$SbCl_5$,[1] and $S_2N_2(SbCl_5)_2$[1] have absorptions at 795 and 663, 800 and 723, and 818 cm^{-1}, respectively. It seems likely that all of the infrared absorptions of $S_2N_2BCl_3$ near this region (at 840 (m), 788 (wm), 728 (s, b), and 682 (mw) cm^{-1}) may result from combinations of S–N and BCl_3 modes. The remaining $S_2N_2BCl_3$ absorptions (at 1115, 950, 610, and 467 cm^{-1}) correspond closely in position and shape to absorptions in $S_2N_2SbCl_5$. Thus the infrared and chemical evidences support formulation of $S_2N_2BCl_3$ and $S_2N_2(BCl_3)_2$ as adducts of the same type as those of S_2N_2 with $SbCl_5$.[1]

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1, UNITED KINGDOM

Infrared Spectra, Laser Raman Spectra, and Force Constants of the Metal–Hexahalo Species $R_2M^{IV}X_6$, $RM^{V}X_6$ [R = $(C_2H_5)_4N$ or Cs; M^{IV} = Ti, Zr, or Hf; M^{V} = Nb or Ta; X = Cl or Br], and WCl_6

BY W. VAN BRONSWYK, R. J. H. CLARK, AND L. MARESCA

Received December 17, 1968

The infrared and laser Raman spectra of a series of metal–hexahalo species of groups IV–VI have been recorded in the range 700–70 cm^{-1}. The compounds are R_2MX_6 [R = $(C_2H_5)_4N$ or Cs; M = Ti, Zr, or Hf; X = Cl or Br], RMX_6 [R = $(C_2H_5)_4N$ or Cs; M = Nb or Ta; X = Cl or Br], and WCl_6. Assignments for the three Raman-active and two infrared-active fundamentals are made; in addition the value for the inactive fundamental ν_6 (t_{2u}) has in some cases been deduced from infrared-active combination bands. Force constants for the hexahalo species have been calculated on the assumption both of a modified Urey–Bradley force field (MUBFF) and of a generalized valence force field (GVFF). The value for ν_6 could thus be calculated and compared with the value deduced from combination bands. For both force fields the average value of the bond stretching force constants for the quadrivalent ions lies below that for quinquevalent ions, which in turn lies below that for WCl_6. For example, on the basis of the MUBFF, K_{av} for the MCl_6^{2-} ions is ~1.0 mdyn/Å, for the MCl_6^{-} ions it is ~1.3 mdyn/Å, and for WCl_6 it is ~1.6 mdyn/Å. This increase in K with increase in the oxidation state of the metal is consistent with previous findings on other complex ions. In addition, $K_{MCl} > K_{MBr}$ in all cases for a given central metal atom. The expected isotopic structure of the a_{1g} mode of an MCl_6 molecule is calculated, but could not, in practice, be resolved for either the $TiCl_6^{2-}$ or the $TaCl_6^{-}$ ions.

Introduction

Although many studies of the vibrational spectra of MX_6 species (X = Cl or Br) of the later transition metals and of the nonmetals have been made, very few have been reported for the corresponding early transition metal species. Recent infrared and Raman spectral measurements[1] on the $TiCl_6^{2-}$ ion have shown that the original data[2] were incorrect and, consequently, that force constant calculations based thereon[3] are unfounded. Accordingly we have recalculated the force constants for this ion, both as the cesium and as the tetraethylammonium salts, in terms (a) of a modified Urey–Bradley force field (MUBFF) and (b) of a generalized valence force field (GVFF). The infrared and Raman data on $ZrCl_6^{2-}$, $HfCl_6^{2-}$, $NbCl_6^{-}$, and $TaCl_6^{-}$ ions, on WCl_6, and also on the corresponding hexabromo species, are nonexistent, fragmentary, or incorrect. We report herein the complete data for all of these ions, usually both as the cesium and as the tetraethylammonium salts, the band assignments, and the force constants according to both the MUBFF and the GVFF bases. The variations of the bond stretching force constants with change of halogen and with change of the oxidation state of the metal atom are delineated. In general, the data have been gathered for the solid state only, owing to the difficulty (if not impossibility) of finding a solvent or solvents in which the species would be both sufficiently soluble and sufficiently stable for adequate spectral measurements to be made. It is recognized that solid-state spectra may be complicated by site symmetry and correlation splitting and also by slight frequency shifts of the normal modes from their values for the isolated ions. However, in those cases for which reliable data in the dissolved as well as the solid states could be obtained ($TiCl_6^{2-}$ ion[1] and $TaCl_6^{-}$ ion, see below) these effects appear to be slight.

Experimental Section

Preparation of Compounds.—The $TiCl_6^{2-}$ and $TiBr_6^{2-}$ ions were prepared as described previously.[1,4]

The tetraethylammonium salts $[(C_2H_5)_4N]_2ZrCl_6$ and $[(C_2H_5)_4N]_2HfCl_6$ were prepared by a modification of the method involving thionyl chloride as solvent.[5] The metal tetrachloride in thionyl chloride was added to a slight stoichiometric excess

---

[1] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

[2] M.-E. P. Rumpf, *Compt. Rend.*, **202**, 950 (1936).

[3] C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1328 (1958).

[4] R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Co., Amsterdam, 1968.

