carried to other temperatures until the activation parameters are known.

The disappearance of $(NC)_5Fe(C_8H_6O_2N)^{4-}$ conforms to the rate law $-d[(NC)_5Fe(C_8H_6O_2N)^{4-}]/dt = k_1'[(NC)_5Fe(C_8H_6O_2N)^{4-}]$. If k_1' is assumed to equal $k_1[H_2O]$, a bimolecular rate constant k_1 can be calculated. The corresponding parameters have been determined for the analogous complex formed in the acetone–$(NC)_5FeNO^{2-}$ reaction. For the acetone–$(NC)_5FeNO^{2-}$ system $k_1 = 2.9 \times 10^{-4}\ M^{-1}\ sec^{-1}$ compared to $7.0 \times 10^{-5}\ M^{-1}\ sec^{-1}$ for the acetophenone–$(NC)_5FeNO^{2-}$ system. The slower reaction for $(NC)_5Fe(C_8H_6O_2N)^{4-}$ results from a larger enthalpy of activation (19.4 kcal/mol compared to 17.8 kcal/mol) rather than any entropy difference (−12 eu for acetophenone compared to −15 eu for acetone).

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CONTRIBUTION FROM THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA, AND WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, ENGLAND

The Preparation and Spectral Properties of Some Hexahalo and Oxopentahalo Complexes of Niobium and Tantalum

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Various preparative routes to the compounds $M^IM^VCl_6$ [M^I = Na, K, Rb, Cs, Tl, $(C_6H_5)_4As$; M^V = Nb, Ta] have been investigated. Magnetic susceptibilities and electronic and vibrational spectral properties of salts containing MCl_6^-, MBr_6^-, MCl_6^{2-}, and MBr_6^{2-} ions are presented and analyzed, together with the concomitant properties of salts of $MOCl_5^{2-}$ and $MOBr_5^{2-}$ ions.

Introduction

In a continuing program[1-3] of hexahalometalate chemistry, interest was focused on niobium and tantalum. The original intent was to made the hexahalometalate(IV) salts by reduction with alkali metal iodides, in the manner used successfully with WCl_6[2,4]

$$2CsI + 2CsMCl_6 \longrightarrow 2Cs_2MCl_6 + I_2$$

and to compare their spectra with those of the analogous molybdenum and tungsten compounds.

Samples of hexahalometalate(V) salts were needed as starting materials. Various preparative approaches to the latter were attempted. In addition, certain physical properties of these compounds were measured.

Previously the hexachlorometalates(V) and hexabromometalates(V) have been prepared two ways: (1) heating mixtures of the solid metal pentahalides with the appropriate alkali metal halide[5] and (2) allowing the same reagents to react in an ICl–$SOCl_2$ solvent system.[6,7] The quadrivalent salts described herein have been synthesized previously by direct reaction of the metal tetrahalides with the appropriate alkali metal halide by McCarley and coworkers.[8]

Experimental Section

Sources of Chemicals.—Niobium(V) and tantalum(V) chlorides and oxides were obtained from Alfa Inorganics and from Columbia Organic Chemicals. Niobium and tantalum bromides were synthesized from the direct reaction of bromine vapor with the respective metal powders[9] obtained from Fairmount Chemicals. Cesium salts and tetraphenylarsonium chloride were obtained from Columbia Organic Chemicals. Iodine monochloride was supplied by K & K Laboratories. Other chemicals were commercial reagent grade materials.

All hexahalometalates(V) were handled in a dry nitrogen atmosphere during isolation and subsequent reaction, as were all hexahalometalates(IV) during synthesis and subsequent handling.

Preparation of Hexahalometalates(V). (a) Reaction in ICl–$SOCl_2$ Solvent System.—The preparation of $CsNbCl_6$ by this method has been described in detail by Bagnall and Brown.[6,7] The $CsNbCl_6$ and $CsTaCl_6$ used in the present work were prepared by this method. *Anal.* Calcd for $CsNbCl_6$: Nb, 21.19; Cl, 48.51. Found: Nb, 21.72, 20.81; Cl, 48.68, 48.69. Calcd for $CsTaCl_6$: Ta, 34.36; Cl, 40.41. Found: Ta, 34.34; Cl, 40.49.

