Far-Infrared Spectra of Compounds Containing the M_6X_{12} Metal Atom Cluster[1a,b]

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Infrared spectra between 50 and 4000 cm^{-1} have been obtained for a number of compounds containing the $(Nb_6Cl_{12})^{n+}$ ($n =$ 2, 3, 4) metal atom cluster. Band assignments are made and compared with those previously reported for compounds containing this unit. The assignments for bands arising from both $(Nb_6Cl_{12})^{n+}$ and terminal ligand stretching modes are established and discussed.

Introduction

Some far-infrared investigations of compounds containing the M_6X_{12} unit (M = Nb, Ta; X = Cl, Br)[2] and the Mo_6X_8 (X = Cl, Br) and W_6Cl_8 units[3] have recently been reported.[4] In the case of the niobium and tantalum compounds, bands were assigned to the fundamental ir-active modes of the M_6X_{12} cluster. For the molybdenum compounds, of the form $(Mo_6-X_8)Y_6^{2-}$, bands were identified as being the F_{1u} (in O_h) ir-active fundamentals and further assigned to M–X, M–Y, X–M–Y, and M–M modes. In the course of spectral and chemical studies of metal atom cluster compounds, we have obtained infrared spectra for a number of compounds containing these units, both in the solid state and in solution. We report here studies of the $(Nb_6Cl_{12})^{n+}$ cluster, in three different oxidation states ($n =$ 2, 3, 4), coordinated to various terminal ligands. Our data, where overlap is present, are in general agreement with those previously reported.[2,3] By examining the changes in the spectra with changes in terminal ligand and oxidation state of the cluster, the band assignments for the $(M_6X_{12})L_6$ species are established and information on the nature of the vibrations giving rise to these bands is obtained.

Experimental Section

Preparation of Niobium Compounds. 1. $(Nb_6Cl_{12})X_2 \cdot nH_2O$ (X = Cl, Br, I, OH).—These compounds were prepared according to the methods employed by Harned.[5,6] A slight modification was used in the reduction of the $NbCl_5$ with cadmium metal in that the reactants were placed in a sealed, evacuated Vycor tube and heated for 12 hr at about 400° and then for 12 additional hr at about 600°. Somewhat higher yields were obtained in this manner. *Anal.* Found for $NbCl_{2.33} \cdot nH_2O$: Nb, 45.9; Cl, 40.1; Cl/Nb, 2.30.

2. $((C_2H_5)_4N)_2[(Nb_6Cl_{12})X_4(C_2H_5OH)_2]$ (X = Cl, Br).—$Nb_6Cl_{14} \cdot nH_2O$ was dissolved in absolute ethanol by refluxing. Excess $(C_2H_5)_4NX$ was added, the solution was stirred well, and the precipitate was filtered off, washed with ethanol and ether, and dried in air. The chloride was light green and the bromide dark

green. *Anal.* Calcd for X = Cl: Nb, 37.8; Cl, 38.4; C, 16.2; H, 4.20; N, 1.90; Cl/Nb, 2.67. Found: Nb, 37.3; Cl, 38.5; C, 15.9; H, 3.64; N, 2.13; Cl/Nb, 2.70. Calcd for X = Br: Nb, 33.7; C, 14.5; H, 3.74; N, 1.69. Found: Nb, 34.0; C, 14.7; H, 3.14; N, 1.78.

3. $((C_2H_5)_4N)_n[(Nb_6Cl_{12})Cl_6]$ ($n =$ 2, 3, 4).—These compounds were prepared as previously reported by the authors.[7]

4. $Ta_6Cl_{14} \cdot 7H_2O$.—This compound was prepared according to the method of Harned.[6] *Anal.* Calcd: Ta, 63.5. Found: Ta, 63.3.

5. $((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]$.—This compound was prepared by air oxidation of ethanolic solutions of $Ta_6Cl_{14} \cdot 7H_2O$ saturated with HCl gas and recovered in the same manner as the corresponding niobium compound. The cocoa brown precipitate was washed with ethanol and ether and dried in air. *Anal.* Calcd: Ta, 52.5; Cl, 30.7; Cl/Ta, 3.00. Found: Ta, 52.6; Cl, 30.8; Cl/Ta, 2.98.

