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Electron Spin Resonance in the Pentachloromethoxoniobate(IV) Ion[1]

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Electron spin resonance at 3.2 cm. has been observed from the $Nb(OCH_3)Cl_5^{2-}$ ion in dilute methanol solution saturated with HCl. Measurements were made at 300 and at 77°K. and both the isotropic and anisotropic g values and hyperfine splittings due to the ^{93}Nb (100%) nucleus were observed. The results are interpreted in terms of an approximate molecular orbital approach to the bonding which takes into account the effect of charge-transfer states.

The pentachloroalkoxo complexes of niobium, previously reported by Wentworth and Brubaker,[2] are mononuclear complexes which show the spin-only paramagnetism expected for a d^1 ion. In the present work, we have studied the e.s.r. spectrum of the methoxo complex in frozen methanol glass and in liquid solution at 300°K. (Figure 1). This is the first e.s.r. study on a well-characterized complex of niobium(IV), and one of the few such studies carried out for a second transition row element.[3,4] Fedotov, *et al.*,[5] have reported resonance absorption from a species assumed to be $NbCl_4$, but no chemical evidence for its identity was given.

Experimental

The sample was prepared by the method of Wentworth and Brubaker,[2] except that the electrolyzed solution was not treated with a nitrogen base to precipitate $Nb(OCH_3)Cl_5^{2-}$ but was instead introduced into a 3-mm. e.s.r. sample tube. The optical spectrum of the solution exhibits the same features as obtained[6] by reflectance measurements on the solid tetramethylammonium salt, indicating that the microsymmetry is the same for the niobium atom in either case. There is a maximum at 500 mμ and end absorption beginning at about 400 mμ.

The spectra were obtained at 3.2 cm. on a Varian V-4500-10A e.s.r. spectrometer with 100-kc. field modulation. The magnet field was calibrated with proton resonance markers. First derivative presentation of the signal was used.

Results

In methanol glass at 77°K. the e.s.r. spectrum may be described by a spin Hamiltonian with axial symmetry.[7]

$$H = g_{\|}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + AS_zI_z + B(S_xI_x + S_yI_y) \qquad (1)$$

where $S = {}^1/_2$, $I(^{93}\mathrm{Nb}:\ 100\%) = {}^9/_2$. At room temperature in liquid solution, the anisotropies are averaged to zero, and the Hamiltonian becomes

$$H = \langle g\rangle\beta H\cdot S + \langle a\rangle I\cdot S \qquad (2)$$

$$\langle g\rangle = (1/3)(g_{\|} + 2g_{\perp}) \qquad (3)$$

$$\langle a\rangle = (1/3)(A + 2B)$$

The eigenvalues of eq. 2 to second order are[8]

$$\omega = \langle g\rangle\beta H_0 + \langle a\rangle m_I + \frac{\langle a\rangle^2}{2\langle g\rangle\beta H_0}[I(I + 1) - m_I^2] \qquad (4)$$

The isotropic line width is approximately the same magnitude as the splitting. The natural line width is probably broadened by the interaction of the chlorine nuclear moments with the electron spin. The end-to-end distance for the isotropic spectrum is about 2000 gauss, and $\langle g\rangle = 1.861 \pm 0.002$ and $\langle a\rangle = 178 \pm 3$ gauss.

Because this ion resembles the vanadyl ion in electronic structure and symmetry type, we may assume that the relative magnitudes of A and B in eq. 1 are the same as for the vanadyl ion.[6,8,9] With this assumption and eq. 4, we may assign the lines on the low-field end of the anisotropic spectrum to the $g_{\|}$ set and determine that

$$|A| = 248 \pm 6 \text{ gauss} \qquad g_{\|} = 1.965 \pm 0.008 \qquad (5)$$

$$|B| = 144 \pm 10 \text{ gauss} \qquad g_{\perp} = 1.809 \pm 0.010$$

The computed value for B fits the spectrum on the high-field end where the set of $g_{\perp}$ lines are expected to go above the base line,[8] but an exact fit is difficult because of the breadth of the lines.

