The specific rates of reaction of e_{aq}^- [13] and Cd^IEDTA with NO_3^- are higher than those with NO_2^-, whereas the specific rates of reaction of H atoms,[13] $Cd^I(aq)$,[5] and $Ni^I(aq)$[5] with NO_2^- are higher than those with NO_3^-. The hydrated electrons are expected to be outer-sphere reducing agents, and a similar mechanism has been suggested for Cd^IEDTA. Hydrogen atoms are most likely an inner-sphere reducing agent,[6,14–16] and the same mechanism has been suggested for $Ni^I(aq)$ and $Cd^I(aq)$.[6] It is, therefore, suggested that the relative reactivities toward NO_3^- and NO_2^- might be used as one of the guides for determining the mechanism of reduction by strong reducing agents.

Acknowledgments.—The authors wish to acknowledge Dr. M. S. Matheson, Professor M. Anbar, and Dr. M. Faraggi for stimulating discussions. We wish to thank the Linac group for their careful operation and Mr. S. Petrek for maintaining the electronic equipment.

---

[13] M. Anabar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

[14] G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1391 (1965).

[15] M. Anbar and D. Meyerstein, *Nature*, **206**, 818 (1965).

[16] J. Halpern and J. Rabani, *J. Amer. Chem. Soc.*, **88**, 699 (1966).

CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
E. I. DU PONT DE NEMOURS AND COMPANY, AIKEN, SOUTH CAROLINA 29801

Volatile Chelates of Quadrivalent Actinides[1]

BY H. A. SWAIN, JR.,[2] AND D. G. KARRAKER

Received November 25, 1969

Tetrakis β-diketonates were synthesized with quadrivalent thorium, uranium, neptunium, and plutonium and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (fod) and with Th^{4+} and U^{4+} and 2,2,6,6-tetramethylheptane-3,5-dione (thd) and then characterized by elemental analysis. X-Ray diffraction data showed $Th(fod)_4$, $U(fod)_4$, and $Np(fod)_4$ were isomorphous, but $Pu(fod)_4$ had a different structure. Vapor pressures measured by a modified Knudsen effusion method were *ca.* 10^{-3} mm at 125° for all fod chelates and at 195° for both thd chelates. ΔH_{subl} increased from 33.1 kcal/mol for $Th(fod)_4$ to 36.4 kcal/mol for $Pu(fod)_4$. ΔS_{subl} values increased nearly linearly with Z for Th^{4+}, U^{4+}, and Np^{4+} fod chelates; the value for ΔS_{subl} for $Pu(fod)_4$ was larger than the value predicted by a linear increase with Z, probably because of the different crystal structure of $Pu(fod)_4$.

Introduction

Lanthanide chelates of the sterically hindered β-diketones 2,2,6,6-tetramethylheptane-3,5-dione (thd)[3] and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (fod)[4] have sufficient volatility to permit gas chromatographic separation of the chelates of adjacent lanthanides.[3,4] Some lanthanide ions have been separated by fractional sublimation of $Ln(thd)_3$ chelates. The possibility of similar separations of actinides led to the study reported in this paper. In this study, $Th(thd)_4$, $U(thd)_4$, and $M(fod)_4$ (M = Th, U, Np, Pu) were prepared, and their vapor pressures and some other physical properties were determined. The preparation and study of the spectra of the fod chelates of Th^{4+} and U^{4+} were reported[5] while this paper was in preparation.

Previous workers[6,7] have prepared over 30 β-diketonates of U^{4+} and obtained some measure of their volatility. In general, the substitution of fluorine for hydrogen ($-CF_3$ for $-CH_3$) and replacement of normal alkyl groups with branched alkyl groups increased volatility. However, the most volatile of these chelates, $U(CF_3COCHCOCF_3)_4$, was too unstable for any practical use. The greater shielding of the M^{4+} ions by the bulky thd and fod ligands offers the possibility for both increased volatility and stability toward oxidation.