A few additional compounds were made for the purpose of infrared studies, but were not characterized by other methods. These include a compound which on the basis of infrared evidence was formulated as $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$ and which was prepared essentially according to the method employed by Cotton and Curtis[8] for the preparation of the corresponding molybdenum compound. In this case, 0.2 g of $Nb_6Cl_{14} \cdot nH_2O$ was dissolved in absolute ethanol, a stoichiometric amount of $AgClO_4$ in methanol was added, and the solution was stirred in the dark for 30 min. After the AgCl was filtered off, 5 ml of DMSO was added, and the solution was concentrated to approximately 10 ml. Upon addition of 20 ml of 2-propanol a dark green precipitate forms which is filtered off, washed with 2-propanol and ether, and dried *in vacuo* at 100°.

A compound, which on the basis of infrared evidence was formulated as $(Nb_6Cl_{12})Cl_2(DMSO)_4$ was produced by dissolving $Nb_6Cl_{14} \cdot nH_2O$ in DMSO and precipitating the material by addition of chloroform.

A compound was prepared by addition of excess $(C_2H_5)_4NBr$ to a solution of $Nb_6Cl_{14} \cdot nH_2O$ in ethanolic HBr, concentration of the solution, and recovery of the precipitate which formed. The compound was formulated as $((C_2H_5)_4N)_4[(Nb_6Cl_{12})Br_6]$. *Anal.* Calcd: Nb, 28.1; Br, 24.2. Found: Nb, 29.1; Br, 23.7. Infrared evidence indicates the material is probably slightly contaminated with the $(Nb_6Cl_{12})^{3+}$ compound.

A compound is prepared by addition of excess N-methylpyridinium iodide to an ethanolic solution of $Nb_6Cl_{14} \cdot nH_2O$ saturated with HI gas followed by concentration of the solution and recovery of the precipitate which forms. The infrared spectrum indicates the presence of $(Nb_6Cl_{12})^{2+}$ and $PyCH_3^+$. A qualitative test shows the presence of iodide. The compound is formulated as $(PyCH_3)_4[(Nb_6Cl_{12})I_6]$. *Anal.* Calcd: Nb, 25.7. Found: Nb, 24.2.

Methods of Analysis.—The compounds are decomposed by boiling with ammoniacal hydrogen peroxide until a clear, colorless solution is obtained. After boiling the solution to expel excess

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

(3) F. A. Cotton, R. M. Wing, and R. A. Zimmerman, *Inorg. Chem.*, **6**, 11 (1967).

(4) The authors are indebted to Dr. M. J. Ware of the University of Manchester, England, for a private communication of ir and Raman data (including polarization studies) on a number of compounds containing the Mo_6X_8 (X = Cl, Br) unit.

(5) H. S. Harned, *J. Am. Chem. Soc.*, **35**, 1078 (1913).

(6) H. S. Harned, *ibid.*, **82**, 4815 (1960).

(7) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **6**, 549 (1967).

(8) F. A. Cotton and N. F. Curtis, *ibid.*, **4**, 241 (1965).

peroxide and ammonia, the solution is cooled to room temperature and made slightly acidic with nitric acid. Niobium is determined as Nb_2O_5 by a standard gravimetric procedure. Halogen is determined gravimetrically as silver halide when only one halogen is present. The carbon, hydrogen, nitrogen, and halogen (in compounds containing more than one halogen) analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Infrared Spectra.—Infrared spectra from 300 to 3900 cm⁻¹ were obtained on a Perkin-Elmer 521 double-beam grating spectrometer. All spectra obtained in this region were of solids, which were prepared principally as Nujol mulls and in a few instances as KBr pellets, both methods yielding identical results. The mulls were held between KRS-5 thallium bromide–thallium iodide windows using tin or lead spacers. Infrared spectra from 50 to 400 cm⁻¹ were obtained on a Perkin-Elmer 301 far-infrared grating spectrometer using double-beam operation. To cover the region 50–400 cm⁻¹, four gratings of 40, 20, 10, and 5 lines/mm were employed, all to first order. Below 300 cm⁻¹, the instrument was flushed continuously with dry nitrogen to remove water vapor which has rotational bands throughout this entire region. These latter bands were used to calibrate the various gratings. Solids were prepared exclusively as Nujol mulls which were held between polyethylene windows. The polyethylene windows employed in this study have a spectrum between 400 and 50 cm⁻¹ which consists of only one weak–medium band at 73 cm⁻¹. This band has been subtracted from all reported spectra. Solution spectra in nitromethane were obtained at approximately 200–400 cm⁻¹, this solvent having a convenient window in this region. Polyethylene liquid cells with 0.2-mm spacers were employed for these measurements. Spectro grade nitromethane was used to prepare the solutions, and Nujol dried over sodium metal was used to prepare the mulls.