The method was also applied to the synthesis of hexahalometalates of Tl, K, and Rb. When TlCl was dissolved in ICl and mixed with $SOCl_2$ solutions of $NbCl_5$ or $TaCl_5$, a precipitate formed upon addition of a considerable excess of $SOCl_2$. *Anal.* Calcd for $TlNbCl_6$: Cl, 41.71. Found: Cl, 42.18. Calcd for $TlTaCl_6$: Cl, 35.57. Found: Cl, 36.70.

The corresponding K and Rb salts were not precipitated by the foregoing procedures, and the precipitate obtained upon addition

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[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **2**, 568 (1963).

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[5] I. S. Morozov, B. G. Korshunov, and A. O. Simonick, *Zh. Neorgan. Khim.*, **1**, 1646 (1956).

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[8] R. E. McCarley, private communication.

[9] A. Cowley, F. Fairbrother, and N. Scott, *J. Chem. Soc.*, 3133 (1958).

of CCl_4 to the $SOCl_2$ solution did not give analyses corresponding to $MNbCl_6$ or $MTaCl_6$.

(b) **Tetraphenylarsonium Salts.**—A solution of 4–5 g of $(C_6H_5)_4AsCl$ in approximately 50 ml of $SOCl_2$ was combined with a solution of 3 g of $NbCl_5$ or 4 g of $TaCl_5$, respectively, in approximately 50 ml of $SOCl_2$. The mixture was evaporated in each case to about 20-ml volume and crystallization was allowed to occur at room temperature. The crystals were removed by filtration and washed sparingly with $SOCl_2$. *Anal.* Calcd for $(C_6H_5)_4AsNbCl_6$: Cl, 30.58; C, 41.84. Found: Cl, 30.59; C, 41.91. Calcd for $(C_6H_5)_4AsTaCl_6$: Cl, 27.38; C, 37.10. Found: Cl, 27.40; C, 36.42.

(c) **Reaction of Mixed Metal Oxides with CCl_4 in a Bomb Reaction.**—$KNbCl_6$ and $KTaCl_6$ were prepared by the reaction of a K_2O–M_2O_5 mixture with CCl_4 in a sealed ampoule at 400°, as described previously.[10,11] The oxide mixture was prepared from ignition of an intimate mixture of K_2CO_3 and a slight excess of niobium or tantalum(V) oxide.

The resulting yellow $KNbCl_6$ and white $KTaCl_6$, the insoluble product in each case of CCl_4 extraction of the reaction mixture, were extremely sensitive to air and moisture, the $KNbCl_6$ turning white even in a tightly closed container. *Anal.* Calcd for $KNbCl_6$: Nb, 26.95; Cl, 61.71. Found: Nb, 26.53; Cl, 60.85. Calcd for $KTaCl_6$: Ta, 41.81; Cl, 49.15. Found: Ta, 41.80; Cl, 48.80.

(d) **Direct Solid-State Reaction of Niobium or Tantalum Pentabromides with Alkali Metal Bromides.**[5]—Niobium(V) or tantalum(V) bromide was ground intimately with CsBr in a 1:1 molar ratio. The mixture was heated at approximately 110°, with regrinding, for 1–2 weeks, until the X-ray powder patterns of the products matched those of $CsNbCl_6$ and $CsTaCl_6$.

Preparation and Reactions of Oxopentahalometalate(V) Salts. (a) **Preparation of Cs_2NbOCl_5 and Cs_2NbOBr_5.**—The method described by Brown[12] was used to prepare Cs_2NbOCl_5. In this method, a solution of $NbCl_5$ and CsCl in concentrated hydrochloric acid is saturated with HCl gas to effect precipitation of Cs_2NbOCl_5. In the present work, the precipitate was washed only with concentrated hydrochloric acid and not with ether or $SOCl_2$. The same method, using CsBr and $NbBr_5$, was used for the preparation of Cs_2NbOBr_5, which precipitated as a red-brown solid upon saturation of the solution with HBr gas. *Anal.* Calcd for Cs_2NbOCl_5: Nb, 16.83; Cl, 32.11. Found: Nb, 16.55, 16.80; Cl, 32.25, 31.60. Calcd for Cs_2NbOBr_5: Nb, 12.00; Br, 51.61. Found: Nb, 11.96; Br, 51.43.

