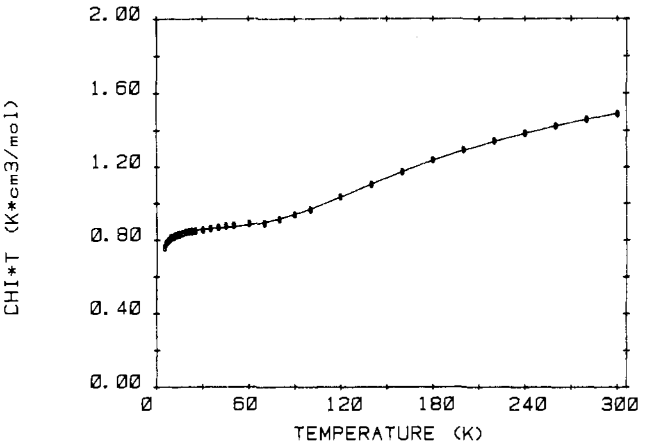

Figure 2. Temperature dependence of the magnetic susceptibility under the form of the χT vs. T curve: (○) experimental points; (—) theoretical curve. The theoretical curve is calculated from the equation below, with

$$\chi_{\text{calcd}} = \frac{N\beta^2 g_1^2}{2k(T-\Theta)} + \frac{2N\beta^2 g_2^2}{3kT}\left[1 + \frac{1}{3}e^{-2J/kT}\right] + 2N\alpha$$

the following "best-fit parameters": $g_1 = 2.16$, $\Theta = -0.75$ K, $g_2 = 2.18$, $-2J = 259$ cm^{-1}, $2N\alpha = 2.4 \times 10^{-4}$ cm^3/mol. The quantity minimized in the least-squares process was $Q = \sum[\chi_{\text{exptl}}T - \chi_{\text{calcd}}T]^2$. The final value of the statistical index $R = Q/N\sum[\chi_{\text{exptl}}T]^2$ was 3.0×10^{-7}.

that the nitrate is monodentate[18] as it is in the salicylaldehyde analogue.[17]

Figure 2 illustrates the magnetic properties of **4** in the form of the χT vs. T curve over the range 5–300 K. This curve exhibits two domains: First, a plateau at $\chi T = 0.8$ K cm^3/mol for temperatures lower than ca. 60 K is indicative of the presence of two independent spins $S = {}^1/_2$. Second, the increase of χT in the upper temperature range reveals an antiferromagnetically coupled system that starts contributing at temperatures higher than 60 K. These properties can be nicely accounted for if one considers that the tetranuclear complex is constituted by two Curie-behaved ions and a binuclear moiety. Fitting the curve under the above assumptions leads to a singlet–triplet separation of 259 cm^{-1} for the dinuclear unit, which is a moderately high value. This model is consistent with Cu2 and Cu2′ forming the coupled pair and Cu1 and Cu1′ being the isolated ions. Owing to the tetragonal symmetry around Cu2 and Cu2′ the magnetic orbitals of each metallic fragment will be of $d_{x^2-y^2}$ type, thus providing a good overlap on the oxygen atoms O1 and O1′. Moreover, by analogy with hydroxy-[19] and alkoxy-bridged[20] complexes, the high value of the Cu2–O1–Cu2′ angles (103°) predicts a significant coupling, in agreement with the observation. At first glance, a coupling could also be predicted between Cu1 and Cu2 since the magnetic orbitals on Cu1 (d_{z^2}) and on Cu2 ($d_{x^2-y^2}$) would overlap on O2 and the Cu1–O2–Cu2 angle is obtuse enough (115°).[19,20] In fact, there is no coupling as evidenced by the value of the Weiss constant ($|\Theta| < 1$ cm^{-1}). We think that the reason for this is probably to be found in the nonplanarity of the system. Actually, the N2–Cu2–O2 axis makes an angle of 129° with the Cu2 basal plane (O1, O1′, O4, O2). This situation is analogous to the folding of dihydroxy-bridged dicopper complexes, which is known to lead to smaller singlet–triplet gaps as a result of a decrease in both the ferromagnetic and the antiferromagnetic contributions to the exchange integral.[21]

In summary, this note reports the synthesis and the magnetic properties of new copper catecholates and describes the X-ray structural characterization of a novel mode of coordination of these ligands. Further work is currently in progress to fully characterize the redox properties of these compounds and study their reactivity.

