

A Study of the Stereochemistry and Magnetic and Spectral Properties of Coordination Compounds of the Niobium(IV) and Tantalum(IV) Chlorides and Bromides and of the Complex Anions NbCl_6^{2-} and NbBr_6^{2-}

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Coordination complexes of the types $\text{NbX}_4 \cdot 2\text{L}$ and $\text{MX}_4 \cdot \text{B}$, where M = Nb or Ta; X = Cl or Br; L = acetonitrile, tetrahydrofuran, tetrahydropyran, or 1,4-dioxane; and B = 2,2'-bipyridyl or 1,10-phenanthroline have been prepared from the tetrahalides. The acetonitrile complexes $\text{NbX}_4 \cdot 2\text{CH}_3\text{CN}$ are useful starting materials for the preparation of the hexahalo salts $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NbX}_6$. The far-infrared spectra ($500\text{--}200\text{ cm}^{-1}$) of the solid complexes $\text{NbX}_4 \cdot 2\text{L}$ and $\text{MX}_4 \cdot \text{B}$ have been recorded and the metal-halogen stretching frequencies assigned. Interpretation of the latter indicates that these complexes have a *cis*-octahedral structure; for $\text{MX}_4 \cdot \text{B}$, the chelating nature of the ligand molecules would in any case make this the most likely structure. The diffuse-reflectance spectra and temperature range magnetic properties of all of the niobium(IV) complexes are compared with related measurements on the "model" octahedral species NbX_6^{2-} . These spectral measurements allow a fairly straightforward assignment of the halogen(π) \rightarrow Nb(d) and $d \leftrightarrow d$ transitions whereas the behavior of the magnetic properties of the complexes over the temperature range $300\text{--}80^\circ\text{K}$ is not generally well understood.

Introduction

The isolation of coordination complexes of the types $\text{MX}_4 \cdot 2\text{L}$ and $\text{MX}_4 \cdot \text{B}$ (M = Nb or Ta; X = Cl, Br, or I; L = pyridine or γ -picoline; B = 2,2'-bipyridyl, 1,10-phenanthroline, or N,N',N',N'-tetramethylethylenediamine)¹⁻⁴ has been achieved using either the metal pentahalides or tetrahalides as starting materials. The use of the former may in some instances be a disadvantage because of possible contamination of the desired complexes by organic oxidation products. For this reason the reactivity of the niobium(IV) halides is of interest.

The thermal stability and ease of preparation of coordination complexes of the type $\text{MX}_4 \cdot 2\text{L}$ are common features of the chemistry of the transition metals of groups IV-VII, and for this reason the isolation of the above niobium(IV) and tantalum(IV) complexes is not unexpected. However, these particular complexes contain metal atoms with d^1 electronic configurations which are isoelectronic with molybdenum(V) and tungsten(V) species (as typified by the MoCl_5^- and WX_6^- anions,⁵⁻⁸ and coordination compounds of the type $\text{MX}_3 \cdot 2\text{L}$, for example⁹), and for this reason, their magnetic and spectral properties are of theoretical interest and should at first sight be amenable to a fairly simple interpretation. We have now carried

out such a study on a range of coordination compounds of niobium(IV) and tantalum(IV) of the types $\text{MX}_4 \cdot 2\text{L}$ and $\text{MX}_4 \cdot \text{B}$, where L = tetrahydrofuran, tetrahydropyran, 1,4-dioxane, or acetonitrile, and B = 2,2'-bipyridyl or 1,10-phenanthroline, the results of which are reported in the present paper. This is part of a general research program directed toward a study of coordination complexes of those transition metal halides in which the central metal atom has electronic configurations of the type d^0 or d^1 .

Experimental Section

All organic reagents and solvents were commercially available.

Preparation of Metal Halides.—Niobium(V) and tantalum(V) chlorides and bromides were prepared by standard literature methods.¹⁰ High-purity samples of niobium(V) and tantalum(V) chlorides were also obtained from Stauffer Chemicals. The purity of all of these halides was confirmed by metal and halogen analyses.

The metal tetrahalides were prepared by aluminum reduction of the corresponding pentahalides, according to the equation $3\text{MX}_5 + \text{Al} \rightarrow 3\text{MX}_4 + \text{AlX}_3$. Since our method varies somewhat from that previously employed,^{3,11} it will be briefly outlined. A weighed amount of the pentahalide was intimately mixed with sufficient aluminum powder¹² to convert 95% of the pentahalide to the tetrahalide. The sealed reaction tube was placed in a tube furnace maintained at 250° , such that the reaction mixture was at one end of the tube. Reduction begins almost immediately at this temperature and color changes can be seen after 30 min. After about 7 days, the "empty" end of the reaction tube was removed from the furnace, the furnace temperature was reduced to $220\text{--}200^\circ$, and the aluminum trihalide and unreacted pentahalide were allowed to sublime to the cooled end of the tube; this separation takes place over a period of about 3 days. The required tetrahalide was separated from the above halides by sealing the tube at a constriction placed between them. The

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(12) The aluminum (99.999%) was obtained from Koch-Light and was stated to contain 1 ppm of iron.

solid tetrahalide was ground to a fine powder in a drybox and then analyzed.

Anal. Calcd for NbCl_4 : Nb, 39.6; Cl, 60.4. Found: Nb, 39.9; Cl, 59.9. Calcd for NbBr_4 : Nb, 22.5; Br, 77.5. Found: Nb, 22.8; Br, 77.2. Calcd for TaCl_4 : Ta, 56.0; Cl, 44.0. Found: Ta, 56.0; Cl, 43.8. Calcd for TaBr_4 : Ta, 36.15; Br, 63.85. Found: Ta, 35.8; Br, 63.9.

Preparation of Complexes.—The metal halides and resulting complexes were very unstable to oxygen and moisture, so that all preparations and the subsequent handling of the desired complexes were carried out on a vacuum line or in a nitrogen-filled drybox. All reactions were carried out in sealed ampoules by treating the metal halide with an excess of the appropriate ligand. The ampoules were refluxed or shaken, etc., until the reaction was complete; they were then opened in a nitrogen atmosphere and the products were worked up on the vacuum line.

$\text{NbX}_4 \cdot 2\text{CH}_3\text{CN}$ ($\text{X} = \text{Cl}$ or Br).—The appropriate tetrahalide was refluxed with acetonitrile for 4 days during which time most of the halide dissolved to yield a brown solution. The reaction mixture was filtered and any insoluble residue was washed with acetonitrile until the washings were almost colorless. The filtrate was then evaporated to dryness to yield the desired complex which was pumped for several hours *in vacuo* to remove any uncoordinated solvent.

These two complexes had infrared spectra (cm^{-1}) characteristic of nitrogen-bonded acetonitrile molecules,¹³ e.g., $\text{NbCl}_4 \cdot 2\text{CH}_3\text{CN}$: 2315 m (combination band ($\nu_3 + \nu_4$)), 2290 s ($\nu(\text{C}\equiv\text{N})$), 1406 m, 1365 m (ν_2), 1150 w, b, 1025 ms, 949 s (ν_4), 819 sh, 800 w.

