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The Trans-Influence and Axial Interactions in Low Spin, Tetragonal Cobalt(II) Complexes Containing Macrocyclic and/or Cyano Ligands. Pulse Radiolytic Studies in Fluid Solution, Electron Paramagnetic Resonance Spectra at 77 K, and Single-Crystal X-Ray Structures[1]

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Abstract: Investigations of the weak interactions between low spin cobalt(II) species and their axial ligands have been performed. X-ray structural studies of six-coordinate $Co(N_4)(OH_2)_2{}^{2+}$ and $Co(N_4)(ClO_4)_2$ complexes, where (N_4) is an equatorially coordinated tetradentate macrocyclic ligand, reveal that the axial Co–ligand bond lengths are 0.3–0.5 Å longer per bond than are the equatorial Co–ligand bond lengths. By means of the pulse radiolytic reductions of the corresponding cobalt(III) complexes, low spin cobalt(II) species of the types $Co^{II}(N_4)L_2$ ($L = NH_3, NO_2^-, CN^-$) and $Co^{II}(CN)_5X$ (X = Cl, CN) have been generated, and the rates of ligand exchange with water in the reduced species have been determined by a kinetic conductivity method. All the cobalt(II) species have been found to be very labile in two (axial) coordination positions, with an appreciable range of rate constants ($k \geqslant 10^3\ s^{-1}$) which depend on both the equatorial and the axial ligands. Electron paramagnetic resonance spectra have provided evidence for interactions with either one or two axial ligands (at 77 K) but on the whole have not provided definitive criteria regarding the coordination number of low spin cobalt(II) species in fluid solution. At least some of the ambiguity may arise because the unpaired electron is in an antibonding orbital. Comparison of the results of this and other studies suggests a strong trans influence in the axial ligand interactions of low spin cobalt(II) complexes. A simple three-center bonding model has been used to describe the weak axial interactions. This model also provides a convenient basis for interpreting the absorption spectrum of a $Co^{II}(N_4)CN$ transient generated in the pulse radiolysis studies. It is inferred that the synergistic trans-influence deduced for low spin cobalt(II) species may be a significant factor in inner sphere electron transfer reactions.

Although the aqueous solution chemistry of low spin cobalt(II) complexes is relevant to the chemistry of such natural systems as the corrinoids[3] and to various issues of concern in the fixation of dioxygen,[4] relatively little is known of the chemical behavior of such systems. Synthetic low spin cobalt(II) systems include the pentacyanocobaltate(II) ion, oxime complexes, Schiff-base complexes, and macrocyclic complexes. The dearth of information regarding the solution chemistry of these cobalt(II) complexes is attributable in part to the difficulties in handling relatively oxygen sensitive species, and in part to the lability of the d^7 electronic configuration.[6-12] In contrast, a substantial literature is developing concerning the structural chemistry of these systems.[13-17] In the solid state the low spin cobalt(II) complexes containing synthetic ligands are tetragonally distorted five-[13] or six-coordinate[14-17] species. Despite the limited correlative solution chemistry, there has been appreciable concern with the nature of the species in solution. Inferences regarding the nature of the low spin cobalt(II) species in solution have been most often based on the 77 K EPR spectra of frozen solutions,[3,4,18-24] and on solid state structural studies.[13-15,25] While both the structural and EPR studies provide evidence for five-[4,13,18,21-23,25,26] and six-coordinate[14,15-17,19,20,22,23] species, a substantial body of opinion seems to have developed that the species in solution are five coordinate.[4,18,21] Some of the low spin cobalt(II) species claimed to be five coordinate[5,21] in aqueous solution are in fact six coordinate diaquo species in the solid state.[15] Since it seemed surprising that the number of axial ligands should decrease as the activity of the ligand is increased, and since the color difference which has come to be associated with five- and six-coordinate cyano and phenylisocyanide complexes[13,22] has not been established as a general property of low spin cobalt(II), we have undertaken to compare solid state, EPR, and solution studies of several low spin cobalt(II) complexes. Since all the solid state structural studies of low spin cobalt(II) complexes reveal tetragonal distortion, we investigated axial ligand lability as the solution property most sensitive to variations in structural and spectroscopic parameters of these complexes. The solvated electron reduction of various cobalt(III) complexes provides a very convenient means of in situ preparation of cobalt(II) complexes with a variety of axial ligands. We have employed the recently reported kinetic conductivity method coupled to pulse radiolysis[11,12] to examine the axial lability of such cobalt(II) complexes.

