order rate constants on molecular iodine added and the increase of exchange rate with addition of traces of tetrabutylammonium halide to the reaction mixture all help to support the proposed reaction scheme.

Conclusion

The use of pseudo-first-order rate constants in a complete nmr line shape fitting to study chemical-exchange reactions requires no *a priori* mechanism to be assumed. In the present case due to the instability of the trimethyltin iodide and the unfavorable magnitude of halogen-exchange rates in the chloride-bromide mixture no activation parameters can be accurately determined. However, from the best fit parameters it is definite that the exchange of halogens among the molecules is by way of the halide ions resulting from the ionization of the trimethyltin halides according to reactions 2 and 3. The extent of ionization may be very small and the rates of ionization and recombination may also be low but the rate constants b_1 and b_{-1} for reaction 5 can be very large. The mere presence of the halide ions will keep the rapid halogen exchange going in reaction 5 which, in dynamic equilibrium, will not change the equilibrium concentrations of the halides and halide ions. Thus the forward specific rate constants a_1 and a_2 for reactions 2 and 3 need not be large for rapid halogen exchange as observed in the trimethyltin systems. The extent of ionization is definitely small as the species Me_3Sn^+ involved in the reactions presents no observable resonance under the highest gain conditions of the Varian HA-100 nmr spectrometer.

Registry No. Trimethyltin chloride, 1066-45-1; trimethyltin bromide, 1066-44-0; trimethyltin iodide, 811-73-4; iodine, 7553-56-2.

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Photochemistry of Aquo- and Hydroxopentacyanocobaltate(III)

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The chemistry of the excited states of cyanocobaltate(III) complexes parallels the known ground-state ligand substitution processes in several cases. The thermally inert $Co(CN)_6{}^{3-}$ undergoes photosubstitution[1-3] to yield $Co(CN)_5(OH_2)^{2-}$ in aqueous media. However, the lack of stereochemical significance for substitution in $Co(CN)_6{}^{3-}$ precludes conclusions regarding whether the photoreaction is a nonthermal process or merely a large acceleration of the thermal substitution rate. The C_{4v} $Co(CN)_5(X)^{n-}$ complexes could potentially yield differences in ground- and excited-state reactivity since there are three possible monosubstitution products. Unfortunately, for $X = Cl^-$,[1] Br^-,[1] I^-,[1] OH_2,[1,3] SCN^-,[4] and $N_3{}^-$,[4] the major photoreaction involves substitution of X to yield $Co(CN)_5(OH_2)^{2-}$ which is the same product that obtains in the ground state.[5,6] Complexes of the formula $Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3{}^{2-}$, OH_2, OH^-) undergo photosubstitution of $SO_3{}^{2-}$ and represent the only reported examples of cyanocobaltate(III) complexes which exhibit wavelength-dependent photochemistry and yield thermally inaccessible substitution products.[7]

We now report the photochemistry of $Co(CN)_5(OH)^{3-}$ and some new aspects of the photochemistry of $Co(CN)_5(OH_2)^{2-}$. The new reactions do not occur thermally at room temperature and are wavelength dependent.

Experimental Section

Preparation of $Co(CN)_5(OH_2)^{2-}$ and $Co(CN)_5(OH)^{3-}$. Aqueous 0.02 *M* solutions of $Co(CN)_5(OH_2)^{2-}$ were prepared by the photolysis of 0.02 *M* $Co(CN)_6{}^{3-}$ in distilled water irradiating with a Pyrex-filtered medium-pressure Hg lamp.[1-3] The $K_3Co(CN)_6$ was obtained from Alfa Inorganics. The hydroxo complex was obtained by making solutions of $Co(CN)_5(OH_2)^{2-}$ basic by the addition of NaOH. The pK_a for the proton of the coordinated water was determined by a spectrophotometric titration and found to be 10.5 ± 0.5. By the analysis for $Co(CN)_4(OH_2)_2{}^-$ described below, the solutions of $Co(CN)_5(OH_2)^{2-}$ showed only small amounts of the diaquo species. The pH 7.9 solutions of $Co(CN)_5(OH_2)^{2-}$ were achieved by dilution of the $Co(CN)_5(OH_2)^{2-}$ solution with pH 7 buffer; pH 1.5 was achieved by the addition of $HClO_4$.