[5] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

TABLE I

ANALYTICAL DATA

Compound	Color	% C		% H		% N		% X	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(C_2H_5)_4N]_2TiCl_6$	Yellow	36.9	37.2	7.7	7.7	5.4	5.5	40.8	38.8
$[(C_2H_5)_4N]_2TiBr_6$	Red	24.4	23.8	5.1	4.9	3.5	3.2	60.85	60.85
$[(C_2H_5)_4N]_2ZrCl_6$	White	34.0	33.8	7.1	6.8	4.95	4.85	37.7	36.5
$[(C_2H_5)_4N]_2ZrBr_6$	White	23.1	22.6	4.85	4.85	3.35	3.1	57.7	57.6
$[(C_2H_5)_4N]_2HfCl_6$	White	29.2	29.1	6.2	6.1	4.3	4.1	32.6	32.1
$[(C_2H_5)_4N]_2HfBr_6$	White	20.9	21.0	4.4	4.4	3.05	2.9	52.2	52.1
$[(C_2H_5)_4N]NbCl_6$	Yellow	22.1	22.6	4.6	4.8	3.2	3.1	48.9	48.2
$[(C_2H_5)_4N]TaCl_6$	White	18.4	18.5	3.85	4.0	2.6	2.6	40.7	40.6
Cs_2TiCl_6	Yellow	...	...	...	...	...	...	40.4	39.1
Cs_2ZrCl_6	White	...	...	...	...	...	...	37.3	37.4
Cs_2HfCl_6	White	...	...	...	...	...	...	32.4	32.0
$CsNbCl_6$	Yellow	...	...	...	...	...	...	48.5	47.7
$CsNbBr_6$	Brown	...	...	...	...	...	...	67.9	66.1
$CsTaCl_6$	White	...	...	...	...	...	...	40.4	40.0
$CsTaBr_6$	Yellow	...	...	...	...	...	...	60.4	59.7
WCl_6	Deep blue	...	...	...	...	...	...	53.6	53.9

of a solution of tetraethylammonium chloride also in thionyl chloride, at room temperature. Acetic anhydride was added to precipitate the required salts; these were collected on a G3 sintered disk under dry nitrogen, washed with acetic anhydride followed by dry ether, and then dried *in vacuo* at room temperature. The tetraethylammonium salts $[(C_2H_5)_4N]NbCl_6$ and $[(C_2H_5)_4N]TaCl_6$ were prepared similarly by mixing the appropriate thionyl chloride solutions[5] and then cooling the resulting solutions in ice; crystallization occurred within 10 min, but the solutions were cooled for 2 hr before separating the precipitate by filtration under dry nitrogen. The compounds were then dried *in vacuo* at room temperature.

The cesium salts Cs_2ZrCl_6 and Cs_2HfCl_6 were prepared under nitrogen by addition of a solution of cesium chloride in the minimum volume of iodine monochloride to a solution of the stoichiometric weight of the appropriate metal tetrachloride in thionyl chloride. Precipitation of the required salts was brought about by addition of acetic anhydride to the above solution and then allowing the mixture to stand for some hours. The precipitates were washed with acetic anhydride and then with ether and finally were dried *in vacuo* at room temperature. The cesium salts $CsNbCl_6$ and $CsTaCl_6$ were prepared similarly[6] by mixing the appropriate iodine monochloride and thionyl chloride solutions and allowing the mixtures to stand for *ca.* 2 hr. The resulting salts were washed with thionyl chloride and dried *in vacuo.*

The tetraethylammonium salts $[(C_2H_5)_4N]_2ZrBr_6$ and $[(C_2H_5)_4]_2HfBr_6$ were prepared by adding a solution of the appropriate metal tetrabromide in thionyl bromide to a slight stoichiometric excess of a solution of tetraethylammonium bromide, also in thionyl bromide, at ~70°. The mixture was cooled, and acetic anhydride was added to bring about precipitation of the required complexes. These were filtered off under dry nitrogen, washed with acetic anhydride followed by dry ether, and then dried *in vacuo* at room temperature.

The salt $CsNbBr_6$ was prepared (a) by heating the stoichiometric amounts of CsBr and $NbBr_5$ in a sealed Pyrex tube under vacuum at ~150° for 2 weeks (the tube being opened under nitrogen and the contents reground several times during this period) and (b) by similarly heating the stoichiometric amounts of CsBr and $NbBr_5$ under vacuum in a Pyrex tube for 2 weeks, but in the presence of IBr (in fivefold weight excess to the total weight of reactants). In case (b), on completion of the reaction, the IBr was removed under vacuum at 80°. In both cases, the product was washed with anhydrous benzene and dried under vacuum. $CsTaBr_6$ was prepared by method (a) above, using $TaBr_5$ in place of $NbBr_5$. It was likewise washed with anhydrous benzene and dried under vacuum.

A commercial sample of tungsten hexachloride was carefully purified by 11 vacuum sublimations at ~275°. The infrared spectrum in the 800–1000-cm^{-1} region was inspected for evidence of oxychloride impurity; none was observed.

The analytical data for the compounds are in Table I. The absence of the most probable impurity in these compounds ($MOCl_4^{n-}$ species) was also established by demonstrating the absence in the 900-cm^{-1} region of the band associated with M=O stretching vibrations.

Infrared Spectra.—The infrared spectra of the compounds were recorded on the Perkin-Elmer 225 (700–200 cm^{-1}) and Grubb-Parsons GM3 (200–70 cm^{-1}) instruments as Nujol mulls between polythene or CsI plates. The mulls were prepared in an efficient drybox under nitrogen. The spectra were calibrated against that of water vapor. The spectra below 200 cm^{-1} were improved by recording them at liquid nitrogen temperatures using a special cell.[7]

Raman Spectra.—The spectra were recorded on a Cary 81 spectrometer using a Spectra-Physics Model 125 He–Ne (6328 Å) laser source. The samples were either wax sealed or vacuum sealed into flat-bottomed Pyrex containers and held in such a way that the laser was normal to the flat surface, the scattered radiation being collected at 180° to the incident beam. Solution Raman spectra were recorded using standard cells.

Both Raman and infrared frequencies are considered to be accurate to ±1 cm^{-1}, except for bands specified as being broad, asymmetric, or shoulders; in these cases the limits are probably ±2 cm^{-1}. The resolution of the Raman instrument is 2 cm^{-1} at best and 5 cm^{-1} at worst for solids.