$\text{TaCl}_4 \cdot 2\text{CH}_3\text{CN}$.—A suspension of tantalum(IV) chloride in acetonitrile was shaken at room temperature. A green solution was initially formed, but after 1 day this had darkened to mustard brown, which became dark brown after a few days. After 2 weeks the solution was filtered, and the excess of solvent was evaporated to leave a dark brown oil which on pumping *in vacuo* yielded the dark brown complex.

$\text{TaBr}_4 \cdot 2\text{CH}_3\text{CN}$.—A similar procedure to that described above gave a deep red solution and a trace of green solid. The dark red-brown complex was isolated when the filtrate was evaporated to dryness.

Unlike their niobium(IV) analogs, the complexes " $\text{TaX}_4 \cdot 2\text{CH}_3\text{CN}$ " had complex infrared spectra (4000–400 cm^{-1}), quite unlike that of "normal" nitrogen-bonded¹³ acetonitrile. The spectra (2500–400 cm^{-1}) are as follows: $\text{TaCl}_4 \cdot 2\text{CH}_3\text{CN}$: 2315 m, 2292 s, ~ 1600 b, sh, 1360 m, ~ 1310 b, sh, 1258 w, 1211 w, ~ 1092 m, b, 1025 ms, 949 w, ~ 850 sh, vb, ~ 800 m, 760 ms, 657 w, 526 mw, 475 w. $\text{TaBr}_4 \cdot 2\text{CH}_3\text{CN}$: 2305 sh, 2288 ms, ~ 1640 mw, b, 1510 m, ~ 1360 m, 1309 mw, 1264 w, 1098 w, 1021 ms, 951 w, 865 sh, ~ 830 sh, ~ 800 m, 740 m, 672 w, ~ 530 w, ~ 455 m.

$\text{NbX}_4 \cdot 2\text{L}$ ($\text{X} = \text{Cl}$ or Br , $\text{L} = \text{C}_4\text{H}_8\text{O}$ or $\text{C}_6\text{H}_{10}\text{O}$).—The tetrahalides were shaken at room temperature with the neat liquid ligands. The desired insoluble complexes were filtered off, washed with solvent, and dried *in vacuo*. Recommended reaction times depended upon the particular complex: $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$, ~ 72 hr; $\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$, ~ 15 hr; $\text{NbX}_4 \cdot 2\text{C}_6\text{H}_{10}\text{O}$, ~ 48 hr. In the case of red-brown $\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$, prolonged reaction resulted in some loss of insoluble product and the formation of a syrupy dark red solution; the latter presumably results from oxygen abstraction and/or polymerization of the solvent.

$\text{NbX}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ ($\text{X} = \text{Cl}$ or Br).—A similar reaction to that described above was employed, but with much longer reaction times (up to 1 week).

The infrared spectra (4000–400 cm^{-1}) of these two complexes were very similar; e.g., $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ had the following absorption bands (1300–400 cm^{-1}): 1288 ms, 1251 s, 1129 s, 1041 m, 1015 s, 1008 sh, 893 ms, 864 s, 834 m, 802 s, 616 s, 487 m, 433 mw.

The Reaction of Tantalum(IV) Chloride and Bromide with Aliphatic Ether Molecules.—Reactions identical with those

described for their niobium(IV) analogs were attempted, but in all cases only dark oils were produced. Several reactions were repeated using benzene or isooctane as diluents, but oils were still formed and no solid products could be isolated.

$\text{MX}_4 \cdot \text{B}$ ($\text{M} = \text{Nb}$ or Ta , $\text{X} = \text{Cl}$ or Br , and $\text{B} = 2,2'$ -Bipyridyl or 1,10-Phenanthroline).—These complexes were prepared by essentially the same procedure, the reaction time being determined solely by the rate at which the tetrahalide lattice could be broken down. The reactions were allowed to proceed until all tetrahalide had been consumed, since the required complexes were only slightly soluble (at most) in the reaction solvent used. Chloroform- or benzene-acetonitrile (9:1 by volume) mixtures were employed as reaction solvents. This general method is illustrated by the preparation of $\text{NbBr}_4 \cdot \text{phen}$ described below.

Niobium(IV) bromide (2.49 g) and 1,10-phenanthroline (1.10 g) were allowed to react in 30 ml of chloroform-acetonitrile (9:1). The reaction mixture was shaken for 5 days and then heated under gentle reflux for a further 2 days. The khaki brown insoluble product was filtered off, washed several times with the redistilled solvent mixture, and dried *in vacuo*.

$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NbX}_6$ ($\text{X} = \text{Cl}$ or Br).—The appropriate acetonitrile complex $\text{NbX}_4 \cdot 2\text{CH}_3\text{CN}$ was treated with tetraethylammonium halide using chloroform-acetonitrile (9:1 by volume) as solvent. Sufficient tetraethylammonium halide was added to ensure that the $\text{NbX}_4 : [(\text{C}_2\text{H}_5)_4\text{N}]\text{X}$ mole ratio was 1:2.2. The reaction mixture was heated under gentle reflux for 2 weeks after which time the reaction mixture was filtered, and the insoluble hexahalo salt was washed several times with solvent to free it from any excess tetraethylammonium halide and finally dried *in vacuo* in the usual way.

$\text{MX}_4 \cdot 2\text{py}$ ($\text{M} = \text{Nb}$ or Ta and $\text{X} = \text{Cl}$ or Br).—The pyridine complexes $\text{NbBr}_4 \cdot 2\text{py}$, $\text{TaCl}_4 \cdot 2\text{py}$, and $\text{TaBr}_4 \cdot 2\text{py}$ were prepared from the tetrahalides by the method described previously by McCarley and coworkers.^{1,2}

Anal. Calcd for $\text{NbBr}_4 \cdot 2\text{py}$: Nb, 16.3; Br, 56.0. Found: Nb, 16.3; Br, 56.3. Calcd for $\text{TaCl}_4 \cdot 2\text{py}$: Ta, 37.6; Cl, 29.5. Found: Ta, 37.7; Cl, 29.6. Calcd for $\text{TaBr}_4 \cdot 2\text{py}$: Ta, 27.5; Br, 48.5. Found: Ta, 27.7; Br, 48.8.

For the preparation of $\text{NbCl}_4 \cdot 2\text{py}$, a modification of the procedure employed by McCarley, *et al.*,¹⁴ was used. Niobium(V) chloride was shaken with pyridine for 3 weeks and the reaction mixture was then evaporated to dryness. The solid mixture remaining was extracted with acetonitrile in a Soxhlet extractor to free the fawn-colored complex $\text{NbCl}_4 \cdot 2\text{py}$ of any reaction by-products (organic oxidation products and $\text{NbCl}_5 \cdot \text{py}$, etc.).¹⁴

Anal. Calcd for $\text{NbCl}_4 \cdot 2\text{py}$: C, 30.6; H, 2.6; N, 7.1; Cl, 36.1; Nb, 23.65. Found: C, 29.5; H, 2.8; N, 6.9; Cl, 36.4; Nb, 23.5.