Other Physical Measurements.—Conductance measurements were performed at 24° on 10^{-3}–10^{-4} M solutions in Spectro grade nitromethane using a dip cell and a Serfass conductance bridge operating at 1000 cps. All molar conductance values reported have been corrected for solvent conductivity.

Results

The infrared (ir) spectra of a series of compounds containing the $(Nb_6Cl_{12})^{n+}$ ($n = 2, 3, 4$) cluster have been obtained in the region of 50–3900 cm⁻¹. For salts containing an organic cation (R), for example, $(C_2H_5)_4N$, the bands due to this cation are not tabulated but were identified by comparison with the spectra of RX (X = Cl, Br).

For the M_6X_{12} species in O_h symmetry, the total vibrational representation is

$$\Gamma_{vib} = 2A_{1g} + A_{2g} + A_{2u} + 3E_g + E_u + 2F_{1g} + 4F_{1u} + 3F_{2g} + 3F_{2u}$$

where the A_{1g}, E_g, and F_{2g} modes are Raman active and the F_{1u} modes are ir active. The M_6X_{12} unit is thus expected to possess four ir-active fundamentals. In addition, if these modes are such that they mainly involve either motions of the bridging halogens (M–X) or motions of the niobium octahedron (M–M) whose frequencies are sufficiently different, then it can be shown that there will be three M–X modes and one M–M mode. For a species of the type $(M_6X_{12})L_n$, it is proposed the metal atom cluster–terminal ligand (L) stretching and bending modes may be interpreted on the basis of a model of the type M^1L_n, where $M^1 = M_6X_{12}$ and may be considered as a massive central "atom." Since the ligands are attached to the metal atoms in the cluster, the stretching modes are desig-

nated as M–L, it being understood that the effective mass of M is considered to be approximately that of M^1. A ligand bending mode is designated as X–M–L.

To identify the M_6X_{12}, M–L, and X–M–L bands, the spectra of the species $(M_6X_{12})L_n$ are compared for different ligands and those bands which remain relatively unshifted in frequency are assigned to vibrations of the M_6X_{12} cluster. The remaining band(s) which exhibit the appropriate frequency shift with L will be assigned as M–L or X–M–L vibrations. The first series of compounds studied was $(Nb_6Cl_{12})L_2 \cdot nH_2O$ (L = Cl, Br, OH), and the observed bands are reported in Table I. The bands above 1500 cm⁻¹ are assigned

TABLE I
INFRARED BANDS (cm⁻¹)[a] OF THE COMPOUNDS
$(Nb_6Cl_{12})L_2 \cdot nH_2O$ (L = Cl, Br, OH)

