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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

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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:

$$M + 6NOF = NOMF_6 + 5NO$$

(M = U, Sb, Nb, Ta).

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_o = 5.234 Å[14]. However, Beal et al. suggested that $NOSbF_6$ is face-centered cubic a_o = 10.19 Å[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 Cu-Kα 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_o = 10.19 Å but we consider it isostructural with $NOUF_6$ with a simple cubic unit cell a_o = 5.087 Å.

$NONbF_6$ and $NOTaF_6$ give cimilar X-ray diffraction patterns which we index with unit cells a_o = 5.105 and 5.110 Å 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.

TABLE 2

The X-ray diffraction patterns for $NOMF_6$

$NOUF_6$

Sato and Kigoshi				Misil, et al.		
d_{obsd}(Å)	I	hkl	d_{calcd}(Å)	d_{obsd}(Å)	I	hkl
5.173	100	100	5.234	5.17	80	100
3.669	80	110	3.701	3.66	100	110
2.996	45	111	3.022	3.00	25	111
2.604	31	200	2.617	2.601	13	200
2.327	76	210	2.341	2.327	40	210
2.122	61	211	2.137	2.136	55	211
1.842	29	220	1.850	1.841	25	220
1.737	29	(300, 221)	1.743	1.737	35	(300, 221)
1.650	33	310	1.650	1.648	30	310
1.573	12	311	1.578	1.572	18	311
1.505	4	222	1.511	1.505	8	222
1.447	6	320	1.452	1.447	13	320
1.395	10	321	1.399	1.395	25	321

$NOSbF_6$

Sato and Kigoshi				Beal, et al.		
d_{obsd}(Å)	I	hkl	d_{calcd}(Å)	d_{obsd}(Å)	I	hkl
5.014	100	100	5.087	5.09	20	200
3.570	80	110	3.597	3.60	80	220
2.921	30	111	2.937	2.942	20	222
2.533	5	200	2.544	2.536	10	400
2.266	20	210	2.275	2.272	50	420
2.071	60	211	2.077	2.074	100	422
1.799	5	220	1.799	1.796	70	440
1.692	40	(300, 221)	1.696	1.693	80	600
1.607	32	310	1.609	1.607	70	620
1.530	12	311	1.534	1.533	60	622
1.466	4	222	1.468	1.469	20	444
1.410	32	320	1.411	1.409	70	640
1.358	4	321	1.360	1.362	90	642
1.272	4	400	1.272	1.272	10	800

$NONbF_6$

d_{obsd}(Å)	d_{calcd}(Å)	I	hkl
5.048	5.105	100	100
3.576	3.610	100	110
2.923	2.923	17	111
2.535	2.553	10	200
2.270	2.283	15	210
2.075	2.084	53	211
1.799	1.805	22	220
1.697	1.702	20	(300, 221)
1.610	1.614	18	310
1.535	1.539	15	311
1.467	1.474	5	222
1.412	1.416	15	320
1.362	1.364	20	321
1.274	1.276	10	400
1.238	1.238	16	(410, 322)
1.202	1.203	11	(411, 330)
1.170	1.171	7	331
1.140	1.142	7	420
1.112	1.114	8	421
1.088	1.088	5	332

$NOTaF_6$

d_{obsd}(Å)	d_{calcd}(Å)	I	hkl
5.073	5.110	82	100
3.587	3.613	100	110
2.936	2.950	30	111
2.541	2.555	12	200
2.274	2.285	31	210
2.076	2.086	51	211
1.801	1.807	21	220
1.698	1.703	30	(300, 221)
1.610	1.616	23	310
1.537	1.541	14	311
1.471	1.475	5	222
1.414	1.417	13	320
1.363	1.366	17	321
1.275	1.278	3	400
1.237	1.239	10	(410, 322)
1.203	1.204	6	(411, 330)
1.171	1.172	6	331
1.141	1.143	5	420
1.113	1.115	5	421
1.089	1.089	3	332

The number of molecules per unit cell were calculated anc 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_o (Å)	5.234	5.087	5.105	5.110
ρ (g/cm^3)	4.205	3.375	2.990	3.901
Σ A	363.167	267.608	239.606	313.529
Σ A / M	0.951	1.007	1.011	0.965

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