Results and Discussion

Spectra and Assignments.—The spectral data on the various species are summarized in Table II in terms of O_h nomenclature. The vibrational modes ν_1 (a_{1g}), ν_2 (e_g), and ν_5 (t_{2g}) are Raman active only, ν_3 (t_{1u}) and ν_4 (t_{1u}) are infrared active only, while ν_6 (t_{2u}) is inactive. The modes ν_1 to ν_3 are either completely or essentially stretching modes, whereas ν_4 to ν_6 are completely or essentially bending modes. The inactive fundamental ν_6 is however permitted as a binary combination band with both ν_2 (to give the components $t_{1u} + t_{2u}$) and ν_5 (to give the components $a_{1u} + e_u + t_{1u} + t_{2u}$). In those cases for which ν_6 could be so deduced, it is included (in parentheses) in Table II. The only fundamental to show appreciable dependence on the cation is ν_3.

The values of the fundamentals call for some com-

---

(6) S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. W. Horner, F. N. Collier, and S. Y. Tyree, *Inorg. Chem.*, **7**, 1859 (1968).

(7) R. J. H. Clark and B. C. Crosse, *J. Chem. Soc.*, *A*, 224 (1969).

TABLE II

SOLID-STATE VIBRATIONAL SPECTRA OF SOME MX_6 ANIONS (X = Cl OR Br) AND WCl_6 (CM^{-1})[a]

Compound	ν_1 (a_{1g})	ν_2 (e_g)	ν_3 (t_{1u})	ν_4 (t_{1u})	ν_5 (t_{1g})	ν_6 (t_{2u})
$[(C_2H_5)_4N]_2TiCl_6$	320 s[b]	271 w	316 s, br	183 s	173 s	. . .
Cs_2TiCl_6	320 s	(272)	334 s	190 s	186 s	(139)
$[(C_2H_5)_4N]_2ZrCl_6$	321 s	250 w, sh	293 s	152 s	151 s	. . .
Cs_2ZrCl_6	326 s	(249)	313 s	162 s	161 s	(112)
$[(C_2H_5)_4N]_2HfCl_6$	326 s	257 w, sh	275 s	145 s	156 s	. . .
Cs_2HfCl_6	333 s	(261)	284 s	150 s	167 s	(110)
$[(C_2H_5)_4N]NbCl_6$	367 s	288 w	333 s[d]	162 s	174 s[c] 183 s	(129)
$CsNbCl_6$	369 s	289 w	333 s	165 s	175 s[c] 183s	(111)
$[(C_2H_5)_4N]TaCl_6$	378 s[b]	298 w	318 s[e]	156 s	179 s	(119)
$CsTaCl_6$	382 s	299 w	320 s	158 s	180 s[c] 188 s	(101)
WCl_6[i]	410 s	315 vw	364 s	158 s	164 w, sh	. . .
$[(C_2H_5)_4N]_2TiBr_6$	190 s	138 w, sh	243 s	119 m	103 m, sh[f]	. . .
$[(C_2H_5)_4N]_2ZrBr_6$	194 s	144 w, sh	223 s	106 m	99 s	. . .
$[(C_2H_5)_4N]_2HfBr_6$[g]	197 s	142 w, sh	189 s[h]	102 m	101 s	. . .
$CsNbBr_6$	224 s	180 w	236 s	112 m	114 vw, sh[f]	. . .
$CsTaBr_6$	232 s	183 w	212 s	107 m	116 s	(75)

[a] Frequencies in parentheses were derived from infrared-active combination bands. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] Polarized in nitromethane solution. [c] Band is split as indicated, presumably owing to solid-state effects. [d] Band is asymmetric with the maximum at 330 cm^{-1} and a shoulder at 352 cm^{-1}. [e] Band is asymmetric with the maximum at 314 cm^{-1} and a shoulder at 331 cm^{-1}. [f] Not resolvable from exciting line. [g] The infrared spectrum of this compound contains an additional unassigned band at 225 (mw) cm^{-1}. [h] Band is asymmetric with a maximum at 186 cm^{-1} and a shoulder at 195 cm^{-1}. [i] The solid state spectrum of WCl_6 is in close agreement with the vapor spectrum, for which ν_1 = 400 cm^{-1}, s, pol, ν_2 = 325 cm^{-1}, w, and ν_5 = 163 cm^{-1}, w (I. R. Beattie and G. A. Ozin, personal communication).

ment, because since the completion of this work, other reports of the Raman spectra of some of the chloro species have appeared. The reported values for the ν_2 mode for these species disagree in some cases with those in Table II; this is perhaps understandable, because for many of the compounds, this fundamental is extremely weak. In one instance[8] the value of ν_2 for the salts $[(C_2H_5)_4N]_2MCl_6$ (M = Zr or Hf) is reported to be 237 cm^{-1} in both cases. No indication of a Raman band at this frequency occurs in our spectra (obtained with a much superior instrument), but ν_2 instead appears as a very weak band at 250 cm^{-1} for the zirconium salt and at 257 cm^{-1} for the hafnium salt.

The Raman spectrum of a freshly prepared solution of zirconium tetrachloride in concentrated hydrochloric acid contains[9] two bands, at 329 (pol) and at 237 (depol) cm^{-1}. Whereas the first band can readily be assigned to the ν_1 (a_{1g}) mode of the $ZrCl_6^{2-}$ ion (*cf.* 321 cm^{-1} for the tetraethylammonium salt and 326 cm^{-1} for the cesium salt, Table II), it seems uncertain whether the second band has been correctly assigned to ν_2 (e_g), because the solid-state values for this mode are around 250 cm^{-1}. A second very recent report[10] of ν_2 (225 cm^{-1}) for zirconium tetrachloride solutions in concentrated hydrochloric acid seems definitely to be incorrect owing to the large and improbable separation between ν_1 and ν_2 (101 cm^{-1}). These solution studies are plagued by the difficulties associated with ensuring the presence of but a single absorbing species. Likewise[10] the Raman spectrum of hafnium tetrachloride in saturated hydrochloric acid is reported to contain three bands, at 331 (strong, pol), 204 (med, depol), and 152 (med, depol) cm^{-1}. The bands have been assigned to ν_1, ν_2, and ν_5, respectively. The agreement with the solid-state values for ν_1 is excellent and for ν_5 is fair. However, the solid-state value for ν_2 is 260 cm^{-1}; this is a reasonable value for a stretching vibration, whereas the apparent solution value of 204 cm^{-1} leads to the highly improbable separation of 127 cm^{-1} between ν_1 and ν_2. Our own measurements on hafnium tetrachloride in hydrochloric acid saturated with hydrogen chloride suggest that some decomposition occurs in this solvent; although ν_1 is observed at 332 cm^{-1}, both ν_2