Experimental Section

A. Preparation of Complexes. Methods of preparation and characterization of the cobalt(III) complexes employed in this study may

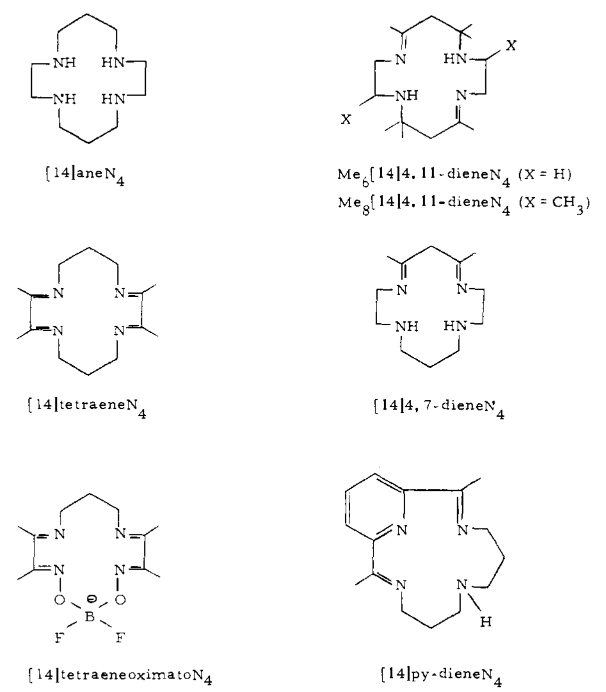


Figure 1. Structural formulas for the macrocyclic ligands. See reference 28 for full names.

be found in the literature.[25-28] We have also previously reported the preparation and characterization of [Co(Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$,[27c,g,30] [Co(Me$_8$[14]4,11-dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$,[27c,30] and [Co([14]tetraeneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$.[27g,28,30] The method of Busch and Long[31] was used for the synthesis of [Co([14]pyridieneN$_4$)](ClO$_4$)$_2$·xH$_2$O.

We used the literature preparation for [Co([14]tetraeneoximatoN$_4$)]Br$_2$.[30] The product was converted to the diaquo perchlorate by addition of silver perchlorate. To prepare Co^{II}([14]tetraeneoximatoN$_4$) species, deoxygenenated solutions of [Co([14]tetraeneoximatoN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$ were reduced with sodium borohydride and filtered in a nitrogen atmosphere; the filtrate was used in the ESR measurements.

B. Electron Paramagnetic Resonance Studies. All experiments were performed under a deoxygenated, nitrogen atmosphere. Samples for EPR studies were prepared by adding oxygen free solvents to the sample under a nitrogen atmosphere, and the solution was outgassed by repeated evacuations. Most of the solvents used were deoxygenated by means of a nitrogen stream passed through the solvent for several hours; pyridine and nitromethane were purified by repeated distillation in vacuo, followed by vacuum distillation into the ESR tube.

The EPR spectra were obtained on a Varian E-4 spectrometer, with DPPH (diphenylpicrylhydrazyl) as a standard, using thin-walled quartz sample tubes.

C. Pulse Radiolysis Studies. The pulse radiolysis of aqueous solutions leads to the primary products indicated in eq 1 (G values, i.e., the number of molecules per 100 eV of radiation absorbed, in parentheses). The OH and H radicals were scavenged with 2-methyl-2-propanol (0.5 M), leaving the hydrated electron to react with the complexes. For the cobalt(III) complexes used in this study the rates of reaction with e_{aq}^- were found to be diffusion controlled.

$$H_2O \rightsquigarrow e_{aq}^-(2.7),\ H_3O^+(2.7),\ OH(2.7),\ H(0.6),\ H_2O_2(0.5) \quad (1)$$

The pulse radiolysis equipment (1.6-MeV electrons from a Van de Graaff generator, pulse duration 0.5 μs) and the 10-MHz kinetic conductivity technique have been described.[11,12] The dose and the conductivity cell constant were always determined before a run of experiments using 10^{-4} M tetranitromethane solutions in the presence of 10^{-2} M propanol. The dose was calculated from $G(C(NO_2)_3^-) = 6.0$ and $\epsilon(C(NO_2)_3^-) = 14\,000$ M^{-1} cm^{-1} at 350 nm. The cell constant was calculated from equivalent conductivities. $\Lambda(H_3O^+) = 350\Omega^{-1}$ M^{-1} cm^2 and $\Lambda(C(NO_2)_3^-) = 40\Omega^{-1}$ M^{-1} cm^2 all at 25 °C. The equivalent conductivities of the intermediates were calculated from the dose per pulse and $G(e_{aq}) = 2.7$. In most of the experiments 500 rads/pulse was sufficient which corresponds to 1.3×10^{-6} mol of hydrated electrons per pulse. The evaluation of the magnitudes of conductivity changes is subject to about a 10% uncertainty due to fluctuations in dosimetry. The relative conductivity changes during any given experiment are subject to about a 10% measuremental uncertainty.