Experimental Section

$M(thd)_4$.—$Th(thd)_4$ and $U(thd)_4$ were prepared[3] by mixing ethanol–water solutions of the NaOH-neutralized β-diketonate and thorium nitrate or $[(C_2H_5)_4N]_2UCl_6$.[8] The chelates precipitated immediately upon mixing the solutions and were purified by recrystallization from petroleum ether (bp 20–40°) and vacuum sublimation. Analytical data are given in Table I.

Attempts to synthesize $Np(thd)_4$ and $Pu(thd)_4$ by the same procedure yielded products that were probably mixtures of $M(thd)_4$ and hydrocarbon-soluble oxidation products, perhaps including $MO_2(thd)_2$. Attempts to obtain pure $Np(thd)_4$ or $Pu(thd)_4$ from the mixture by fractional crystallization were also unsuccessful. An attempt to prepare $Pu(thd)_3$ in the presence of air resulted in the immediate oxidation of Pu^{3+} to higher plutonium oxidation states.

$M(fod)_4$.—$M(fod)_4$ compounds were prepared by the procedure of Springer, *et al.*,[4] rather than that of Wiedenheft.[5] Methanol–water solutions of the NaOH-neutralized β-diketonate and $[(C_6H_5)_4N]_2MCl_6$ or MCl_4 were mixed, and the crude $M(fod)_4$

---

[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] ORAU Research Participant at the Savannah River Laboratory, 1967–1968.

[3] K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

[4] C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

[5] C. Wiedenheft, *ibid.*, **8**, 1174 (1969).

[6] H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer, and R. A. Lad, *J. Amer. Chem. Soc.*, **75**, 2446 (1953).

[7] H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *ibid.*, **78**, 2790 (1956).

[8] J. P. Bibler and D. G. Karraker, *Inorg. Chem.*, **7**, 982 (1968).

precipitated immediately. Pure $M(fod)_4$ was obtained by recrystallization from petroleum ether. The yields were essentially quantitative; analytical data are given in Table I.

TABLE I

ANALYTICAL DATA FOR $M(thd)_4$ AND $M(fod)_4$ COMPOUNDS

Compound	Color	Mp, °C	% metal		% carbon		% hydrogen	
			Calcd	Found	Calcd	Found	Calcd	Found
$Th(thd)_4$	White	219	24.56	24.1	54.78	54.90	7.88	8.00
$U(thd)_4$	Brown	208	24.54	24.3	54.43	54.61	7.84	7.88
$Th(fod)_4$	White	156	16.43	16.6	33.99	33.94	2.83	2.80
$U(fod)_4$	Greenish brown	147	16.78	16.8	33.85	33.70	2.82	2.76
$Np(fod)_4$	Green	...	16.73	16.25	33.87	...	2.82	...
$Pu(fod)_4$	Brown	...	16.84	16.92	33.83	...	2.82	...

Vapor Pressure Measurements.—Vapor pressures of Th^{4+} and U^{4+} chelates were measured by a modified Knudsen effusion method, as previously described in vapor measurements on $Ln(fod)_3$ chelates.[9] The major modification from the normal Knudsen effusion method was a continuous weight measurement with an automatically recording vacuum microbalance. This method has the advantage that spurious effusion rates caused by volatile impurities, variations in temperature, or decomposition of the sample are indicated by nonlinearity of the weight–time chart and can be discarded. Weight–time data were not accepted unless the initial point in a series of measurements at random temperatures could be reproduced at the end of the series. As an example, a series of measurements at 80, 95, 75, 100, and 80° would not be accepted unless both measurements at 80° agreed.