(b) **Attempted preparation of Cs_2TaOCl_5 and Cs_2TaOBr_5.** All attempts to precipitate Cs_2TaOCl_5 from concentrated hydrochloric acid, as described for Cs_2NbOCl_5, resulted in a product with a Cl:Ta ratio of 2 or less. A similar approach failed to produce Cs_2TaOBr_5.

(c) **Reaction of Cs_2NbOCl_5 with CCl_4 in a Bomb.**—Approximately 5 g of cream-colored Cs_2NbOCl_5, mixed with some excess Nb_2O_5, was placed in a 110-ml ampoule containing 32 ml of CCl_4. The sealed ampoule was heated at 400° for 20 hr. Analyses of the resulting yellow solid corresponded to the expected mixture of $CsNbCl_6$ and CsCl.

(d) **Reaction of Cs_2NbOCl_5 with Refluxing Hexachloropropylene.**—Approximately 2–3 g of Cs_2NbOCl_5 was refluxed overnight with approximately 30 ml of C_3Cl_6. The color of the solid became a somewhat deeper yellow. However, an infrared spectrum of the solid product showed an intense peak in the region of 915 cm^{-1}, comparable in position and intensity to the band in Cs_2NbOCl_5 starting material.

Preparation of Hexahalometalates(IV). (a) **Reaction of CsI with $CsMX_6$.**—An equimolar mixture of CsI with $CsNbCl_6$ or $CsTaCl_6$ was ground intimately for 5–10 min in an agate mortar and placed in one end of a 14-mm o.d. Pyrex tube. The tube was stoppered tightly with a rubber stopper, and the end containing the reaction mixture was heated in a tube furnace several days, usually with one or two regrindings of the solid mixture. Iodine crystals formed at the cool end of the tube and the residue in the hot zone became purple in each case.

In a similar manner, CsI was combined with brown $CsNbBr_6$ and yellow $CsTaBr_6$. Upon heating and regrinding, the $CsNbBr_6$ mixture became dark green, and the $CsTaBr_6$ mixture became dark blue-green, with iodine subliming to the cool end of the tube. The temperatures required for reaction in the several cases were: Cs_2NbCl_6, 200°; Cs_2TaCl_6, 300°; Cs_2NbBr_6, 250°; Cs_2TaBr_6, 310°. *Anal.* Calcd for Cs_2NbCl_6: Nb, 16.26; Cl, 37.23. Found: Nb, 16.53; Cl, 35.44; oxidation state of Nb, 3.97. Calcd for Cs_2TaCl_6: Ta, 27.44; Cl, 32.26. Found: Ta, 27.29, 26.90; Cl, 30.10, 29.98; oxidation state of Ta, 3.95. Calcd for Cs_2NbBr_6: Nb, 11.08; Br, 57.20. Found: Nb, 10.78, 11.04; Br, 56.49. Calcd for Cs_2TaBr_6: Ta, 19.54; Br, 51.76. Found: Ta, 19.64; Br, 50.02; oxidation of Ta, 3.99.

(b) **Reaction of CsI with $CsMCl_6$ in Hexachlorobutadiene.**—Approximately 7 g of a finely ground equimolar mixture of CsI with $CsNbCl_6$ or $CsTaCl_6$, respectively, was suspended in 30 ml of dry hexachlorobutadiene, and the mixtures were refluxed for several days. At the end of this time, the solution in each case was dark reddish purple. The $CsNbCl_6$ mixture contained a purple solid, similar in appearance and analysis to that obtained by the method in part a above. The $CsTaCl_6$ mixture was a black solid instead of the purple observed in part a and contained a carbonaceous residue. Both were removed by filtration, washed with CCl_4, and dried. *Anal.* Calcd for Cs_2NbCl_6: Nb, 16.26; Cl, 37.23. Found: Nb, 16.85; Cl, 35.39, 35.70. Calcd for Cs_2TaCl_6: Ta, 27.44; Cl, 32.26. Found: Ta, 27.94; Cl, 30.32; C, 4.0.