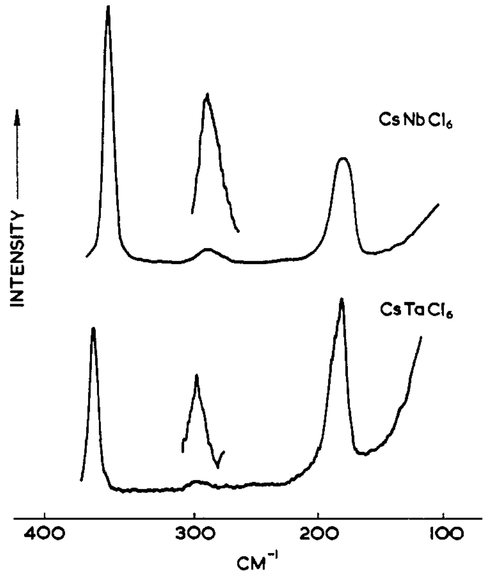

Figure 1.—Raman spectra of solid $CsNbCl_6$ and $CsTaCl_6$; the insets show ν_2 at the maximum sensitivity of the instrument in each case.

---

(8) D. M. Adams and D. C. Newton, *J. Chem. Soc., A*, 2262 (1968).
(9) W. P. Griffith and T. D. Wickins, *ibid., A*, 675 (1967).
(10) J. E. D. Davies and D. A. Long, *ibid., A*, 2560 (1968).

and ν_5 are obscured beneath increasing Rayleigh background.

There is no agreement between the solid-state Raman spectra of $NbCl_6^-$ ion salts and the solution Raman spectra of either $[(C_2H_5)_4N]NbCl_6$ in acetonitrile or niobium pentachloride in saturated hydrochloric acid.[10] Clearly in neither case in solution is the $NbCl_6^-$ ion the sole or even the principal scattering species; this emphasizes the critical importance of the solid-state data.[10a]

In the case of the $TaCl_6^-$ ion, there is excellent agreement between the solid-state Raman values of ν_1, ν_2, and ν_5 (382, 299, and 184 cm^{-1}, respectively, for the cesium salt; 378, 298, and 179 cm^{-1}, respectively, for the tetraethylammonium salt) and the Raman values for these modes in nitromethane solution[10] (380 (vs, pol), 295 (w, depol), and 180 (s, depol) cm^{-1} for the tetraethylammonium salt). Our own measurements on the $TaCl_6^-$ ion in nitromethane solution agree with the above, ν_1, ν_2, and ν_5 having the respective values 380 (vs, pol), 297 (w), and 179 (m) cm^{-1}. Hence the $TaCl_6^-$ ion is genuinely the predominant species in nitromethane solution. However, it is clearly not the absorbing species in a solution of $TaCl_5$ in >12 *M* HCl, because the only Raman band reported[9] for this solution occurs at 312 (pol) cm^{-1}. Further, the Raman spectrum[11] of $PCl_4^+TaCl_6^-$ gives rise to bands at 384, 156, and 188 cm^{-1}; although the first and third bands are clearly to be associated with ν_1 and ν_5, the second band cannot be ν_2 as supposed by the original authors. The present work shows that ν_2 is near 300 cm^{-1}, as would be expected for a mode which involves bond stretchings.

In a recent report[12] of the infrared spectrum of tungsten hexachloride in carbon disulfide, carbon tetrachloride, and benzene solutions both in the fundamental and in the combination band regions, values for the Raman-active fundamentals ν_1, ν_2, and ν_5 were deduced (408, 312, and 206 cm^{-1}) from the values for ν_3 and ν_4 (367 and 165 cm^{-1}, respectively). Our Raman study, the first on a neutral metal hexachloride, indicates that the first two Raman-active fundamentals do in fact occur near to the above values, at 410 and 315 cm^{-1}, respectively. Our experimental value for ν_5 (164 cm^{-1}) indicates that the infrared-active combination band observed at 570 cm^{-1} by Evans and Lo[12] cannot be attributed to $\nu_3 + \nu_5$ ($364 + 164 = 528$ cm^{-1}) as they supposed. The alternative assignment of $\nu_1 + \nu_4$ ($410 + 158 = 568$ cm^{-1}), however, satisfactorily accounts for this band. The weak shoulder observed in the spectrum of a saturated solution of WCl_6 in CS_2 at 215 cm^{-1} and assigned[12] to $\nu_2 - \nu_6$ probably arises from $WOCl_4$ impurity; this shoulder cannot therefore be used as a basis for determining ν_6 as suggested.[12] Since the completion of this work, another report[13] of the Raman spectrum of tungsten hexachloride has appeared, in which ν_1, ν_2, and ν_5 were reported to occur at 410 s, 377 m, br, and 266 m, br cm^{-1}, respectively. An argon ion laser emitting ~1 W (4880 Å) was employed. Our observation is that tungsten hexachloride shows signs of decomposition when its Raman spectrum is being studied using 6328-Å helium–neon excitation of 50 mW and that the decomposition is more pronounced using an argon ion laser; we therefore consider helium–neon excitation to be more satisfactory. Moreover, our values for ν_2 and ν_5 are well in accord with the expected trends in these values along the series $HfCl_6^{2-}$, $TaCl_6^-$, and WCl_6 (Table II).

Some reports of the infrared-active fundamentals of these ions have also appeared; these are in essential agreement with the present values. They refer to ν_3 for the ions $TiCl_6^{2-}$ (ref 1 and references therein), $ZrCl_6^{2-}$,[5] $HfCl_6^{2-}$,[14] and $NbCl_6^-$ and $TaCl_6^-$,[5,6,11] and to ν_4 for the ions $TiCl_6^{2-}$ [1,8] and $NbCl_6^-$ and $TaCl_6^-$.[5,6,11] Apart from the data[1] for the $TiBr_6^{2-}$ ion, all of the bromo salts have been studied here for the first time.

