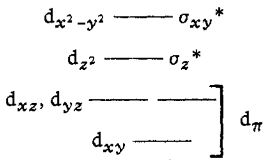
The one-electron energy level ordering for $Co(CN)_5(X)^{n-}$ is



For isoelectronic, isostructural $W(CO)_5(py)$,[17] wavelength-dependent yields of the type obtained here are rationalized by consideration of the bonding changes occurring upon one-electron LF excitation. It is likely that population of σ_z^* and σ_{xy}^* have very different effects on ligand lability with the former tending to give loss of the OH^- or OH_2 and axial CN^- while σ_{xy}^* should labilize the equatorial CN^-'s. The trend for efficiency of CN release as a function of wavelength is like that for CO release from $W(CO)_5(py)$ where the two LF states account for the observations.[17] Assuming a total possible reaction yield of unity the maximun $\Phi_{\text{loss OH}^-}/\Phi_{\text{loss CN}^-}$ is ~20 at 366 nm while for $\Phi_{\text{loss OH}_2}/\Phi_{\text{loss CN}^-}$ the experimental ratio is in excess of 200.[18] Thus, for the OH^- case there is a dramatic lowering of the ratio which is consistent with the prediction that the Co-OH π bonding will tend to be strengthened in the LF states since the π^* level is depopulated.[19,20] Alternate explanations for differing reactivity of $Co(CN)_5(OH)^{3-}$ and $Co(CN)_5(OH_2)^{2-}$ exist and include the possibility that electrostatic effects may assist more efficient CN^- release from the more highly charged complex.[21]

Registry No. $Co(CN)_5(OH_2)^{2-}$, 14842-83-2; $Co(CN)_5(OH)^{3-}$, 16893-73-5.

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(17) M. Wrighton, G. S. Hammond, and H. B. Gray, *Mol. Photochem.*, in press.

(18) This is a very conservative estimate since we are taking 0.2 as the minimum quantum yield for photoexchange of H_2O which is the yield obtained for the production of $Co(CN)_5I^{3-}$ by irradiation of $Co(CN)_5OH_2{}^{2-}$ in the presence of 2 *M* I^- at 380 nm.[1b]

(19) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, in press.

(20) J. I. Zink, *J. Amer. Chem. Soc.*, 94, 8039 (1972).

(21) We thank a referee for suggesting that we point this out.

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Nuclear Magnetic Relaxation of the Antimony-121 Nucleus in Tetramethylantimony Cation

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One of the interesting aspects of the chemistry of tetraphenylantimony ions is their ability to form five-coordinate derivatives in the solid state. X-Ray diffraction studies of both hydroxyltetraphenylantimony[1] and methyloxytetraphenylantimony[2] show them to be pentacoordinate trigonal bipyramids with OH and OCH_3, respectively, in one of the axial positions. Recent studies of the vibrational spectroscopy of tetraphenylantimony cation[3] indicate that it may exist in aqueous solution as the five-coordinate cation species $(C_6H_5)_4SbOH_2{}^+$. To provide more evidence on the geometry of tetraphenylantimony cation in aqueous solution, we have studied the nuclear relaxation of the ^{121}Sb nucleus in tetramethylantimony cations and tetraphenylantimony cations using pulsed nmr spectroscopy. Tetramethylantimony cation is known to be tetrahedral in aqueous solution[4] and will provide a model of tetrahedral symmetry.

