CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF STONY BROOK, STONY BROOK, NEW YORK 11790

Experimental Evidence Concerning the Electronic Structure of the Nb_6Cl_{12} Cluster[1a,b]

BY RAYMOND A. MACKAY[1c] AND ROBERT F. SCHNEIDER

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The preparation of the compounds $((C_6H_5)_4N)_n(Nb_6Cl_{12})Cl_6$ ($n = 2, 3, 4$) is described as are the results of conductance measurements, magnetic susceptibility studies, far-infrared absorption, and electron spin resonance studies on these compounds. The solution esr spectrum shows ^{93}Nb nuclear hyperfine structure. The above results are interpreted in the light of the structure and bonding of these niobium complexes.

Introduction

In the course of some studies on staphylonuclear complexes, we have prepared and isolated a series of salts containing the anionic complexes $(Nb_6Cl_{12})L_6^{n-}$ (n = 2, 3, 4). Three of these are of particular interest: $((C_2H_5)_4N)_4(Nb_6Cl_{12})Cl_6$ (I), $((C_2H_5)_4N)_3(Nb_6Cl_{12})Cl_6$ (II), and $((C_2H_5)_4N)_2(Nb_6Cl_{12})Cl_6$ (III), since they represent three distinct oxidation states of the Nb_6Cl_{12} cluster. McCarley, *et al.*,[2] have observed similar oxidation–reduction chemistry in the analogous Ta_6Cl_{12} system and have demonstrated[3] a two-electron oxidation of the $Nb_6Cl_{12}^{2+}$ species by polarography in aqueous solution. Schafer[4] has reported a paramagnetic $(Ta_6Cl_{12})Cl_3$ in the analogous series of tantalum complexes. We report here the preparation and some physical properties of the compounds I, II, and III listed above. The results of analyses, conductance measurements, magnetic susceptibility studies, electron spin resonance, far-infrared absorption, polarography, and ultraviolet–visible absorption are presented and the implications on proposed schemes for the electronic structure of such complexes are considered.

Experimental Section

(1) **Preparation of $Nb_6Cl_{14} \cdot nH_2O$.**—This compound was prepared by the method of Harned, *et al.*,[5] and was used in the preparation of each of the subsequent compounds.

(2) **Preparation of $((C_2H_5)_4N)_4(Nb_6Cl_{12})Cl_6$ (I).**—$Nb_6Cl_{14} \cdot nH_2O$ is dissolved in absolute ethanol by refluxing and the solution transferred to a three-neck flask fitted with a gas bubbling tube, a dropping funnel with a pressure equalizing side arm which contains a large stoichiometric excess of $(C_2H_5)_4NCl$ dissolved in absolute ethanol, and a gas outlet tube leading to an oil bubbler. The gas inlet system is arranged to permit a regulated flow of HCl gas, N_2 gas, or a mixture of both. The solution is purged with nitrogen for about 30 min, an ice bath then placed around the flask, the nitrogen flow reduced, and HCl gas bubbled through the solution for 10–15 min. The $(C_2H_5)_4NCl$ solution is then added and the stirring, provided by a Teflon-encased spin bar and magnetic stirrer, momentarily increased. After the HCl flow has been continued for an additional 10 min, it is stopped and the solution again purged with nitrogen to remove excess HCl gas. The solution is quickly transferred to a round-bottom flask which is placed on a rotating evaporator fitted with a guard (collector) tube. The solution is concentrated on the evaporator, which is under vacuum from a water aspirator, using a hot water bath. When a precipitate appears, the flask is let cool and removed from the evaporator, and the brownish green material filtered off, washed with ethanol and ether, and dried in air.

