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.

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Notes

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

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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-

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

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

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[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.

gion 40–600 cm^{-1} on a Beckman IR-11 instrument. All spectra were obtained on solids prepared as Nujol mulls. In the cases where the compounds were air sensitive, samples were mulled in the drybox with sodium-dried Nujol and sealed between thin polyethylene sheets in a special airtight cell. Polyethylene windows were used exclusively in the region 600–40 cm^{-1}, and NaCl windows at higher wave numbers. The accuracy and reproducibility of the reported band maxima are estimated to be within ±2 cm^{-1}.

Results and Discussion

Most of the compounds studied in this investigation were salts of the type $R_n[(M_6X_{12})Y_6]$, where R is a tetralkylammonium or *n*-propylammonium cation. The spectra of such compounds in the region 600–4000 cm^{-1} were characteristic only of the organic cation; hence these data are not recorded here. Data illustrating the effect of the cation on the cluster spectra are given in Table I. It is seen that the change in cation has only minor effects on the spectra of the anions $(Nb_6Cl_{12})Cl_6{}^{n-}$, especially in regard to the wave numbers of the strongest bands. The data for the two $(C_2H_5)_4N^+$ salts are in good agreement with those of Mackay and Schneider[3] for the same compounds.

TABLE I

COMPARISON OF IR SPECTRA FOR SALTS OF DIFFERENT CATIONS[a]

$R_2[(Nb_6Cl_{12})Cl_6]$		$R_3[(Nb_6Cl_{12})Cl_6]$		$R_4[(Nb_6Cl_{12})Cl_6]$
$(C_2H_5)_4N^+$	$n\text{-}C_3H_7NH_3^+$	$(C_2H_5)_4N^+$	$n\text{-}C_3H_7NH_3^+$	$(CH_3)_4N^+$
354 vs				
	357 vs	343 vs	343 vs	334 vs
336 s, sh				
302 vs	300 s	290 vs	287 vs	281 vs
267 vs	263 vs, br	252 vs	249 vs	239 vs
196 s				
	196 s	198 ms	200 m	203 vs
190 s				
. . .	176 w, 154 w	. . .	158 w	. . .
142 s	141 vw	141 w	. . .	147 mw
115 m	. . .	122 w	. . .	132 w
71 m	85 m	70 vw	83 m	77 w
64 w	. . .	64 vw	. . .	64 m

[a] Band maxima are listed in cm^{-1}; intensities are: v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Spectra for the compounds containing the octahedral anions $(M_6X_{12})Y_6{}^{n-}$ are collected in Table II. Using a model similar to that of previous authors[3,4] six infrared-active T_{1u} fundamentals are predicted: four arising from the $M_6X_{12}{}^{n+}$ cluster, one from stretching of the M–Y bonds, and one from bending (or wagging) of the M–Y bonds (X–M–Y modes). Close inspection of the data indicates that unambiguous assignment of the bands is difficult because in some cases the requisite number is not observed. Extensive mixing of certain of the normal modes also is evident from the band shifts and intensity changes which occur upon substitution of the Y ligands.

It is important to note that in the complexes $(M_6Cl_{12})Cl_6{}^{n-}$ (M = Nb or Ta) the first three strong bands shift to higher wave number by *ca.* 10–12 cm^{-1} with unit increase in oxidation state of the $M_6Cl_{12}{}^{n+}$ cluster. This shift is consistent with an increase in both the M–X and M–Y bond strength as the average oxidation state of the metal atoms increases. Mackay and Schneider[3] discussed this effect in relation to the $M_6X_{12}{}^{n+}$ modes but failed to consider that the effect also should be operative with the M–Y modes. Both Mackay and Schneider and Mattes[4] assigned the latter mode to the band at *ca.* 200 cm^{-1} in the spectra of $(Nb_6Cl_{12})Cl_n$ compounds. Significantly this band undergoes a small shift to *lower* wave number as the cluster oxidation state increases. Thus we believe this assignment must be incorrect. There is now good evidence which indicates the shift of the M–Y modes to higher wave number should be at least as great as the shift of $M_6X_{12}{}^{n+}$ modes upon oxidation.