Supplementary Material Available: Listings of anisotropic thermal parameters, interatomic distances and angles, and hydrogen atom coordinates (5 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

---

(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; pp 232, 246.

(19) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110.

(20) Mikuriya, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1086–1091.

(21) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567–576.

Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Ammonolysis of Niobium(V) Bromide

L. Maya

Received October 2, 1986

The chemistry of transition-metal compounds in liquid ammonia is of interest because it provides an added perspective to the more extensively studied behavior of these compounds in aqueous systems. Ammonolytic reactions are more sensitive than the parallel hydrolytic processes to the polarizing power of the central atom and lead to a variety of products in which only a portion of the original ligands are displaced by amide. Hydrolysis, on the other hand, leads in general to fully hydroxo-substituted derivatives. However, in both cases, the products are susceptible to undergoing additional condensation through the formation of amido, imido, hydroxo, or oxo bridges.

The ammonolytic reactions can also be utilized as synthetic tools in providing oxygen-free derivatives containing strong metal–nitrogen bonds. It is in this area that our interest is focused since the derivatives can be used as intermediates to prepare precursors that can be thermally converted into advanced ceramic materials such as nitrides or carbonitrides.

Niobium nitrides and carbonitrides are materials with desirable properties such as hardness, thermal stability, and particularly, in the case of cubic forms, superconductivity.[1] The ammonolysis of niobium halides provides a synthetic route to the nitride. This has been previously examined by Fowles and Pollard,[2] who found, through tensimetric determinations, that the initial ammonolytic reaction leads to the ammonia-soluble derivative $NbCl_3(NH_2)_2$. Evaporation of the ammonia left a solid residue that, upon thermal treatment, produced NbN. Additional work by Allbutt and Fowles[3] showed that long-term ammonolysis leads to an insoluble residue having a formula corresponding to $NbBr(NH_2)_2NH$. (The structure of a similar tantalum analogue has been recently established.[4]) More recent developments in this area include the work of Sinitsyna,[5] who performed dry ammonolysis reactions between the niobium halides and an excess of the corresponding ammonium halide to produce niobium halide nitrides, $NbNX_2$. Finally, Grebtsova et al.[6] studied the thermal conversion of the ammonolysis residue of $NbCl_5$ into NbN by a variety of techniques.

The present work was undertaken to better characterize the ammonolytic intermediates as well as the thermal decomposition products and also to explore the use of these intermediates in the preparation of derivatives that could be converted into carbonitrides similar to previous work in the titanium system.[7]

---

(1) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic: New York, 1971.

(2) Fowles, G. W. A.; Pollard, F. H. *J. Chem. Soc.* **1952**, 4938.

(3) Allbutt, M.; Fowles, G. W. A. In *Developments in Inorganic Nitrogen Chemistry*; Colburn, C. B., Ed.; Elsevier: Amsterdam, 1966; Vol. 1.

(4) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; ChotaVuru, G. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1069.

(5) Sinitsyna, S. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1977**, *22*, 402.

(6) Grebtsova, O. M.; Troitskii, V. N.; Shulga, Yu M. *J. appl. Chem. USSR* (*Engl. Transl.*) **1985**, *58*, 2011.

(7) Maya, L. *Inorg. Chem.* **1986**, *25*, 4213.

0020-1669/87/1326-1459$01.50/0

Experimental Section

Electronic grade ammonia was further purified by contact with sodium metal. Niobium(V) bromide (Alfa Inorganics) was dissolved in liquid ammonia at -50 °C, filtered, and dried under vacuum at room temperature. This procedure produced a free-flowing powder containing between 7 and 8 mol of NH_3/mol of $NbBr_5$. Sodium acetylide was prepared according to ref 8. All other reagents were AR quality and used without additional purification.