Analyses.—Niobium and tantalum analyses were performed by hydrolysis of the sample with aqueous ammonia, precipitating the hydrous oxide of niobium or tantalum. The oxide was filtered, washed, ignited to 800–850°, cooled, and weighed. Halide analyses were performed gravimetrically on the filtrate. Carbon analyses were done by Triangle Chemical Laboratories, Inc., Chapel Hill, N. C.

Oxidation states were determined by dissolving the sample in an excess known quantity of Ce(IV) solution in 2 *N* H_2SO_4. The solutions were then back-titrated with standard Fe(II) solution. In the case of Cs_2TaBr_6, the titer of Ce(IV) solution was corrected for the amount of Ce(IV) consumed by oxidation of the bromide ion to bromine, calculated from the bromine analysis of the sample.

Magnetic Moments.—Magnetic susceptibilities were determined for representative samples at 20° using a Gouy balance and a variable-flux permanent magnet described earlier.[13]

X-Ray Powder Patterns.—X-Ray powder patterns were determined for representative samples using a 114.59-mm Norelco powder camera and Cu $K\alpha$ radiation.

Visible and Ultraviolet Spectra.—Spectra were determined on samples which had been ground with freshly fused KCl and pressed into pellets. The pellets were layered so as to have an outside coating of KCl, and the pellet mixtures were handled in a dry nitrogen atmosphere during grinding and loading into the pellet die. The spectra were obtained using a Cary Model 14 double-beam recording spectrophotometer. For the solution spectra reported, $NbCl_5$ or $TaCl_5$ was dissolved in 12 *N* HCl, presumably furnishing the $MOCl_5^{2-}$ ion in solution, for comparison to the spectra of the solid material.

Infrared Spectra.—The infrared spectra of the compounds were recorded using Grubb–Parsons grating spectrometers, Types DM2 (double beam, 455–200 cm^{-1}) and GM3 (single beam, 200–70 cm^{-1}), as Nujol mulls between polyethylene plates of thickness 0.055 cm. The instruments were calibrated by reference to part of the rotational spectra of water vapor,[14] and the

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[10] E. R. Epperson, S. M. Horner, K. Knox, and S. Y. Tyree, Jr., *Inorg. Syn.*, **7**, 169 (1963).

[11] W. W. Horner, F. N. Collier, and S. Y. Tyree, Jr., *Inorg. Chem.*, **3**, 1388 (1964).

[12] D. Brown, *J. Chem. Soc.*, 4944 (1964).

[13] S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 112 (1962).

[14] L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Natl. Bur. Std.*, **A66**, 223 (1962).

TABLE I

Ion[a]	Absorption spectra, cm^{-1}						Ref
$NbCl_6^-$			29,400	34,500		43,500	
$NbCl_6^{2-}$	20,400	(25,600)[b]	(30,500)	34,800	40,000	43,500	
$NbOCl_5^{2-}$			29,800	(36,360)		43,500	
$NbOCl_5^{2-}$ (aq soln)			(30,800)	35,600		43,500	
$MoCl_6^-$		24,100	28,250	32,800	36,430	41,150	1
$MoCl_6^{2-}$	22,200	25,800	27,780	32,750	35,710	40,820	1
$MoOCl_5^{2-}$	14,100	22,420	28,010	32,260		40,000	17
$TaCl_6^-$			30,800	36,400		42,400	
$TaCl_6^{2-}$	20,800	26,000	(29,000)	(38,500)		42,200	
$TaOCl_5^{2-}$ (aq soln)				37,000			
WCl_6^-		27,400	32,260	35,700	39,200	42,800	2
WCl_6^{2-}	19,230		31,750	35,500	39,400	42,600	
$WOCl_5^{2-}$	14,200	25,190	32,790	37,170			17
$NbBr_6^-$			(18,900)	23,300	28,000	33,300	
$NbBr_6^{2-}$		(16,500)	(19,700)	24,400	28,600	(34,500)	
$NbOBr_5^{2-}$			(21,700)	25,300	28,000	33,900	
$MoOBr_5^{2-}$	14,290		21,280	24,100	26,530		17
$TaBr_6^-$			(21,000)	24,400	30,000	33,300	
$TaBr_6^{2-}$	14,800	(17,100)	18,200	24,900	29,400	(33,800)	
$TaOBr_5^{2-}$				24,400	28,500	28,500	
WBr_6^-	14,900		18,900	23,500			18
WBr_6^{2-}			20,100	25,200		33,000	17
$WOBr_5^{2-}$	14,290			25,640			17