Analytical Procedures.—For the metal analyses, a weighed amount of compound was hydrolyzed with a 0.880 M ammonia solution and then ignited to the oxide (Nb_2O_5 or Ta_2O_5). Halogen was determined by the usual silver halide gravimetric procedure or, in the case of some of the 2,2'-bipyridyl and 1,10-phenanthroline complexes, by the standard Volhard method.

Carbon, hydrogen, and nitrogen were determined in the micro-analytical laboratory in this department. In the case of $\text{TaCl}_4 \cdot 2\text{CH}_3\text{CN}$ and $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$, no C, H, and N analyses are reported since these complexes were found to decompose rapidly during their handling. Also, samples of $\text{NbBr}_4 \cdot \text{bipy}$ and $\text{TaCl}_4 \cdot \text{phen}$ failed to give reproducible C, H, and N analyses, but the reason for this is not clear although it may be due to the difficulty of completely decomposing these complexes. However, metal and halogen analyses, together with their spectroscopic and magnetic properties, leave little doubt that $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$, $\text{NbBr}_4 \cdot \text{bipy}$, and $\text{TaCl}_4 \cdot \text{phen}$ were of the usual stoichiometry and of acceptable purity.

Physical Measurements.—Visible and ultraviolet spectra were

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TABLE I
 ANALYTICAL DATA FOR COORDINATION COMPLEXES OF THE NIOBIUM(IV) AND TANTALUM(IV) HALIDES

Compound	Color	% C		% H		% N		% X		% M		μ_{eff} , BM	Temp, °K
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
NbCl ₄ ·2CH ₃ CN	Pale orange-brown	15.2	14.9	2.1	2.1	8.8	8.0	44.8	44.6	29.3	29.5	1.55	293
NbBr ₄ ·2CH ₃ CN	Dark brown	9.7	9.7	1.2	1.9	5.7	4.9	64.6	63.9	18.8	18.9	1.34	291
TaCl ₄ ·2CH ₃ CN	Dark brown	35.0	34.8	44.7	43.9	0.45	293
TaBr ₄ ·2CH ₃ CN	Dark red-brown	8.2	8.0	1.0	1.6	4.8	4.4	54.9	52.7	31.05	30.6	0.46	293
NbCl ₄ ·2C ₄ H ₈ O	Pale yellow-brown	37.4	36.5	24.5	24.7	1.53	292
NbBr ₄ ·2C ₄ H ₈ O	Red-brown	17.3	16.4	2.9	3.1	57.4	57.9	16.7	16.9	1.35	293
NbCl ₄ ·2C ₅ H ₁₀ O	Pale yellow	29.5	28.8	4.95	5.1	34.85	34.7	22.8	22.9	1.54	292
NbBr ₄ ·2C ₅ H ₁₀ O	Light brown	20.5	19.7	3.45	3.6	54.7	53.7	15.9	15.9	1.51	293
NbCl ₄ ·2C ₄ H ₈ O ₂	Pale yellow	23.4	23.4	3.9	4.2	34.5	34.9	22.6	22.9	1.61	294
NbBr ₄ ·2C ₄ H ₈ O ₂	Red-brown	16.3	15.2	2.7	3.0	54.3	54.2	15.8	16.1	1.55	294
NbCl ₄ ·bipy	Violet-purple	30.7	30.7	2.1	2.1	7.2	6.9	36.3	36.1	23.8	23.9	1.41	296
NbBr ₄ ·bipy	Dark green	56.2	56.9	16.3	16.6	1.34	294
TaCl ₄ ·bipy	Dark green	25.1	24.5	1.7	1.6	5.85	5.7	29.6	29.6	37.8	37.7	0.81	293
TaBr ₄ ·bipy	Dark green	18.3	18.1	1.2	1.4	4.3	4.2	48.7	48.8	27.55	27.5	0.89	297
NbCl ₄ ·phen	Purple	34.7	34.5	1.9	2.1	6.7	6.7	34.2	34.2	22.4	22.1	1.41	293
NbBr ₄ ·phen	Khaki brown	24.3	24.2	1.4	1.5	4.7	4.6	53.9	53.7	15.7	15.4	1.38	293
TaCl ₄ ·phen	Dark blue	28.8	29.3	36.0	35.8	0.95	295
TaBr ₄ ·phen	Dark blue-green	21.2	20.4	1.2	2.3	4.1	4.1	46.95	47.1	26.6	26.6	0.91	297
[(C ₂ H ₅) ₄ N] ₂ NbCl ₆	Pale brown	33.9	34.5	7.1	6.6	4.95	5.1	37.6	37.6	16.4	16.5	1.16	293
[(C ₂ H ₅) ₄ N] ₂ NbBr ₆	Yellow	23.1	22.4	4.8	4.9	3.4	3.3	57.6	57.5	11.15	11.3	1.20	296

measured on Unicam SP 700 and 800 spectrophotometers, and infrared spectra, on Perkin-Elmer 337 and Grubb-Parsons DM 4 (4000–400 and 400–200 cm⁻¹, respectively) spectrophotometers. Mulls and reflectance samples were prepared in a nitrogen-filled drybox equipped with a gas-recirculating system. Solution samples were prepared on a vacuum line.

Magnetic susceptibility measurements were made on a Newport Instruments variable-temperature Gouy balance system, based upon the original design of Figgis and Nyholm;¹⁵ HgCo(CNS)₄ was used as calibrant. Diamagnetic corrections were estimated from Pascal's constants, and the magnetic moments were calculated using the expression $\mu_{eff} = 2.84(\chi_m T)^{1/2}$.

Results and Discussion

The complexes prepared in the present work, together with their analytical data and room-temperature magnetic moments, are shown in Table I. Where appropriate, the infrared spectra (4000–400 cm⁻¹) of these complexes are listed in the Experimental Section. The acetonitrile and other complexes were extremely sensitive to air and moisture and had to be handled with the utmost caution. The 2,2'-bipyridyl and 1,10-phenanthroline derivatives were more stable but still liable to hydrolysis and oxidation unless anhydrous oxygen-free conditions were maintained.

Niobium(IV) and tantalum(IV) chloride and bromide react with chloroform or benzene solutions of 2,2'-bipyridyl and 1,10-phenanthroline with the formation of the highly colored, solvent-insoluble complexes of empirical formula MX₄·B. The addition of acetonitrile to the appropriate reaction mixture was found to favor the formation of a homogeneous product, free of any unreacted tetrahalide. The reason for this is almost certainly that the halides dissolve in the added acetonitrile with the resulting formation of the reaction intermediates MX₄·2CH₃CN. Confirmation of this is afforded by the observation that such acetonitrile

complexes can be isolated by direct reaction of this reagent with the tetrahalides. While this work was in progress, it was brought to our attention that McCarley was carrying out a detailed investigation of these particular complexes,^{16,17} and we have therefore not studied them in any great detail. We note, however, that, while NbX₄·2CH₃CN complexes have infrared spectra (4000–400 cm⁻¹) characteristic of normal nitrogen-bonded acetonitrile molecules,¹⁸ the products which analyze closely for TaX₄·2CH₃CN have much more complex spectra (see Experimental Section). This seems to bear out the observation of Kilty and McCarley¹⁶ that the tantalum(IV)-acetonitrile systems are not straightforward and that a mixture of products results.

