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CRYSTALLOGRAPHIC DATA ON BIS-TETRAFLUOROAMMONIUM HEXAFLUORONICKELATE (IV), $(NF_4)_2NiF_6$

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SUMMARY

X-ray diffraction studies on both powdered and single crystal samples of $(NF_4)_2NiF_6$ have shown that the compound crystallises in a tetragonal form derived from the K_2 $PtCl_6$ structure. The space group is I 4/m and the unit cell dimensions are : a = 6.828 (5) Å, c = 9.270 (9) Å, c/a = 1.358, and Z = 2.

INTRODUCTION

The compound $(NF_4)_2NiF_6$, which was first prepared and characterized by Christe [1], is just one example of a very interesting group of perfluoroammonium salts. These compounds, which have been proposed as fluorine sources for chemical lasers, [2-4] are also interesting from a structural point of view, since anions with the central atom tetra, penta or hexa-coordinated [5] have been found associated with the tetrafluoroammonium ion.

The original syntheses were carried out by Christe and his co-workers and the vibrational spectra given in their papers allow straightforward identifications of the compounds. The X-ray powder patterns have also been given, and as far as $(NF_4)_2NiF_6$ is concerned, its pattern has been indexed [1] on a tetragonal cell with parameters a = 10.457 Å, c = 10.953 Å, V = 1197.7 Å^3, Z = 16/5.

This is the same type of structure which has been proposed for the other kwnown $(NF_4)_2MF_6$-type salts such as (M = Ge, Sn, Ti) [5, 3, 6].

Current interest in this laboratory in high oxidation state species and in compounds related to chemical laser technology, led us to prepare the title compound. Chemical analysis and vibrational spectroscopy indicated that the compound was of sufficient purity for the X-ray powder pattern to be reliable enough to be exploited to gain more information on the crystal structure. Partial data were also obtained from single crystals, and the combined information permitted the space group, the unit-cell parameters and molecular structure of $(NF_4)_2NiF_6$ to be determined.

EXPERIMENTAL

The compound was prepared by the indirect metathetical process described in the original paper [1]. Purification was achieved by alternating the in-cold-HF filtration [1] and BrF_5 [7] treatments. Spectroscopic and elemental analyses, showed that the compound had the composition (mol %) : $(NF_4)_2NiF_6$: 98.9 ; Cs_2NiF_6 : 0.9 ; NF_4SbF_6 : 0.2. Single crystals were obtained by slow evaporation of an HF solution containing a sample with the above composition, and these were introduced into 0.5 mm i.d. quartz capillaries in a nitrogen filled dry box. One of the best crystals which could be obtained, although large and somewhat imperfect was studied by Weissenberg and precession spinning crystal techniques. The hkl (l=0,1) layers about the c-axis were obtained with the Weissenberg diffractometer. The intensities of the reflections, which were found to be strongly affected by absorption, have been estimated visually using an intensity scale.

RESULTS

From the single crystal study, the unit cell emerged as body - centred tetragonal (I) with a = 6.828 (5) Å ; c = 9.270 (9) Å ; c/a = 1.358. The c/a ratio close to $\sqrt{2}$ and the body-centered unit cell indicate that the structure can be derived from a distorted face-centred cubic cell with a volume twice as large, corresponding to 9.65 × 9.65 × 9.27 Å. This allows the assignment of the X-ray powder pattern with the extinction rule : h+k+l=2n.

TABLE I

Powder Pattern of $(NF_4)_2NiF_6$

hkl	d calc (Å)	d obs. (Å)	Int	ref.[1] dobs. (Å)
101	5.497	5.50	vs	5.46 vs
110	4.828	4.82	vw	–
200	3.414	3.41	m	3.42 ms
112	3.344	3.35	ms	3.31 s
211	2.900	2.89	m	2.880 ms
103	2.815	2.82	mw	–
202	2.749	2.74	w	2.742 mw
220	2.414	2.41	m	2.407 mw
004	2.318	2.313	w	–
213	2.172	2.162	s double	2.150 s
310	2.159			
114	2.089	2.088	w	–
312	1.957	1.951	vw	1.954 w
204	1.917	1.912	trace	–
321	1.855	1.849	m	1.846 m
303	1.832	1.829	trace	
105	1.789	1.788	mw	
400	1.707	1.702	vw	
224	1.672	1.668	w	
411	1.630	1.626	m	
330	1.609	1.609	m	
314	1.580	1.583	mw	
006	1.545	1.545	w	
332	1.520	1.520	w	

The main lines with the exception of the reflection at 2.82 Å, which is part of a characteristic triplet correspond to those given by Christe [1].