[a] All spectra reported in this work are of Cs salts. [b] Bands in parentheses were observed only as shoulders.

resulting frequencies are believed to be accurate to ±1 cm^{-1} for sharp bands and ±2 cm^{-1} for broad bands.

In order to increase the sharpness of bands, it is desirable to record the spectra at liquid nitrogen temperatures. To this end, a special cell was designed for both instruments, that for the DM2 being shown in Figure 1. Both instruments are purged of water vapor by passing a slow stream of very dry air through the optical paths. Trace residual water vapor in this air stream is then frozen out on the brass catcher foils in front of and behind the sample by addition of liquid nitrogen to the funnel which connects with the catcher foils. Then the sample itself is independently lowered to ~77°K by addition of liquid nitrogen to the second funnel, that which connects directly with the sample holder. This technique avoids the possibility of ice freezing on the outside of the polyethylene plates containing the sample. The assistance of Dr. R. W. Cattrall in designing the cell is acknowledged. The cell for the GM3 instrument is designed similarly.

Owing to the extreme sensitivity of the compounds to hydrolysis and, in the case of the quadrivalent derivatives, to oxidation also, the mulls were prepared in a nitrogen-filled drybox under rigorously anhydrous conditions. The samples were sealed in glass ampoules in a nitrogen atmosphere in Chapel Hill and sent to University College, where the contents of the sealed ampoules were broken directly into Nujol. The spectra were also recorded in the 1000-cm^{-1} region in order to be sure that no significant amounts of oxo impurities were present.[15]

Results and Discussion

The products of the reduction of $CsNbCl_6$ and $CsTaCl_6$, respectively, with cesium iodide show analyses approaching those of the compounds Cs_2NbCl_6 and Cs_2TaCl_6. The analyses showed low chloride results by *ca.* 2% on a number of preparations. The hexabromometalate(IV) salts gave correspondingly low bromide analyses, as did the products of the reaction of CsI with $CsMCl_6$ in refluxing hexachlorobutadiene. The possible formation of polynuclear compounds under the reaction conditions used would account for the low halogen content of the compounds. Alternatively, extreme sensitivity of the compounds to air and moisture may have resulted in poor analytical results. In spite of rigorous exclusion of air and moisture during preparation, very small peaks in the Nb–O region of the infrared spectrum were usually observed for the hexahalometalate(IV) salts, apparently simply from the handling required to obtain the spectrum.

The observed physical properties present strong evidence that the preparative methods used in this work do yield Cs_2MX_6, albeit impure. The visible and ultraviolet spectra, reported earlier,[16] are shown in Table I,[1,2,17,18] along with the spectra of some Mo and W compounds for comparison. Typical spectra of $CsNbCl_6$, Cs_2NbCl_6, and Cs_2NbOCl_5 are shown in Figure 2.