Niobium was determined as Nb_2O_5 by ignition in air in a Pt crucible. Nitrogen was determined after acid hydrolysis as ammonia with an ion-selective electrode. Nitrogen in the refractory nitride products was liberated by a vacuum-fusion procedure and quantified by gas chromatography. Bromide was determined with an ion-selective electrode and by neutron activation in the refractory samples. Sodium was determined by neutron activation analysis. Carbon was determined as CO_2 in a Leco carbon analyzer.

Infrared spectra were obtained with a Model 60 Digilab FTIR spectrophotometer on KBr pellets prepared in a glovebox. ESCA was performed by using Al Kα radiation at 250 W. Magnetic susceptibility was measured in a micromagnetic susceptometer, described in ref 9, on solid samples sealed in a capillary tube. The temperature was varied between 4.2 and 300 K, and the applied fields were varied between 5 and 15 kG.

All manipulations were done in an inert-atmosphere glovebox (O_2 and $H_2O \leq 1$ ppm) and on a vacuum line. Reactions were performed, unless otherwise stated, at room temperature in heavy-walled ampules. Separations of ammonia-soluble and ammonia-insoluble reaction products were accomplished in ampules provided with a side arm by repeated decantation followed by washings with ammonia distilled from the side arm.

Pyrolyses were done in quartz containers connected to the vacuum line. Condensable products were collected in a U trap for further analysis. One run was performed under a helium flow while the evolved volatiles were monitored with a mass spectrometer.

Results and Discussion

In the course of this study a number of ammonolytic products were isolated and characterized, including $NbBr(NH_2)_2NH$ obtained as an insoluble precipitate from the long-term ammonolysis of $NbBr_5$. Another compound, $Nb_6Br_9N_7$, was obtained as an intermediate in the thermal decomposition of the solid residue remaining after the evaporation of excess ammonia from the short-term ammonolysis. These two compounds were derivatized with sodium acetylide and the products characterized. The pyrolysis, to 800 °C, of all the above compounds was examined.

Long-Term Ammonolysis. An ampule loaded with $NbBr_5$ and liquid ammonia produced initially a clear dark red liquid, which, in the course of 2 weeks, slowly faded to a light brown color and deposited a precipitate containing 70% of the initial niobium. This material had a composition corresponding to $NbBr(NH_2)_2NH$, compound I. (Anal. Calcd: Nb, 42.27; Br, 36.35; NH_3, 23.2. Found: Nb, 42.43; NH_3, 24.29.) An equivalent material was isolated by Allbutt and Fowles from the ammonolysis of $NbCl_5$.[2]

Ammonolytic reactions of metal halides, in some instances, are either slow or do not proceed to completion because of the back reaction caused by buildup of ammonium halide byproduct. Thus, the removal of this material can promote the ammonolysis. This strategy was used in an additional experiment using KBH_4 as a mild base to neutralize the ammonium bromide produced. In this case the reaction was completed after it was allowed to stand overnight. The product of this reaction had the same composition as compound I and did not incorporate borohydride or potassium. The yield of compound I in this reaction was also 70%. Hydrogen was produced as byproduct of the neutralization reaction to the extent of 4.2 mol/mol of Nb.

The infrared spectrum of compound I showed strong NH vibrations at (in cm^{-1}) 3277, 3203, 3127, 1597, and 1250 and a strong broad band at 694. Minor bands and shoulders were at 1402, 878, and 553. The infrared spectra of this and other compounds will be discussed in a subsequent section.

The photoelectron spectrum of compound I showed the following binding energies (in eV): N(1s), 397.1; Nb($3d_{5/2}$), 205.4; Br(3d), 69.0. These are referenced to the C(1s) level at 284.6 eV. Brief exposure of the sample to air caused a shift in the N(1s) energy to 401.4 eV and a marked increase in the N and Br peak intensities. This phenomenon is interpreted as being the result of hydrolysis and formation of an ammonium bromide coating on the surface of the solid. A similar observation was made in the case of titanium bromo amides.[7]

Table I. Products of the Thermal Decomposition of the Ammonolytic Mixture

	A[a]	1	2	3
wt % Nb	40.55	40.26	39.85	40.07
wt % Br	52.32	51.83	51.26	52.72
wt % NH_3	8.66	8.49	8.06	8.75

[a] Calculated for $Nb_6Br_9N_7$.

