22.2 kK. This places –SeCN below –Br (19.9 and 24.1 kK)[19] in the spectrochemical series. Although we did not observe a band in the visible region in the spectrum of the rhodium(III) selenocyanate complex, Schmidtke[22] has observed a very weak band at 18.2 kK. This is lower than the value of 19.4 kK reported[10] for the corresponding thiocyanate complex, in agreement with the conclusion stated above.

Acknowledgments.—We wish to thank Dr. C. Pecile for suggesting the integrated absorption intensity measurements and for providing us with a copy of his paper prior to publication. This research was supported by the University of Delaware Research Foundation.

---

[22] H.-H. Schmidtke, *J. Inorg. Nucl. Chem.*, in press.

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

Reactions of Niobium Tetrahalides with Some Tertiary Amines[1]

BY T. M. BROWN AND GERALD S. NEWTON[2]

Received January 28, 1966

The reactions of the niobium tetrahalides with triethylamine have been studied under the conditions described (72 hr at 25 or 50°). Only with niobium tetrachloride was a product obtained free of unreacted tetrahalide. Comparison of its visible reflectance spectrum and diamagnetic character with the spectra and magnetic properties of niobium tetrachloride and other compounds containing the niobium–niobium bond suggests that at least partial retention of the metal–metal bond may have occurred. Similar results were obtained when $NbCl_4$ was placed in an excess of N,N,N′,N′-tetramethylpropylenediamine or N,N′-dimethylpiperazine. The reactions with N,N,N′,N′-tetramethylethylenediamine yield the monoadducts, $NbX_4 \cdot C_6H_{16}N_2$ (X = Cl, Br, I), as the major reaction products. Partial reduction of the metal also occurred, resulting in the formation of the diamine dihydrohalides and organic oxidation products. The visible and ultraviolet spectra of the $NbX_4 \cdot C_6H_{16}N_2$ complexes were examined over the range 220 to 670 mμ. Two low-intensity transitions were observed in the visible region as expected for a tetragonally distorted complex.

Introduction

The known chemistry of niobium(IV) may be conveniently divided into two parts: (1) binary compounds, *i.e.*, the oxide and simple halides, and (2) complex compounds in which reaction of the tetrahalides, and in some cases the pentahalides, with donor ligands has occurred. The simplest coordination compounds of niobium(IV) are the highly colored hexahalo complexes, A_2NbX_6 (A = K, RB, Cs; X = Cl, Br, I), recently prepared by Torp[3] by fusion of the tetrahalides with stoichiometric amounts of alkali metal halides. In addition, the coordination compounds, $NbX_4 \cdot 2L$ and $NbX_4 \cdot B$ (X = Cl, Br, I; L = pyridine, acetonitrile; B = 2,2′-bipyridine, 1,10-phenanthroline), have been reported.[3–5] The visible and ultraviolet spectra of these complexes were studied and the behavior of the hexahalo and acetonitrile complexes was found to be in accord with simple ligand field theory.

The visible spectra of the tetrahalides in pyridine solution, however, yielded quite unusual results in that the extinction coefficients were much higher than expected for simple d–d transitions and were comparable in magnitude to those expected of charge-transfer transitions which are not usually found in the visible region of the spectrum. McCarle and Torp[4] attributed these absorption bands to charge transfer from filled π orbitals of ligand pyridine to metal atom d orbitals. The fact that the absorptions occur at progressively shorter wavelengths in the order Cl > Br > I indicates a possible reversal of the usual spectrochemical series. The investigators reason that if pyridine is a strong π-bonding ligand in these complexes, the order of π bonding of halogens is Cl < Br < I and is sufficient to offset the normal order of the spectrochemical series.

Carnell and Fowles have studied[6,7] the action of primary, secondary, and tertiary amines on the niobium(V) chlorides and bromides. With most primary amines, the aminobasic metal halides, $MX_3(NHR)_2 \cdot NH_2R$, resulted. With secondary amines, the analogous products, $MX_3(NR_2)_2 \cdot NHR_2$, resulted. With trimethylamine, highly insoluble products were obtained, possibly mixtures, but giving the over-all composition $MX_5 \cdot 2N(CH_3)_3$. None of these reactions resulted in reduction to the tetravalent state.

In view of the π-bonding ability of the ligands present in compounds of the type $NbX_4 \cdot 2L$, it was of interest to study the properties of niobium tetrahalide

---

[1] This work was supported by the National Science Foundation, Grant No. GP-3810.

[2] NASA Predoctoral Fellow, 1964–1965.

[3] B. A. Torp, Doctoral Dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1964.

[4] R. E. McCarley and B. A. Torp, *Inorg. Chem.*, **2**, 540 (1963).