It should be observed that the charge-transfer bands of MX_6^- and MX_6^{2-} salts correspond quite closely. Such similarity of energies is predictable, since the more electronegative pentavalent metal simply abstracts more electronic charge from the surrounding ligands, so that the effective nuclear charge on the metal is nearly the same for MX_6^- and MX_6^{2-}. In addition to the charge-transfer bands, the MX_6^{2-} salts exhibit one or two lower energy bands, presumably d–d bands, corresponding to the $^2T_{2g} \rightarrow {}^2E_g$ transition. The presence of two such bands is predictable from Jahn–Teller splitting of the excited state.

The X-ray data also lend strength to the formulation of the salts as Cs_2MX_6. All such compounds prepared in the present work showed patterns of the cubic K_2PtCl_6 structure, the patterns being essentially the same as for Cs_2WCl_6.[2] The compounds Cs_2NbOCl_5

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(15) A. Sabatini and I. Bertini, *Inorg. Chem.*, **5**, 204 (1966).

(16) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Nucl. Chem. Letters*, **1**, 43 (1965).

(17) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

(18) B. J. Brisdon and R. A. Walton, *ibid.*, 2274 (1965).

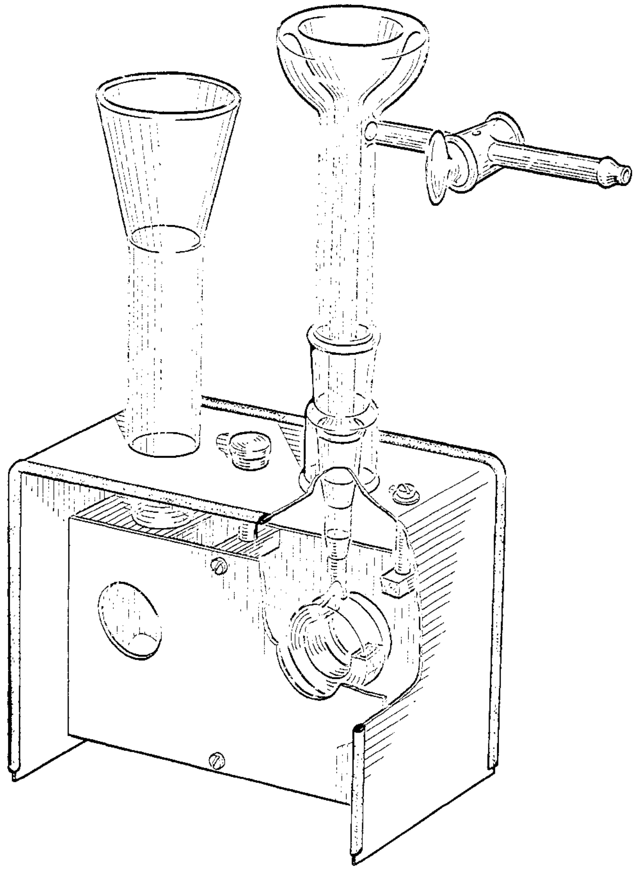

Figure 1.—Apparatus for recording spectra on the GM3 instrument at liquid nitrogen temperature.

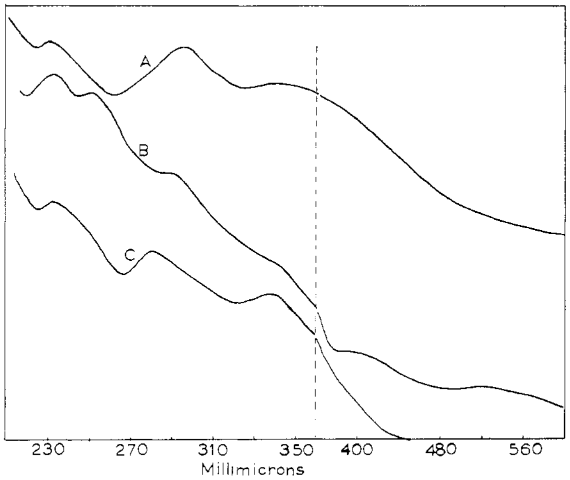

Figure 2.—The ultraviolet and visible absorption spectra of compounds in KCl pellets: (A) $CsNbCl_6$; (B) Cs_2NbCl_6; (C) Cs_2NbOCl_5.

