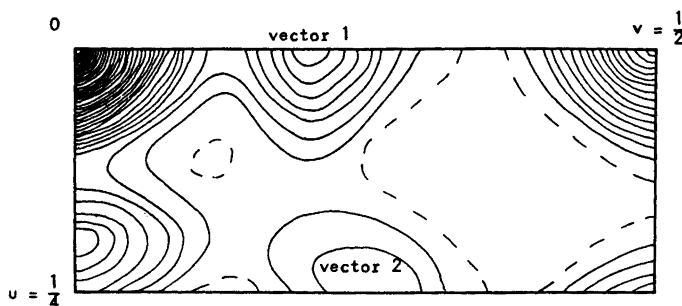
Fig. 1. The Patterson function P(*uvw*) at *w* = 0.

CRYSTAL DATA

$(NH_4)_3[TiF_5(O_2)]$; $M = 229.0$ g mol^{-1}
Cubic, $Fm3m$ (No. 225), $Z = 4$
$a = 9.231(5)$ Å (Peyronel:[1] $a = 9.20$ Å)
$V = 787(1)$ Å^3
$D_c = 1.934$ g cm^{-3}
$\mu(CuK\alpha) = 103$ cm^{-1}

A list of observed and calculated structure factors is available from the author R.S. on request.

STRUCTURE DETERMINATION

The unit cell contains four formula units. The four titanium atoms thus might occupy the positions 4a of space group $Fm3m$. The Patterson function ought to resemble the structure since vectors involving the titanium atoms will appear at atomic positions if the titanium atoms are not disordered and thus occupy the positions 4a. The Patterson function (the section at $w = 0$ is given in Fig. 1) showed two crystallographically independent diffuse peaks at about 2 Å from the origin, which were interpreted as Ti−F and Ti−O vectors. Fluorine and oxygen atoms thus occupy two positions (denoted by 1 and 2) of the type 0yz. Vectors at ¼00 and ¼¼¼ were interpreted as Ti−N(1) and Ti−N(2) vectors. The data could not be analysed in terms of ordered fluorine and oxygen atoms. Furthermore, since it was evident that it would not be possible to distinguish between oxygen and fluorine, all atoms coordinated to titanium were treated as fluorine atoms (F(1) and F(2), respectively). The disordered fluorine and oxygen electron distribution was accounted for in the calculated structure factors by introducing partial fluorine atoms within the disordered peaks in such a way that the observed peak shapes were reproduced. Since the ratio between the heights of the Patterson peaks 1 and 2 is about 2.5 and there is a total of twenty-eight oxygen and fluorine atoms, vector 1 was accounted for by twenty partial fluorine (and oxygen) atoms F(1) in positions 96j of space group $Fm3m$ while vector 2 was taken to be due to eight partial fluorine (and oxygen) atoms F(2), also in positions 96j.

A least-squares refinement was undertaken at this stage. After three cycles of refinement the R-value was 0.083. Both an electron density map and a difference map were calculated. The latter showed the hydrogen atoms H(1) and H(2) bonded to N(1) and N(2), respectively. Since there were six peaks around N(1) it was apparent that the hydrogen atoms H(1) were also disordered. Introduction of these hydrogen atoms, with appropriate occupancy factors, into the least-squares refinement reduced the R-value to 0.058 after three more cycles. The temperature parameters of the hydrogen atoms were kept constant and were given the value $B = 5.0$ Å^2. All shifts were less than 10 % of the corresponding standard deviations after the last cycle. The results from the refinement were checked by calculating a three-dimensional electron density difference map. This showed only small residual maxima, the largest maximum having a magnitude of about 5 % of the height of a nitrogen peak in the F_o-synthesis. The atomic parameters are given in Table 2.

Table 2. Atomic coordinates, expressed as fractions of the cell edges, and isotropic thermal parameters for $(NH_4)_3[TiF_5(O_2)]$. Space group $Fm3m$, $Z = 4$. The numbers in parentheses are the standard deviations of the last significant figures. The temperature factor $= \exp(-B \sin^2 \theta/\lambda^2)$. The thermal parameters of the hydrogen atoms were assigned the value 5.0 Å^2 and were not refined. Note that F(1) and F(2) include the oxygen atoms as well.

Atom	Position	Occupancy factor	x	y	z	B
Ti	4a	1	0	0	0	3.07(9)
N(1)	4b	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	4.9(7)
N(2)	8c	1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	5.0(3)
F(1)	96j	0.208	0	0.046(1)	0.205(1)	4.9(3)
F(2)	96j	0.083	0	0.112(3)	0.180(3)	5.4(6)
H(1)	24e	0.667	0.388(13)	0	0	5.0
H(2)	32f	1	0.185(6)	0.185(6)	0.185(6)	5.0

DISCUSSION

The capped octahedron model proposed by Hampson and Pauling for ammonium heptafluorozirconate and applied to ammonium pentafluoroperoxotitanate by Peyronel is without doubt incorrect since this requires fluorine and oxygen atoms along the [111] direction and a slight disorder of the heavy atoms. These conditions were not observed. Instead, the many partial fluorine and oxygen sites are consistent with a disordered orientation of an ordered pentagonal bipyramidal arrangement of ligands (Fig. 2) such as that found in the ion $[NbF_5(O_2)]^{2-}$.[6]

The observed interatomic distances

Ti $-$ F(1)	1.938(14) Å
Ti $-$ F(2)	1.959(39) Å
N(1) $-$ H(1)	1.03(12) Å
N(2) $-$ H(2)	1.04(9) Å

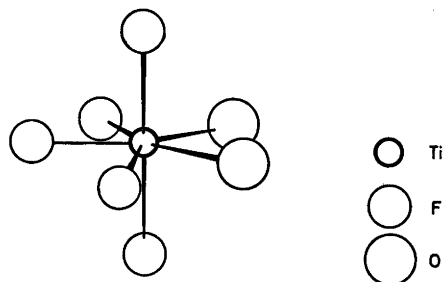are very probable, which is a further indication of the correctness of the structure.

REFERENCES

1. Peyronel, G. *Gazz. Chim. Ital. 71* (1941) 620.
2. Hampson, G. C. and Pauling, L. *J. Am. Chem. Soc. 60* (1938) 2702.
3. Hurst, H. J. and Taylor, J. C. *Acta Crystallogr. B 26* (1970) 417.
4. Piccini, A. *Z. Anorg. Allg. Chem. 10* (1895) 438.
5. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
6. Stomberg, R. *To be published.*

Fig. 2. The ion $[TiF_5(O_2)]^{3-}$.