Analysis for CN^- Release. Release of CN^- from the $Co(CN)_5(OH_2)^{2-}$ or $Co(CN)_5(OH)^{3-}$ leads to the formation of the diaquo or dihydroxo complex[7] which we find can be reproducibly detected in small amounts by the addition of pH 7 (buffered) solutions of 0.5 *M* Na_2SO_3 resulting in the formation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ identified by its characteristic absorption maximum at 316 nm (ϵ 32,000)[8] and a shoulder at ~380 nm[7]. The unreacted $Co(CN)_5(OH_2)^{2-}$ yields $Co(CN)_5(SO_3)^{4-}$ ($\epsilon_{max,\ 316 nm} = 420$). The anation of the diaquo species is extremely rapid, but anation of the $Co(CN)_5(OH_2)^{2-}$ required approximately 30 min at room temperature. When no further optical density changes could be detected, the optical density at 316 nm was recorded for nonirradiated and irradiated $Co(CN)_5(OH_2)^{2-}$ or $Co(CN)_5(OH)^{3-}$ solutions after addition of the $SO_3{}^{2-}$ solution. Qualitative determination of CN^- release is made by noting the characteristic odor of HCN upon addition of $HClO_4$ to irradiated solutions of $Co(CN)_5(OH)^{3-}$.

Quantum Yield Determinations. Corning glass[9] filters and filter solutions were used to isolate the 313-, 366-, 405-, and 436-nm Hg lines from the output of either a 450- or 550-W Hanovia medium-pressure Hg lamp. The light intensity at each wavelength was determined by ferrioxalate actinometry[10] under the same conditions as for irradiation of the cyanocobaltate(III) solutions.

The $Co(CN)_5(OH_2)^{2-}$ at either pH 7.9 or 1.5 was irradiated in a fixed position and a stream of N_2 was passed through the solution for several minutes before irradiation and continuously during the photolysis to remove HCN formed in the preparation of the aquo complex and during its photolysis. Either 2.5- or 3.0-cm^3 aliquots were irradiated, and at least three duplicates were photolyzed in each case. Failure to bubble N_2 continuously at pH 7.9 resulted in diminished yields, but did not markedly affect pH 1.5 results.

Either 2.5- or 3.0-cm^3 aliquots of the $Co(CN)_5(OH)^{3-}$ (pH 13) were irradiated either in a fixed position or in a merry-go-round.[11]

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(1) (a) A. W. Adamson and A. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); (b) A. W. Adamson, A. Chiang, and E. Zinato, *ibid.*, **91**, 5468 (1969).

(2) L. Moggi, F. Bolletta, V. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

(3) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 5254 (1971).

(4) M. Wrighton, D. Bredesen, H. B. Gray, and G. S. Hammond, *J. Chem. Soc., Chem. Commun.*, 1018 (1972).

(5) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

(6) A. Haim, R. J. Grassie, and W. K. Wilmarth, *Advan. Chem. Ser.*, No. **49** (1965).

(7) M. Wrighton, H. B. Gray, G. S. Hammond, and V. Miskowski, *Inorg. Chem.*, **12**, 740 (1973).

(8) H. H. Chen, M.-S. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

(9) For the transmittance spectra of Corning glass filters see Bulletin CFG, Corning Glass Works, Corning, N. Y. 14830, 1970.

(10) (a) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **235**, 518 (1956).

(11) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

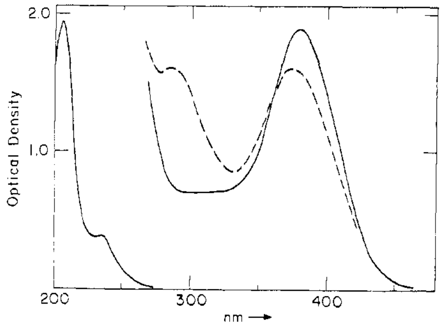

Figure 1. Absorption spectra of $Co(CN)_5(OH_2)^{2-}$ in H_2O (pH ∿7) (——) and $Co(CN)_5(OH)^{3-}$ in 0.1 *M* NaOH (- - - -). The concentration for the low-energy absorptions is 6.79×10^{-3} *M* and for the high-energy region is 9.74×10^{-5} *M*.