The only symmetry elements detected are the 4-fold axis and the mirror plane perpendicular to it. There is no diagonal mirror plane (hkò ≠ kho and hkl ≠ khl).

This means that the Laüe group 4/m can be chosen, so that the space group I 4/m (n° 87 of the International Crystallographic Tables) is retained. The crystal data can therefore be summarized as follows : $F_{14}N_2Ni$ M = 353, red tetragonal crystals, a = 6.828 (5) Å, c = 9.270 (9) Å, V = 432 Å^3, Z = 2, D_c = 2.71 gcm^{-3}, space group I 4/m.

The atomic positions are derived from those of K_2PtCl_6 and are as given in Table II.

TABLE II

Atomic Positions of $(NF_4)_2NiF_6$

Ni	2a	000
N	4d	01/2 1/4, 1/2 0 1/4
F_1	8h	xy0, $\bar{x}\bar{y}$0, $\bar{y}$x0, y$\bar{x}$0
F_2	4e	00z, 00$\bar{z}$
F_3	16i	xyz (general positions)

Considering that only a small number of parameters had to be determined, a model was tested and refined by the least-square method using the Busing-Levy 1962 XFLS computer program and visual intensity estimation of 47 independent hko and kl1 reflections*.

The refinement led to the values given in Table III for the positional parameters, for which, with an overall temperature factor and two scale factors, R, of 0.12 was obtained.

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* List of observed and calculated structure factors are available from the authors.

TABLE III

Atomic Positional Parameters

	x	y	z
F_1	0.131	0.223	0
F_2	0	0	0.185
F_3	0.144	0.567	0.166

DISCUSSION

From the results of this study, it is clear that the structure of $(NF_4)_2NiF_6$ consists of octahedral NiF_6^{2-} anions and tetrahedral NF_4^+ cations, in an anti-fluorite type structure. The space group I 4/m imposes a site symmetry 4/m (C_4^h) for the nickel and $\bar{4}$ (S_4) for the nitrogen atoms, so that axial distortion of the octahedron NiF_6^{2-} and the tetrahedron NF_4^+ is allowed as well as rotation of the ions around their respective axes. The positional parameters are estimated with an unequal accuracy so that, on the one hand, the parameters x and y of the F_1 and F_3 atoms lead to relatively accurate values of the rotation angles. (-15° (1) and + 20° (1) respectively from diagonal positions (x = y)). On the other hand since the coordinate z for the atoms F_2 and F_3 are not accurately known, neither the axial distortion of the polyhedra, nor the atomic distances involving those atoms can be given precisely. The Ni-F_1 and Ni-F_2 distances are equal to 1.76 (3) Å and 1.72 (6) Å respectively. The N-F distances are between 1.30 and 1.40 Å and the F-F distances are approximately 2.5 and 2.2 Å in the octahedron and the tetrahedron respectively. The inter-polyhedron F-F distances are between 2.6 and 3.2 Å.

The present study should be considered as a first step giving the proper model towards the structure of $(NF_4)_2NiF_6$. To obtain more accurate information on positional and thermal parameters, it would be necessary to use more precise intensity measurements from appropriate single crystals. It would also be worthwhile investigating the Ge, Sn and Ti analoguous NF_4^+ salts, since it is highly probable that these compounds can also be described in terms of the K_2PtCl_6 derived structure.

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REFERENCES

1 K.O. Christe, Inorg. Chem. 16, 2238 (1977).

2 D. Pilipovich, U.S patent 3, 963, 542 (1976).

3 K.O. Christe, C.J. Schack and R.D. Wilson, Inorg. Chem. 16, 849 (1977).

4 K.O. Christe, R.D. Wilson and C.J. Schack, Inorg. Chem, 16, 937 (1977).

5 K.O. Christe, C.J. Schack and R.D. Wilson, Inorg. Chem. 15, 1275 (1976).

6 K.O. Christe and C.J. Schack, Inorg. Chem. 16, 353 (1977).

7 K.O. Christe, C.J. Schack and R.D. Wilson, J. of Fluorine Chem. 8, 541 (1976).