Discussion

Having obtained the experimental e.s.r. parameters, we turn to a molecular orbital treatment in an effort to interpret them in terms of the bonding. If one neglects the methyl group, the pentachloromethoxoniobate(IV) ion has C_{4v} symmetry. The pertinent molecular orbitals are

$$\phi^*_{\pi1} = N_{\pi1}(\Psi d_{xz} - \lambda^{O}{}_{\pi1}\Psi^{O}{}_{p\pi} - \lambda^{Cl}{}_{\pi1}\Psi^{Cl}{}_{p\pi}) \qquad (6)$$

$$\phi^*_{\pi2} = N_{\pi2}(\Psi d_{xy} - \lambda^{Cl}{}_{\pi2}\Psi^{Cl}{}_{\pi p})$$

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(1) Supported by the U. S. Atomic Energy Commission under grant AT-(11-1)-1001.

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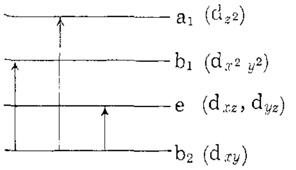
$$\phi^*_{\sigma 2} = N_{\sigma 2}(\Psi d_{x^2-y^2} - \lambda^{Cl}_{2s}\Psi^{Cl}_{2s} - \lambda^{Cl}_{p\sigma}\Psi^{Cl}_{p\sigma})$$

where, following Kon,[10] the metal s and p orbitals have been used to form hybrids but we have included covalent σ and π overlap of the ligand orbitals. The postulated order of the energy levels is as follows



The peak in the visible spectrum at 19,900 cm.$^{-1}$ can be assigned to the $b_2 \rightarrow b_1$ transition. The charge-transfer band which begins at 23,600 cm.$^{-1}$ probably masks the $b_2 \rightarrow a_1$ transition. In locating the energy levels and making spectral assignments, we have used the results of Ballhausen and Gray[11] on the similar vanadyl ion.

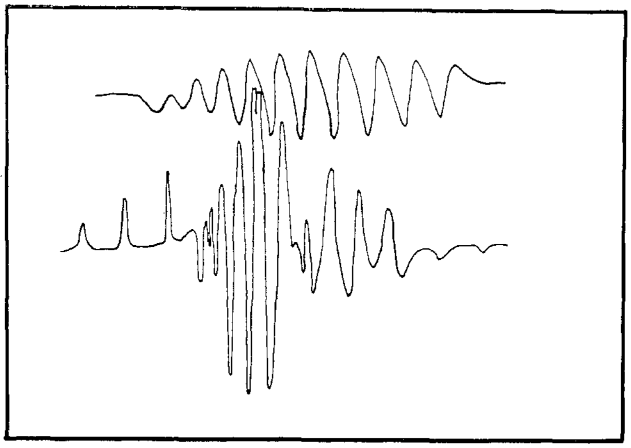


Figure 1.—E.s.r. spectra of the $[Nb(OCH_3)Cl_5]^{2-}$ ion in CH_3OH saturated with HCl: upper spectrum at room temperature; lower spectrum at liquid N_2 temperature; magnetic field increasing toward the right.

The $b_2 \rightarrow$ e transition was not observed, presumably due to the low intensity of the band and the experimental difficulties in the near-infrared region. Powdered samples of $[(CH_3)_4N]_2[Nb(OCH_3)Cl_5]$ in KBr pellets gave no absorption bands at either room temperature or at 77°K. in the region from 4000 to 14,000 cm.$^{-1}$ that were not given by samples of $(CH_3)_4NBr$ in the same matrix. It is of interest to note that the absorption band, in the visible region, assigned to the $b_2 \rightarrow b_1$ transition is perfectly symmetrical at room temperature and shows no sign of structure of the type observed by Ortolano, Selbin, and McGlynn[12] even though the spin coupling constant is much larger for niobium than it is for vanadium.