The reaction of NbX₄·2CH₃CN with the appropriate tetraethylammonium halide in mixed chloroform-acetonitrile as solvent yielded the hexahaloniobates(IV) [(C₂H₅)₄N]₂NbX₆. Their preparation and characterization is important since they are considered as model compounds in our subsequent discussions of the magnetic and spectral properties of the niobium(IV) and tantalum(IV) coordination complexes.

The ether molecules tetrahydrofuran, tetrahydropyran, and 1,4-dioxane reacted with the niobium(IV) halides to give the usual type of complex NbX₄·2L. In marked contrast, the tantalum(IV) halides gave dark oils from which no solid complexes could be isolated. The infrared spectra of the tetrahydrofuran and tetrahydropyran complexes closely resemble those of their vanadium(IV) analogs VCl₄·2C₄H₈O and

(16) P. A. Kilty and R. E. McCarley, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. O120.

(17) T. A. Dougherty and R. E. McCarley, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. O121.

(18) R. A. Walton, *Quart. Rev. (London)*, **19**, 126 (1965), and references therein.

(15) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

$\text{VCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}^{19}$ and are characteristic of these coordinated ether molecules.

In contrast with the usual tendency of transition metal tetrahalides to form 1:1 adducts with 1,4-dioxane, in which the ligand molecules are bridging, the stoichiometry of the niobium(IV)-1,4-dioxane complexes prepared in the present study implies that the complex either is eight-coordinate with bridging 1,4-dioxane molecules or, alternatively, is six-coordinate and contains *monodentate* ligand molecules. It has been shown^{20,21} that a differentiation of the mode of 1,4-dioxane bonding on the basis of infrared spectral measurements is rarely unambiguous, since even when the complex is known to contain bridging 1,4-dioxane molecules (*e.g.*, $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$),²² the ligand bands are often little changed from those of the free ligand. However, it is our experience that for 1,4-dioxane complexes of the early transition series halides, *e.g.*, $\text{TiCl}_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ ²³ and $\text{VCl}_4 \cdot \text{C}_4\text{H}_8\text{O}_2$,¹⁹ the ligand spectrum is drastically altered by complex formation, a probable consequence of the formation of strong metal-oxygen bonds, whereas in complexes derived from the nickel(II) and cobalt(II) halides the spectral changes are often small. In the present instance, the infrared spectra of $\text{NbX}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ were not significantly more complex than for other 1,4-dioxane complexes (except in the 900–800- cm^{-1} region), but a new absorption band, absent in the free ligand and in other dioxane complexes,²¹ was observed at $\sim 485 \text{ cm}^{-1}$. The latter observation may indicate the presence of 1,4-dioxane molecules of lower symmetry (*i.e.*, *monodentate*) than the corresponding "free" or bridging molecules. In an attempt to confirm this we recorded the Raman spectrum of $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ using He-Ne laser excitation,²⁴ but, other than an intense line at 334 cm^{-1} , assigned to $\nu(\text{Nb}-\text{Cl})$ (see the following section), no ligand bands were located, so we were unable to confirm whether this molecule contained noncentrosymmetric (*i.e.*, *monodentate*) ligand molecules. However, the presence of an intense infrared absorption band at 1129 cm^{-1} , at almost the same frequency as the antisymmetric C-O-C stretching vibration of free 1,4-dioxane, leads us to conclude that "free" ether groups are present and that $\text{NbX}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ is six-coordinate and contains *monodentate* ligand molecules. Such a conclusion is supported by far-infrared spectral measurements to be discussed next.

Stereochemistry of the Complexes.—Far-infrared spectral measurements in the 500–200- cm^{-1} region

were used as a guide to the stereochemistry, *i.e.*, *cis*- or *trans*-octahedral, of the complexes prepared in the present work. These data are listed in Table II, together with our conclusions as to their stereochemistries. The distinction between *cis* and *trans* isomers is based upon the following symmetry arguments. A species of the type *trans*- $\text{MX}_4 \cdot 2\text{L}$ should have one infrared-active M-X stretching mode (e_u symmetry), whereas the related *cis* isomer is expected to have four such modes (symmetry $2a_1 + b_1 + b_2$).²⁶ In the latter instance the four absorption bands associated with these four modes may not always be observed because either accidental band degeneracies or the inherent weakness of some of these bands give rise to a simpler spectrum. In the present instance the complexity of the chloride spectra (with the exception of the pyridine complexes) is good evidence for the *cis* stereochemistry. For the bromide complexes, the absorption bands assigned to $\nu(\text{Nb}-\text{Br})$ were located near the limit of our measurements (200 cm^{-1}) so that these assignments are less certain. However, there can be little doubt that the bromide complexes of 2,2'-bipyridyl and 1,10-phenanthroline are *cis*, and our assignments for $\text{NbBr}_4 \cdot 2\text{CH}_3\text{CN}$ are in keeping with the results of a recent single-crystal X-ray study of this complex.¹⁶

It is important to note that $\nu(\text{Nb}-\text{Cl})$ modes of $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ occur at frequencies characteristic of a six-coordinate niobium(IV) species,^{27,28} which is further evidence of the *monodentate* 1,4-dioxane molecules. Also, as mentioned in the previous section, the Raman spectrum of this solid complex had $\nu(\text{Nb}-\text{Cl})$ at 334 cm^{-1} , the same frequency as the most intense $\nu(\text{Nb}-\text{Cl})$ mode in the infrared spectrum. This infrared-Raman coincidence is evidence for a *cis*-octahedral structure, and rules out the *trans* isomer for which the mutual-exclusion principle should hold.

We have also recorded the far-infrared spectra of the previously reported pyridine complexes^{1,2} but consider our spectral assignments in Table II tentative. The spectra in those regions in which $\nu(\text{Nb}-\text{X})$ vibrations occur are generally less complex than the 2,2'-bipyridyl and 1,10-phenanthroline *cis* complexes, but more complex than might be anticipated for the *trans* isomers.

The infrared-active niobium-halogen stretching vibrations (ν_3) of the NbX_6^{2-} anions are at ~ 305 (s, vb) and 222 (s) cm^{-1} for X = Cl and Br, respectively. These vibrations are at lower frequencies than the related modes of the NbX_6^- anions,^{29–31} in agreement with the usual observation that $\nu(\text{M}-\text{X})$ frequencies of related species decrease as the oxidation state of the central metal atom decreases.

(19) B. E. Bridgland, G. W. A. Fowles, and R. A. Walton, *J. Inorg. Nucl. Chem.*, **27**, 383 (1965).

(20) R. A. Walton, *Inorg. Chem.*, **5**, 643 (1966).

(21) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Chem. Soc., A*, 1842 (1968).

(22) O. Hassel and J. Hvovlef, *Acta Chem. Scand.*, **8**, 1953 (1954).

(23) G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Chem. Soc.*, 5873 (1963).