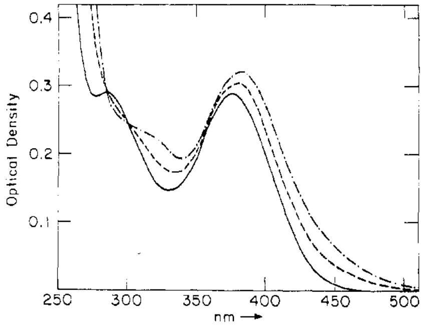

Figure 2. Spectral changes occurring upon 313-nm photolysis of $Co(CN)_5(OH)^{3-}$ in 0.1 *M* NaOH: ——, starting material; - - - -, ~17% conversion; – · – ·, ~40% conversion to $Co(CN)_4(OH)_2{}^{3-}$.

Correction was made for the lack of 100% light absorption at 436 nm. Quantum yield determinations in all cases were made for an absolute conversion of <2%.

Spectra. Electronic absorption spectra and optical density measurements were determined using either a Cary 17 spectrophotometer or a Perkin-Elmer 165 uv-vis spectrophotometer.

Results and Discussion

Electronic Spectra. The electronic absorption spectra of $Co(CN)_5(OH)^{3-}$ and $Co(CN)_5(OH_2)^{2-}$ are shown in Figure 1. Following the assignments of Gutterman and Gray[12] the first transition is identified as the ${}^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1)$ transition. The second absorption maximum for the aquo complex occurs at 232-nm which is higher energetically than the second ligand field (${}^1A_{1g} \rightarrow {}^1T_{2g}$) band for the O_h $Co(CN)_6{}^{3-}$. Thus, it is unlikely that this band is a ligand field transition in the lower symmetry aquo complex. We can associate this transition with a component of the charge-transfer absorption. The second absorption maximum for the hydroxo complex, however, is lower in energy than the second ligand field band in $Co(CN)_6{}^{3-}$. Energetically this band falls near the expected position of the ${}^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2b_1)$ ligand field band. However, argument could be made that this absorption is a charge-transfer transition involving the hydroxo group. For either the aquo or hydroxo complex, though, it is expected that electronic absorption in the range 260-350 nm will result in substantial population of the $d_{x^2-y^2}$ ($\sigma_{xy}{}^*$) orbital at the expense of the lower d_π orbital.[13] Band maxima, molar extinction coefficients, and spectral assignments are detailed in Table I.

Photochemistry. Irradiation of $Co(CN)_5(OH_2)^{2-}$ is known to yield substitution of the H_2O.[1b] We find that, in addition, loss of CN^- occurs with very modest efficiency to yield a diaquo species. The initial quantum yields for CN^- loss from $Co(CN)_5(OH_2)^{2-}$ are shown in Table II.

Table I. Spectroscopic Data for $Co(CN)_5(X)^{n-}$ Complexes[a]

Complex	Band max, nm (ε)	Assignment
$Co(CN)_5(OH_2)^{2-}$	380 (280)	$d_{xz}, d_{yz} \rightarrow d_{z^2}$ (${}^1A_1 \rightarrow {}^1E$)
	315–280 (∿100)	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (${}^1A_1 \rightarrow {}^1E$)
	232 (3950)	CT
	206 (20,000)	Co(III) → CN^- π^*
$Co(CN)_5(OH)^{3-}$	375 (236)	$d_{xz}, d_{y^2} \rightarrow d_{z^2}$ (${}^1A_1 \rightarrow {}^1E$)
	288 (240)	$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (${}^1A_1 \rightarrow {}^1E$) + CT (?)

[a] Room-temperature aqueous solutions; natural pH for $Co(CN)_5(OH_2)^{2-}$ and in 0.1 *M* NaOH for $Co(CN)_5(OH)^{3-}$.