In order to obtain bonding parameters from our e.s.r. data we use the equations of Golding.[7] We have included the effects of covalent bonding

$$A = P\langle r^{-3}\rangle(4/7)N_{\pi 2}^2 - \langle a\rangle$$

$$B = P\langle r^{-3}\rangle(2/7)N_{\pi 2}^2 - \langle a\rangle \qquad (7)$$

where $P = g_e g_n B_{en}$ and is defined as positive for the case of ^{93}Nb which has a positive nuclear moment. $\langle r^{-3}\rangle$ is the reciprocal cube of the average radial distance of the outer electrons from the nucleus. In order to obtain the bonding coefficient, $N_{\pi 2}$ in eq. 7, we need to estimate $\langle r^{-3}\rangle$ for Nb^{4+}. For this purpose we use the empirical formula of Korol'kov[13,14]

$$\langle r^{-3}\rangle = \frac{\xi}{5.84Z}\left[C - 0.09 \ln \frac{\langle r^{-3}\rangle}{Z}\right]^{-1} \qquad (8)$$

where ξ is the spin–orbit coupling constant in cm.$^{-1}$, Z is the atomic number, and C is a constant depending on the period in which the element is found. To determine C for the 4d series, we use $\langle r^{-3}\rangle = 3.913$ a.u. computed for Nb^{3+} by Freeman and Watson.[15] The spin–orbit coupling constants for Nb^{3+} and Nb^{4+} are 670 and 748 cm.$^{-1}$, respectively.[16] If we use the values for Nb^{3+}, the constant, C, becomes 0.600 for the 4d series. If we substitute $C = 0.600$ into eq. 8 and make several iterations, we obtain $\langle r - ^3\rangle = 4.26$ for Nb^{4+}. From eq. 7 we now compute that $N_{\pi 2}^2 = 0.62$. The size of this coefficient indicates fairly extensive π-bonding by the chlorine atoms in the xy plane to the d_{xy} orbital of the niobium. The g values are given by

$$g_{\parallel} = 2.0023 - \frac{8\xi N_{\pi 2}^2 N_{\sigma 2}^2}{\Delta E(b_2 \rightarrow b_1)} + \frac{8\xi N_{\pi 2}^2(1 - N_{\sigma 2}^2)}{\Delta E_{\parallel}\text{ (charge transfer)}} \qquad (9)$$

$$g_{\perp} = 2.0023 - \frac{2\xi N_{\pi 2}^2 N_{\pi 2}^2}{\Delta E(b_2 \rightarrow e)} + \frac{2\xi N_{\pi 2}^2(1 - N_{\pi 1}^2)}{\Delta E_{\perp}\text{ (charge transfer)}} \qquad (10)$$

where we have neglected overlap terms, but have included a correction term for the presence of low-lying charge-transfer bands as introduced by Lacroix and Emch.[17] Following Ballhausen and Gray,[11] we assign the observable charge-transfer band at 30,000 cm.$^{-1}$ to $\Delta E_{\perp}$ and estimate $\Delta E_{\parallel} = 43{,}000$ cm.$^{-1}$ by comparing the relative electronegativities of chlorine and oxygen. In eq. 9 we take[9] $\xi = 748$ cm.$^{-1}$, ΔE ($b_2 \rightarrow b_1$) = 19,900 cm.$^{-1}$, and $\Delta E_{\parallel} = 43{,}000$ cm.$^{-1}$ and $g = 1.965$. We obtain $N_{\sigma 2}^2 = 0.45$, a value which is indicative of a rather covalent σ-bond between the chlorines and the niobium. Similarly, we might use eq. 10 to obtain $N_{\pi 1}^2$ if the quantity ΔE ($b_2 \rightarrow$ e) were known. If the transition $b_2 \rightarrow$ e lies in the near-infrared region as expected, $N_{\pi 1}^2$ would be of about the same magnitude as $N_{\pi 2}^2$, which is reasonable. It must be emphasized that these values are the result

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of an incomplete theoretical treatment and are dependent upon spectral assignments which must be considered tentative until more is known about second row transition metal spectra. The assumption that the ΔE ($b_2 \rightarrow e$) transition is of high enough energy to lie in the near-infrared region is supported by the room temperature e.s.r. spectrum for this complex, which is easily observed. The existence of an e.s.r. spectrum at room temperature implies a long relaxation time and a substantial separation of the ground and first excited electronic levels.