TABLE II

VAPOR PRESSURE RESULTS

Compound	Measurement range, °C	$\ln P(\text{mm}) = -A/T + B$		ΔH_{subl}, kcal/mol	ΔS_{subl}, cal/mol deg
		A	B		
$Th(thd)_4$	118–136	18304 ± 371	36.918 ± 0.935	36.4 ± 0.7	65.4 ± 1.9
$U(thd)_4$	119–136	17932 ± 184	35.625 ± 0.315	35.6 ± 0.3	59.8 ± 0.6
$Th(fod)_4$	71–94	16654 ± 382	38.743 ± 1.069	33.1 ± 0.8	64.0 ± 2.1
$U(fod)_4$	70–94	17238 ± 173	39.875 ± 0.484	34.3 ± 0.3	66.3 ± 1.0
$Np(fod)_4$	77–95	17779 ± 354	41.419 ± 0.980	35.3 ± 0.7	69.3 ± 2.0
$Pu(fod)_4$	76–90	18455 ± 947	43.602 ± 0.267	36.7 ± 1.9	73.4 ± 5.3

The two Pyrex glass Knudsen cells were nearly cylindrical, 3 cm high, and 2 cm in diameter. The areas of the orifices were determined by calibration with the effusion rate of benzophenone[10] as 7.52×10^{-3} and 1.21×10^{-2} cm² ± 1.2%. Microscopic measurement of the orifices yielded areas of 7.74×10^{-3} and 1.21×10^{-2} cm², respectively. Effusion rates were measured over the range from 0.1 to 8 mg/hr. The sensitivity of the Ainsworth recording vacuum microbalance was ±10 μg with the Knudsen cell suspended. The pressure of the vacuum system was below 10^{-6} mm.

The cell containing the samples was heated by an oil bath that surrounded the vacuum system for the region 10 cm above and below the Knudsen cell. The oil bath was continuously stirred and heated by a thermoregulator-controlled immersion heater. Because the vacuum prevented direct heat transfer between the heating bath and the Knudsen cell, a calibration curve was obtained by simultaneously measuring the temperature of the oil bath and a dummy cell with an enclosed thermometer in the sample position. During effusion measurements, the temperature of the sample was obtained from the calibration curve and the temperature of the oil bath. Stem and calibration corrections were applied to all thermometer readings; cell temperatures could be reproduced to ±0.4°, which corresponds to about 4% uncertainty in the calculated vapor pressures.

The vapor pressures of $Np(fod)_4$ and $Pu(fod)_4$ were measured in an apparatus enclosed in a glove box to minimize the hazard to personnel from radioactivity. Because the apparatus had to be enclosed in a glove box, an electrical furnace was used instead of an oil bath, and thus direct temperature measurements were not attempted. Temperatures were determined in this system from a calibration of the furnace control settings against cell temperatures calculated from the effusion rates of benzophenone and $Er(thd)_3$.[9] The uncertainty in temperature measurements in this system is ±0.6°, which corresponds to an uncertainty in vapor pressure of ±6%.

The uncertainty in temperature measurements is considered large enough to include the self-cooling of the cell from evaporation of the sample, calculated to be 10^{-2}–10^{-3} cal/sec for the effusion rates of this work. The relatively large orifices of the Knudsen cells tend to minimize the importance of surface diffusion of the sample along the orifice walls.[11] A conservative estimate of the magnitude of surface diffusion, assuming a surface diffusion coefficient of 10^{-4} cm²/sec, indicates the ratio of diffused sample to effused sample to be about 0.05. The vapor pressure measurements are considered accurate to ±10%.

Miscellaneous Data.—X-Ray diffraction data on powdered samples were obtained with nickel-filtered copper radiation and were recorded with a Norelco diffractometer for $Th(fod)_4$ and $U(fod)_4$ and on Ilford G film for $Np(fod)_4$ and $Pu(fod)_4$. Line intensities were estimated visually from film. Melting points were measured with a block melting point apparatus. Carbon–hydrogen–nitrogen content was measured with an F & M Model 185 CHN analyzer. Metal analyses were performed by standard methods.[8]

Results

Vapor Pressures.—Vapor pressures were calculated from the well-known Langmuir equation using the rate of weight loss of the sample, the size of the orifice in the effusion cell, the temperature of measurement, and the monomeric molecular weight. The effusing vapors were assumed to be simple molecules, and mass spectra[12] showed no evidence of dimers or polymeric species.