[5] M. Allbutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, **6**, 299 (1964).

[6] P. J. H. Carnell and G. W. A. Fowles, *J. Chem. Soc.*, 4113 (1959).

[7] P. J. H. Carnell and G. W. A. Fowles, *J. Less-Common Metals*, **4**, 40 (1962).

complexes in which the nitrogen-containing ligand did not have the ability to function as a π-bonding ligand. In this work, the action of various tertiary amines on the niobium tetrahalides is described.

Experimental Section

General Precautions.—Due to the reactive nature of niobium(IV) compounds, all operations were carried out using standard vacuum line techniques or in a dry argon atmosphere.

Materials.—Niobium metal was supplied by the Union Carbide Corp. Best results, in terms of reaction times and yields, were obtained with this metal after the following treatment. The metal was thoroughly washed with ether, acetone, sodium hydroxide, hydrochloric acid, and finally with water. The metal was dried, then heated at *ca.* 500° and 2×10^{-6} mm pressure for 6 hr. The tube containing the metal was sealed off under vacuum and stored in a drybox. Niobium pentachloride was purchased from Alfa Inorganics, Inc., and used as received. Reagent grade bromine was dried over phosphorus pentoxide for 48 hr and thoroughly degassed on the vacuum line prior to transfer under vacuum to a clean flask for storage. Reagent grade iodine was outgassed immediately before use by pumping for several hours at 10^{-4}–10^{-5} mm pressure.

Triethylamine and N,N,N′,N′-tetramethylethylenediamine were purchased from Eastman Chemicals. N,N,N′,N′-Tetramethylpropylenediamine and N,N′-dimethylpiperazine were prepared by the formaldehyde–formic acid methylation of propylenediamine and piperazine, respectively. A large quantity of the amine was allowed to stand over solid KOH and BaO for 24 hr, refluxed over KOH–BaO overnight, and then distilled through an 80-cm column packed with glass tubing. The constant-boiling fraction was collected in a dry flask containing a few grams of fresh BaO. The amine was outgassed on the vacuum line at about 10^{-5} mm and vacuum distilled into a storage flask containing dry BaO.

Other solvents used were either reagent grade or Spectro Grade and were purified by allowing them to stand over phosphorus pentoxide for 48 hr and outgassing at *ca.* 10^{-5} mm. The solvents were then vacuum distilled into a clean, dry flask containing a small amount of thoroughly outgassed P_2O_5 and stored under vacuum.

Analytical Methods.—The complexes were analyzed for niobium and halide content in the following manner. A sample was placed in a vessel constructed in such a manner that liquids could be added without exposure to the air. The sample was hydrolyzed in the absence of air with an excess of 1:1 ammonia, heated to ensure complete hydrolysis, and then neutralized with dilute nitric acid. The hydrous niobium pentoxide was filtered off, thoroughly washed with water, and ignited at 800° to Nb_2O_5 in a porcelain crucible. The volume of the filtrate was reduced by evaporation to about 50 ml, and determination of halide was carried out by a standard Volhard procedure. As a check on this method, niobium was also determined by direct ignition of the sample to the pentoxide after digestion with ammonia. Repeated analysis of pure tetrahalides indicated agreement between theoretical and found values of ±0.3%.

Carbon, hydrogen, and nitrogen analyses were done by Midwest Microlab, Inc., Indianapolis, Ind.

The determination of oxidation states was accomplished by placing a sample in excess ferric sulfate solution and titrating the ferrous ion produced with standard cerium(IV) solution using ferroin indicator. Analyses of iodide complexes were hindered by oxidation of iodide to iodine, and reliable determinations could not be obtained by this method.

The niobium content of solutions used for spectral work was determined by the spectrophotometric method of Telep and Boltz.[8]

Preparation of Niobium(IV) Halides.—Niobium tetrachloride was obtained by the reduction of $NbCl_5$ with niobium metal according to the procedure of McCarley and Torp.[4] The material was identified by its X-ray powder pattern, all lines observed corresponding to those reported in the literature, and by analysis for niobium. *Anal.* Calcd for $NbCl_4$: Nb, 39.6. Found: Nb, 39.8.

Niobium pentabromide was prepared by reaction of the elements at 400–450° in a sealed tube for several days followed by reduction of the $NbBr_5$ obtained to $NbBr_4$ with niobium metal.[4] The material was identified by X-ray analysis and niobium determination. *Anal.* Calcd for $NbBr_4$: Nb, 22.5. Found: Nb, 22.4.

Niobium pentaiodide was prepared by reaction of the elements at 510° in a sealed tube for 48 hr followed by decomposition to the tetraiodide and iodine.[9] X-Ray analysis and niobium determination confirmed that the tetraiodide had been obtained. *Anal.* Calcd for NbI_4: Nb, 15.5. Found: Nb, 15.8.