TABLE II

INFRARED SPECTRA[a] OF THE ANIONS $(M_6X_{12})Y_6{}^{n-}$

$(Nb_6Cl_{12})F_6{}^{4-}$ [b]	$(Nb_6Cl_{12})Br_6{}^{2-}$ [c]	$(Nb_6Cl_{12})I_6{}^{3-}$ [d]	$(Nb_6Br_{12})Br_6{}^{2-}$ [d]	$(Nb_6Br_{12})Cl_6{}^{2-}$
320 vs	352 vs	343 vs	262 vs	268 vs, br
278 w	276 vw	276 w	220 vs	219 w
236 w	228 vs	216 vs	171 s	184 ms
205 vw	157 m		138 s	169 w
171 w		172 s		156 w
595 m, sh		141 m		126 ms
575 s		108 s		93 w
552 s				
430 vs, br				
$(Ta_6Cl_{12})Cl_6{}^{3-}$ [b]	$(Ta_6Cl_{12})Cl_6{}^{2-}$ [b]	$(Ta_6Cl_{12})Br_6{}^{2-}$ [b]	$(Ta_6Br_{12})Br_6{}^{2-}$ [b]	$(Ta_6Br_{12})Cl_6{}^{2-}$ [b]
324 vs	336 vs[e] (F)[g]	337 vs[f] (F)[g]	. . .	256 vs (F)[g]
. . .	318 s, sh	321 s, sh	. . .	244 s, sh
283 s	294 s[e] (F)	283 w[f] (F)	230 vs (F)[g]	230 vs (F)
243 vs	259 vs[e] (F)	260 w[f] (F)	196 vs (F)	181 m (F)
171 w	164 m[e] (F)	192 vs[f] (F)	161 vs (F)	150 m (F)
153 vw	160 w	. . .	134 s (F)	127 s (F)
140 s	140 s[e] (F)	146 s[f] (F)	98 m (F)	99 w (F)
118 m	118 m[e] (F)	82 m[f] (F)	82 m (F)	
	67 w, br			

[a] Band maxima and intensities are the same as in Table I. [b] $(C_2H_5)_4N^+$ salt. [c] $n\text{-}C_3H_7NH_3^+$ salt. [d] $(n\text{-}C_4H_9)_4N^+$ salt. [e] Bands of similar intensity and wave number also were found in the spectrum of $Cs_2[(Ta_6Cl_{12})Cl_6]$. [f] Bands of similar intensity and wave number also were found in the spectrum of $Cs_2[(Ta_6Cl_{12})Br_6]$. [g] Bands designated by (F) are considered to be fundamentals.

Chemical evidence derived from substitution reactions indicates that the terminal halides Y are most firmly bound in the $M_6X_{12}{}^{4+}$ derivatives.[5a] However recent structural information is more convincing. We illustrate here by comparing M–X and M–Y bond distances in the compounds $K_4[(Nb_6Cl_{12})Cl_6]$[7] and $((CH_3)_4N)_2[(Nb_6Cl_{12})Cl_6]$.[6] In the former compound average Nb–Cl (X) and Nb–Cl (Y) distances of 2.49 and 2.59 Å were found; in the latter compound these distances were 2.42 and 2.46 Å, respectively. Thus the much greater decrease of the M–Y distance upon the two-unit oxidation supports proportionately stronger M–Y bonding, and accordingly the M–Y stretching mode should be shifted to higher wave number.

As noted by other authors[2–4] the bands of highest wave number at 334–357, 324–337, 262, and 230 cm^{-1}, respectively, in the $Nb_6Cl_{12}{}^{n+}$, $Ta_6Cl_{12}{}^{n+}$, $Nb_6Br_{12}{}^{n+}$, and $Ta_6Br_{12}{}^{n+}$ series are shifted only slightly by substitution at the M–Y positions. This is good evidence for assignment of these bands to one of the M_6X_{12} modes. In order of descending wave number the next

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(7) A. Simon, H. G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **361**, 235 (1968).

two bands undergo significant changes in both wave number and intensity on substitution of Y; *e.g.*, compare the spectra of $(M_6Cl_{12})Cl_6^{2-}$ with those of $(M_6Cl_{12})Br_6^{2-}$. These changes signify strong mixing of the normal modes arising from the $M_6X_{12}^{n+}$ unit and the M–Y bonds. However, the appearance of the strong bands at 172, 192, and 256 cm^{-1} in the spectra of $(Nb_6Cl_{12})I_6^{3-}$, $(Ta_6Cl_{12})Br_6^{2-}$, and $(Ta_6Br_{12})Cl_6^{2-}$, respectively, certainly indicates that the M-Y modes should be assigned higher wave numbers than those given by Mackay and Schneider or by Mattes.

It is notable that the spectra provided here by the $(Ta_6X_{12})Y_6^{2-}$ compounds each show six bands of sufficient intensity to merit designation as the six T_{1u} fundamentals. Only five of the fundamentals were recognized by Mackay and Schneider for the $(Nb_6Cl_{12})Y_n$ series and by Mattes for all of the compounds $(M_6X_{12})X_n$ (M = Nb, Ta; X = Cl, Br; n = 2, 3, 4). The data given here still do not permit identification of the sixth fundamental in the $(Nb_6Cl_{12})Y_6^{n-}$ complexes.[8] Mattes associated the unobserved fundamental with the metal–metal stretching modes (T_{1u}), whereas Mackay and Schneider associated it with the M–Y wagging modes (T_{1u}). This hitherto unidentified band can now be designated for the tantalum cluster anions; it is the fundamental of lowest wave number in the data given for each of these anions in Table II.