Short-Term Ammonolysis. The ammonolysis of $NbBr_5$ by contact with liquid ammonia at -50 °C for 60 min, followed by evaporation of excess ammonia at room temperature, produced residues that, in different runs, showed a mole ratio of NH_3:$NbBr_5$ between 7 and 8. These results are in agreement with the observations of Fowles and Pollard,[2] who also established from their tensimetric determinations that 2 mol of ammonium halide are produced in the ammonolysis; thus, the residue can be represented as $NbBr_3(NH_2)_2{\cdot}2NH_4Br{\cdot}(4 - x)NH_3$ where $x \leq 1$. Attempts to separate the ammonium bromide by sublimation under vacuum (10^{-3} mmHg) at 220 °C liberated ammonia and NH_4Br. The course of this process was monitored by conducting material balances in addition to analyzing the residue by FTIR and X-ray diffraction. Eventually, after exhaustive sublimation (about 8 h for a 2-g load), a residue with little residual ammonium bromide was obtained. The amount of sublimed ammonium bromide corresponded to 3.5 mol/mol of Nb, clearly in excess of the initial 2:1 relation. Evidently internal elimination and additional ammonolysis had taken place. The residues of three independent preparations showed a composition corresponding to $Nb_6Br_9N_7$, compound II. Analytical results are given in Table I. Supporting evidence that this is the correct formulation for this material is described below.

The Nb:N mole ratio of 1:1.17, which initially was assumed to be a deviation from a 1:1 ratio due to analytical errors, was confirmed by repeated analyses. This value was also reported by Fowles and Pollard[2] for one of the intermediates in the thermal decomposition of the ammonolytic residue of $NbCl_5$. However, they did not pursue the characterization of that material.

Crucial to the formulation of compound II is a knowledge of the oxidation state of the niobium. Attempts to determine it by direct chemical means using potentiometric titrations with either Ce(IV) or Cr(VI) failed because of the formation of insoluble intermediates. The atomic ratios of Nb:Br:N of 1:1.5:1.17 suggested Nb(V), providing the nitrogen was present as nitride. The fact that niobium is in the V oxidation state is supported by the observation of a 206-eV value for the binding energy of the $3d_{5/2}$ level of Nb in the photoelectron spectrum of this material. In addition to this, the magnetic susceptibility measurements showed diamagnetic behavior. The molar susceptibility was found to be about -1×10^{-4} emu/mol. The presence of imide or amide ligands would have implied a lower oxidation state, and probably, paramagnetic behavior would have been observed. The IR spectrum showed very weak N–H vibrations, due mostly to residual NH_4Br. Hydrogen analyses gave values of 0.03%, 0.1%, and 0.3%, depending on the method used. The 0.1% value is considered as more reliable on the basis of material balances. This amount of hydrogen is in the form of NH_4Br, which is estimated to be present at ~3% by weight, in agreement with the intensity of the ν_4 band at 1400 cm^{-1}.

The overall process leading to the formation of compound II, based on repeated experiments, is represented by

$$6NbBr_5 + 46NH_3 \xrightarrow{\text{room temperature}} 6[NbBr_3(NH_2)_2{\cdot}2NH_4Br{\cdot}3.66NH_3] \xrightarrow[\Delta]{220\ ^\circ C} Nb_6Br_9N_7 + 21NH_4Br + 18NH_3$$

---

(8) Greenlee, K. W.; Henne, A. L. *Inorg. Synth.* **1946**, *2*, 79.

(9) Nave, S. E.; Huray, P. G. *Rev. Sci. Instrum.* **1980**, *51*, 7.