Preparation of N,N,N′,N′-Tetramethylethylenediamine Dihydrohalides.—The N,N,N′,N′-tetramethylethylenediamine dihydrohalides were prepared by adding a slight excess of the appropriate hydrohalic acid to a 1:1 aqueous solution of the diamine. The salt was then precipitated by addition of a large excess of acetone. The salt was collected on a sintered-glass filtering funnel, washed with cold water and acetone, and then air dried. The white, crystalline salt was recrystallized from anhydrous methanol and dried for several hr at 110°. *Anal.* Calcd for $C_6H_{16}N_2 \cdot 2HCl$: Cl, 37.5. Found: Cl, 37.4. Calcd for $C_6H_{16}N_2 \cdot 2HBr$: Br, 57.5. Found: Br, 57.4. Calcd for $C_6H_{16}N_2 \cdot 2HI$: I, 68.2. Found: I, 68.2.

Preparation of Niobium(IV) Halide Complexes.—Reactions at room temperature were carried out in vessels fitted with a Teflon-covered stirring bar, stopcock, and joint for attachment to the vacuum line. A finely ground sample of niobium(IV) halide, typically 2–5 g, was placed in the tared vessel in a drybox and evacuated, and the sample weight was obtained. Excess ligand (approximately 20 ml) was vacuum distilled into the vessel at room temperature and the reaction allowed to proceed with stirring. For reaction periods longer than 48 hr, the vessels were returned periodically to the vacuum line to ensure that no loss of vacuum had occurred. At the end of a given time period, the excess ligand was distilled off at room temperature (*ca.* 10^{-5} mm). The residue was vacuum dried at *ca.* 2×10^{-6} mm until a constant weight was attained. The approximate amount of ligand reacted was calculated from the weight gain data. All reactions at elevated temperatures were carried out in sealed tubes. Tetrahalide was placed in a reaction tube which was fitted with a removable stopcock in a drybox. The tube was then evacuated and excess ligand distilled onto the halide. The ligand was frozen out at −78°; the tube was sealed off under vacuum and suspended in a bath at the desired temperature. After a given time period, the tubes were broken open under a dry nitrogen atmosphere and placed in a drying vessel. The drying vessel was attached to a vacuum line, and the excess ligand was distilled off. The residue was vacuum dried for 48–72 hr at *ca.* 2×10^{-6} mm.

Purification of the reaction products was achieved by extraction in a Soxhlet-type continuous extractor containing a fritted-glass filter.

Reactions with Triethylamine.—The reactions of the niobium(IV) halides with excess triethylamine yielded finely divided dark brown powders after 72 hr reaction time. The excess amine remained clear and colorless throughout the course of the reaction, indicating negligible solubility of the tetrahalide or the reaction product in the ligand. Constant weight was attained after 72 hr drying. The approximate stoichiometry of the resulting compounds as indicated by analysis is given in Table I. X-Ray analysis of the products showed only tetrahalide diffraction lines, indicating that any product formed was amorphous.

When $NbCl_4$ was treated with an excess of triethylamine for 124 hr, the resulting material was amorphous, giving no X-ray

---

(8) G. Telep and D. F. Boltz, *Anal. Chem.*, **24**, 163 (1952).

(9) J. D. Corbett and P. X. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

TABLE I

MOLE RATIO OF $(C_2H_5)_3N:NbX_4$

Halide	Reaction temperature 25°	50°	90°
$NbCl_4$	0.98[a]	0.3	0.75
$NbBr_4$	0.3	0.1	...
NbI_4	0.1	...	...

[a] This value was obtained from weight gain data.

diffraction pattern. This compound was insoluble in triethylamine, benzene, carbon tetrachloride, chloroform, and dimethylformamide. When heated for 72 hr at 50° or for 12 hr at 75° under a dynamic vacuum (2×10^{-6} mm pressure), this compound showed no loss in weight or development of crystallinity. Analysis indicated that a product of less than 1:1 stoichiometry had been formed. *Anal.* Calcd for $NbCl_4 \cdot 0.9(C_2H_5)_3N$: Nb, 28.5; Cl, 43.6; N, 3.87. Found: Nb, 28.4; Cl, 43.8; N, 3.90; oxidation state, 4.1.

Reactions with N,N,N',N'-Tetramethylpropylenediamine and N,N-Dimethylpiperazine.—The reaction of $NbCl_4$ with the abovementioned amines yielded results similar to those obtained for triethylamine with $NbCl_4$. Due to the amorphous character of the resulting materials and apparent lack of any definite compound formation, additional work with these amines was not carried out.

