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X-RAY DIFFRACTION OF NOMF_6 (M = U, Sb, Nb, Ta)*

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SUMMARY

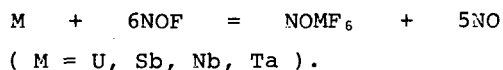
Four nitrosyl fluorometallate salts (NOUF_6 , NOSbF_6 , NONbF_6 , NOTaF_6) were synthesized by the reaction between N_2O_4 -HF mixtures and the metal. X-ray diffraction and density studies indicate that NOUF_6 , NOSbF_6 , NONbF_6 and NOTaF_6 are isostructural and have simple cubic unit cells containing one molecule.

INTRODUCTION

During the past twenty five years a number of papers have been published on nitrosyl fluorometallate salts[1], [2], [3].

* This paper is taken in part from the Dr. Eng. dissertation of N. Sato

The basic reactions by which these salts are synthesized can be exemplified by the interaction of nitrosyl fluoride with the respective metals, as shown in the following equation:



A reaction between N_2O_4 and liquid HF gave compounds such as NOF 3HF and NOF 6HF[4],[5],[6] which are potentially cheap sources of NOF and may permit their use on a large scale.

Since N_2O_4 -HF solution is so reactive and available for processes which are impossible in other solutions, the application of this non-aqueous solution on an industrial scale may be economic. These concepts arose through the work at Brookhaven National Laboratory on the reprocessing of reactor fuels[7]. One of the present authors reported that many nitrosyl fluorometallate salts can be obtained easily using the N_2O_4 -HF mixtures[8],[9],[10],[11].

Recently we have extended this process to the investigation of separating and refining metallic components, such as Nb and Ta, from their sources[12],[13].

The X-ray diffraction pattern for each salt are useful in order to understand and follow the whole process. However, there is still not much known about the structures of these salts due to the extreme reactivity of the salts both as oxidizing and as fluorinating agents. These four nitrosyl fluorometallate salts $NOMF_6$ (M = U, Sb, Nb and Ta) have similar thermal properties that is, they sublime at relatively low temperatures after one or two phase transitions. Musil, et al reported that $NOUF_6$ had a simple cubic unit cell with lattice constant $a_0 = 5.234 \text{ \AA}$ [14]. However, Beal et al. suggested that $NOSbF_6$ is face-centered cubic $a_0 = 10.19 \text{ \AA}$ [15].

EXPERIMENTS, RESULTS AND DISCUSSION

Preparation of NOMF_6 (M = U, Sb, Nb, Ta)

For NOUF_6 , the 20mole% NO_2 -80mole% HF solution prepared as described previously[8] was added to metallic uranium in a reaction vessel made of Kel-F plastic. The reaction vessel was kept at room temperature for 1 or 2 days until all the metal had dissolved. A whitish-blue compound was obtained by centrifuging the solution. For NOSbF_6 , 20mole% NO_2 -80mole% HF solution was added slowly to the metallic antimony until all the metal had dissolved at room temperature and had been converted to a white precipitate. The same method was used to prepare NONbF_6 and NOTaF_6 , and white precipitates were obtained. These four products have been identified as NOMF_6 by chemical and DTA-TG analyses. All the products were analyzed for metal ion, fluorine and nitrogen as previously described[8] and the results are shown in Table 1. From DTA-TG results, the phase transition temperature and sublimation point of each product coincided with those reported by Kigoshi, and it was clear that no compounds other than NOMF_6 were present.

X-ray powder photographs were obtained using a Teflon plate and $\text{Cu-K}\alpha$ irradiation through a nickel filter. NOMF_6 was put on the plate and packed in with a plastic cover in an inert atmosphere box.

X-ray diffraction studies

The X-ray diffraction pattern for each nitrosonium salt is given in Table 2. The X-ray diffraction pattern for NOUF_6 reported by Musil, et al. is also given and the two sets of data for NOUF_6 are in close agreement.

TABLE 1

Chemical analyses of NOMF_6 .

Component (%)		NOUF_6	NOSbF_6	NONbF_6	NOTaF_6
M	Calcd	62.31	45.81	39.22	55.69
	Found	62.38	45.11	39.42	55.75
F	Calcd	29.84	42.89	48.12	35.08
	Found	29.56	42.99	48.20	35.07
N	Calcd	3.62	5.27	5.91	4.31
	Found	3.45	4.76	5.92	4.31

The X-ray diffraction pattern for NOSbF_6 reported by Beal, et al. is also given in Table 2 and the two sets of data for NOSbF_6 agree in inter-planar spacing d and intensity I . However, Beal, et al. indexed the data with a face-centered cubic unit cell in which $a_0 = 10.19 \text{ \AA}$ but we consider it isostructural with NOUF_6 with a simple cubic unit cell $a_0 = 5.087 \text{ \AA}$.

NONbF_6 and NOTaF_6 give similar X-ray diffraction patterns which we index with unit cells $a_0 = 5.105$ and 5.110 \AA respectively.

Densities and number of molecules per unit cell of NOMF_6

The densities of NOMF_6 at room temperature were determined by volume displacement in Kel-F oil. A polypropylene picnometer was used. The results are given in Table 3.

The number of molecules per unit cell were calculated and are given in Table 3. The results show that the simple cubic unit cell contains one molecular unit.

TABLE 3

Densities and number of molecules per unit cell of NOMF_6 .

	NOUF_6	NOSbF_6	NONbF_6	NOTaF_6
M	382.025	265.696	236.909	324.944
a_0 (Å)	5.234	5.087	5.105	5.110
ρ (g/cm ³)	4.205	3.375	2.990	3.901
ΣA	363.167	267.608	239.606	313.529
$\Sigma A / M$	0.951	1.007	1.011	0.965

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