The fact that a hexanuclear cluster unit of niobium atoms is formed in this system is not unusual considering the tendency of this element, as well as that of Ta and W, to behave in this fashion. Particularly interesting is the presence of hexanuclear units in Nb(V) systems such as the hydrolytic species of $Nb_6O_{18}(OH)^{7-}$ and in $K_{14}Nb_{12}O_{37}$.[10-12]

Grebtsova et al.[6] did not observe the corresponding chloride derivative of compound II in their thermogravimetric analysis apparently because of the relatively large sample size of ammonolytic mixture taken and the relatively fast heating rate.

The IR spectrum of compound II is very simple. After subtraction of the NH_4Br contribution, it exhibits a strong band at 768 cm^{-1} with a shoulder at 704 cm^{-1} and much weaker bands at 3350 (br), 1597, and 1259 cm^{-1}.

The photoelectron spectrum of compound II showed bands at 396.6 eV for N(1s), 206.0 eV for Nb(3 $d_{5/2}$), and 69.0 eV for Br(3d). This material is less sensitive to hydrolysis but it showed a behavior similar to that of compound I upon exposure to air, indicating the growth of NH_4Br on the surface.

Compound II was found to be susceptible to further ammonolysis. Contact with liquid ammonia produced at −50 °C a solid having a composition corresponding to $Nb_6Br_5(NH)_{10}(NH_2)_5$. (Anal. Calcd: Nb, 46.42; Br, 33.66; NH_3, 21.48. Found: Nb, 46.96; Br, 32.54; NH_3, 22.23.) The formulation of this material, which quite likely is polymeric in nature, as well as similar ones to follow, does not represent known structures; they are the simplest expressions consistent with the material and ionic balances. Alternate formulations whereby two amide ligands can be represented as an imide and ammonia are also possible.

Treatment of compound II in a sealed ampule with liquid ammonia at room temperature produced NH_4Br as a soluble species and $Nb_6Br_4(NH)_{11}(NH_2)_4$. (Anal. Calcd: Nb, 50.39; Br, 28.9; NH_3, 23.05. Found: Nb, 49.07; Br, 28.27; NH_3, 22.35.) The material balance for this experiment is described by

$$Nb_6Br_9N_7 + 13NH_3 \rightarrow 5NH_4Br + Nb_6Br_4(NH)_{11}(NH_2)_4$$

It is significant that in this treatment no hydrogen or nitrogen were produced, which would have indicated a redox reaction. This constitutes further support that the niobium in compound II is in the V oxidation state.

The relatively low values of the N(1s) binding energies for compounds I and II of 397.1 and 396.6 eV, respectively, suggest considerable electron transfer from the niobium to the nitrogen ligands.[13,14] These values suggest a charge of about −2 on the basis of a correlation developed by Hendrickson et al.,[14] which covered values between 407 and 397 eV, and correlated with charges of +3 to −2 as calculated by an extended Hückel molecular orbital method. It is interesting to note the 0.5-eV shift in the N(1s) values between compound I and II, which seems to indicate subtle differences in electron transfer to amide–imide ligands, on one hand, as compared to the nitride ligands in compound II. This difference is more evident in the IR spectra. Compounds I and II showed strong bands at 694 and 768 cm^{-1}, respectively. These bands appear to be due to M–N vibrations that are shifted to higher energies than those of amines of transition metals, which occur between 510 and 300 wavenumbers.[15] The amines show N(1s) binding energies of about 400 eV. It is apparent that both spectroscopies are sensitive to bonding interactions of M–N moieties in these types of compounds, showing a trend of higher binding energies associated with lower M–N vibration frequencies.