Tetrachloro(N,N,N',N'-tetramethylethylenediamine)niobium(IV).—In the reaction of $NbCl_4$ with the diamine, a red solid was noticeable after several hours of stirring at room temperature. The excess diamine slowly became deep red as the reaction proceeded. X-Ray diffraction data indicated that the tetrahalide had reacted completely after 96 hr. Weight gain data indicated an apparent reaction of 1.6 moles of diamine per mole of $NbCl_4$. It was apparent from the analysis that neither a simple 1:1 nor a 1:2 adduct had been obtained. The oxidation state was less than four, indicating that some reduction of the tetrahalide had occurred.

The red product was extracted for 72 hr with the diamine, thereby removing a considerable amount of material consisting mostly of a dark red viscous liquid which fumed and turned black upon exposure to the atmosphere. This material contained niobium and chloride and smelled strongly of amines. Extraction was continued with benzene for 24 hr and with the diamine for an additional 24 hr. The red material appeared to be insoluble in the diamine as well as in chloroform, carbon tetrachloride, and diethyl ether.

The X-ray diffraction pattern of the unextracted red product obtained from this treatment contained a number of lines which could be attributed to the diamine dihydrochloride salt. In addition, an infrared spectrum of the product contained bands clearly indicating the presence of the diamine dihydrochloride salt. *Anal.* Calcd for 3:1 molar mixture of $NbCl_4 \cdot C_6H_{16}N_2$ and $C_6H_{16}N_2 \cdot 2HCl$: Nb, 22.4; Cl, 39.9; C, 23.2; H, 5.4; N, 9.1. Found: Nb, 23.2; Cl, 38.8; C, 22.8; H, 5.9; N, 9.2; oxidation state, 3.9.

Positive identification of the complex $NbCl_4 \cdot C_6H_{16}N_2$ was obtained by rapidly washing a sample of the material with ice water to remove the diamine salt followed immediately by vacuum drying.

An X-ray diffraction pattern and infrared spectrum of the resulting compound indicated that the diamine dihydrochloride salt had been removed. Analysis of a sample of the complex obtained by washing with water confirmed the 1:1 stoichiometry. *Anal.* Calcd for $NbCl_4 \cdot C_6H_{16}N_2$: Nb, 26.5; Cl, 40.4. Found: Nb, 27.1; Cl, 40.1.

A reaction carried out at 100° gave similar results. The red product obtained after 72 hr reaction at 100° and extraction with the diamine for 72 hr appeared to be an equimolar mixture of the monoadduct and the diamine dihydrochloride.

Tetrabromo(N,N,N',N'-tetramethylethylenediamine)niobium(IV) and Tetraiodo(N,N,N',N'-tetramethylethylenediamine)niobium(IV).—A deep blue solid resulted from the reaction of niobium(IV) bromide with the diamine after 72 hr reaction time at room temperature. The solid, after extraction with the diamine for 72 hr and benzene for 24 hr, was a 3:2 molar mixture of the monoadduct, $NbBr_4 \cdot C_6H_{16}N_2$, and the dihydrobromide salt of the diamine, $C_6H_{16}N_2 \cdot 2HBr$, as indicated by analysis and X-ray and infrared data. Reaction of $NbBr_4$ with the diamine at 100° under conditions similar to those used in the tetrachloride reaction resulted in a light gray powder having an X-ray diffraction pattern identical with that of the diamine dihydrobromide salt. Niobium content was found to be less than 0.5%.

The reaction of niobium(IV) tetraiodide with the diamine resulted in an olive-green product containing the diamine dihydroiodide as indicated by X-ray and infrared data. The mixture had an elementary composition corresponding approximately to 74 parts of $NbI_4 \cdot C_6H_{16}N_2$, 10 parts of $C_6H_{16}N_2 \cdot 2HI$, and 16 parts of other substances.

Attempts to effect further purification of the products were unsuccessful. The materials appeared to react with nitromethane, acetonitrile, and dioxane. Rapid hydrolysis prevented washing with water or methanol. Extraction of the products with benzene over extended periods of time (weeks) did not yield a sufficient amount of material to be of value.

X-Ray Diffraction Measurements.—All X-ray data were obtained using a Debye–Scherrer 114.59-mm diameter camera. Samples were passed through a 200-mesh sieve and packed in 0.3-mm glass capillaries. The samples were exposed to Ni-filtered Cu Kα radiation for 3–8 hr on a General Electric XRD-5 at power settings of 50 kv and 16 ma.

Spectral Measurements.—Infrared absorption spectra were obtained with a Perkin-Elmer Infracord Model 137 using the KBr pellet technique. Repeated scans indicated the samples were stable for at least 0.5 hr.