Table II. Quantum Yields for Release of Cyanide from $Co(CN)_5(OH_2)^{2-}$ and $Co(CN)_5(OH)^{3-}$ [a]

Complex irrdtd	pH	Φ_{313}	Φ_{366}	Φ_{405}	Φ_{436}
$Co(CN)_5(OH_2)^{2-}$	1.5	0.003	0.001		
	7.9	0.002	0.0006		
$Co(CN)_5(OH)^{3-}$	13	0.06	0.047	0.024	0.022

[a] Quantum yields are ±10%.

The $Co(CN)_5(OH)^{3-}$ is significantly more photoreactive than the aquo species toward CN^- release. Initial quantum yields for CN^- release were found to be wavelength dependent and the data are included in Table II. Conversion to $Co(CN)_4(OH)_2{}^{3-}$ was measured to be as high as 90%. Spectral changes occurring upon 313-nm photolysis of $Co(CN)_5(OH)^{3-}$ are shown in Figure 2. The same spectral changes that occur upon 313-nm photolysis also obtain upon 366-nm excitation. The product of 313-nm photolysis has absorption maxima at about 383 and 315 nm compared to 375 and 286 nm for the $Co(CN)_5(OH)^{3-}$. These absorption band positions are consistent with a predominantly *cis*-$Co(CN)_4(OH)_2{}^{3-}$ product,[14] and the spectrum resembles that of $Co(CN)_4(en)^-$.[15] However, a mixture of *cis*- and *trans*-$Co(CN)_4(OH)_2{}^{3-}$ is likely since *trans*- to *cis*-$Co(CN)_4(X)(OH_2)^{n-}$ isomerization is thought to occur thermally.[7]

The wavelength-dependent yields implicate at least two reactive excited states giving CN^- substitution at different efficiencies. This is to be contrasted to the photosubstitution of $Co(CN)_6{}^{3-}$ which gives the same quantum yield for $Co(CN)_5(OH_2)^{2-}$ formation upon 254-, 313-, or 366-nm direct excitation[1,2] and upon biacetyl sensitization.[4,16] The $Co(CN)_5(N_3)^{3-}$ and $Co(CN)_5(SCN)^{3-}$ complexes give the same quantum yield for biacetyl sensitization and 436-nm excitation[4] which is consistent with complete decay of the lowest LF (ligand field) singlet excited state to the lowest LF triplet excited state. Complexes of the general formula *trans*-$Co(CN)_4(SO_3)(X)^{n-}$ show only modest wavelength effects for quantum yields for loss of $SO_3{}^{2-}$.[7]

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(12) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971).

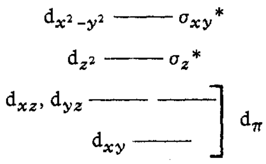
(13) For a discussion of the LF spectra of cobalt(III)-ammine complexes see R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(14) Ligand field considerations suggest that the first d-d transition will be shifted to considerably lower energy for *trans*-$Co(CN)_4(OH_2)_2{}^-$ while the *cis*-$Co(CN)_4(OH_2)_2{}^-$ should be only slightly red shifted from the $Co(CN)_5(OH_2)^{2-}$ lowest d-d absorption. The lowest d-d absorption maxima for $Co(CN)_6{}^{3-}$, $Co(CN)_5(SO_3)^{4-}$, and *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ follow the predicted sequence with the position in the trans disubstituted complex being approximately twice as far removed from the first $Co(CN)_6{}^{3-}$ absorption as the monosubstituted complex. For theory see C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, pp 106-107; see also ref. 13.

(15) K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968).

(16) G. B. Porter, *J. Amer. Chem. Soc.*, **91**, 3980 (1969).

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.

[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-

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

[2] A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 91, 297 (1969).

[3] J. B. Orenberg, M. D. Morris, and T. V. Long, *Inorg. Chem.*, 10, 933 (1971).

[4] H. Siebert, *Z. Anorg. Allg. Chem.*, 273, 161 (1953).

[5] A. A. Abragam, "Principles of Nuclear Magnetism," Oxford University Press, New York, N. Y., 1961, Chapter 8.

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

[7] R. A. Dwek, Z. Luz, and M. Shporer, *J. Phys. Chem.*, 74, 2232 (1970).

[8] M. Broze and Z. Luz, *J. Phys. Chem.*, 73, 1600 (1969).