The vapor pressures calculated for each compound were fitted to the expression

$$\ln P(\text{mm}) = \frac{-A}{T} + B$$

by a least-squares computer program.

Heats of sublimation (ΔH_{subl}) and entropies of sublimation (ΔS_{subl}) were obtained by equating the experimental vapor pressure equation (with P in atmospheres) to the standard thermodynamic equations

$$\ln P(\text{atm}) = \ln K_{\text{subl}} = \frac{\Delta F}{-RT} = \frac{\Delta H - T\Delta S}{-RT}$$

Equating terms of the same power in T

$$\Delta H_{\text{subl}} = AR \qquad \Delta S = R(B - \ln 760)$$

The constants for the vapor pressure equation, ΔH_{subl}, and ΔS_{subl} are given in Table II, and the vapor pres-

---

(9) H. A. Swain, Jr., and D. G. Karraker, proposed for publication.

(10) K. Neumann and E. Völker, *Z. Phys. Chem., Abt. A*, **161**, 33 (1932).

(11) W. L. Winterbottom and J. P. Hirth, *J. Chem. Phys.*, **37**, 784 (1962).

(12) K. Ernst, Lawrence Radiation Laboratory, private communication.

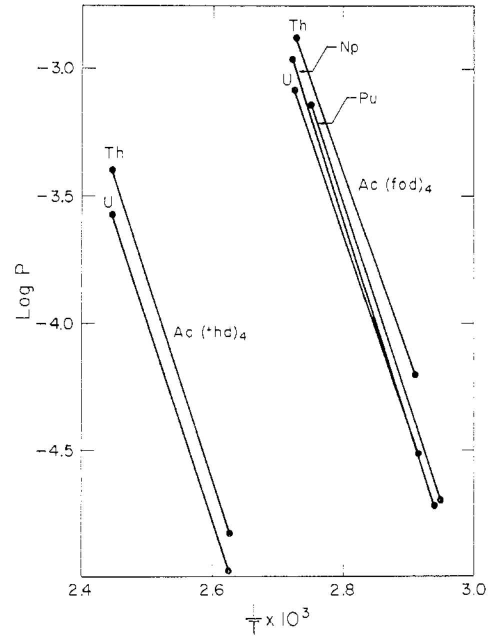

Figure 1.—Vapor pressures of actinide(IV) chelates.

sures are shown in Figure 1. Errors shown in Table II reflect only the precision of the data fitting.

Mass Spectra.—Preliminary results[10] on the mass spectra of vaporized U(thd)$_4$ and U(fod)$_4$ showed, within the error of mass calibration, a small peak for the ML$_4^+$ and major peaks at m/e corresponding to ML$_3$(L − CH$_3$)$^+$, ML$_3^+$, and ML$_2$CO$^+$ (L = fod or thd). When the accelerating voltage of the ion beam was decreased from 70 to 17 V, the ML$_3$(L − CH$_3$)$^+$ peak increased relative to other peaks. No peaks heavier than ML$_4^+$ were observed. The mass spectra appear consistent with the assumption that U(thd)$_4$ and U(fod)$_4$ are vaporized as simple molecules; other chelates are assumed to vaporize similarly.

X-Ray Diffraction.—Partial X-ray diffraction data for M(fod)$_4$ compounds are given in Table III. The diffraction patterns demonstrate that Th(fod)$_4$, U(fod)$_4$, and Np(fod)$_4$ are isomorphous, but Pu(fod)$_4$ has a different crystal structure. The diffraction patterns of all M(fod)$_4$ compounds have a large number of lines which suggest that these compounds have complicated crystal structures of low symmetry.