Cl	Cl[b]	Br	Br[b]	OH
3900–50	3900–130	3900–50	3900–30	3900–98
				3576 s, sp
3512 sh	3503 sh	3300 s	3540 sh	
3228 s, b	3283 ms	3172 s	3315 s	2988 s, b
2412 sh	3120 ms	2268 w	3260 sh	
		1723 vw	3180 sh	
		1691 vw		
1619 m	1590 m	1623 sh	1615 sh	1639 mw
		1599 ms	1595 m	1604 m
		1399 vw		
		1383 vw		
675 mw, b	600 m	1091 w, b		1009 w
758 vw		436 w, b		841 sh
436 vw		379 sh		755 mw
404 sh		364 sh		416 sh
393 sh		361 m	371 sh	409 m
387 sh		356 sh	359 sh	397 sh
381 mw	342 sh	346 sh	354 sh	355 sh
340 s	336 s	344 ms	341 sh	328 m
	329 sh	336 ms	336 m	283 sh
280 mw	304 sh	322 sh	325 sh	274 mw
257 sh	291 sh	264 vw	276 mw	265 w
247 mw	283 s	242 sh	271 sh	240 mw
233 sh	253 sh	231 m	231 s	225 m
208 w	247 ms	196 w		219 m
166 w	239 sh	151 sh	158 mw	180 sh
147 mw	230 s	127 w	153 mw	177 mw
			121 w	156 w
			104 mw	150 sh
			99 mw	137 w

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad; sp, sharp.   [b] Heated on vacuum line at 130° for 20 hr.

to free water, and for L = OH the sharp band at 3576 cm⁻¹ is assigned to the O–H stretch of the hydroxide ion according to the criteria described by Nakamoto.[9] Below 1500 cm⁻¹ there are between 15 and 19 bands and shoulders, most of which are due to the lattice water. It may be noted that the major features in the spectra of the $(Nb_6Cl_{12})L_2 \cdot nH_2O$ (L = Cl, Br) compounds are in agreement with those observed by Boorman and Straughan[2] on the same compounds. The complexity of the spectra makes their interpretation rather difficult and suggests that the spectra of com-

(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

pounds containing the Nb_6Cl_{12} cluster with no lattice water or lattice solvent should be much less complex. This is substantiated by the spectra of the compounds $R_n[(NbCl_{12})L_6]$ (L = Cl, Br, I), $R_2[(Nb_6Cl_{12})L_4(C_2H_5OH)_2]$ (L = Cl, Br), and $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$, which contain no uncoordinated solvent. The bands observed for these compounds are reported in Tables II and III.

TABLE II

INFRARED BANDS $(CM^{-1})^a$ OF COMPOUNDS CONTAINING THE $(Nb_6Cl_{12})^{2+}$ CLUSTER

		Compound			
I[b]	II[c]	III[d]	IV[e]	V[f]	VI[g]
		Range, cm⁻¹			
3900–98	3900–98	3900–98	3900–98	3900–70	3900–100
					439 s
340 s	340 vs	340 s	347 vs	341 vs	339 vs
280 ms	271 m	279 s	280 m	273 ms	288 m
237 m	230 ms	234 ms	228 s	221 s	241 m
202 mw		198 m			
	157 wm		157 ms		
147 w		143 w	148 sh	148 m	
					100 ms

^{a} s, strong; m, medium; w, weak; v, very; sh, shoulder; sp, sharp. ^{b} $R_2[(Nb_6Cl_{12})Cl_4(C_2H_5OH)_2]$, R present, no other bands observed, R = $(C_2H_5)_4N$. ^{c} $R_2[(Nb_6Cl_{12})Br_4(C_2H_5OH)_2]$, R present, no other bands observed, R = $(C_2H_5)_4N$. ^{d} $R_4[(Nb_6Cl_{12})Cl_6]$, R present, no other bands observed, R = $(C_2H_5)_4N$. ^{e} $R_4[(Nb_6Cl_{12})Br_6]$, R present, no other bands observed, R = $(C_2H_5)_4N$. ^{f} $R_4[(Nb_6Cl_{12})I_6]$ R present, no other bands observed, R = $PyCH_3$. ^{g} $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$, bands due to coordinated DMSO and free ClO_4^- ion observed: 1095 ms, 1024 w, 981 m, 946 ms, 852 w, 619 m, sp.