All of the above discussion emphasizes the great care needed in the interpretation of solution-state data, particularly Raman data, for these very readily hydrolyzable hexahalo species. We have therefore concentrated our attention on solid-state spectra, for which the species under study are not in doubt. We recognize that the selection rules relevant to the solid compounds are not necessarily those pertaining to O_h symmetry, but in practice little deviation therefrom is apparent. The assignments in Table II are substantiated by the consistency of the force constant calculations presented below.

The observed infrared-active combination bands for the various cesium salts, together with their assignments, are given in Table III. The strongest of these would be expected to be $\nu_1 + \nu_3$, $\nu_2 + \nu_3$, $\nu_3 + \nu_5$, and $\nu_2 + \nu_4$ by analogy with the known results for metal hexafluorides,[15] and in general this is found to be the case. The value for ν_6 was obtained in practice only from the combination band $\nu_2 + \nu_6$ because $\nu_5 + \nu_6$ (which is also infrared active) would be expected to lie in the region of the fundamental ν_3 and therefore to be obscured. In the case of $CsTaCl_6$, a very weak band occurs at 378 cm^{-1} which can be attributed to the formally inactive (in O_h) mode ν_1. In addition, in two or three cases there is evidence for certain formally forbidden first overtones. Their frequencies, together with the frequencies of other very weak bands (readily assignable to ternary combination bands), provide additional evidence for the correctness of the assignments of the fundamentals. Some of these are included as a footnote to Table III.

Force Constant Calculations.—The force constants for the various octahedral species have been calculated on the bases of both (A) the MUBFF and (B) the GVFF.

(A) The MUBFF includes, besides the bond stretch-

(10a) Note Added in Proof.—It has since been shown [I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc., A*, 2765 (1968)] that a satisfactory spectrum of $[(C_2H_5)_4N]NbCl_6$ can be obtained in acetonitrile if the latter is sufficiently dry.

(11) P. Reich and H. Preiss, *Z. Chem.*, **7**, 115 (1967).

(12) J. C. Evans and G. Y. S. Lo, *J. Mol. Spectry.*, **23**, 147 (1968).

(13) R. A. Walton, *Chem. Commun.*, 1385 (1968).

(14) R. J. H. Clark and W. Errington, *J. Chem. Soc., A*, 258 (1967).

(15) H. H. Claassen, J. G. Malm, and H. Selig, *J. Chem. Phys.*, **36**, 2890 (1962); H. H. Claassen, H. Selig, and J. G. Malm, *ibid.*, **36**, 2888 (1962).

TABLE III

INFRARED-ACTIVE BINARY COMBINATION BANDS (CM^{-1})[a]

Assignment	Cs_2TiCl_6 Obsd	Cs_2TiCl_6 Calcd	Cs_2ZrCl_6 Obsd	Cs_2ZrCl_6 Calcd	Cs_2HfCl_6 Obsd	Cs_2HfCl_6 Calcd	$CsNbCl_6$ Obsd	$CsNbCl_6$ Calcd	$CsTaCl_6$ Obsd	$CsTaCl_6$ Calcd	$CsNbBr_6$ Obsd	$CsNbBr_6$ Calcd	$CsTaBr_6$ Obsd	$CsTaBr_6$ Calcd
$\nu_1 + \nu_3$	652 w	654	630 w	639	610 w	617	694 vw	702	694 vw	702	454 w	460	...	444
$\nu_2 + \nu_3$	600 w, br	606	560 w	(562)	545 w, br	(545)	610 w	622	611 w	619	...	416	...	395
$\nu_3 + \nu_5$	526 vw?	520	466 w	474	445 vw, br	451	498 vw, br	512	...	504	...	350	319 w	328
$\nu_1 + \nu_4$	503 vw, br	510	...	488	480 w, br	483	...	534	...	540	323 w	336	...	338
$\nu_2 + \nu_4$	464 vw	462	...	(411)	...	(411)	442 w	454	440 w	437	293 w, br	292	292 w	289
$\nu_2 + \nu_6$	411 w	(411)	361 w, sh	(361)	...	(371)	400 w, sh	(400)	400 vw, br	(400)	...	...	258 vw, br	(258)

[a] In addition to the bands listed, very weak bands also occur at the following frequencies (cm^{-1}): Cs_2TiCl_6, 695 ($\nu_1 + \nu_4 + \nu_5 = 696$), 552 ($3\nu_5 = 558$); Cs_2ZrCl_6, 680, ($\nu_1 + \nu_2 + \nu_6 = 687$), 610 ($2\nu_2 + \nu_6 = 610$, $2\nu_3 = 626$); Cs_2HfCl_6, 704 ($\nu_1 + \nu_2 + \nu_6 = 704$), 650 ($\nu_1 + \nu_4 + \nu_5 = 650$), 629 ($2\nu_2 + \nu_6 = 632$), 525 ($2\nu_2 = 522$); $CsNbCl_6$, 652 ($2\nu_3 = 666$); $CsTaCl_6$, 642 ($2\nu_3 = 640$), 552 ($2\nu_5 + \nu_4 = 526$), 378 ($\nu_1 = 382$). Suggested assignments are given; these are not always consistent with infrared activity (assuming isolated anions of O_h symmetry) but may be permitted because of lattice effects. Difference bands were not observed. Frequencies in parentheses were used to determine ν_6, and in some cases ν_2 as well. The remaining two infrared-active binary combination bands, $\nu_4 + \nu_5$ and $\nu_5 + \nu_6$, are invariably obscured by ν_3.

ing (K), angle bending (H), and repulsive (F) force constants, the interaction force constants associated with *trans* bond stretches (k) and with adjacent angle bends (h).[16] These five force constants have been calculated from the five observed fundamentals in each case with the assistance of a program written for the University College IBM 360 computer. The results are in Table IV. From these force constants, a value for the inactive fundamental ν_6 was calculated for each ion. The agreement between the calculated value and the value determined from the infrared-active combination bands is reasonable.