Acetylide Derivatives. Parallel reactions of compounds I and II with excess sodium acetylide to replace the bromide were conducted in liquid ammonia. These produced dark brown precipitates after overnight standing at room temperature. Separation of unreacted sodium acetylide and the resulting NaBr byproduct into the side arm left, after ammonia evaporation, derivatives Ia and IIa. These materials were found to be salt-like in that incorporation of sodium was observed, similar to the acetylide of transition metals prepared by Nast.[16] Compounds Ia and IIa had idealized compositions corresponding to $Na_4Nb_6(C{\equiv}C)_4(N)_8NH$ and $Na_5Nb_6(C{\equiv}C)_5(N)_5(NH)_5$, respectively. The composition of derivative Ia suggests that compound I may also contain hexanuclear niobium clusters. The IR spectrum of Ia showed no N–H vibrations. The only significant features were a very strong band at 662 cm^{-1} with shoulders at 854, 762, and 583 cm^{-1}. Weak bands were observed at 1904, 2003, and 2162 cm^{-1}, which appear to be due to bridging acetylide moieties.[17,18] The IR spectrum of IIa is quite similar to that of Ia. The most salient feature is a strong band at 680 cm^{-1} with shoulders at 843, 757, and 584 cm^{-1} and weak bands at 1917, 2032, and 2167 cm^{-1}. In addition to these, bands were observed at 3348 and 3220 cm^{-1}. It is not clear whether these two bands are due to N–H or C–H vibrations. If the latter is correct, compound IIa would have to be formulated as $Na_5Nb_6(C{\equiv}CH)_5(N)_{10}$.

Table II. Pyrolysis of Derivatives and Intermediates

expt	compd	wt loss	XRD	chem anal., wt % C	N	Br	Na
1	Ia	30.6	Nb[C,N]	4.37	6.15	0.07	1.03
2	IIa	34.8	Nb[C,N]	13.73	3.52	0.97	2.29
3	I	50.9	Nb_4N_3		10.8	5.3	
4	II	71.6	NbN			1.6	
5	II	66.8	Nb_4N_3			5.2	

Pyrolysis of Derivatives and Intermediates. Samples of the derivatives Ia and IIa and the intermediate ammonolytic compounds were pyrolyzed under vacuum. A summary of the results obtained is given in Table II. Compound Ia was found to decompose violently upon reaching 100 °C. Part of the initial sample was ejected out of the heating zone but still within the outer quartz tube connected to the vacuum line. The experiment was continued and samples of the ejected material as well as material subjected to heating to 800 °C were examined for X-ray diffraction (XRD), with the same pattern found for the two materials. Evidently the ejected material converted by an energetic exothermic process into the final carbonitride at a relatively low temperature. The X-ray diffraction patterns of $Nb_4N_{3.92}$, Nb_4N_3, and NbC are similar to the point of being indistinguishable when the lines are slightly diffuse. It is now known whether the products obtained from the pyrolysis are true solid solutions of a carbonitride or a two-phase mixture of a nitride and a carbide.

The pyrolysis of compound Ia was repeated by using this time an assembly made of three quartz tubes, each sealed at one end, nested within each other and having their openings in opposite directions. This assembly prevented the ejection of material from the inner tube, and created a tortuous pathway for the evolved volatiles. The heating rate was reduced, and no violent decomposition was observed in this experiment. The residue was characterized by chemical analysis and XRD. Most of the initial sodium present was sublimed and deposited as a metallic film in the colder portions of the apparatus. No significant amounts of volatiles other than traces of ammonia and acetylene were collected inthe −196 °C trap. Pyrolysis of compound IIa in a tortuous path assembly produced a residue that had a stoichiometric excess of carbon over the amounts of niobium and nitrogen present. Apparently some of the carbon was present as an amorphous residue, which was actually detected by the presence of a weak band in the Raman spectrum at 1346 wavenumbers.[19] The relatively high sodium and bromine contents of the residue are due to the fact that the initial product was mechanically contaminated at the time

---

(10) Neuman, G. *Acta Chem. Scand.* **1964**, *18*, 278.

(11) Nelson, W. H.; Tobias, R. S. *Can J. Chem.* **1964**, *42*, 731.

(12) Tobias, R. S.; Freidline, C. E. *Inorg. Chem.* **1965**, *4*, 215.

(13) Ramqvist, L.; Hamrin, K.; Johanson, G.; Fahlman, A.; Nordling, C. *J. Phys. Chem. Solids* **1969**, *30*, 1835.