Table I

Salt	Concn, *M*	Solvent	T_2, msec
$(CH_3)_4SbI$	1.0	H_2O	0.14
$(CH_3)_4SbI$	0.1	H_2O	0.24
$(CH_3)_4SbI$	0.1	Methanol	0.07
$[(C_6H_5)_4Sb]_2SO_4$	0.5	H_2O	Not obsd
$(C_6H_5)_4SbCl$	0.1	Methanol	Not obsd
$SbCl_6{}^-$	~1	5 *m* HCl	0.15
$SbCl_4{}^-$	~1	5 *m* HCl	Not obsd

Both the naturally abundant antimony isotopes, ^{121}Sb and ^{123}Sb, have magnetic dipole moments and electric quadrupole moments. ^{121}Sb is the more favorable from an nmr standpoint because of its higher natural abundance (57.25%) and its higher intrinsic sensitivity (0.16 relative to ^1H at constant field). Unfortunately, the liquid-phase resonances of both isotopes tend to be extremely broad when antimony is in a site of less than cubic symmetry due to the large electric quadrupole coupling constant. We have been unable to find any recorded values for the relaxation times of antimony nuclei as salts in the liquid phase in the literature.

For nuclei with large electric quadrupole moments the dominant mechanism of nuclear relaxation is due to the interaction of the quadrupole moment with the electric field gradient at the nucleus. Equation 1 relates the quadrupole coupling constant ($e^2Qq/\hbar$) to the magnetic relaxation times, T_1 and T_2.[5,6]

$$\frac{1}{T_1}=\frac{1}{T_2}=\frac{3}{125}\left(\frac{e^2Qq}{\hbar}\right)^2\tau_c \qquad (1)$$

The asymmetry parameter is taken to be zero. If the molecular symmetry is cubic or higher, the electric field gradient vanishes and T_2 increases, usually by about three orders of magnitude. This behavior is shown in relaxation times of various boron compounds. In tetrahedral ions such as $^{11}BH_4{}^-$, T_1 is about 10 sec. In three-coordinate boron compounds, values of T_1 are about 10 msec.[6] Similarly, T_2's for ^{55}Mn and ^{187}Re, both of which have large quadrupole moments, have been observed in solution only as tetrahedral oxy anions.[7,8]

Results and Discussion

T_2 values for the ^{121}Sb resonance of the tetramethylantimony cation under various conditions are listed in Table I. No signal was observed in solutions of the tetraphenylantimony salts, because T_2 in these solutions is shorter than the receiver dead time of the pulsed spectrometer (~10 μsec). Tetramethylantimony cation in aqueous solution gives a signal which is directly observable on an oscilloscope at concentrations above about 0.05 *M*. T_2 for this ion in aqueous solu-

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(1) K. Shem, W. E. McEwen, S. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *J. Amer. Chem. Soc.*, 90, 1719 (1968).

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(6) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971, Chapter 4.

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tion is about 200 μsec and is dependent on both concentrations and temperature. An Arrhenius plot of the longitudinal relaxation rate gives a value of 3.8 kcal/mol. This value is consistent with a correlation time, τ_c, produced by diffusional translation or reorientation.[7] The decrease in T_2 with increasing salt concentration is probably due to ion pairing at higher concentrations. Ion pairing would tend to distort the tetrahedral symmetry of the tetramethylantimony cation and reduce T_2. Ion pairing would also explain the relatively small T_2 value of tetramethylantimony cation in methanol, since the reduced dielectric constant of this solvent would tend to enhance the equilibrium concentration of ion pairs. Solutions of tetraphenylantimony sulfate in water and tetraphenylantimony fluoride and chloride in methanol were also studied but signals were not observed because of extremely short T_2's in these solutions. An upper limit of 10 μsec can be placed on the T_2 values for these ions. The octahedral structure of $SbCl_6^-$ is reflected in its relatively long relaxation time. The short T_2 of $SbCl_4^-$, on the other hand, indicates a nontetrahedral geometry for this anion as expected from the lone pair in the antimony valence shell.[9]

The extremely short relaxation found for tetraphenylantimony cations in aqueous solution demonstrates that the geometry of these ions deviates significantly from tetrahedral in aqueous solution. This result confirms the inferences made from a study of the vibrational spectra of tetraphenylantimony cation in aqueous solution.[3] From limited Raman evidence the authors also proposed that tetraphenylantimony chloride is tetracoordinate in methanolic solution. If tetraphenylantimony chloride were tetrahedral in methanolic solution, one would expect to observe a ^{121}Sb relaxation time comparable to that observed for the tetramethylantimony cation in methanol. Our data, therefore, do not support the previous interpretation of the Raman data.