Diffuse reflectance measurements were obtained on a Cary Model 14 spectrophotometer equipped with a reflectance attachment and a photocell which allowed the region from 220 to 700 mμ to be scanned. Samples were diluted in a drybox with $MgCO_3$ and firmly packed in a layer 1–2 mm thick against one face of a standard 1-cm square absorption cell. The sample was backed by a glass slide held firmly in place by a paper spacer and the cell sealed with a strip of tape.

Solution spectra were also obtained with the Cary Model 14. A cell similar to that described by McCarley and Torp[4] was used. After each spectral measurement, the cell was opened and the solution removed for analysis.

Conductivity Measurements.—A conductivity cell with removable electrodes was constructed which allowed a weighed sample to be placed in the cell under an inert atmosphere. The apparatus was then evacuated on the vacuum line and solvent distilled in from a weighing flask. An Industrial Instruments, Inc., conductivity bridge, Model RC-16B2, equipped with external capacitance of up to 0.1 μf was used for measurements.

Magnetic Susceptibility Measurements.—Powdered samples were placed in evacuated quartz bulbs 1 cm long and 0.7 cm in diameter. Magnetic susceptibitity measurements were obtained at room temperature using a Faraday balance. Corrections for the diamagnetism of the quartz bulbs were applied in all cases.

Results and Discussion

Several preliminary experiments were carried out which indicated the advisability of working with tertiary rather than primary or secondary amines in studying the behavior of the niobium(IV) halides.

The reaction of $NbCl_4$ with excess ethylenediamine proceeded vigorously with the evolution of HCl at room temperature. After 72 hr, excess ethylenediamine was distilled from the reaction mixture and the black, polymeric-appearing product was dried at *ca.* 2×10^{-6} mm for 48 hr. Weight gain data indicated an apparent mole ratio, ethylenediamine:$NbCl_4$, of 5.28 for the product. Continued vacuum drying resulted in significant weight loss, and the apparent mole ratio dropped to 4.31. After 200 hr constant weight still had not been attained.

Reactions of $NbCl_4$ with diethylamine also proceeded vigorously with gas evolution at room temperature. Weight gain data after 72 hr reaction time and 48 hr drying indicated a mole ratio of 9.37 moles of diethylamine per mole of $NbCl_4$. Again the product could not be dried to constant weight.

In these reactions, at least partial solvolysis of the Nb–X bond undoubtedly occurred with formation of Nb–N linkages and formation of HX as was observed[7] in reactions of the niobium pentahalides with primary and secondary amines. The nature of the products seems to indicate that reduction of niobium may have occurred along with the possible production of organic polymers as oxidation products.

Reactions with Triethylamine.—The reactions of the niobium tetrahalides with triethylamine occurred very slowly and did not yield well-defined mono- or diadducts. Only in the reaction with $NbCl_4$ was the reaction complete, as indicated by the absence of diffraction lines of the tetrahalide in X-ray powder diffraction patterns. Compounds having the stoichiometry $NbCl_4\cdot 0.9(C_2H_5)_3N$, $NbBr_4\cdot 0.3(C_2H_5)_3N$, and $NbI_4\cdot 0.1(C_2H_5)_3N$ were obtained after 72 hr reaction time at room temperature. Longer reaction times would undoubtedly yield compounds containing additional $(C_2H_5)_3N$.

The diadducts analogous to those obtained with pyridine and acetonitrile might be expected to result from the reactions of the niobium tetrahalides with triethylamine. The failure of this to occur and the low degree of reactivity exhibited by the tetrahalides under the conditions described may be due to several factors. The polymeric structure of the tetrahalides presumably leads to a relatively high crystal energy which would lend considerable stability to the compounds. This stability coupled with the relatively weak coordinating ability of the tertiary amine would undoubtedly contribute to the lack of reactivity observed. Possible steric requirements might also be significant. Studies of reactions with other amines, *e.g.*, trimethylamine and triisopropylamine, are being carried out to determine the influence of such effects. Several authors[7,10,11] have commented on the fact that rarely do tertiary amines form stable complexes with metal halides and then only upon prolonged reaction times when reduction of the metal may become a factor.

The fact that the niobium tetrahalides and the products formed show no apparent solubility in the amine is significant. In the reported reactions with pyridine and acetonitrile, the tetrahalides went into solution, with reaction, and the diadducts formed exhibited at least slight solubility in the ligand. The absence of appreciable solubility with the tertiary amine results in a heterogeneous solid–liquid reaction which would be expected to occur slowly.