Discussion

The M(fod)$_4$ chelates are air-stable, hydrocarbon-soluble compounds that are easily prepared, purified, and handled. The vapor pressures of U(fod)$_4$, Np(fod)$_4$, and Pu(fod)$_4$ are the same within the precision of the measurements; Th(fod)$_4$ is slightly less volatile. The values calculated for ΔH_{subl} show a nearly linear increase with atomic number, as do the ΔS_{subl} for Th(fod)$_4$, U(fod)$_4$, and Np(fod)$_4$. ΔS_{subl} for Pu(fod)$_4$ is considerably greater than would be expected from a linear extrapolation with Z, perhaps as a consequence of different crystal structure of Pu(fod)$_4$.

Th(thd)$_4$ and U(thd)$_4$ are much less volatile than the M(fod)$_4$ chelates. The fod ligand is structurally derived from the thd ligand by substituting –C$_3$F$_7$ for –C(CH$_3$)$_3$. Both the asymmetry of the fod ligand and the presence of a fluorocarbon group would be predicted[7,8] to increase the volatility of M(fod)$_4$ chelates as compared to that of M(thd)$_4$ chelates. The inability to prepare pure Np(thd)$_4$ and Pu(thd)$_4$ and the slow oxidation of U(thd)$_4$ by air may indicate that ligand repulsion decreases the stability of these compounds.

TABLE III

PARTIAL X-RAY DIFFRACTION DATA FOR M(fod)$_4$ COMPOUNDS

Th(fod)$_4$^{a}		U(fod)$_4$^{a}		Np(fod)$_4$^{b}		Pu(fod)$_4$^{b}	
d, Å	I/I_0	d, Å	I/I_0	d, Å	Rel intens	d, Å	Rel intens
10.85	1	10.85	3	10.84	s	12.65	w
9.80	2	9.74	2	9.65	m	10.54	s
						9.52	m
8.59	3	8.52	2	8.54	m	8.35	m
7.91	2	7.86	2	7.82	m	8.20	w
7.11	1	7.08	1	7.10	w	7.70	m
6.84	3	6.84	2	6.78	m	6.98	s
6.48	2	6.46	2				
6.31	3	6.30	8	6.32	m	5.54	m
						4.90	m
5.99	3	5.97	3	5.96	m	4.51	s
5.61	1	5.61	1			4.19	w
5.52	2	5.49	3	5.49	w	4.14	w
5.28	2	5.28	2	5.23	w	3.97	vw
5.01	10	5.00	10	4.97	s	3.80	vw
						3.65	vw
4.79	5	4.78	8	4.76	m	3.39	vw
4.72	3	4.71	2			3.20	w
4.54	10	4.54	9	4.52	s	2.95	vw
		4.52	9			2.87	vw
4.26	8	4.25	8	4.24	s	2.75	vw
4.11	2	4.11	5	4.12	w	2.69	vw
4.02	2	4.00	3	4.01	w	2.63	vw
3.97	2	3.94	5	3.89	w	2.47	vw
3.93	2					2.31	vw
3.89	2	3.88	2			2.09	vw

^{a} Diffractometer. ^{b} Film. Abbreviations: s, strong; m, medium; w, weak; v, very.

The vapor pressure, ΔH_{subl}, and ΔS_{subl} for Pa^{4+} chelates may be estimated from an interpolation of these quantities between Th^{4+} and U^{4+} compounds. These Pa^{4+} chelates would be difficult to prepare because of the rarity of protactinium and the instability of its quadrivalent oxidation state. For Pa(fod)$_4$