(3) **Preparation of $((C_2H_5)_4N)_3(Nb_6Cl_{12})Cl_6$ (II).**—$Nb_6Cl_{14} \cdot nH_2O$ is dissolved in absolute ethanol by refluxing, and the solution is placed in an ice bath and saturated with HCl gas. The ice bath is then removed and oxygen gas bubbled through the solution for about 30 min. Excess $(C_2H_5)_4NCl$ is added, and the solution is stirred well and then concentrated on a rotating evaporator with a hot water bath until a precipitate appears. The brown material is filtered off, washed with ethanol and ether, and dried in air. Alternatively, iodine (with no HCl gas) may be used as the oxidizing agent.

(4) **Preparation of $((C_2H_5)_4N)_2(Nb_6Cl_{12})Cl_6$ (III).**—$Nb_6Cl_{14} \cdot nH_2O$ is dissolved in absolute ethanol by refluxing and chlorine gas is passed through the solution for about 20 min. Upon addition of excess $(C_2H_5)_4NCl$ an olive-green precipitate appears which is let settle, filtered off, washed with ethanol and ether, and dried in air. Bromine may also be used as the oxidizing agent, but a large excess of bromine is to be avoided since infrared evidence indicated that this leads to complexes containing polyhalide anions.

(5) **Physical Measurements.**—Conductance measurements were made at 24° on nitromethane solutions at concentrations of 10^{-3}–10^{-4} M. Polarographic studies were made on a Sargent recording polarograph in DMSO solution with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. Both a rotating platinum electrode and a dropping mercury electrode were used. Infrared spectra were obtained from Nujol mulls and nitromethane solutions on a Perkin-Elmer Model 521 (300–3900 cm^{-1}) using KRS-5 windows and on a Perkin-Elmer Model 301 (50–400 cm^{-1}) using polyethylene windows. Magnetic susceptibility measurements were carried out using a Gouy Balance. Electron spin resonance spectra were obtained on a Varian V4500 spectrometer system operating at 9.5 GHz, with a field modulation frequency of 100 kc/sec. Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer using 10-mm quartz cells with the solvent as reference.

(6) **Analyses.**—Niobium and chlorine were determined as Nb_2O_5 and AgCl after appropriate degradation of the complexes. Carbon, hydrogen, and nitrogen analyses were carried out by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Results

The analytical results and molar conductances in nitromethane are given in Table I. The molar conductances are consistent with formulations of II and

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[1] (a) Taken in part from a thesis for the Ph.D. degree presented to State University of New York at Stony Brook; (b) work supported by National Science Foundation Grant GP3838; (c) NSF Cooperative Graduate Fellow.

[2] R. E. McCarley and J. H. Espenson, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

[3] R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *Inorg. Chem.*, **4**, 1491 (1965).

[4] H. Schafer and H. Schnering, *Angew. Chem.*, **76**, 833 (1964).

[5] H. S. Harned, C. Pauling, and R. B. Corey, *J. Am. Chem. Soc.*, **82**, 4815 (1960).

TABLE I

ANALYSES AND MOLAR CONDUCTANCES IN NITROMETHANE

	% Nb		% Cl		% C		% H		% N		Concn, M	Molar conductance, ohms^{-1} cm^2 mole^{-1}
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$((C_2H_5)_4N)_4(Nb_6Cl_{12})Cl_6$ (I)	32.4	32.5	37.0	37.2	20.9	22.4	4.42	4.70	3.34	3.26	1.27×10^{-4}	334
$((C_2H_5)_4N)_3(Nb_6Cl_{12})Cl_6$ (II)	35.2	35.2	39.8	40.2	17.7	18.2	3.81	3.78	2.62	2.65	1.34×10^{-4}	283
$((C_2H_5)_4N)_2(Nb_6Cl_{12})Cl_6$ (III)	38.2	38.3	43.6	43.8	14.6	13.3	2.89	2.77	2.10	1.93	1.35×10^{-4}	178

III to be 3:1 and 2:1 electrolytes, respectively. The value obtained for compound I seems reasonable for a 4:1 electrolyte and is further supported by a value of 334 ohm^{-1} cm^{-1} mole^{-1} found by us for the compound $[(MO_6Cl_8)(DMSO)_6](ClO_4)_4$.