The lesser extent of reaction at 50° than at room temperature may be due to the rapid formation of an insoluble product layer on the tetrahalide surface at the higher temperature. The lack of reactivity of the niobium pentahalides with trimethylamine even at long reaction periods (months to years) has been attributed to such effects.[7] The fact that the reaction with $NbCl_4$ at 90° for 72 hr resulted in a greater consumption of the halide may be due to a greater solubility of the product at that temperature. The possibility of rapid diffusion of the triethylamine through a product layer could also become an important factor at elevated temperature. Although variables such as particle size and stirring rate (which were not controlled) may have considerable effect in these heterogeneous reactions, the above results definitely indicate an order of reactivity chloride > bromide > iodide in the simple coordination of the niobium(IV) halides with triethylamine. This is the same order of reactivity observed in the simple complexing reactions with pyridine.[4] The above conclusions do not, however, preclude the possibility of simple dissociation of the adducts at 50°.

The nature of the products obtained in these reactions is somewhat obscure. Only in the reaction with $NbCl_4$ was a product obtained free of unreacted tetrahalide. The stoichiometry indicated by weight gain data and analysis may be due to a mixture of products rather than the incomplete formation of definite 1:1 or 1:2 adducts. As in the case of niobium(IV) chloride, which has been shown[4] to be diamagnetic, a magnetic susceptibility measurement at room temperature of the niobium(IV) chloride–triethylamine adduct also showed this solid to be diamagnetic. The visible reflectance spectrum of the brown adduct of $NbCl_4$ of approximate 1:1 composition is similar to that of the tetrahalides. The spectra of $NbCl_4$ and $NbBr_4$ are ill defined but exhibit one very broad peak at 388 and 390 mμ, respectively. The $NbCl_4$–triethylamine adduct shows a similar broad peak at 380 mμ. The compounds prepared by Wentworth and Brubaker[12] also show similar visible spectra. The dimeric $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and the polymeric $Nb(OC_2H_5)_4$ in which the Nb–Nb bond is assumed to be present exhibit only single absorptions at 365 and 380 mμ, respectively.

If this single visible band and the diamagnetism are characteristics of the presence of the metal–metal bond, then it would appear that the Nb–Nb bond is retained in the $NbCl_4$–triethylamine adduct. Mixtures of the monomeric adduct with the dimeric, tetrameric, etc., adducts having the Nb–Nb bond intact would account for the visible reflectance spectrum, diamagnetism, and the analytical results. Such a mixture of products might fail to allow crystallinity and result in the observed amorphous nature of the products.

---

(10) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

(11) G. W. A. Fowles and C. M. Pleass, *ibid.*, 1674 (1957).

(12) R. A. P. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 47 (1964).

Reactions with N,N,N′,N′-Tetramethylenediamine.—The above results indicated that the niobium(IV) halides will react only reluctantly with tertiary amines. It is well known that the inclusion into a single ligand molecule of two electron-donor atoms greatly enhances the formation and stability of metal–organo complexes. This additional stability is referred to as the chelate effect. It was, therefore, decided to study the action of the bidentates N,N,N′,N′-tetramethylethylenediamine (hereafter referred to as the diamine), N,N,N′,-N′-tetramethylpropylenediamine, and N,N′-dimethylpiperazine on the tetrahalides. Only in the case of N,N,N′,N′-tetramethylethylenediamine was a definite compound formed. The reaction of the diamine with the tetrahalides apparently proceeds *via* two simultaneous or, quite probably, consecutive reactions. Although some reduction of the metal occurred, the major products obtained were monoadducts of the type $NbX\cdot C_6H_{16}N_2$. This behavior resulted in complex mixtures as reaction products.

The analysis and oxidation state indicated the possible presence of a mixture of the monoadduct $NbCl_4\cdot C_6H_{16}N_2$ and the diamine dihydrochloride $C_6H_{16}N_2\cdot 2HCl$.

The presence of diamine dihydrochloride was confirmed by examination of infrared spectra and X-ray diffraction patterns. Formation of the salt resulted in shift of the C–H absorption band centered at 2850 cm^{-1} to lower wavenumbers and caused the appearance of a broad N–H "ammonium" band at 2500 cm^{-1}. A number of other bands characteristic of the diamine were also observed to shift or disappear. The spectrum of the red reaction product was nearly identical with that of the salt except for the absorption bands at 945 and 910 cm^{-1} in the fingerprint region. The broad band at 2500 cm^{-1} characteristic of the salt was present in the spectrum of the reaction product.