TABLE III

INFRARED BANDS $(CM^{-1})^a$ OF $((C_2H_5)_4N)_n[(Nb_6Cl_{12})Cl_6]$ (n = 2, 3, 4) AND $((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]^b$

$(Nb_6Cl_{12})^{2+}$	$(Nb_6Cl_{12})^{3+}$	$(Nb_6Cl_{12})^{4+}$	$(Ta_6Cl_{12})^{3+}$
		Range, cm⁻¹	
3900–98	3900–98	3900–98	3900–80
340 s	346 s	353 s	327 vs
279 s	290 s	302 s	285 m
234 ms	251 s	267 s	244 s
198 m	198 m	193 mw	
143 w	142 mw	141 mw	140 mw

^{a} s, strong; m, medium; w, weak; v, very. ^{b} For all compounds, $(C_2H_5)_4N$ present. No other bands observed.

Inspection of Table II shows that the band at about 200 cm⁻¹ for L = Cl moves to 157 and 100 cm⁻¹ for L = Br and I, respectively, and appears at 439 cm⁻¹ for L = DMSO. The band at about 145 cm⁻¹ remains relatively unshifted, but appears to be of variable intensity and is not observed for two of the compounds. It may be seen that the terminal ligands appear to have an effect on the relative intensities of the bands and it is possible that the band at about 145 cm⁻¹, which is generally weak or weak–medium, may not be observed for the two compounds (L = Br, DMSO) due to very low intensity. At this point, we then assign the bands observed at about 340, 280, 232, and possibly 145 cm⁻¹ to the M_6X_{12} unit. These assignments are in agreement with those of Boorman and Straughan.[2] The other band, observed at various frequencies, is then assigned as an M–L stretch. An

ir-active bending mode might be expected at lower frequencies, but is not observed. Most of the compounds were only studied to about 100 cm⁻¹ so that either the bending mode lies below 100 cm⁻¹ (for L = Cl, Br, I), which is quite possible, or it has such a low intensity that it is not observed. The terminal halogen stretching frequencies are lower than those generally observed for octahedral, tetrahedral, or square-planar transition metal complexes.

Using the preceding assignments, the band at 409 cm⁻¹ for $(Nb_6Cl_{12})(OH)_2 \cdot nH_2O$ (Table I) may be assigned as the M–O stretch. The ir spectra above 500 cm⁻¹ of $[(Nb_6Cl_{12})(DMSO)_6](ClO_4)_2$ and $(Nb_6Cl_{12})Cl_2(DMSO)_4$ indicate that these compounds contain DMSO ligands which are coordinated to niobium through the oxygen and do not contain free DMSO, according to the criteria of Cotton, et al.[8,10] The former compound also contains the bands of the free perchlorate ion. The observation of the Nb–O stretching frequency at 439 cm⁻¹ also confirms the coordination of DMSO through the oxygen. The Nb–O stretch for $(Nb_6Cl_{12})Cl_2(DMSO)_4$ occurs at 430 cm⁻¹, indicating that a given ligand stretching frequency is fairly independent of the nature of other terminal ligands which may be present. In addition, the M–L stretching frequency appears to be most sensitive to the atom in L to which M is attached rather than to the structure of the ligand, as indicated by Nb–O (OH) at 409 cm⁻¹ and Nb–O (DMSO) at 439 cm⁻¹. Inspection of Table II also shows that the positions of the M_6X_{12} bands are not appreciably affected by the nature of the terminal ligands, indicating that there is little interaction between the M–L and M_6X_{12} modes.

Let us now consider the effect of increasing the positive charge of the cluster on the M_6X_{12} frequencies. For metal–halogen complexes, an increase of one unit in the oxidation state of the metal causes an increase in the metal–halogen stretching frequency of about 30 cm⁻¹, for example,[11] as shown below.

Compd	ν_3, cm⁻¹	Compd	ν_3, cm⁻¹
$((C_2H_5)_4N)W^VCl_6$	329	$K_2Ir^{IV}Cl_6$	333
$Cs_2W^{IV}Cl_6$	308	$K_3Ir^{III}Cl_6$	296

Inspection of Table III shows that there is a uniform increase of the three highest M_6X_{12} bands with increasing charge on the cluster (i.e., increasing oxidation state).