(14) Hendrickson, D. N.; Hollander, J. M.; Jolly, W. L. *Inorg. Chem.* **1969**, *8*, 2642.

(15) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1970.

(16) Nast, R. *Spec. Publ.—Chem Soc* **1959**, *No. 13*, 103.

(17) Hagihara, N. *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **1978**, *35*, 61.

(18) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1960.

(19) Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126.

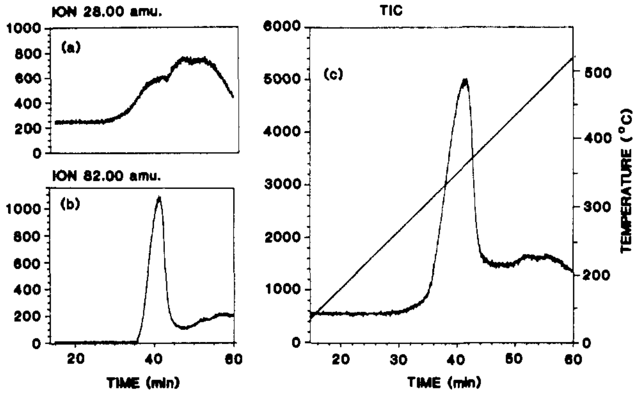

Figure 1. Mass spectra vs. time of volatiles evolved in the thermal decomposition of $Nb_6Br_9N_7$: (a) N_2; (b) HBr. Part c: total ion current vs. temperature (the straight line shows the temperature gradient in the experiment).

of emptying the ampule with about 5% NaBr. No significant amounts of volatiles were collected in the pyrolysis of this compound.

Pyrolysis of compound I in the tortuous path assembly produced Nb_4N_3. The condensable volatile products in this case were NH_3, NH_4Br, and $NbBr_5$. Chemical analysis of the residue showed 5.3% Br. This compares with 6.1% residual chlorine in the 800 °C product isolated by Grebtsova et al., who found that heating to 1000 °C eliminates the residual halide.

The pyrolysis of compound II showed some interesting behavior. The tortuous path assembly produced a residue with the X-ray pattern of Nb_4N_3 and a Br content of 5.2%, while the product of the pyrolysis in a single tube had the X-ray pattern of hexagonal NbN and a Br content of 1.6%. The effect of the experimental conditions in forming these two distinct phases was confirmed in additional experiments. The tortuous path assembly produced in a number of experiments a metallic coating in the hot portion of the assembly. A SIMS analysis of the coating showed Nb^+, NbN^+, and NbO^+. Examination by transmission electron microscopy of the coating showed the diffraction patterns of NbN, Nb_4N_3, and Nb_2O_5. The crystallites had dimensions in the 10–40-nm range. The presence of oxide might be due to exposure to air or diffusion from the quartz substrate. The formation of NbN coatings by a chemical vapor deposition route is an interesting phenomenon. The conditions controlling this process have not been established, but, apparently, the vapor species $NbBr_5$ and HBr, isolated and identified by FTIR, in conjunction with thermal gradients have a significant role in the transport reaction.

In addition to $NbBr_5$ and HBr, nitrogen was also detected in a separate experiment by mass spectroscopic analysis of the volatiles. The $NbBr_5$ was condensed in the colder portions of the assembly and was not detected by MS. The profile of volatile production as a function of temperature is given in Figure 1. The hydrogen in the HBr collected in the decomposition of $Nb_6Br_9N_7$ is provided by a residual NH_4Br contamination of compound II. It is seen that nitrogen evolution occurs particularly at high temperatures while HBr is evolved within a narrow temperature range.

Conclusions

Niobium(V) bromide produces, depending on the experimental conditions, a series of ammonolytic intermediates showing metal to halide ratios of 2.0, 1.5, 1.0, 0.83, and 0.75. Particularly interesting from a chemial and structural point of view is the formation of a hexanuclear compound, $Nb_6Br_9N_7$. The intermediates are readily converted into acetylide derivatives of high metal content that yield upon thermal treatment niobium carbonitrides or mixed nitride–carbide phases. The amount of carbon introduced may be a variable susceptible to control given the variability of the metal to halide ratio in the intermediates.