Rapid washing with ice water removed the salt with little or no hydrolysis of the complex. An examination of the X-ray and infrared data indicated the absence of the salt and only coordinated diamine, for the broad N–H absorption at 2500 cm^{-1} was absent, along with the strong C–H absorption of the free amine at 2850 cm^{-1}. The disappearance of the absorption at 2580 cm^{-1} has been shown[13] to occur upon coordination of tertiary amines with metals. The bands at 945 and 910 cm^{-1} which are not observed in the salt were still present. Further confirmation of the composition of this red complex was obtained by examination of its electronic spectra which exhibited two low-intensity absorptions in the visible region. The visible spectra of the water-washed product and of the salt–complex mixture taken in benzene were identical. The spectrum is discussed in detail below.

As the temperature of the reaction was increased, the rate of reduction also increased as indicated by the formation of additional diamine dihydrochloride. At room temperature a 3:1 molar mixture of complex and hydrochloride salt was obtained while at 100° a 1:1 molar mixture was obtained for the same reaction period

The increased amount of diamine salt is an indication of greater extent of reduction than that obtained at room temperature. Apparently the reduced metal products, as well as the organic oxidation products, are soluble in the diamine and are largely removed by the extraction procedure.

Similar results were obtained for the tetrabromide and tetraiodide although reduction apparently occurs at a faster rate. With $NbBr_4$ and NbI_4 reduction is complete at the higher temperature and the greater part of the reduced niobium species as well as the organic oxidation products is soluble in the diamine.

The above results, coupled with the fact that the complexes were essentially nonconducting in benzene solution, indicate that the monoadducts are the major products of the reactions with the diamine for short time periods at room temperature. The formation of the complex may be the first step in the slow reduction of the metal. Other reductions by N,N,N′,N′-tetramethylethylenediamine have been observed[10] in the reactions with chloroplatinic acid, H_2PtCl_6, and potassium hexachloroiridate(IV), K_2IrCl_6.

The nature of the oxidation products of the diamine obtained in these reactions is obviously complex. It is known that the oxidation of tertiary amines often leads to tars except in cases of oxidation by peracids and hydrogen peroxide.[14]

The agreement between solution and reflectance measurements further confirmed that the reaction products obtained were substantially complex–salt mixtures with no appreciable amounts of lower oxidation state metal complexes present. The visible spectra obtained for the pure $NbCl_4\cdot C_6H_{16}N_2$ complex and the complex–salt mixture were identical. This is a good indication that the peaks obtained for the tetrabromide and tetraiodide complex–diamine dihydrohalide salt mixtures most likely result from the complex and are not due to the presence of other substances.

The visible spectra of complexes of the type $MX_4\cdot B$ (B = bidentate ligand) can be interpreted with the aid of simple ligand field theory. Under the perturbing influence of an octahedral field the ^2D ground state of niobium(IV) is split into a lower lying $^2T_{2g}$ term and an upper ^2E_g term. The nonequivalence of the six ligands introduces at least a tetragonal component to the ligand field. It has been shown that even though the symmetry of the ligand field is C_{2v} it can be treated as D_{4h}.[15] The tetragonal distortion splits the lower $^2T_{2g}$ term into the terms $^2B_{2g}$ (usually lower lying) and ^2E_g, and the upper ^2E_g term into $^2A_{1g}$ and $^2B_{1g}$ (in the nomenclature for D_{4h} symmetry). Thus two transitions are expected in the visible region, $^2B_{2g} \rightarrow {}^2A_{1g}$ and $^2B_{2g} \rightarrow {}^2B_{1g}$. From the positions of the absorption bands the magnitude of the ^2E_g splitting may be estimated.

---

[13] J. T. Braunholtz, E. A. V. Elsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958).

[14] D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 439.

[15] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 107.

Table II

Absorption Maxima of the $MbX_4 \cdot C_6H_{16}N_2$ Complexes

Complex	Conditions	Peak positions (cm^{-1}) (extinction coefficients in parentheses)				
$NbCl_4 \cdot C_6H_{16}N_2$	Benzene	19,800 (30)	23,260 (13)	33,330 (1000)		
	Solid	19,420	23,260	33,330	38,760	
$NbBr_4 \cdot C_6H_{16}N_2$[a]	Benzene	17,860 (45)	21,980 (26)	30,490 (590)		
	Solid	17,490	21,740 sh	30,300	36,230	38,760
$NbI_4 \cdot C_6H_{16}N_2$[a]	Benzene	15,750 (230)	18,180 (240)	22,220 sh (820)	24,690 sh (1200)	
		27,250 (2400)	33,110 sh (5400)			
	Solid	15,750	...	22,470	24,940	
		26,670	31,750			

[a] Data were obtained using the mixtures of tetrahalide complex–diamine dihydrohalide salt.