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Tetrahedral Bromide Complexes of Nickel(II) in Organic Solvents

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A spectrophotometric study of complexes of nickel(II) with bromide in acetone solution has shown that two tetrahedral complexes are formed. One complex is known to be $NiBr_4^{-2}$, and the other is shown to be a solvated complex of the type $Ni(solv)Br_3^-$. The same complexes are formed in tetrahydrofuran, dimethylacetamide, methyl ethyl ketone, acetonitrile, and nitromethane.

Introduction

In recent years, much attention has been directed to the use of organic solvents as convenient media for the production of halide complexes of the transition metals. In the case of nickel(II), where no definite evidence for complexes other than the monohalo has been found for aqueous solution,[1] complexes with up to four coordinated halides can be formed in organic solvents. Chloride complexes of nickel(II) have been studied in nitromethane,[2-4] acetonitrile,[4-7] dimethylformamide,[3,7-9] dimethylacetamide,[7] ethanol,[3] and trimethyl phosphate.[5] Bromide complexes have been studied in nitromethane,[2-4] acetonitrile,[4] dimethylformamide,[3] and acetone.[10,11] The investigators, using spectrophotometric, conductometric, and magnetic techniques, have shown that the highest halide complex produced in these solvents is tetrahedral NiX_4^{-2}, and that various other complexes can be formed, the higher complexes being tetrahedral and the lower complexes octahedral. We have investigated the behavior of the nickel(II)–bromide system in various organic solvents with the view of obtaining more definite information as to the structure and absorption spectra of the different species produced in these solvents. The present paper deals with the higher, tetrahedral complexes.

The spectrum of the tetrahedral tetrabromo nickelate ion is now well known, both in the solid state and in solution.[2-4] Goodgame, Goodgame, and Cotton observed the solvolysis of $NiBr_4^{-2}$ to a lower tetrahedral complex in acetonitrile and nitromethane and postulated the lower complex to be $NiBr_3(solv)^-$, where "solv" represents a coordinated solvent molecule. Šramko has observed the formation of a species with similar spectral characteristics as one of the steps in the production of $NiBr_4^{-2}$ by the addition of bromide to acetone solutions of nickelous perchlorate[11] and has also assigned the species the formula $NiBr_3^-$. This assignment is reasonable, but a more conclusive demonstration of the nature of the species and a more precise picture of its absorption spectrum seems desirable. In the present investigation, acetone was employed as a solvent for a detailed study of the higher complexes. The results obtained for acetone solution were used to interpret observations in other solvents.

Experimental

Materials.—Nickelous perchlorate hexahydrate was recrystallized G. F. Smith Co. $Ni(ClO_4)_2 \cdot 6H_2O$. The nickel content of the salt was checked by gravimetric analysis with dimethylglyoxime. Anhydrous nickelous bromide was prepared by treating nickelous carbonate with hydrobromic acid and evaporating to dryness. The composition was checked by bromide analysis. Tetraethylammonium tetrabromonickelate was prepared according to Gill and Nyholm.[2] Lithium bromide was Mallinckrodt N.F. VIII, recrystallized from water and ethanol, dried at 110°, and stored in a vacuum desiccator. Tetraethylammonium bromide was recrystallized Eastman salt. Lithium perchlorate was G. F. Smith Co. $LiClO_4$.

All solvents were Spectro grade. Acetone, acetonitrile, and tetrahydrofuran were dried over magnesium sulfate and redistilled, then passed through an alumina column. Nitromethane was purified according to Larson and Iwamoto.[12]

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