Registry No. $(CH_3)_4SbI$, 2185-78-6; $SbCl_6^-$, 17949-89-2; ^{121}Sb, 14265-72-6; tetraphenylantimony cation, 15912-81-9.

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[9] The $SbCl_6^-$ resonance was observed at 780 ppm to the high field of tetramethylantimony cation.

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Erbium Hectoboride

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This note reports the preparation and characterization of single-phase erbium hectoboride, together with the electron microprobe and wet chemical analyses that were performed to determine more exactly the erbium to boron ratio. Previously, binary borides of composition MB_{50-100} (historically labeled as hectoborides) have been reported for yttrium,[1] ytterbium,[2,3] gadolinium,[2] holmium,[3] and plutonium.[4] In fact, Spear and Solovyev[5] have found that all of the lanthanide rare earth metals with the exception of lanthanum, cerium, and praseodymium form a hectoboride compound. However, the exact metal to boron ratio of this class of compounds has never been established with certainty. This uncertainty may simply result from the complexity of the structure and reflect variations in the degree of metal and/or boron occupancy of equivalent lattice sites. On the other hand, a reliable chemical analysis of this type of compound had never been performed prior to the investigation described in this note. Instead, the chemical compositions of MB_{50}, MB_{66}, MB_{70}, and MB_{100} have been inferred from less accurate means. For example, Smith and Gilles[2] have established the composition as GdB_{100} on the strength of relative intensities of X-ray diffraction maxima from patterns obtained on samples of overall compositions GdB_{49}, GdB_{99}, and GdB_{199}. In the case of YB_{66} the formula was inferred on the basis of the crystal structure analysis, as significant boron impurity precluded a meaningful direct chemical analysis.[6] Formulas have also been approximated from the known compositional makeup of the starting materials before synthesis; however, the final synthesized composition is almost certainly altered due to the preferential loss of one constituent.

Experimental Section

An assortment of arc-melted erbium–boron samples were prepared using β-rhombohedral boron of 99.98% purity and erbium sponge of 99.9% purity as the starting materials. Spectrographic analysis of the boron showed a total metal impurity level of less than 300 ppm, the major impurities in the erbium were calcium (<200 ppm), oxygen (300–700 ppm), and total rare earths (<400 ppm).

Using a water-cooled copper crucible, the samples were arc-melted in a glove box that had been evacuated to less than 10^{-5} Torr and back-filled with argon. Prior to each melt, a zirconium button was melted as an oxygen getter. Each erbium–boron button was flipped and remelted 4 times to ensure sample homogeneity. The resulting arc-melted buttons were of the order of 2–4 g, with compositions ranging from 93 to nearly 100 mole % boron. A button single phased with respect to erbium hectoboride was sought, upon which a reliable wet chemical analysis could be made.

Results and Discussion

Seven ingots with compositions ranging from 93 to nearly 100 mole % boron were prepared and cursorily examined by metallographic analysis. Six ingots were two phased, composed of either ErB_{12} and what appeared to be the hectoboride or the hectoboride and free boron. One sample was single phase, and because the starting composition was ErB_{70}, this ingot was felt to be pure erbium hectoboride. X-Ray diffraction analysis confirmed the single-phase nature of this button. The indexed pattern for this button is given in Table I [nickel-filtered copper radiation (λ_α 1.54178, λ_{α_1} 1.54051) and a Debye-Scherrer camera (diameter 114.6 mm) were used]. The lattice parameter was determined using selected back-reflection lines and a combination of Nelson–Riley and least-squares procedures. The structure is face-centered cubic with $a_0 = 23.440$, $\sigma = 0.003$ Å, com-

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