Polarographic studies in DMSO of the salts containing $(Nb_6Cl_{12})Cl_6{}^{3-}$ (II) and $(Nb_6Cl_{12})Cl_6{}^{2-}$ (III) each give two waves of equal height at +0.70 ± 0.5 v and −0.10 ± 0.5 v relative to a sce. Apparently, these two half-waves coalesce into the single one reported at 0.426 v (relative to hydrogen) for aqueous solutions by McCarley, *et al.*[2] We propose that these two half-waves correspond to the processes[6]

$$[Nb_6Cl_{12}]^{2+} \longrightarrow [Nb_6Cl_{12}]^{3+} + e^-$$

and

$$[Nb_6Cl_{12}]^{3+} \longrightarrow [Nb_6Cl_{12}]^{4+} + e^-$$

We note here also that, while in aqueous solution, iodine is a sufficiently strong oxidant to cause the two-electron oxidation,[2] in ethanol it effects only a one-electron oxidation of $[Nb_6Cl_{12}]^{2+}$.

The magnetic data are of particular interest. Robin and Kuebler[7] report that $Nb_6Cl_{14}\cdot 7H_2O$ is diamagnetic but has a large temperature-independent paramagnetism (850×10^{-6} cgs unit). Schafer[8] has measured the susceptibility of anhydrous Nb_6Cl_{14} and finds that this compound is also diamagnetic. These and several other relevant measurements show that the 2+ state of the Nb_6Cl_{12} species is diamagnetic.

Our bulk susceptibility data on compound II follow closely (from 77 to 300°K) the equation $\chi = [(3.23 \pm 0.001) \times 10^{-1}]/T - (358 \pm 23) \times 10^{-6}$ cgs unit. From the temperature dependence, we calculate a magnetic moment μ_{eff} of 1.615 ± 0.003 BM. The diamagnetic corrections we use are ($-\chi_D \times 10^6$ cgs unit): C, 6.00; H, 2.93; N, 5.55; H_2O, 13; Cl^-, 26; Nb($2^1/_3$+), 25; Nb($2^1/_2$+), 23.5; Nb($2^2/_3$+), 22. The last three values were calculated from the value given by Selwood[9] for Nb^{5+} and from the slope of the corrections given for molybdenum as a function of its oxidation state. These corrections yield for compound II a temperature-independent paramagnetism (χ_{TIP}) of 588×10^{-6} cgs unit. The same corrections applied to the uncorrected susceptibility reported for $Nb_6Cl_{14}\cdot 7H_2O$ by Robin[7] yield for that compound $\chi_{\text{TIP}} = 845 \times 10^{-6}$ cgs unit, and for Nb_6Cl_{14}, the uncorrected data of Schafer yield $\chi_{\text{TIP}} = 574 \times 10^{-6}$ cgs unit. Our measured susceptibility of compound III is

$$\chi = \frac{(2.8 \pm 0.2) \times 10^{-2}}{T} - (376 \pm 51) \times 10^{-6} \text{ cgs unit}$$

The temperature-dependent term for this compound yield an effective moment of 0.47 ± 0.02 BM, which we attribute entirely to the contamination of compound III with a paramagnetic impurity. McCarley[10] has since prepared the identical compound in a pure state and obtained a value of 0.02 BM from measurements of its magnetic susceptibility.

The electron spin resonance spectrum of the paramagnetic compound II was obtained for the solid and solutions in ethanol, nitromethane, and DMSO all at room temperature and in DMF at temperatures down to −60°. The spectrum (see Figure 1) of the solid showed a single broad resonance with a width of approximately 1000 gauss and corresponding to an average *g* value of 1.95 ± 0.05.