TABLE IV

MUBFF FORCE CONSTANTS OF SOME MX_6 ANIONS AND WCl_6

Compound	K (mdyn/Å)	H (mdyn/Å)	F (mdyn/Å)	k (mdyn/Å)	h (mdyn/Å)	ν_6 (calcd) (cm^{-1})	ν_6 (exptl) (cm^{-1})
$[(C_2H_5)_4N]_2TiCl_6$	1.03_9	0.055	0.18_3	0.36_6	0.002	121	...
Cs_2TiCl_6	1.09_3	0.085	0.17_3	0.35_4	−0.002	133	139
$[(C_2H_5)_4N]_2ZrCl_6$	0.96_6	−0.022	0.25_7	0.15_9	0.013	95	...
Cs_2ZrCl_6	1.02_3	−0.017	0.27_7	0.08_8	0.011	104	112
$[(C_2H_5)_4N]_2HfCl_6$	1.01_3	−0.013	0.25_5	0.18_8	0.019	93	...
Cs_2HfCl_6	1.05_7	−0.003	0.27_1	0.17_6	0.015	105	110
$[(C_2H_5)_4N]NbCl_6$	1.27_6	−0.013	0.32_7	0.22_6	0.001	126	129
$CsNbCl_6$	1.28_1	−0.016	0.33_3	0.22_9	0.004	123	111
$[(C_2H_5)_4N]TaCl_6$	1.35_9	−0.021	0.34_2	0.25_5	0.016	111	119
$CsTaCl_6$	1.35_9	−0.022	0.35_8	0.25_8	0.015	118	101
WCl_6	1.61_9	−0.099	0.43_6	0.14_7	0.038	76	...
$[(C_2H_5)_4N]_2TiBr_6$	0.64_5	−0.009	0.24_3	0.08_1	0.003	71	...
$[(C_2H_5)_4N]_2ZrBr_6$	0.78_4	−0.017	0.24_1	0.02_3	0.003	68	...
$[(C_2H_5)_4N]_2HfBr_6$	0.72_9	−0.026	0.26_6	0.03_4	0.012	64	...
$CsNbBr_6$	1.11_7	0.013	0.25_3	0.23_1	−0.009	85	...
$CsTaBr_6$	1.14_6	−0.001	0.29_0	0.22_6	−0.001	83	75

The MCl stretching force constants lie in the range 0.97–1.62 mdyn/Å and are much more reasonable in comparison with those calculated[16] on the same basis for the $SnCl_6^{2-}$ (1.00 mdyn/Å), $SeCl_6^{2-}$ (1.34 mdyn/Å), $ReCl_6^{2-}$ (1.34 mdyn/Å), and $OsCl_6^{2-}$ (1.34 mdyn/Å) ions than that originally reported for the $TiCl_6^{2-}$ ion (3.10 mdyn/Å).[3] The latter value is based on the incorrect Raman values[2] for this ion and lies in the region of the stretching force constants of MF_6^{n-} ions.

There is little difference among the K values for the $TiCl_6^{2-}$, $ZrCl_6^{2-}$, and $HfCl_6^{2-}$ ions (average value 1.03 mdyn/Å) or between those for the $NbCl_6^-$ and $TaCl_6^-$ ions (average value 1.30 mdyn/Å). However, these average K values increase with increase in the oxidation state of the central metal atom in the expected manner:[17] M(IV), 1.03 mdyn/Å; M(V), 1.30 mdyn/Å; W(VI), 1.62 mdyn/Å.

The MBr stretching force constants are considerably lower than the corresponding MCl stretching force constants in each case (by 0.18–0.39 mdyn/Å) and are in the unexpected order TiBr < HfBr < ZrBr.

For each anion, the value of K for the tetraethylammonium salt lies below that for the cesium salt (by ~0.05 mdyn/Å). This is a general result and is related to the observation that the highest vibrational frequencies for an anion always occur where the anion is in a lattice in which the dimensions of the available sites are smallest.

Of the other force constants, the largest is usually F, the XX repulsive force constant. This increases with increase in the oxidation state of the central metal atom in agreement with the expected decrease in MX bond lengths (and consequent increase in $X \cdots X$ repulsive interaction) the higher the oxidation state of the metal atom. The other force constants are generally small.

It is worth noting that if the value of ν_2 for the $HfCl_6^{2-}$ ion is taken to be 204 cm^{-1}, as suggested by Long and Davies,[10] then ν_6 is found to be imaginary on the basis of MUBFF calculations. This is further evidence for the incorrectness of their assignment.

If the values for ν_2 and ν_5 given in ref 13 for WCl_6 are used instead of those in Table II, then the resulting values for both K (2.34 mdyn/Å) and k (0.52 mdyn/Å) are excessively large and clearly not in accordance with the trends exhibited by the other molecules. Similarly, according to the GVFF treatment (see below), the value for f_r (3.03 mdyn/Å) for WCl_6 is again excessive if the values of ref 13 are used for ν_2 and ν_5, and moreover there is no real solution to the 2 × 2 matrix involving the t_{1u} modes.

(B) The GVFF includes,[18,19] besides the bond stretching (f_r) and angle bending (f_α) force constants, the following interaction constants: f_{rr} and f_{rr}' which

---

(16) J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964); W. Yeranos, *Z. Physik. Chem.* (Frankfurt), **45**, 72, 77 (1965).

(17) L. A. Woodward, *Trans. Faraday Soc.*, **54**, 1271 (1958); R. J. H. Clark in "Halogen Chemistry," Vol. 3, V. Gutman, Ed., Academic Press, London, 1967, p 85.

(18) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 268.

(19) I. R. Beattie, T. Gilson, K. Livingstone, V. Fawcett, and G. A. Ozin, *J. Chem. Soc., A*, 712 (1967).