(24) The pale yellow color of this complex made such a measurement seem feasible.²⁵ This measurement was carried out using a Cary 81 Raman spectrophotometer on a sample of the complex sealed under nitrogen in a Pyrex tube.

(25) I. R. Beattie, *Chem. Brit.*, **3**, 347 (1967).

(26) I. R. Beattie, M. Webster, and G. W. Chantry, *J. Chem. Soc.*, 6172 (1964).

(27) If $\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ was eight-coordinate, $\nu(\text{Nb}-\text{Cl})$ would be expected at significantly lower frequencies since the frequency of metal-halogen stretching modes appears to decrease with increase in coordination number.²⁸

(28) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(29) For $[(\text{C}_2\text{H}_5)_4\text{N}]\text{NbCl}_6$ and $[(\text{C}_2\text{H}_5)_4\text{N}]\text{NbBr}_6$, ν_3 is located at 333 and ~ 235 (doublet) cm^{-1} , respectively.^{30,31}

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

(31) D. Brown and P. J. Jones, *ibid.*, **A**, 247 (1967).

TABLE II
FAR-INFRARED SPECTRA (450-200 cm^{-1}) AND STEREOCHEMISTRY OF COMPLEXES

Complex	$\nu(\text{Nb-X})$	Ligand bands	Unassigned	Stereochemistry
$\text{NbCl}_4 \cdot \text{bipy}$	338 s, 330 sh, 288 m, 247 vw?	415 mw, 355 sh		<i>cis</i>
$\text{NbBr}_4 \cdot \text{bipy}$	~ 260 sh, 240 sh, ~ 215 s	420 m, 364 m	~ 310 sh	<i>cis</i>
$\text{TaCl}_4 \cdot \text{bipy}$	~ 335 sh, 316 s, 298 ms, 248 w, b?	422 vw, 372 sh, 357 sh	455 vw	<i>cis</i>
$\text{TaBr}_4 \cdot \text{bipy}$	265 sh, 248 sh, 220 s, b	419 m, 364 s	325 ms	<i>cis</i>
$\text{NbCl}_4 \cdot \text{phen}$	~ 360 sh, 348 s, 330 s, 310 s, 260 m	425 m, 275 mw, 237 w		<i>cis</i>
$\text{NbBr}_4 \cdot \text{phen}$	263 sh, 247 sh, ~ 230 s, b	430 mw, 279 m	314 m, 302 w	<i>cis</i>
$\text{TaCl}_4 \cdot \text{phen}$	~ 325 s, ^a 288 m	427 w, 275 sh	~ 380 sh, 255 w, sh	<i>cis</i>
$\text{TaBr}_4 \cdot \text{phen}$	265 m, 255 m, ~ 225 sh, 214 s	429 mw, 285 sh	390 mw, 325 m	<i>cis</i>
$\text{NbCl}_4 \cdot 2\text{py}$	361 sh, ~ 340 sh?, 330 s	429 mw	238 m	Uncertain
$\text{NbBr}_4 \cdot 2\text{py}$	280 w, sh?, 260 sh, 245 s, 230 sh?	429 w	325 w	<i>cis</i> ?
$\text{TaCl}_4 \cdot 2\text{py}$	318 sh?, 310 s	Possibly <i>trans</i>
$\text{TaBr}_4 \cdot 2\text{py}$	~ 215 sh, 208 s	432 w	...	Uncertain
$\text{NbCl}_4 \cdot 2\text{CH}_3\text{CN}$	370 sh, 356 s, 335 s	413 sh, 400 sh	247 w	<i>cis</i>
$\text{NbBr}_4 \cdot 2\text{CH}_3\text{CN}$	280 s, 253 s, 238 sh	414 mw, 400 mw	350 m	<i>cis</i>
$\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$	333 vs, b, ^a 270 m, 235 mw	<i>cis</i>
$\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$	290 sh, 270 s, ~ 245 sh	...	330 w	<i>cis</i>
$\text{NbCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$	347 s, 332 s, 278 m, 247 m	417 m, 295 mw	...	<i>cis</i>
$\text{NbBr}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$	248 sh, 234 vs	415 mw, 304 m, 293 ms	...	Probably <i>cis</i>
$\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	347 sh, 334 s, 288 ms, 248 m	430 w, 304 ms	...	<i>cis</i>
$\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	~ 240 s, vb ^b	438 w, 312 s	...	Probably <i>cis</i>

^a Probably a doublet. ^b At least a triplet.

TABLE III
MAGNETIC PROPERTIES (μ_{eff}) OF NIOBIUM(IV) COMPLEXES

	Temp, °K											
	313	293	273	253	233	213	193	173	153	133	113	93
$\text{NbCl}_4 \cdot \text{bipy}$	1.42	1.41	1.41	1.40	1.39	1.38	1.37	1.36	1.35	1.34	1.33	1.31
$\text{NbBr}_4 \cdot \text{bipy}$	1.36	1.34	1.32	1.30	1.28	1.26	1.23	1.21	1.19	1.16	1.13	1.10
$\text{NbCl}_4 \cdot \text{phen}$	1.39	1.41	1.40	1.40	1.40	1.40	1.39	1.38	1.38	1.37	1.34	1.34
$\text{NbBr}_4 \cdot \text{phen}$	1.39	1.38	1.37	1.37	1.37	1.37	1.37	1.37	1.36	1.36	1.35	1.36
$\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$	1.55	1.54	1.53	1.54	1.53	1.51	1.51	1.50	1.49	1.47	1.47	1.45
$\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}$	1.37	1.39	1.37	1.36	1.35	1.35	1.35	1.34	1.34	1.33	1.33	1.30
$\text{NbCl}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$	1.54	1.54	1.55	1.56	1.56	1.55	1.55	1.53	1.53	1.53	1.52	1.51
$\text{NbBr}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O}$	1.52	1.51	1.50	1.49	1.49	1.48	1.47	1.46	1.45	1.43	1.42	1.41
$\text{NbCl}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	1.61	1.61	1.62	1.61	1.60	1.60	1.60	1.59	1.58	1.57	1.56	1.54
$\text{NbBr}_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	1.56	1.55	1.55	1.55	1.54	1.54	1.53	1.52	1.51	1.50	1.48	1.46
$[(\text{C}_2\text{H}_5)_3\text{N}]_2\text{NbCl}_6$	1.19	1.16	1.16	1.09	1.05	1.02	0.99	0.97	0.94	0.89	0.86	0.83
$[(\text{C}_2\text{H}_5)_3\text{N}]_2\text{NbBr}_6$	1.23	...	1.16	1.22	1.15	1.08	1.19	1.18	1.19	1.18	1.17	1.20

Magnetic Properties.—Previous literature values for the room-temperature magnetic moments of complexes of the niobium(IV) halides are quoted in the range 1.6–1.0 BM, with much lower values (usually less than 1 BM) for the tantalum(IV) analogs.^{1,2,4} The magnetic moments of the complexes prepared in the present work are listed in Table I and can be seen to fit in well with these previous trends. The values we report for the complexes $\text{MCl}_4 \cdot \text{B}$ ($\text{B} = 2,2'$ -bipyridyl and 1,10-phenanthroline), as prepared from the tetrachlorides, are at variance with earlier measurements.⁴ In particular, μ_{eff} for $\text{NbCl}_4 \cdot \text{B}$ (1.41 BM) are significantly higher (by ~ 0.4 BM) than the values reported for the same complexes prepared from the pentachloride.⁴ The lower moments of the latter products may be a reflection on the difficulty sometimes

encountered in isolating pure products from reduction reactions. The temperature range magnetic properties of the niobium(IV) complexes are shown in Table III.