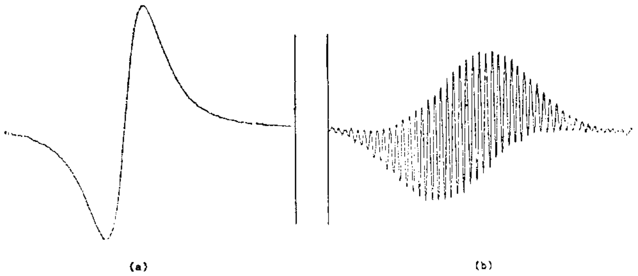

Figure 1.—Esr spectra of $((C_2H_5)_4N)_3(Nb_6Cl_{12})Cl_6$: (a), polycrystalline solid; (b), nitromethane solution.

The solution spectrum at room temperature in ethanol, nitromethane, and DMSO solvents is a symmetrical multiline pattern of 49 detectable components, a low resolution trace of which is shown in Figure 1. Since the nuclear spin of ^{93}Nb (100% natural abundance) is $^9/_2$, the number of lines expected in the hyperfine splitting of a single electron delocalized uniformly over six equivalent Nb atoms is 55. The outermost components of such a pattern are expected to be of very low relative intensity and inability to observe the outermost 3 lines on each side of the pattern is not considered significant. The existence of twelve further equivalent chlorine nuclei each with spin $^3/_2$ would seem to make difficult an attempt at establishing further delocalization of the electron to the bridging chlorine atoms.

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[6] We write the electrode processes schematically since the state of complexation of the cluster species in DMSO solution is uncertain.

[7] M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, **4**, 978 (1965).

[8] V. Simon, H. Schnering, H. Wohrle, and H. Schafer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

[9] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 78.

[10] P. B. Fleming, T. A. Dougherty, and R. E. McCarley, *J. Am. Chem. Soc.*, **87**, 159 (1967).

TABLE II

FAR-INFRARED BANDS OF I, II, AND III (cm^{-1}) IN NUJOL MULLS AND NITROMETHANE SOLUTIONS

$((C_2H_5)_4N)_4(Nb_6Cl_{12})Cl_6$ (I)	340 s	279 s	234 ms	198 m	143 w[a]
$((C_2H_5)_4N)_3(Nb_6Cl_{12})Cl_6$ (II)	346 s	290 s	251 s	198 m	142 w[a]
$((C_2H_5)_4N)_2(Nb_6Cl_{12})Cl_6$ (III)	353 s	302 s	267 s	193 wm	141 wm[a]

[a] Not observed in nitromethane solution because of solvent interference; s, strong; m, medium; w, weak.

TABLE III

ULTRAVIOLET–VISIBLE ABSORPTION BANDS OF $((C_2H_5)N)_n(Nb_6Cl_{12})Cl_6$ IN ETHANOL AND NITROMETHANE[a]

	$n = 4$ (2+)		$n = 3$ (3+)		$n = 2$ (4+)	
Band	C_2H_6O (ε)	CH_3NO_2 (ε)	C_2H_5OH	CH_3NO_2 (ε)	C_2H_5OH	CH_3NO_2 (ε)
A		7.6 (1.5)		7.6 (1.6)		
	10.8[a] (4.3)		10.4[c]			
B		9.9 (1.5)		9.9 (1.6)	10.7	10.7 (0.9)
C	17.0[b] (0.5)	15.3[b] (0.3)	*d*	14.6[b] (0.3)	*d*	14.4[b] (0.4)
D	19.8[b] (1.0)	18.8[b] (0.9)	18.2[b]	18.0[b] (0.9)	17.5[b]	18.5[b] (0.8)
E	24.7 (11.8)	22.7 (11.2)	23.5	22.7 (11.8)	22.1	21.9 (14.0)
F	30.8[b] (4.3)		*d*		*d*	
G	35.5 (16.0)		34.7		33.7	
H	43.5[b] (39.0)		43.5[b]		42.7[b]	
I	46.7 (83.0)		45.9		45.6	

[a] Frequencies in kK, ε in l. $mole^{-1}$ cm^{-1} × 10^3. [b] Shoulder. [c] Independent evidence shows that this band is a superposition of two close lying bands. [d] Probably obscured by other bands.