TABLE V

GVFF FORCE CONSTANTS OF SOME MX_6 ANIONS AND WCl_6

	mdyn/Å						Cm⁻¹ [c]	
Compound	f_r[a]	f_{rr}'	f_{rr}	f_α	$f_{\alpha\alpha}$[b]	$f_{r\alpha}$	ν_6(calcd)	ν_6(exptl)
$[(C_2H_5)_4N]_2TiCl_6$	1.600	0.134	0.101	0.264	0.054	0.320	122	. . .
Cs_2TiCl_6	1.631	0.127	0.095	0.326	0.073	0.370	131	139
$[(C_2H_5)_4N]_2ZrCl_6$	1.399	0.188	0.141	0.240	0.061	0.278	107	. . .
Cs_2ZrCl_6	1.407	0.203	0.152	0.305	0.085	0.319	114	112
$[(C_2H_5)_4N]_2HfCl_6$	1.472	0.187	0.140	0.168	0.020	0.166	110	. . .
Cs_2HfCl_6	1.522	0.198	0.149	0.210	0.032	0.213	118	110
$[(C_2H_5)_4N]NbCl_6$	1.852	0.240	0.180	0.298	0.065	0.353	127	129
$CsNbCl_6$	1.866	0.244	0.183	0.300	0.066	0.354	127	111
$[(C_2H_5)_4N]TaCl_6$	1.980	0.251	0.188	0.204	0.018	0.206	127	119
$CsTaCl_6$	1.998	0.262	0.197	0.224	0.025	0.235	129	101
WCl_6	2.232	0.320	0.240	0.344	0.102	0.422	116	. .
$[(C_2H_5)_4N]_2TiBr_6$	0.985	0.178	0.134	0.296	0.085	0.271	73	. . .
$[(C_2H_5)_4N]_2ZrBr_6$	1.064	0.177	0.133	0.313	0.099	0.297	70	. . .
$[(C_2H_5)_4N]_2HfBr_6$	1.046	0.195	0.146	0.268	0.074	0.246	71	. . .
$CsNbBr_6$	1.618	0.186	0.139	0.366	0.106	0.418	81	. . .
$CsTaBr_6$	1.682	0.213	0.159	0.277	0.059	0.327	82	75

[a] To obtain a value for f_r it has been assumed that $f_{rr}' = {}^4/_3 f_{rr}$; for reasons see text. [b] The assumption $f_{\alpha\alpha} = f_{\alpha\alpha}'$ has been made; for reasons see text. [c] A comparison of ν_6(calcd) and ν_6(found) is somewhat artificial as the assumptions imply that $\nu_6 = \nu_5\sqrt{2}$.

denote *cis* and *trans* bond stretching interactions, respectively; $f_{\alpha\alpha}$ and $f_{\alpha\alpha}'$ which denote angle bending interactions, the former when the three bonds involved are mutually perpendicular and the latter when the three bonds involved are coplanar; and $f_{r\alpha}$ which is the interaction constant, involving an angle and one of the bonds enclosing it. Following usual practice, it was assumed that the force constants associated with stretch–bend and bend–bend interactions are zero if the two internal coordinates do not have a bond in common. For this field, it is necessary to assume certain relationships between the force constants in order to reduce their number (7) to the number of observable fundamentals (5). The first of these assumptions is that $f_{\alpha\alpha} = f_{\alpha\alpha}'$. The second involves a relationship between f_{rr}' and f_{rr} in order to solve for f_r (f_{rr} and the sum $f_r + f_{rr}'$ are both uniquely determined). The relationship assumed herein, namely, that $f_{rr}' = {}^4/_3 f_{rr}$, was chosen because the coefficient $^4/_3$ is the minimum value which would give a real solution to the 2×2 matrix involving ν_3 and ν_4 for all of the compounds dealt with in this work. The results are in Table V.

The MCl bond stretching force constants (f_r) lie in the range 1.40–2.23 mdyn/Å and display the same trends as discussed above for the MUBFF force constants; *i.e.*, (i) the average values for f_r for each group increase with the oxidation state of the central atom (*viz.*: M(IV), 1.50; M(V), 1.90; WCl_6, 2.23 mdyn/Å), (ii) the f_r values for the tetraethylammonium salts are slightly lower than those for the cesium salts of the same hexachlorometalate ion (by ~0.03 mdyn/Å), and (iii) and f_r values for the hexabromometalates are considerably lower than those for the hexachlorometalates (by ~0.5 mdyn/Å).

A comparison of ν_6 (exptl) with ν_6 as determined from combination bands has little value for this force field because the assumptions automatically result in the relationship $\nu_6 = \nu_5/\sqrt{2}$. The values so calculated have, however, been included in Table V.

Chlorine Isotopic Effects.—An attempt has been made to demonstrate the expected isotopic splitting of the ν_1 (a_{1g}) vibration of the $TiCl_6^{2-}$ ion in nitromethane solution. The relative and percentage abundances of the different isotopic species present in natural abundance are listed in Table VI, together with the calculated values for ν_1 for each species. The total frequency separation between ν_1 for $Ti^{35}Cl_6^{2-}$ and $Ti^{37}Cl_6^{2-}$ (8.8 cm^{-1}) depends linearly on the value of ν_1 and on the fixed ratio $(35/37)^{1/2}$. However, even by use of the narrowest slits on the Cary 81, we were unable to resolve the potential structure of the ν_1 band. This must be partly because the solvent we were forced to use (for solubility reasons) leads typically to broader bands than is the case with nonpolar solvents and partly because three of the isotopic species can exist as both *cis* and *trans* isomers. These are the species $Ti^{35}Cl_4{}^{37}Cl_2{}^{2-}$ and $Ti^{35}Cl_2{}^{37}Cl_4{}^{2-}$ (for each of which the *cis*:*trans* abundance ratio is 4:1) and $Ti^{35}Cl_3{}^{37}Cl_3{}^{2-}$ (for which this ratio is 1:1).