$$\ln P(\text{mm}) = \frac{-17{,}100}{T} + 39.5$$

$$\Delta H_{\text{subl}} = 34 \text{ kcal/mol}$$

$$\Delta S_{\text{subl}} = 65.3 \text{ cal/mol deg}$$

and for Pa(thd)$_4$

$$\ln P(\text{mm}) = \frac{-18{,}100}{T} + 38.1$$

$$\Delta H_{\text{subl}} = 36 \text{ kcal/mol}$$

$$\Delta S_{\text{subl}} = 62.6 \text{ cal/mol deg}$$

The volatility of the M(fod)$_4$ chelates is approximately equal to that of Er(fod)$_3$[9] despite molecular weights of about 1400, compared to 1052 for Er(fod)$_3$. The shielding of the M^{4+} ion by the fod ligands more than compensates for their larger molecular weight; the volatility of M(fod)$_3$ chelates would be predicted to be considerably lower, perhaps less than La(fod)$_3$. Although volatilization does not appear to be a practical method for separating U(fod)$_4$, Np(fod)$_4$, and Pu(fod)$_4$, it may be useful for separating these actinides from light lanthanides and trivalent actinides.

Acknowledgments.—The authors are grateful to K. Ernst, Lawrence Radiation Laboratory, Livermore, Calif., for mass spectrometric information and to W. J. Kerrigan for assistance in construction of the apparatus.

Notes

CONTRIBUTION NO. 2605 FROM THE INSTITUTE FOR
ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Chemistry of Polynuclear Metal Halides. VIII. Infrared Spectra of Some $Nb_6X_{12}{}^{n+}$ and $Ta_6X_{12}{}^{n+}$ Derivatives[1]

BY P. B. FLEMING, J. L. MEYER, W. K. GRINDSTAFF,
AND R. E. MCCARLEY

Received August 22, 1969

Recent studies of the infrared spectra of compounds containing $M_6X_{12}{}^{n+}$ cluster species have been reported by Boorman and Straughan,[2] Mackay and Schneider,[3] and Mattes.[4] Certain characteristic bands arising from the $M_6X_{12}{}^{2+}$ (M = Nb or Ta; X = Cl or Br) cluster units were first identified by Boorman and Straughan[2] in derivatives where the associated anions and coordinated neutral donor ligands were varied, *e.g.*, among Cl^-, Br^-, $SO_4{}^{2-}$, $BF_4{}^-$, H_2O, and C_5H_5N. Mackay and Schneider[3] reported a more extensive investigation of $Nb_6Cl_{12}{}^{n+}$ complexes in each of the states with $n = 2$, 3, or 4. Principally by exchanging outer ligands Y and L in the complexes $(Nb_6Cl_{12})Y_nL_{6-n}{}^{(m-n)+}$, where m is the cluster oxidation state, they identified four allowed ir bands arising from the Nb_6Cl_{12} cluster unit and also those arising from vibrations of the outer Nb–Y or Nb–L bonds.

In the most recent study Mattes[4] reported the ir spectra for a larger number of derivatives $(M_6X_{12})X_n$, with M = Nb, Ta; X = F, Cl, Br, I; $n = 2, 3, 4$. A normal-coordinate analysis was performed in the attempt unambiguously to assign the observed bands and calculate force constants. However ir data which we have obtained indicate that certain of the assignments made in the previous studies are incorrect. Since the Raman spectra needed to confirm the assignments finally will be difficult to obtain on these highly colored compounds, we report here the results of our study, with suggestions for changes in previous ir band assignments.

Experimental Section

Preparation of Compounds.—Most of the compounds used in this study were prepared as previously reported,[5] with the exception of the compounds noted below.

$[(C_4H_9)_4N]_3[(Nb_6Cl_{12})I_6]$.—A compound approaching this composition was prepared by dissolving $Nb_6Cl_{14}\cdot 8H_2O$ in ethanol, refluxing with a large excess of tetra-*n*-butylammonium iodide, cooling, and filtering. The solution was then evaporated to near dryness, and the above procedure was repeated in a fresh solution of ethanol–$((C_4H_9)_4N)I$. Upon concentrating and cooling the solution, dark crystals were obtained. These were filtered, washed successively with chloroform and ether, and then dried *in vacuo*. *Anal.* Calcd for $C_{48}H_{108}N_3Nb_6Cl_{12}I_6$: Nb, 22.56; Cl, 17.22; I, 30.81; C, 23.31; H, 4.41. Found: Nb, 24.21; Cl, 17.65; I, 28.84; C, 21.63; H, 4.03; Cl/Nb, 1.91; I/Nb, 0.87.