Acknowledgment. Analytical services were provided by the Analytical Chemistry Division of the Oak Ridge National Laboratory. I am very grateful to Gilbert M. Brown for providing the mass spectra of evolved volatiles and to J. R. Moore and S. E. Nave for performing the magnetic susceptibility measurements. This research was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

Contribution from the Centro de Investigación
en Polímeros y Materiales, Universidad de Sonora,
Hermosillo, Sonora, Mexico, and Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Electroconductive Tetrathiafulvalene Salt of Copper Iodide: $(TTF)_{4/3}CuI_2$

Michiko B. Inoue,[1a] Catalina Cruz-Vázquez,[1a]
Motomichi Inoue,*[1a] Quintus Fernando,[1b]
and Kenneth W. Nebesny[1b]

Received September 16, 1986

In our previous papers,[2-4] we reported that copper(II) chloride and bromide function as excellent oxidants to form highly electroconductive tetrathiafulvalene (abbreviated as TTF) salts. The resulting compounds can be formulated as $[(TTF)_n]^{\bullet +}Cu^IX_2$ (X = Cl, Br), in which each TTF moiety carries a fractional charge of $+1/n$. The electrical and magnetic properties vary markedly depending on the composition (i.e. the value of n), which can be readily controlled by using different halides and a variety of solvents. This flexibility in the design of different types of conducting complexes can be attributed to the difference in the stabilization of the Cu^I state of the halides in the various solvents. This observation has prompted us to investigate the synthesis and properties of the copper iodide–TTF salts. Copper(II) iodide, however, is not stable, and a TTF–CuI_2 complex cannot be prepared by the method that was used for the synthesis of the chlorides and bromides. In this study, we report the synthesis and physical properties of $(TTF)_{4/3}CuI_2$. This compound has been characterized by IR and X-ray photoelectron spectroscopy (XPS) measurements.

Results and Discussion

Copper(II) acetate did not react with excess TTF in common organic solvents such as methanol, tetrahydrofuran, and acetonitrile, in contrast with the reactions of TTF with $CuCl_2$ and $CuBr_2$. When an alkylammonium iodide was added to a mixture of copper(II) acetate and TTF in methanol, a reaction occurred immediately and $(TTF)_{4/3}CuI_2$ was formed. In this reaction, the oxidant CuI_2 was prepared in situ. In the X-ray powder diffraction pattern of the product, a peak attributable to CuI was not found, indicating that the material was not contaminated by CuI. When tetrahydrofuran was used as a solvent instead of methanol, a TTF-CuI_2 complex was obtained. Its IR spectrum, however, indicated that the material was contaminated by an acetate. When acetonitrile was employed as a solvent, the resulting material did not contain copper but had the composition $(TTF)I_{0.7}$; this compound had been prepared by a reaction between TTF and I_2.[5] In the acetonitrile solutions, copper(II) ions act as oxidants, but

---

(1) (a) Universidad de Sonora. (b) University of Arizona.
(2) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Chem. Commun.* **1985**, 1043.
(3) Inoue, M. B.; Inoue, M.; Fernando, Q.; Nebesny, K. W. *Inorg. Chem.* **1986**, *25*, 3976.
(4) Inoue, M.; Inoue, M. B.; Cruz-Vázquez, C.; Roberts, S.; Fernando, Q. *Synth. Met.* **1987**, *19*, 641.
(5) Anal. Calcd for $C_6H_4S_4I_{0.7}$: C, 24.58; H, 1.37; I, 30.30. Found: C, 25.29; H, 1.40; I, 30.78. The preparation of this compound was reported by: Wudl, F.; Schafer, D. E.; Walsh, W. H., Jr.; Rupp, L. W.; DiSalvo, F. J.; Waszczak, J. V.; Kaplan, M. L.; Thomas, G. A. *J. Chem. Phys.* **1977**, *66*, 377 and references therein.