TABLE VI

CALCULATED ISOTOPIC SPLITTING OF THE ν_1 (a_{1g}) VIBRATION OF THE $TiCl_6^{2-}$ ION

Dinegative ion	Rel abundance[a]	% abundance[b]	ν_1, cm^{-1}
$Ti^{35}Cl_6$	729	18.57	322.1
$Ti^{35}Cl_5{}^{37}Cl$	1458	36.09	320.6
$Ti^{35}Cl_4{}^{37}Cl_2$	1215	29.23	319.1
$Ti^{35}Cl_3{}^{37}Cl_3$	540	12.63	317.6
$Ti^{35}Cl_2{}^{37}Cl_4$	135	3.07	316.1
$Ti^{35}Cl^{37}Cl_5$	18	0.40	314.7
$Ti^{37}Cl_6$	1	0.02	313.3

[a] Based on the ratio ^{35}Cl:^{37}Cl = 3:1. [b] Based on the precise nuclidic abundances of 75.53% (^{35}Cl) and 24.47% (^{37}Cl).

An attempt to observe the isotopic splitting pattern for the ν_1 mode of the $TaCl_6^-$ ion in nitromethane solution was also unsuccessful using both He–Ne (6328 Å) laser excitation with a 1.8-cm^{-1} slit width and Ar$^+$ (4880- and 5145-Å) laser excitation with a 1.0-cm^{-1} slit width. In the case of the Ar$^+$ excitation, the band is asymmetric on the low-frequency side, as expected, and has a width at half-peak-height of 7.5 cm^{-1}.

Conclusion

The vibrational spectra and force constants of the hexahalo anions of the early transition elements are internally consistent and comparable with those of the later transition and post-transition element hexahalo anions.

The bond stretching force constants on both the MUBFF and the GVFF bases exhibit the expected trends with respect to changing the oxidation state of the metal atom and changing the halogen from chloride to bromide. The difference between the bond stretching force constants K(MUBFF) and f_r(GVFF) for a given hexahalo species arises because of the different restoring forces assumed in the two treatments. The GVFF method takes into account both *cis* (f_{rr}) and *trans* (f_{rr}') bond stretching interactions, whereas the MUBFF method retains the latter (as k) but replaces the former by an XX repulsive interaction (F). The force constant matrix elements (F_{nn}) formed in each treatment are different and lead to the conclusions[16,18]

$$F_{11} - 4F = K + k;\ F = (\lambda_1 - \lambda_2)/3.3\mu_X \quad \text{(MUBFF)}$$

$$F_{11} - 4f_{rr} = f_r + f_{rr}';\ f_{rr} = (\lambda_1 - \lambda_2)/6\mu_X \quad \text{(GVFF)}$$

where $\lambda = 5.889 \times 10^{-2}\nu^2$ and μ_X = reciprocal mass of X.

As the magnitudes of F and f_{rr} are clearly different, the other constants K, k and f_r, f_{rr}' must likewise be different, despite their having the same physical significance.

The occurrence of a negative force constant (H) in the MUBFF treatment arises because of the distinction made between the adjacent XX repulsions (F) and the bond angle bending forces (H), a distinction which is not justified. The only requirement is that the sum $H + 0.55F$ be positive,[18] which is true in every case. The matter is aggravated by the arbitrary assumption[18] that the nonadjacent XX repulsive force constants equal $-0.1F$.

Acknowledgment.—L. M. thanks the University of Padova for a leave of absence, and W. v. B thanks the I.C.I. Co. Ltd. for the award of a fellowship. Part of this research was supported by NATO Grant No. 341, which is gratefully acknowledged. We are also grateful to the University of London for the use of the Cary 81 laser Raman spectrometers.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ARIZONA STATE UNIVERSITY, TEMPE, ARIZONA 85281

Studies of Some Niobium and Tantalum Hexaisothiocyanate Complexes[1,2]

BY G. F. KNOX AND T. M. BROWN

Received January 6, 1969

The reaction of potassium thiocyanate with $NbCl_5$, $NbCl_4$, and $TaCl_5$ in acetonitrile gives the complex anions $Nb(NCS)_6^-$, $Nb(NCS)_6^{2-}$, and $Ta(NCS)_6^-$, respectively. Metatheses between $KM(NCS)_6$ (M = Nb, Ta) and tetrabutylammonium chloride and tetraphenylarsonium chloride give rise to compounds containing these cations. Infrared data indicate that the thiocyanate groups are nitrogen bonded in all cases. A detailed study of the conductance of these compounds in acetonitrile showed that dissociation takes place at low concentrations which must be taken into account when interpreting the visible–ultraviolet spectra.

Introduction

The preparation and partial characterization of the hexaisothiocyanate complexes of niobium(V)[3] and tantalum(V)[3,4] have been reported. The relatively low frequency of the CN stretch in these d^0 complexes was of interest and led us to an investigation of the similar niobium(IV) complex, a d^1 case. Further studies have been made on all of the +5 complexes since the original reports. While this work was being completed, Boland and coworkers[5,6] reported the preparation of several complexes of niobium(V) and tantalum(V) containing thiocyanate ion. A more complete examination of the acetonitrile solutions of these complexes indicated that dissociation occurs at concentrations used to obtain the visible–ultraviolet spectra and must be taken into account when interpreting the results. The results of these investigations are now presented along with a description of the niobium(IV) complex.

Experimental Section

Since some of the starting materials, as well as the products of the following syntheses, were unstable in the presence of oxygen or water vapor, all work was carried out in an inert-atmosphere drybox or under vacuum. All solvents and vessels used in the reactions were thoroughly dried by accepted methods. The elemental analyses of C, H, N, S, and As were carried out by Alfred Bernhardt Laboratories, Mülheim, Germany. Nio-

---

(1) Abstracted in part from the Ph.D. dissertation submitted by G. F. Knox to the Graduate School of Arizona State University, Tempe, Ariz., 1968.

(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(3) T. M. Brown and G. F. Knox, *J. Am. Chem. Soc.*, **89**, 5296 (1967).

(4) H. Boland and E. Tiede, *J. Less-Common Metals*, **13**, 224 (1967).

(5) H. Boland and E. Zenker, *ibid.*, **14**, 397 (1968).

(6) H. Boland, E. Tiede, and E. Zenker, *ibid.*, **15**, 89 (1968).