McCarley, *et al.*,^{1,2} found that the magnitude of the magnetic moments of $\text{MX}_4 \cdot 2\text{py}$ ($\text{M} = \text{Nb}$ or Ta and $\text{X} = \text{Cl}$, Br , or I) decrease in the order $\text{Cl} > \text{Br} > \text{I}$ and concluded that this order was directly related to the distortion of the complexes from regular octahedral symmetry; the greater the distortion, the more the magnetic moments approach the spin-only value. This order required an apparent reversal of the accepted ligand field strengths $\text{Cl} > \text{Br} > \text{I}$. However, to us this seems to be an oversimplification since Figgis^{3,2} has shown that the effective magnetic moment arising

from the ${}^2T_{2g}$ ground term of a transition metal complex ion in a cubic ligand field is dependent not only upon Δ , the separation between the orbital levels of the ${}^2T_{2g}$ term created by an axial ligand field, but also upon λ , the spin-orbit coupling constant, and k , the so-called orbital reduction factor, which has in the past sometimes been equated with the metal ion t_{2g} orbital delocalization.³³ There seems no reason why Δ should be the only variable for a series of complexes of the type $MX_4 \cdot 2L$, where only X changes, and a consideration of all of these parameters would seem more appropriate. From the calculated data of Figgis,³² we have attempted to fit the temperature range magnetic properties of our niobium(IV) complexes using graphical procedures. It is convenient to use the parameter $\nu = \Delta/\lambda$ ³² in these procedures, and it should also be noted that the splitting Δ , due to the axial field component, is defined as positive when the orbital *singlet* lies lowest. Only in the case of $NbX_4 \cdot bipy$ were unique fits apparently obtained: X = Cl, $k = 0.8$, $\nu = +2.3$, $\lambda = 650 \text{ cm}^{-1}$; X = Br, $k = 0.7$, $\nu = +1$, $\lambda = 430 \text{ cm}^{-1}$.

The difficulty of determining unique fits for the other complexes is almost certainly due to the small variation of μ_{eff} with temperature (Table III). This is in line with observations for related systems,³⁴ in which a similar lack of variation was noted. Since we only obtained fits for $NbX_4 \cdot bipy$, any discussion on the magnitude of the parameters k , ν , and λ would seem inappropriate, although it is clear that only when Δ is *positive, i.e.*, when the orbital singlet lies lowest, does agreement with theory appear satisfactory. What is significant is that the magnetic moments of $[(C_2H_5)_4N]_2NbX_6$ are smaller than those for $NbX_4 \cdot 2L$, an apparent reflection of the more regular octahedral structure of the former—as the distortion parameter Δ increases, so μ_{eff} should *tend toward* the spin-only value.³² For $NbX_4 \cdot 2L$ it does not seem justified to infer^{1,2} that μ_{eff} depends only upon Δ , the ground-state distortion, and that the latter is necessarily determined by the difference between X and L in the spectrochemical series.

Electronic Absorption Spectra.—To aid the spectral assignments of the complexes $NbX_4 \cdot 2L$ and $NbX_4 \cdot B$ we first measured the electronic absorption spectra of the hexahalo salts $[(C_2H_5)_4N]_2NbX_6$. These solid-state and solution spectra are shown in Table IV, together with the band assignments. Solid-state spectra are illustrated in Figure 1. The absorption bands in the 15–25-kK region are assigned to $d \leftrightarrow d$ transitions, the appearance of two absorption bands implying a considerable distortion of the excited 2E_g term, even though the hexahalo anions are formally of O_h symmetry. Bearing in mind that the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of the VCl_6^{2-} anion^{35,36} is located at 15 kK, the $d \leftrightarrow d$

TABLE IV
ELECTRONIC ABSORPTION SPECTRA AND ASSIGNMENTS OF THE
HEXAHALONIOBATE(IV) ANIONS NbX_6^{2-}

Medium	Absorption max, kK ^a	
	$d \leftrightarrow d$	$X(\pi) \rightarrow Nb$
$[(C_2H_5)_4N]_2NbCl_6$		
DR ^b	~16.4 sh, 23.8 sh, b	31.4 sh, 35.4, 38.0 sh, 44.8
CH ₃ CN	24.4 sh (<100)	28.6 sh (<420), 31.85 sh (<2400), 34.8 (9600), 40.2 (9000)
CH ₃ CN + added $[(C_2H_5)_4N]Cl$	~19.4 sh?, ~24.5 sh	~28.0 sh, 31.6 sh, 34.8, 40.5
$[(C_2H_5)_4N]_2NbBr_6$		
DR	~15.8 sh?, ~18.5 sh	22.8 sh, 26.4, 29.5, 32.2, 35.4, 37.4 sh, 45.0
CH ₃ CN	~15.0 sh, b?, ~19.0 sh?	27.0 (7800), 29.3 (11,500), 31.35 (12,800), 33.0 sh?, ~40.0 sh?
CH ₃ CN + added $[(C_2H_5)_4N]Br$	15.9 (95), ~21.5 sh?	24.0 (<590), 26.7 (3500), 29.0 (10,500), 33.1 (3100), 36.4 sh (~3000), 38.2 (3200)

^a Molar extinction coefficients in parentheses. ^b DR = diffuse reflectance.

transitions of NbX_6^{2-} occur at frequencies consistent with the expected increase in $10Dq$ for a metal halide of the second transition series. For both NbX_6^{2-} anions, these transitions were usually located as shoulders on the low-energy side of the more intense halogen(π) \rightarrow Nb(d) transitions (see later). For this reason and because we did not observe a single absorption band assignable to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition, we have not attempted to estimate a value of $10Dq$ for these anions.

It is now apparent that for a hexahalo anion of the type MX_6^{n-} , the order of increasing energy of the halogen π orbitals is usually $t_{1g} > t_{1u}(\pi + \sigma) > t_{2u} > t_{2g}$.^{37,38} Assuming such an order, we have recently measured and assigned the room-temperature electronic absorption spectra of transition metal hexahalo anions of groups IV–VI, in which the central metal atoms contain d^0 or d^1 electronic configurations.^{39,40} From these measurements and the previously noted trends⁴¹ in the frequencies of absorption bands of MX_6^{n-} species, within a particular transition series, we would expect that the $NbCl_6^{2-}$ anion should show its $Cl(\pi) \rightarrow Nb(d)$ transitions at frequencies characteristic of its position within the $4d^n$ series: $ZrCl_6^{2-}$, $NbCl_6^{2-}$, $MoCl_6^{2-}$, $TcCl_6^{2-}$, etc. Thus the $ZrCl_6^{2-}$ and $MoCl_6^{2-}$ anions have their first *Laporte-allowed* halogen(π) \rightarrow metal(d) transition (*i.e.*, $t_{1u}(\pi + \sigma) \rightarrow M(t_{2g})$) at 41.7 and 27.8 kK, respectively.^{39,41} For $NbCl_6^{2-}$, a

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(40) R. A. Walton, P. C. Crouch, and B. J. Brisdon, *ibid.*, **24A**, 601 (1968).