and Cs_2NbOBr_5 also showed the same cubic X-ray powder pattern, in agreement with the work of Brown.[12] The alkali metal hexahalometalate(V) salts, on the other hand, exhibited the more complex pattern observed previously for $CsWCl_6$.[2]

The magnetic moments of the compounds prepared are shown in Table II. In cases where only a slight net paramagnetism was exhibited, the corrected molar susceptibility is given. Many compounds which should exhibit diamagnetism showed a slight paramagnetism. However, the Nb_2O_5 used to synthesize the starting materials also showed a net paramagnetism of about 50×10^{-6} cgsu. Therefore the slight paramagnetism of some niobium(V) compounds may be attributed to impurities in the starting materials. The magnetic moments of the Cs_2MX_6 salts are consistent with those predicted on the basis of the Kotani theory. Indeed, the moments are comparable to those of the d^1 compounds $((C_2H_5)_4N)MoCl_6$ and $((C_2H_5)_4N)WCl_6$ reported by Brisdon and Walton,[19] 1.31 and 0.66 BM, respectively.

Table II

Magnetic Susceptibilities

Compound	μ_{eff}, BM	χ_M', cgsu
Cs_2NbCl_6	1.24	
Cs_2NbCl_6 (from C_4Cl_6 suspension)	1.24	
Cs_2NbBr_6	1.18	
Cs_2TaCl_6		97×10^{-6}
Cs_2TaBr_6		145×10^{-6}
$KNbCl_6$	Diamagnetic	
$CsNbCl_6$		65×10^{-6}
$CsTaCl_6$	Diamagnetic	
Cs_2NbOCl_5	Diamagnetic	
Cs_2NbOBr_5		90×10^{-6}

Although data on metal–chlorine and metal–bromine stretching frequencies are now quite well documented,[20] data on halogen–metal–halogen bending frequencies are very sparse. The present study of the infrared spectra was undertaken to obtain information about the effects of different counterions on the infrared-active stretching and bending fundamentals of metal hexahalo anions of niobium and tantalum and to compare these vibrational frequencies with those of corresponding complexes of molybdenum and tungsten.[21] The results are given in Table III. Figures 3 and 4 show typical spectra.

In the case of the $NbCl_6^-$ ion, ν_3 (the antisymmetric stretching vibration) and ν_4 (the antisymmetric bending vibration) are both almost independent of the cation, lying at 333 ± 2 cm^{-1} and at *ca.* 165 cm^{-1}, respectively. Thus the size of the cation ($K^+ < Tl^+ < Cs^+ < (C_2H_5)_4N^+ < (C_6H_5)_4As^+$) has a negligible effect on the vibrational frequencies of the $NbCl_6^-$ ion. More typically, the highest vibrational frequencies for an anion occur in those lattices where the dimensions of the available sites are smallest, as has been observed for cyanide ions isomorphously diluted into alkali halide crystals[22] and for different salts of the tetrahedral MX_4^{2-} ions (M = first-row transition metal; X = Cl, Br, or I).[23] The vibrational frequencies of the corresponding tantalum salts show more dependence on the cation, and in the case of the cesium salt there is evidence for the resolution of the triple degeneracies of

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[19] B. J. Brisdon and R. A. Walton, *J. Inorg. Nucl. Chem.*, **27**, 1101 (1965).

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TABLE III

INFRARED-ACTIVE ABSORPTION BANDS IN THE SALTS RMX_6 AND R_2MX_6 (M = Nb or Ta; X = Cl or Br)

Salt	ν_3 (t_{1u})	ν_4 (t_{1u})
	Pentavalent Derivatives	
$KNbCl_6$	333 vs, br	176 s, 163 s
$TlNbCl_6$	335 vs, br	165 s, vbr
$CsNbCl_6$	333 vs	165 s, vbr
$(C_2H_5)_4NNbCl_6$[a]	333 vs	...
$(C_6H_5)_4AsNbCl_6$	331 vs	163 s
$KTaCl_6$	315 vs, asym	154 s
$TlTaCl_6$	333 vs, asym	164 s, br
$CsTaCl_6$	328 s, 317 vs, 307 vs	164 ms, 157 s, 150 s
$(C_2H_5)_4NTaCl_6$	330 vs	...
$(C_6H_5)_4AsTaCl_6$	316 vs	155 s
	Tetravalent Derivatives	
Cs_2NbCl_6	314 s	165 s
Cs_2NbBr_6	236 vs	112 s
Cs_2TaCl_6	297 vs	160 s
Cs_2TaBr_6	217 vs	109 s