$\nu(2+)$, cm⁻¹	$\nu(3+) - \nu(2+)$, cm⁻¹	$\nu(4+) - \nu(3+)$, cm⁻¹
340	6	7
279	11	12
234	12	16

An increase of less than 30 cm⁻¹ per unit increase in oxidation state for M_6Cl_{12} is not surprising since the change in oxidation state of each metal atom is only one-sixth of the change in oxidation state of the cluster. The above three bands are then assigned as the $3F_{1u}$ ir-active fundamental M–X frequencies. The three high-

(10) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

(11) D. M. Adams, H. A. Gebbie, and R. D. Peacock, *Nature*, **199**, 278 (1963).

est bands for $((C_2H_5)_4N)_3[Ta_6Cl_{12}]Cl_6$ (Table III) are in good agreement with the niobium M–X bands, being slightly lower in frequency as may be expected, since for two transition metals in the same group the metal which is lower in the periodic table has lower metal–halogen frequencies for the same oxidation state.

Boorman and Straughan[2] identify bands at 330–320, 235–230, 190–175, and 145–140 cm^{-1} as the four F_{1u} ir-active modes of $[Ta_6Cl_{12}]^{2+}$. These bands are in general agreement with those observed by us for $[Ta_6Cl_{12}]^{3+}$, except for the presence of the band at 175–190 cm^{-1} and the absence of the 285- cm^{-1} band. They report a weak band at about 284 cm^{-1} for $Ta_6Cl_{14}\cdot 8H_2O$ and anhydrous Ta_6Cl_{15}. The terminal chlorine stretch should occur at about 200 cm^{-1} or slightly lower by comparison with the niobium analog, and it is possible that this is the band observed at 175–190 cm^{-1}. If their assignments for $[Nb_6Br_{12}]^{2+}$ (270–280, 200–210, 170–180, 145 cm^{-1}) are correct, then it would appear that the three highest bands are associated with modes involving primarily motions of the halogen atoms. This supports the same conclusion reached above by consideration of the frequency shift with change in oxidation state. We may also note that a band at 340–350 cm^{-1} in $(M_6Br_{12})Cl_2$ (hydrated) (M = Nb, Ta) is reported by Boorman and Straughan and ascribed to a vibration of the bridging chloride ions between the $[Nb_6Br_{12}]^{2+}$ clusters. While we are in agreement that the chloride ions do not occupy internal positions in the cluster, we do not consider it likely that there are bridging terminal ligands in any of these cluster compounds except, of course, for the anhydrous substances. It has been demonstrated by the compounds reported here and by other studies[8,12–14] that the clusters coordinate all six terminal positions. Thus, a compound of the type $M_6X_{14}\cdot nH_2O$ should be formulated as $[(M_6X_{12})Cl_2(H_2O)_4]\cdot(n-4)H_2O$. This band at 340–350 cm^{-1} appears in the $(M_6Br_{12})L_2$ spectra only for L = Cl, and it may be due to a mixing (interaction) of the M–X and M–L modes, since at least one of the modes may now occur at nearly the same frequency as the M–L mode.

All of the M_6X_{12} species appear to have a corresponding band at about 140–145 cm^{-1} suggesting that this band be assigned to the M_6X_{12} unit. This band, for the $(Nb_6Cl_{12})^{n+}$ series (Table III), is seen to remain approximately constant, in fact decreasing by 1 cm^{-1} per unit increase in oxidation state of the cluster. An M–M band might be expected to show such behavior since removing electrons from the metal atom cluster and increasing the metal oxidation state should tend to weaken the metal–metal bonding, the $(Nb_6Cl_{12})^{2+}$ state itself being classically electron deficient. Metal–metal stretching bands have been observed in Raman spectra and the M–M frequencies found to occur in the region 120–200 cm^{-1} for a wide range of metals,[15]

for example, as shown below for the compounds $MM^1(CO)_{10}$.

Compd	M–M^1	Cm^{-1}
$Mn_2(CO)_{10}$	Mn–Mn	157
$MnRe(CO)_{10}$	Mn–Re	182
$Re_2(CO)_{10}$	Re–Re	128

In a recent ir study of compounds containing the Ta_6X_{12} (X = Cl, Br) cluster,[16] the ir-active mode which involves mainly a motion of the tantalum atoms (Ta–Ta) has been assigned to a band occurring at 140 cm^{-1}.