(41) See, for example, C. K. Jørgensen, "Halogen Chemistry," Vol. 1, Academic Press, New York, N. Y., 1967, p 265.

(33) For a full discussion of the significance of k , see M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, in press.

(34) See, for example, J. Lewis, F. E. Mabbs, and R. A. Walton, *J. Chem. Soc.*, A, 1366 (1967).

(35) G. W. A. Fowles and R. A. Walton, *J. Inorg. Nucl. Chem.*, **27**, 735 (1965).

(36) P. A. Kilty and D. Nicholls, *J. Chem. Soc.*, 4915 (1965).

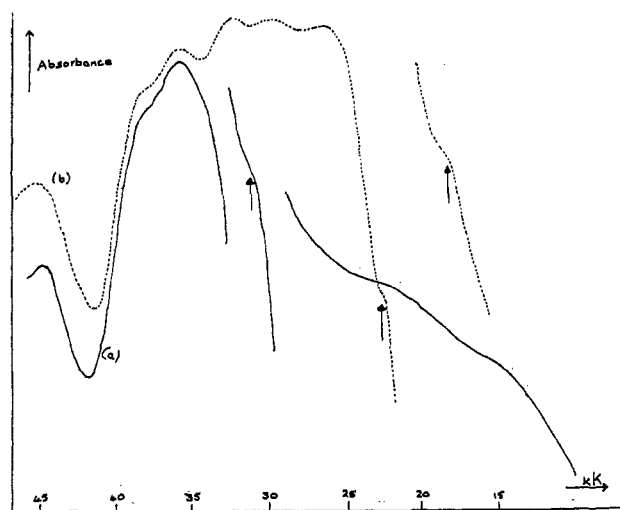


Figure 1.—Diffuse-reflectance spectra of $[(C_2H_5)_4N]_2NbX_6$: (a) $X = Cl$; (b) $X = Br$. (Weak shoulders are marked by an arrow.)

band frequency somewhere intermediate between these is anticipated. We accordingly propose the following assignments, utilizing the solution data in acetonitrile (band maxima in kK): ~ 28.0 , $t_{1g}(\pi) \rightarrow Nb(t_{2g})$; 31.65 , $t_{1u}(\pi + \sigma) \rightarrow Nb(t_{2g})$; 34.8 , $t_{2u}(\pi) \rightarrow Nb(t_{2g})$. From the assignment of the first Laporte-allowed transition (31.65 kK), we calculate^{38,41} an optical electronegativity (χ_{opt}) for Nb(IV) of 1.85. This value fits in well with the trend for Zr(IV) (1.60),³⁹ Nb(IV) (1.85), Mo(IV) (2.0),⁴² and Tc(IV) (2.25),⁴² it is less than the value for isoelectronic Mo(V)⁴⁰ but comparable to that for Nb(V).⁴²

The similarity between the solid and solution spectra of $[(C_2H_5)_4N]_2NbCl_6$ is good evidence that in solution the spectrum is that of the authentic $NbCl_6^{2-}$ anion.^{43,44} Addition of a large excess of tetraethylammonium chloride to such a solution did not affect the band positions, indicating the absence of significant solvolysis. On the other hand, solution data for $NbBr_6^{2-}$ indicate that this anion dissolves initially in acetonitrile with reaction, since the spectrum is altered, and closely approaches that of the solid-state species, on the addition of tetraethylammonium bromide.

The increase in the complexity of the spectrum of the $NbBr_6^{2-}$ anion, relative to $NbCl_6^{2-}$, is due in large part to the spin-orbit coupling effects of the halogen.^{38,41} In addition, the bathochromic shift of ~ 5 kK occurs on passing from $NbCl_6^{2-}$ to $NbBr_6^{2-}$, as ex-

(42) See ref 41, p 306.

(43) Horner and Tyree⁴⁴ reported the electronic absorption spectra of the $NbCl_6^{2-}$ and $NbBr_6^{2-}$ anions but did not specify the cations present or the medium in which these measurements were carried out. However, the agreement between their data for $NbCl_6^{2-}$ and ours is quite good; the bands they observed at 30.5 (sh), 34.8, 40.0, and 43.5 kK are clearly seen by us in the spectrum of solid $[(C_2H_5)_4N]_2NbCl_6$ at 31.4 (sh), 35.4, 38.0 (sh), and 44.8 kK. However, their spectrum of the $NbBr_6^{2-}$ anion is far less complex than we observed or than is anticipated^{38,41} for a hexabromo anion.

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

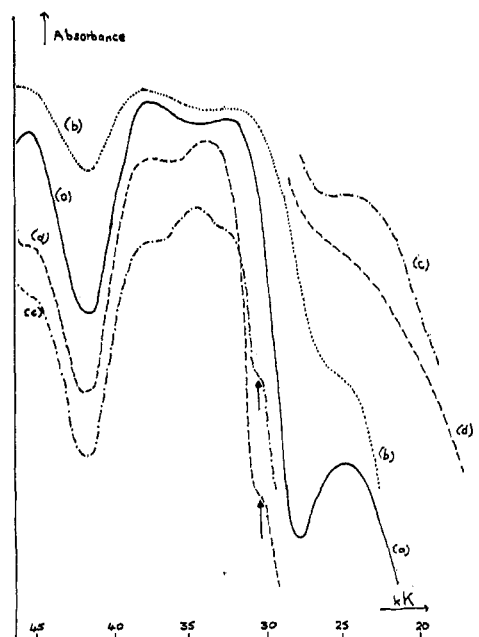


Figure 2.—Diffuse-reflectance spectra of $NbCl_4 \cdot 2L$: (a) $L = CH_3CN$; (b) $L = C_4H_8O$; (c) $L = C_4H_8O_2$; (d) $L = C_6H_{10}O$.

pected from the optical electronegativity difference between Cl and Br.⁴¹

A consideration of the complexes $NbX_4 \cdot 2L$, where L is CH_3CN or an ether molecule, would lead us to expect similarities with the spectra of NbX_6^{2-} , although the $d \leftrightarrow d$ transitions of the former should be particularly sensitive to both changes in ligand symmetry and the differences between X and L in the spectrochemical series. Using the spectral assignments for NbX_6^{2-} as a model, we have carried out a similar analysis of the spectra of $NbX_4 \cdot 2L$, in terms of $d \leftrightarrow d$ and $X(\pi) \leftrightarrow Nb(d)$ transitions (Table V). Once again, the former are invariably located as shoulders on the low-energy side of the rising absorption leading to the $X(\pi) \rightarrow Nb(d)$ transitions, and, other than noting that more than one $d \leftrightarrow d$ transition is usually observed, we will not comment further on these transitions.