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

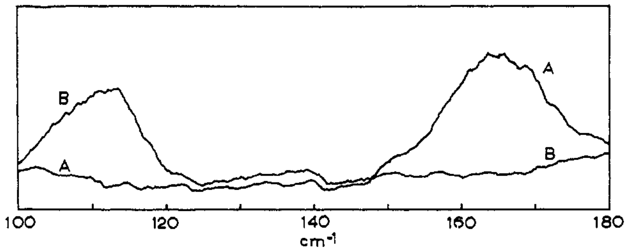

Figure 3.—The ν_4 (t_{1u}) infrared absorption spectra using the GM3 instrument: (A) Cs_2NbCl_6; (B) Cs_2NbBr_6.

ν_3 and ν_4 in the crystalline state (most obviously when the spectrum is recorded at 77°K).

The effect of lowering the oxidation state of transition metal from 5 to 4 is to lower ν_3 by *ca.* 20 cm^{-1}, but there is no effect on ν_4 (as evidenced by a comparison of the data for the various cesium salts). Coupling of the present data with those on the corresponding molybdenum and tungsten hexachloro anions (cesium salts)[21] yields the following frequency (cm^{-1}) orders: ν_3: Ta(IV) (297) < W(IV) (308) < Nb(IV) (314) < Mo(IV) (325); ν_4: Ta(IV) (160) < W(IV) (166) ~ Nb(IV) (165) < Mo(IV) (170); *i.e.*, both ν_3 and ν_4 increase with decreasing size of the central metal atom. The same frequency order prevails for the hexabromo complexes: ν_3: Ta(IV) (217) ~ W(IV) (214) < Nb(IV) (236); ν_4: Ta(IV) (109) < Nb(IV) (112). However, Adams, *et al.*,[21] have assigned a band occurring at 60–78 cm^{-1} in the spectrum of the WBr_6^{2-} ion as ν_4. In view of the internal consistency of the above results, it seems most probable that the band they observed is a lattice vibration and that ν_4 for this ion should be near 110 cm^{-1}. Moreover, ν(MBr)/ν(MCl) for ν_3 and ν_4 typically lies in the range 0.68–0.76,[20] and this is not possible if ν_4 for the WBr_6^{2-} ion lies near 70 cm^{-1}.

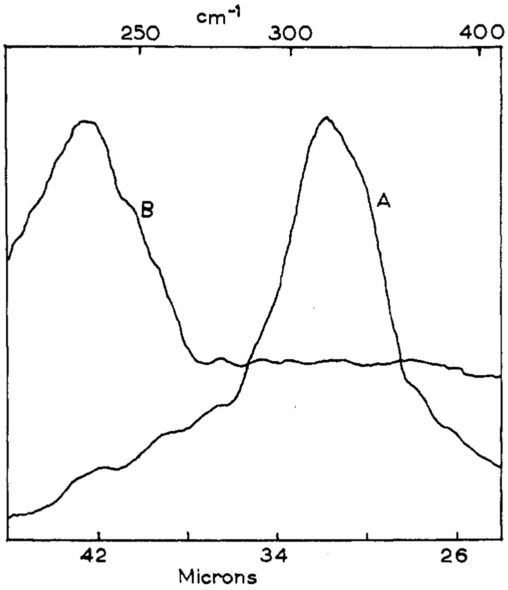

Figure 4.—The ν_3 (t_{1u}) infrared absorption spectra using the DM2 instrument: (A) Cs_2NbCl_6; (B) Cs_2NbBr_6.

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