The persistence of the symmetric solution spectrum in DMF down to −30° leads us to believe that the splitting is intrinsically isotropic. We are able to fit the observed spectrum in nitromethane with the Hamiltonian $\mathcal{H} = -g\beta HS + aI \cdot S$. Because of the large total nuclear spin, the second-order contributions to the energy levels of the above Hamiltonian were included but they are found to produce corrections which border on the limits of the experimental error. The constants we obtain from the spectrum are $g = 1.948 \pm 0.003$ and $a = 20.6 \pm 0.5$ gauss.

To substantiate the similarity of the three compounds in question, we present the results of infrared spectroscopic investigations. Table II summarizes the absorption bands observed in the far-infrared region. Above 400 cm^{-1}, only bands due to $(C_2H_5)_4N^+$ are observed. The close similarity of the spectra are to be noted as are the systematic shifts upward in frequency with increase in oxidation state of the first three bands. We are able to account for these three bands as motions involving primarily the bridging chlorines[11] while the fourth, relatively unshifted band corresponds to the F_{1u} infrared-active stretch of the six terminal chlorine atoms. The lowest band is tentatively considered to involve primarily a motion of the Nb_6 octahedron.

The increase of frequency with increasing oxidation state is not uncommon in transition metal halide complexes. The identity of the mull and solution spectra supports the view that crystallographic distortions are minimal.

The ultraviolet–visible absorption spectra of compounds I, II, and III in ethanol and in nitromethane are given in Table III. The compounds are only slightly soluble in ethanol and for that reason those solutions were prepared by boiling the solids in ethanol. The solubilities in nitromethane are sufficiently high so that nitromethane solutions were made up at room temperature.

The qualitative similarities in the spectra of the three compounds in a given solvent are to be noted, as should also the differences in the spectra between the nitromethane and ethanol solutions. The most striking qualitative feature is the lack of observation of band A in the doubly oxidized species.

Conclusions

We conclude from the bulk magnetic properties of the compounds I, II, and III as a function of oxidation state of the Nb_6Cl_{12} cluster that, in the absence of a reordering of the electronic energy levels, the topmost filled orbital in the cluster is nondegenerate. We further conclude from the fact that the symmetric electron spin resonance pattern of the compound containing the cluster in the 3+ state is explained by a single hyperfine interaction constant that this orbital is delocalized symmetrically over the entire Nb_6 octahedron.

That there is no significant reordering of the electronic energy levels is likely from the close similarity of the ultraviolet–visible absorption spectra of the three compounds. The absence of a band in the 4+ state is expected since a level which previously contained 2 and 1 electrons (in the 2+ and 3+ states, respectively) is now empty. Transitions *to* that level are expected on other grounds to occur at lower frequency.

The infrared results show that there is no drastic change in geometry as the cluster is oxidized. The agreement between solution and solid (mull) spectra shows that the local symmetry of the complex is high even in the solid state.

The bulk susceptibility data on the 3+ state (μ_{eff} = 1.62 BM) indicate that the observed paramagnetism corresponds quite closely to that expected from the spin-only value for one electron. The closeness of g (1.95) to the free-electron value further supports this description and yields independently for $\mu_{eff} = g\sqrt{S(S+1)}$ the value 1.69 BM assuming $S = 1/2$.

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[11] R. Mackay and R. F. Schneider, to be published.

There is, therefore, no extensive spin–orbit coupling in this system.

Two recent studies of esr on niobium(IV) complexes have been reported. Rasmussen, *et al.*,[12] have studied NbCl$_5$(OCH$_3$)$^{2-}$ and find an average (both the hyperfine interaction and g tenson are anisotropic) hyperfine interaction constant $a = 178 \pm 3$ gauss with $g = 1.861 \pm 0.002$. Lardon and Gunthard[13] have examined what is presumed to be NbCl$_6^{2-}$ and find $a = 177.4 \pm 0.1$ gauss and $g = 1.892 \pm 0.001$. The former complex has niobium(IV) in an approximately tetragonal (C_{4v}) environment. This corresponds to the same local symmetry about a niobium atom in our complexes.