For a particular halogen, the complexes show strikingly similar spectra in the regions in which the $X(\pi) \rightarrow Nb(d)$ transitions are located (see Figure 2). These spectra are also closely related to those of the parent NbX_6^{2-} anions themselves and would seem to confirm our earlier observations, based upon a comparative study of the electronic spectra of TiX_6^{2-} and $TiX_4 \cdot 2L$,³⁹ that the electron-transfer spectra of related species of the types MX_6^{2-} and $MX_4 \cdot 2L$ are very similar and due entirely to $X(\pi) \rightarrow M(d)$ transitions, thus ruling out transitions involving the ligand molecules, L , e.g., $L \rightarrow M(d)$.

The spectra of the complexes $NbX_4 \cdot 2py$ and $NbX_4 \cdot B$, where $B = 2,2'$ -bipyridyl or 1,10-phenanthroline, now present a further complication in that we have the added possibility of transitions arising from the metal atom nonbonding t_{2g} set to an antibonding molecular

TABLE V
 ELECTRONIC ABSORPTION SPECTRA AND ASSIGNMENTS OF COMPLEXES OF THE NIOBIUM(IV) HALIDES

Complex	Medium	Absorption max, kK ^a	
		d ↔ d	X(π) → Nb or Ta
NbCl ₄ ·2CH ₃ CN	DR ^b	24.4	32.3, 37.2, 45.4
	CH ₃ CN	15.4 (10), 26.3 (150)	~32.8 sh, 38.0 (13,400), 43.1 (15,500)
NbBr ₄ ·2CH ₃ CN	DR	16.6 sh, 20.2 sh	24.5, 29.9, 36.7, 44.9
	CH ₃ CN	16.0 sh	26.3 sh, 30.8 (8400), 35.6 (7800), 38.2 (6800)
NbCl ₄ ·2C ₄ H ₈ O	DR	~25.5 sh	31.6, ~35.0 sh, 37.4, 45.6
NbBr ₄ ·2C ₄ H ₈ O	DR	19.4 sh, 22.0	24.6, 26.8, 30.2 sh, br, 36.8, ~45.0
NbCl ₄ ·2C ₅ H ₁₀ O	DR	~25.8 sh, vb	30.0 sh, 33.4, ~37.1 sh, 45.2
NbBr ₄ ·2C ₅ H ₁₀ O	DR	19.6 sh, 22.0 sh	24.7 sh, 26.4, 29.6, 32.5, 36.0, 45.1
NbCl ₄ ·2C ₄ H ₈ O ₂	DR	14.7?, 23.5	29.6 sh, 32.0 sh, 34.0, 36.5 sh, ~45.0?
NbBr ₄ ·2C ₄ H ₈ O ₂	DR	18.8 sh, 22.0 sh	24.4, 26.0, 30.2, 32.7, 36.0, 45.4
NbCl ₄ ·bipy ^c	DR	17.0, 25.0 sh	29.0, ~31.0 sh, 37.0, 45.0
NbBr ₄ ·bipy ^c	DR	17.0 sh, 19.0	16.3, 30.6, 35.6, 45.0
NbCl ₄ ·phen ^c	DR	~19.0 b, ^d 23.2	28.2, 31.2, 36.6, 45.4
NbBr ₄ ·phen ^c	DR	18.8 sh, ^d 21.5	25.5, ~29.0 b, 37.0, 45.5
NbCl ₄ ·2py ^c	DR	18.2, 24.3	33.4 sh, 35.6, 45.0
NbBr ₄ ·2py ^c	DR	15.6	25.4, 27.0, 31.0, 33.1, 33.1, ~35.0 b, 45.0

^a Molar extinction coefficients in parentheses. ^b DR = diffuse reflectance. ^c Assignments for these complexes are tentative because of the possibility that some of the absorption bands may be due to transitions of the type Nb(*t*_{2g}) → ligand(π*). ^d Further absorptions were observed at 16.3 sh? (NbCl₄·phen) and 15.5 and 13.6 sh (NbBr₄·phen) kK.

orbital composed mostly of antibonding ligand π orbitals.⁴⁵ Such transitions are well known⁴⁶ in related systems. As a result of this further possibility, the d ↔ d transitions of these complexes are likely to be partially masked. McCarley and Torp¹ reported that the spectra of pyridine solutions of NbX₄·2py (X = Cl or Br) were characterized by absorption bands in the 24–20-kK region, whose ε_{max} values (~1000) indicated that they were not the expected d ↔ d transitions. In the present work, in which we carried out diffuse-reflectance spectral measurements on these and the related 2,2'-bipyridyl and 1,10-phenanthroline complexes (see Table V), we found prominent absorption bands in this same region and so have not attempted more detailed assignments. However, we do note that the halogen(π) → Nb(d) transitions occur at similar frequencies to the other complexes listed in Table V and also that the dissolution of the complexes NbX₄·B in acetonitrile, in which they are slightly soluble,⁴ occurs with reaction since the solution spectra in this solvent are significantly different from the diffuse-reflectance spectra recorded in Table V.⁴⁷

(45) We rule out the alternative possibility, namely, ligand(π) → M(*t*_{2g}), since the analogous d⁰ species TiX₄·bipy³⁹ do not reveal absorption bands in the 45–10-kK region which can be assigned to such a transition.

(46) See, for example, C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p 191.

(47) We have also recorded the diffuse-reflectance spectra of the tantalum(IV) complexes TaX₄·2py and TaX₄·B, but these are not discussed in the present paper. However, a description of the spectra can be obtained on request from R. A. W.

Finally, we wish to mention a rather unusual feature of the electronic spectra of most of the complexes which we have so far not discussed. All of the complexes show an as yet unexplained absorption band at ~10 kK, which has a low extinction coefficient—ε_{max} ~10 where estimates are possible—and is particularly prominent in the diffuse-reflectance spectra. Within the series of complexes NbX₆²⁻, NbX₄·2CH₃CN, and NbX₄·2(ether), this band is virtually invariant in frequency (10.0 ± 0.6 kK), but for the tertiary amine complexes it may occur as low as ~8 kK. We have as yet no explanation for this spectral feature. What is fairly definite is that it does not seem to owe its origin to a d ↔ d transition of the type ²T_{2g} → ²E_g or a corresponding transition in a low-symmetry ligand field, since this would imply a very low and unacceptable value for 10Dq. Also, we can rule out its origin in the decomposition of the complexes during handling procedures since the complexes were recovered unchanged after the measurements. A possible explanation, which incidentally would not seem to be borne out by the magnetic properties of the complexes,⁴⁵ is that we are seeing a transition between the split components of the ground state. However, since this band is also observed in the spectra of the hexahalo salts, this seems rather unlikely but not impossible. We hope that future work may resolve this problem.

(48) With such a large ground-state distortion, the magnetic moments of these complexes should approach the spin-only value (1.73 BM) and become temperature independent.³²