$[(CH_3)_4N]_4[(Nb_6Cl_{12})Cl_6]$.—This compound was prepared according to a method developed by Koknat.[6] Complete details of the synthesis will be given in a subsequent paper. *Anal.* Calcd for $C_{16}H_{48}N_4Nb_6Cl_{18}$: Nb, 37.36; Cl, 42.77; N, 3.75; C, 12.88; H, 3.24. Found: Nb, 37 28; Cl, 42.54; N, 3.82; C, 12.78; H, 3.28; Cl/Nb, 2.99.

Several compounds containing DMSO (dimethyl sulfoxide) are reported in the results. These were prepared as follows, but their composition is nominally that reported since analytical data were not obtained. The hexakis adducts $[(M_6X_{12})(DMSO)_6](ClO_4)_n$ (M = Nb, Ta; X = Cl, Br) were synthesized by dissolving the appropriate cluster hydrate $(M_6X_{12})X_n\cdot mH_2O$ in a minimum volume of DMSO, adding a small excess of $AgClO_4$ to precipitate the outer halide ligands, and stirring the solution overnight. The silver halide precipitate was removed by filtration, and the desired perchlorate salt was precipitated by the addition of chloroform, filtered, washed successively with ethanol and ether, and dried in air. *These perchlorate compounds were found to be shock sensitive and hazardous*, but small amounts (1–10 mg) could be handled normally with caution.

The compounds of nominal compositions $(Nb_6Cl_{12})Br_2(DMSO)_4$ and $(Ta_6Cl_{12})Cl_3(DMSO)_3$ were prepared by dissolving the appropriate hydrated cluster halide in DMSO, adding chloroform or ether to precipitate the compound, washing with the same solvent, and drying in air. The compound $(Nb_6Cl_{12})Cl_3(DMSO)_3$ was prepared by dissolving a weighed sample of $((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$ in a few milliliters of DMSO, adding the calculated quantity of $AgClO_4$ to precipitate three of the terminal chloride ligands per mole of cluster, and stirring for 3 hr. After filtering to remove AgCl, the desired compound was precipitated with addition of a large volume of chloroform, filtered, and washed with the same solvent. The product apparently contained extra DMSO of crystallization and may be formulated as $[(Nb_6Cl_{12})Cl_3(DMSO)_3]\cdot 3DMSO$. *Anal.* Calcd for $Nb_6Cl_{15}C_{12}H_{36}S_6O_6$: Nb, 35.8; Cl, 34.2; C, 9.3; H, 2.3. Found: Nb, 36.1; Cl, 35.7; C, 10.4; H, 2.6.

Infrared Spectra.—Spectra were measured over the region 600–4000 cm^{-1} on a Beckman IR-7 instrument and over the re-

---

[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] P. M. Boorman and B. P. Straughan, *J. Chem. Soc.*, 1514 (1966).

[3] R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **7**, 455 (1968).

[4] R. Mattes, *Z. Anorg. Allg. Chem.*, **364**, 279 (1969).

[5] (a) B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, **9**, 1343 (1970); (b) P. B. Fleming, T. A. Dougherty, and R. E. McCarley, *J. Amer. Chem. Soc.*, **89**, 159 (1967); (c) P. B. Fleming, L. A. Mueller, and R. E. McCarley, *Inorg. Chem.*, **6**, 1 (1967); (d) P. J. Kuhn and R. E. McCarley, *ibid.*, **4**, 1482 (1965).

[6] F. W. Koknat and R. E. McCarley, on the preparation and structure determination of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$, to be published.