Finally, it may be seen from a comparison of the ir bands in the solids with those obtained in nitromethane solution (Table V) that solid-state effects are minimal, since the solid state and solution spectra are the same to within 1–4 cm^{-1}. The conductance data (Table VI) indicate that the complexes are not appreciably dissociated in nitromethane solution, and this is consistent with the presence of the niobium–terminal chlorine stretching frequency in the solution spectra.

TABLE IV

BAND ASSIGNMENTS FOR $(Nb_6Cl_{12})L_n$

M$_6$X$_{12}$ mode		M–L mode	
Band freq,[a] cm^{-1}	Assignment	Band freq,[a] cm^{-1}	Assignment
340	Nb–Cl	200	Nb–Cl
280	Nb–Cl	157	Nb–Br
232	Nb–Cl	100	Nb–I
145	Nb–Nb	409	Nb–OH
		439	Nb–O (DMSO)

[a] Since the frequencies vary by a few reciprocal centimeters from compound to compound, the values given are averages for the $(Nb_6Cl_{12})^{2+}$ compounds in Table II.

TABLE V

COMPARISON OF INFRARED BANDS OF SOME Nb_6Cl_{12} COMPOUNDS FOR SOLID AND NITROMETHANE SOLUTION[a]

(Nb$_6$Cl$_{12}$)$^{n+}$ compound[b]		
$R_4[(Nb_6Cl_{12})Br_6]^{2+}$	$R_3[(Nb_6Cl_{12})Cl_6]^{3+}$	$R_2[(Nb_6Cl_{12})Cl_6]^{4+}$
Range, cm^{-1}		
400–180	400–180	400–180
343 ms (347)	343 ms (346)	353 m (353)
278 w (280)	292 m (290)	305 w (302)
226 m (228)	254 m (251)	269 mw (267)
	197 w (198)	193 vw (193)

[a] Frequencies for solids are given in parentheses. s, strong; m, medium; w, weak; v, very. [b] R = $(C_2H_5)_4N$.

TABLE VI

MOLAR CONDUCTANCE IN CH_3NO_2 AT 24° FOR CONCENTRATIONS IN THE RANGE 10^{-3}–10^{-4} M

Compound[a]	Λ[b]	Electrolyte
$R_2[(Nb_6Cl_{12})Cl_6]$	178	
$R_2[(Nb_6Cl_{12})Cl_4(C_2H_5OH)_2]$	156	2:1
$R_2[(Nb_6Cl_{12})Br_4(C_2H_5OH)_2]$	158	
$R_3[(Nb_6Cl_{12})Cl_6]$	283	3:1
$R_4[(Nb_6Cl_{12})Cl_6]$	334	4:1

[a] R = $(C_2H_5)_4N$. [b] Corrected for conductivity of pure solvent. Λ given in units of mhos cm^2 mole^{-1}. Errors are $\pm 5\%$.

(12) J. E. Fergusson, B. H. Robinson, and C. J. Wilkins, *J. Chem. Soc.*, 486 (1967).

(13) R. A. Mackay, Ph.D. Thesis, State University of New York at Stony Brook, June 1966.

(14) R. E. McCarley, *Chem. Eng. News*, **44**, 42 (May 30, 1966).

(15) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, **17**, 616 (1966).

(16) R. E. McCarley, J. Meyer, B. G. Hughes, and J. G. Converse, paper presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

Conclusions

(1) The four ir-active fundamentals of the $(Nb_6Cl_{12})^{n+}$ cluster (n = 2, 3, 4) are established as 340–353, 279–302, 234–267, and 141–143 cm^{-1}. It appears likely that the three highest bands are associated primarily with motion of the halogens and the lowest band is associated primarily with a motion of the metal atoms.

(2) The M–L stretching frequencies for the (Nb_6Cl_{12})-L^n species are established as 409, 439, 200, 157, and 100 cm^{-1} for L = OH, DMSO, Cl, Br, and I, respectively.