Data from the spectra of the DMSO adducts in the region below 600 cm^{-1} are given in Table III. All of these adducts have a strong band in the range 429–440 cm^{-1}, which may be assigned as the metal–oxygen stretching fundamental of coordinated DMSO. This is in accord with the assignment of the Nb–O stretch in compound II at 439 cm^{-1} by Mackay and Schneider.[3] Field and Kepert[9] also reported the Nb-O stretch at 417–449 cm^{-1} in the spectra of a series of oxygen donor–cluster complexes. It is significant that the M–O stretching modes for these cluster adducts are in the same wave number range of 410–500 cm^{-1} as reported for a large series of simple metal ion-DMSO complexes.[10]

TABLE III

INFRARED SPECTRA[a] OF DMSO–CLUSTER ADDUCTS IN THE REGION 40–500 CM^{-1}

I[b]	II[c]	III[d]	IV[e]	V[f]	VI[g]
435 vs	437 vs	440 vs	429 vs	440 s	433 s, br
338 s, br	340 vs	334 vs, br	337 w	330 vs, br	325 ms, br
290 s, br	. . .	. . .	312 w	262 m	. . .
252 s	270 ms	268 ms	262 vs	247 m, sh	. . .
240 m, sh	240 s	240 s	229 vs	227 m	224 s
198 mw	. . .	196 vw	. . .	192 w	199 w
118 vw	. . .	133 vw	165 w	140 w	145 w

[a] Band maxima and intensities same as in Table I. [b] I = $(Nb_6Cl_{12})Cl_3(DMSO)_3$. [c] II = $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$. [d] III = $(Nb_6Cl_{12})Br_2(DMSO)_4$. [e] IV = $[(Nb_6Br_{12})(DMSO)_6](ClO_4)_2$. [f] V = $(Ta_6Cl_{12})Cl_3(DMSO)_3$. [g] VI = $[(Ta_6Cl_{12})(DMSO)_6](ClO_4)_3$.

The strong cluster band at high wave number is present in the spectra of all of the DMSO adducts, and it is shifted only slightly from the value observed for the $(M_6X_{12})Y_6^{n-}$ ions of appropriate cluster oxidation state. In the spectrum of IV the two weak bands at 337 and 312 cm^{-1} evidently arise from a trace of free DMSO retained in the complex. The band in the region 224 to 240 cm^{-1} becomes more intense with increasing substitution of DMSO on the cluster (compare the spectra of I and V with those of II and VI). Consequently this latter band may arise from a ligand-dependent mode, possibly M–O–S or X–M–O bending. Finally, the bands at 290 cm^{-1} in I and 262 cm^{-1} in V apparently arise from the terminal Nb–Cl and Ta–Cl stretching vibrations, respectively, since they are absent in spectra of the ions completely substituted with DMSO.

In summary it should be emphasized that definite assignments of all bands in these spectra cannot be made at this time. Indeed this must await a normal-coordinate analysis which takes account of mixing of the normal modes and which is based on more complete data, especially from Raman spectra. However the data reported here allow the following tentative conclusions.

(1) A band arising from the metal–metal stretching vibrations is not readily identified in $M_6X_{12}^{n+}$ clusters.

(2) Bands arising from the M–Y stretching vibrations are unambiguously identified only in those cases where they occur outside the immediate wave number range of the $M_6X_{12}^{n+}$ vibrational modes, *e.g.*, as in $(M_6X_{12})(DMSO)_6^{n+}$ or $(Ta_6Br_{12})Cl_6^{n-}$.

(3) Only one of the four bands arising from the $M_6X_{12}^{n+}$ vibrational modes (usually the one of highest frequency) undergoes little change in intensity or frequency with substitution of the Y atoms.

(4) The mixing of the normal modes appears to be less extensive in the $Ta_6X_{12}^{n+}$ compounds—hence the requisite fundamental bands can be identified with greater confidence.

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[8] The number of bands in the region 400–600 cm^{-1} for $(Nb_6Cl_{12})F_6^{4-}$ indicates a complicated structure where the terminal fluorine atoms probably occupy two or more nonequivalent positions in the compound $((C_2H_5)_4N)_4[(Nb_6Cl_{12})F_6]$.

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[10] B. F. G. Johnson and R. H. Walton, *Spectrochim. Acta*, **22**, 1853 (1966).

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Preparation of Cubic Chloro Complex Compounds of Trivalent Metals: Cs_2NaMCl_6[1a]

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The recent syntheses of $Cs_2NaAmCl_6$[2] and $Cs_2NaBkCl_6$[3] suggested that similar compounds might be

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[1] (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Participant in the summer Undergraduate Training Program in Nuclear Chemistry.

[2] K. W. Bagnall, J. B. Laidler, and M. A. A. Stewart, *J. Chem. Soc., A*, 133 (1968).

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