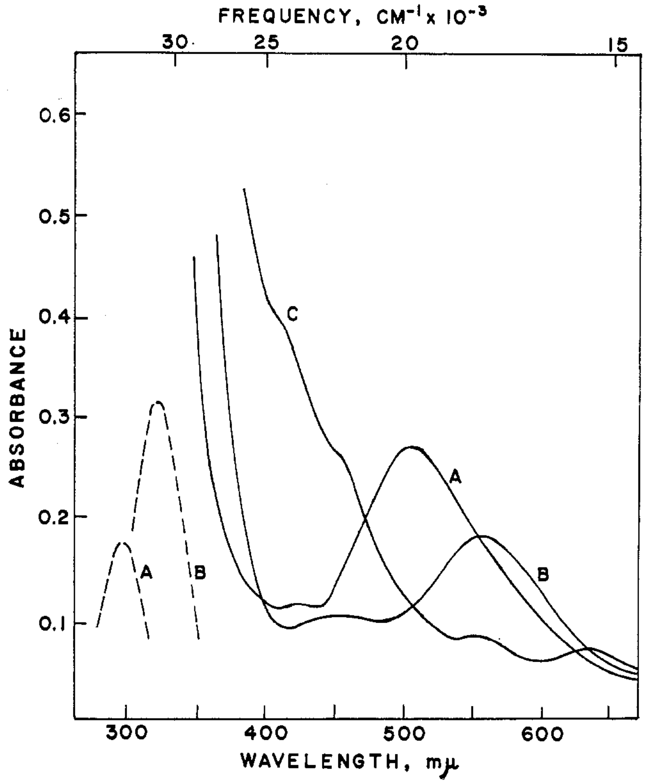

Figure 1.—Spectra in benzene of $NbCl_4 \cdot C_6H_{16}N_2$ (curve A: solid line, 9.4×10^{-3} *M;* dotted line, 1.8×10^{-4} *M*), $NbBr_4 \cdot C_6H_{16}N_2$ (curve B: solid line, 4.2×10^{-3} *M;* dotted line, 5.4×10^{-4} *M*), $NbI_4 \cdot C_6H_{16}N_2$ (curve C: 3.3×10^{-4} *M*).

The observed transitions are shown in Figure 1 and tabulated in Table II. It can be seen that two low-intensity transitions occur in the visible region for each complex and several higher intensity peaks occur in the ultraviolet region. All the observed absorptions show a shift to progressively longer wavelengths in the order Cl < Br < I. The solution and solid-state spectra agree quite well, suggesting that similar species are present in the solid and in solution. The higher energy, low-intensity transition is not resolved well in the reflectance spectra of the chloride and bromide complexes and could not be resolved at all in the spectra of the iodide complex.

The low-intensity visible transitions are attributed to the two d–d transitions expected. From the energies of these transitions, the calculated magnitude of the ^2E_g splitting is 3840, 4350, and 2430 cm^{-1} for the chloride, bromide, and iodide complexes, respectively (it is not known which of the two terms, $^2A_{1g}$ or $^2B_{1g}$, is higher). Comparison of these data with that of Torp[3] on the hexahalo and diacetonitrile complexes indicates an order of ligand field strength $CH_3CN > C_6H_{16}N_2 > Cl > Br > I$. The magnitude of the ^2E_g splitting here is of the same order ($\sim$3000 cm^{-1}) as was observed in the acetonitrile complexes. The extinction coefficients of these transitions are somewhat higher than usually observed for simple d–d transitions. This effect increases in the order Cl < Br < I and is probably indicative of vibronic coupling and/or vibronically induced borrowing of intensity from the strong ultraviolet absorption bands.

The higher intensity absorptions observed can be attributed to charge-transfer transitions from halogen to metal. These peaks shift to longer wavelengths in the order Cl < Br < I. The charge-transfer transitions of the iodide complex are shifted sufficiently to appear in the visible region, as was observed with the diacetonitrile complex of niobium tetraiodide.

These data are consistent with that expected of a tetragonally distorted octahedral complex and thus serve as confirmation that the simple monoadducts were obtained in the reaction of the niobium tetrahalides with tetramethylethylenediamine.

The reaction of $NbCl_4$ with N,N,N′,N′-tetramethylpropylenediamine and N,N′-dimethylpiperazine yielded results similar to those obtained with triethylamine. As with triethylamine, reaction occurred very slowly and no apparent solubility of the tetrahalide or the products formed was observed in the amine. This behavior is not unreasonable in view of the greater degree of bond strain which would result with these ligands compared to that for the N,N,N′,N′-tetramethylethylenediamine complex. These results further verify the lack of coordinating ability of tertiary amines and indicate that the metal–nitrogen bonds in the N,N,-N′,N′-tetramethylethylenediamine complexes are probably relatively weak.

Acknowledgment.—The authors wish to thank Mr. Richard D. Mounts for the preparation of several of the ligands used in the course of this work.