Our value of the hyperfine interaction constant of 20.6 ± 0.5 gauss is slightly less than *one-sixth* of both the constants reported above (29.7 gauss). It supports strongly the use of niobium d orbitals as the basis for the metal–metal bonding within the octahedron. An orbital which can potentially be effective in bonding together the metal octahedron is an a_{2u} (representation of the group O_h) orbital which has been shown by Cotton and Haas[14] to arise from the metal d_{xy} orbitals. Kettle[15] has pointed out that this orbital can be considered to be of a three-center (maximum density above the octahedral faces) type, and we propose that the a_{2u} orbital is in fact the only reasonable choice for the top filled level in the Nb$_6$Cl$_{12}^{2+,3+}$ species. This is consistent with the bonding scheme given by Cotton and Haas[14] for values of $p \geq 8.3$.[16] It further suggests that the scheme of Robin and Kuebler[7] does not explain the magnetic properties without a substantial reordering of levels.

This work then supports the general principles and assumptions used by Cotton and Haas in their molecular orbital treatment of the M$_6$X$_{12}$ unit and suggests that proper inclusion of the effects of the chlorine atoms (both bridging and terminal) may well produce an energy level scheme of more than qualitative significance.

We wish to mention further that we have looked for both niobium and chlorine nuclear quadrupole resonance in these compounds. We have searched the region from 10 to 40 Mc at both 24 and −196° with a superegenerative spectrometer incorporating coherence control of the type described by Peterson and Bridenbaugh[17] with no success. We have also searched the region from 2 to 16 Mc at 24° with a Varian Model V-4210 broad-line nmr spectrometer and probes, again without success. The sharpness of the hyperfine components of the esr absorption suggests that the field gradient at niobium is relatively small so that a niobium quadrupole resonance could be expected to fall in the range which we have investigated. The chlorine resonance should certainly fall in this region. The lack of observation of any resonances whatever may be attributable to broadening by the large number of protons due to the tetraethylammonium cation.

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(15) S. F. A. Kettle, *Theoret. Chim. Acta* (Berlin), **3**, 211 (1965).

(16) p is defined in ref 15 as the product of the metal atom Slater orbital exponent and the metal–metal internuclear separation.

(17) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Inst.*, **35**, 698 (1964).

Contribution from the Department of Chemistry, University of Louisville, Louisville, Kentucky,
and Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

Magnetic Properties and Electronic Structure of Lanthanum Hydrides[1]

By WILLIAM G. BOS[2] and H. S. GUTOWSKY

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Previously, the nuclear magnetic properties of the lanthanum hydrides have been interpreted in terms of a protonic model while the bulk susceptibilities have been attributed to a hydridic structure. The experimental results and their theoretical relation to the electronic structure are discussed. A simple band model is used to show that the hydridic structure also can account for the magnetic resonance results. Application of the band model to other metallic hydrides is considered briefly.

Three different models have been used to describe the bonding in metallic hydrides: the protonic model, the atomic model, and the hydridic model. In the protonic model the hydrogen is supposed to exist as an essentially bare proton, the hydrogen electrons having been lost to the conduction band of the metal. In the hydridic model, on the other hand, the hydrogen species is pictured as carrying a full negative charge. The atomic model is an intermediate version; it considers these hydrides to be alloylike in character with a partial charge, either positive or negative, on the hydrogen. The general arguments for and against each of these models have been reviewed by Gibb[3] and by Libowitz.[4]

Nuclear magnetic resonance shifts, similar to the Knight shifts observed in metals, have been observed

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(1) Presented at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966.

(2) Department of Chemistry, University of Louisville, Louisville, Ky.

(3) (a) T. R. P. Gibb, Jr., Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 99; (b) *Progr. Inorg. Chem.*, **3**, 315 (1962), see especially pp 335–372.

(4) G. G. Libowitz, "Solid State Chemistry of Binary Metal Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1965.