(3) The M–L frequencies are largely independent of the nature of any other terminal ligands which may be present. For a given M, the M–L frequency depends primarily on the atom in the terminal ligand to which M is attached.

(4) There is little interaction between the M–L and M_6X_{12} modes when there is no overlap of frequencies.

(5) The terminal ligands are not appreciably dissociated when the compounds are dissolved in nitromethane solution.

(6) There are no appreciable solid-state effects on the ir spectra of these compounds.

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Electrical Properties of the Group IV Disulfides TiS₂, ZrS₂, HfS₂, and SnS₂[1,2]

BY LAWRENCE E. CONROY AND KYU CHANG PARK

Large single crystals of TiS₂, ZrS₂, HfS₂, and SnS₂ have been prepared by the chemical transport method. All four disulfides were found to be n-type semiconductors with the CdI₂ (C6) structure. Room-temperature electrical conductivity values were 1.4 × 10³ ohm^{-1} cm^{-1} for TiS₂, 7.6 × 10^{-1} ohm^{-1} cm^{-1} for ZrS₂, 3.0 × 10^{-3} ohm^{-1} cm^{-1} for HfS₂, and 9.6 × 10^{-9} ohm^{-1} cm^{-1} for SnS₂. Both TiS₂ and ZrS₂ exhibited typical degenerate semiconductor behavior at room temperature. Energy gap values for HfS₂ and SnS₂ were 2.1 and 2.2 eV, respectively. Magnetic susceptibility values at room temperature were 0.52, 0.61, 0.44, and 0.41 BM, respectively, for TiS₂, ZrS₂, HfS₂, and SnS₂.

Introduction

The disulfides of the group IV elements Ti, Zr, Hf, and Sn have remarkably similar properties, characterized by high metallic luster. TiS₂, ZrS₂, HfS₂, and SnS₂ all crystallize in the hexagonal (C6) CdI₂ structure[3] which consists of a hexagonal close-packed sulfide lattice with metal atoms in alternate layers of the octahedral holes. Alternatively, the structure may be described as planar sheets of MS₆ octahedra joined at their edges. The optical and electronic transport properties of this group of compounds is of interest from several aspects. (1) They exhibit pseudo-metallic properties. In addition to the metallic luster, high room-temperature electrical conductivities have been reported for TiS₂[4-6] and ZrS₂.[4] (2) They constitute a group of isostructural compounds in which one may hope to examine effects on the optical and electron-transport properties arising from the substitution of metal atoms, differing in size, nuclear charge, and d-orbital configuration, in the same anion (or nonmetal atom) lattice. Optical properties of these compounds have been reported by Greenaway and Nitsche,[7] but electrical conductivity data on single crystals have been reported only for TiS₂[6] and SnS₂,[8] and the literature lacks any data on the temperature dependence of conductivity, Hall mobility, or charge-carrier concentration of any of these compounds. This research was directed toward the characterization of single crystals of TiS₂, ZrS₂, HfS₂, and SnS₂.

Experimental Section

Materials.—Titanium metal sponge (99.99%, United Mineral and Chemical Corp.), zirconium metal sponge (99.99%, K & K Laboratories, Inc.), hafnium metal sponge (99.9%, Electronic Space Products, Inc.), purified sulfur (J. T. Baker), and purified SnS₂ (City Chemical Corp.) were employed as starting materials. Resublimed reagent grade iodine was used in the chemical transport reactions.

Preparation of Single Crystals.—Single crystals of TiS₂, ZrS₂, HfS₂, and SnS₂ were prepared by utilizing chemical transport reactions, in a procedure similar to that employed by Greenaway and Nitsche.[7,9] All reactions were carried out in Vycor tubes ranging in size from 1.5 to 2.5 cm i.d. and 10–15 cm in length, employing iodine vapor (5 mg/cm³) as the transport agent. SnS₂ crystals were prepared from SnS₂ powder. The transition

(1) This research is taken from the thesis presented by Kyu Chang Park to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, Aug 1967.

(2) Presented before the Division of Inorganic Chemistry at the 154th Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

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