The time-dependent signals from both conductivity and spectrophotometric techniques were stored in a Biomation 810 transient recorder, transferred automatically to paper tape, and evaluated on a PDP 11 computer.

X-ray Structure Determinations. Co([14]aneN$_4$)(ClO$_4$)$_2$. A single crystal of dimensions 0.30 × 0.30 × 0.40 mm was mounted in a glass capillary under anaerobic conditions. The x-ray examination was on a Syntex P2$_1$ diffractometer withMo Kα radiation which had been diffracted from a highly oriented graphite monochromator whose diffraction vector was parallel to that of the sample. The takeoff angle was approximately 4°. Rotation and axial photographs indicated the triclinic crystal system. Lattice constants were obtained from least-squares refinement of 15 reflections (λ 0.710 69 Å). The crystal data are: $a = 10.953$ (1), $b = 8.677$ (1), $c = 9.181$ (1) Å; $\alpha = 84.55$ (1), $\beta = 87.40$ (1), $\gamma = 89.42$ (1)°; $\rho_{(calcd)} = 1.74$ g cm^{-3}; $Z = 2$; $\mu = 1.38$ cm^{-1}. The lattice constants above correspond to a body-centered cell. This nonconventional cell is close to orthogonal, minimizing correlations, and was thus used throughout the structural study. The lattice transformation to the reduced primitive cell is

$$\begin{bmatrix} -\tfrac{1}{2} & \tfrac{1}{2} & -\tfrac{1}{2} \\ \tfrac{1}{2} & -\tfrac{1}{2} & -\tfrac{1}{2} \\ -\tfrac{1}{2} & -\tfrac{1}{2} & \tfrac{1}{2} \end{bmatrix}$$

and yields $a = 8.241$ Å, $b = 8.421$ Å, $c = 8.019$ Å, $\alpha = 116.34°$, $\beta = 95.31°$, and $\gamma = 113.13°$. Intensity data for $\sin\theta/\lambda < 0.538$ were collected by the θ–2θ scan technique. Each reflection was scanned from $2\theta(K\alpha_1) - 0.8°$ to $2\theta(K\alpha_2) + 1.0$ at 2°/min with backgrounds measured at both ends of the scan for a total time equal to the scan time. The intensities of three standard reflections varied less than 2% from their means throughout the data collection. Standard deviations were assigned[33] as follows: $\sigma(I) = [\sigma_{counter}(I)^2 + (0.04I)^2]^{1/2}$ where $\sigma_{counter} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, and K = ratio of scan time to background time. Extinction and absorption corrections were not applied. Data for which $I \geqslant 3\,\sigma(I)$ were used in solution and refinement of the structure. Of the 2300 data examined, 1107 were considered observed.

Presumption of the centrosymmetric space group $I\bar{1}$ requires that the cobalt resides on an inversion center. A difference Fourier synthesis revealed all non-hydrogen atoms. Isotropic least-squares refinement, including anomalous scattering for cobalt and chlorine, resulted in $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.10$ with no evidence of perchlorate disorder. A difference synthesis yielded the positions of 12 hydrogen atoms.

Anisotropic least-squares refinement of all non-hydrogen atoms with fixed contributions from the hydrogen atoms with thermal parameters of 5.0 Å^2 converged to $R = 0.044$, $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.065$, an error of fit of 2.15 and residual electron density less than 0.5 e/Å^3. Atomic parameters are given in Table SI.[34]

[Co(Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)$_2$](BF$_4$)$_2$. A preliminary report of this structure may be found in ref 15a. A crystal of dimensions 0.11 × 0.26 × 0.33 mm was mounted on a glass fiber with Silastic adhesive. Precession photographs were uniquely consistent with the monoclinic space group $P2_1/c$. Subsequent x-ray examination and data collection for this compound were with Zr-filtered Mo Kα radiation on a Picker card-controlled diffractometer. Final lattice constants were obtained from least-squares refinement of 22 reflections (λ 0.709 26 Å). The crystal data are: $a = 7.893$ (7), $b = 9.518$ (7), $c = 16.813$ (13) Å; $\beta = 107.16$ (2)°; $\rho_{(flotation)} = 1.49$, $\rho_{(calcd)} = 1.51$ g cm^{-3}; $Z = 2$; $\mu = 8.3$ cm^{-1}. Intensity data for $\sin\theta/\lambda < 0.595$ were collected by the θ–2θ scan technique with a takeoff angle of 2.7°. Each reflection was scanned from $K\alpha_1 - 1.0°$ to $K\alpha_2 + 1.0°$ at 2°/min with background counts of 15 s at each end of the scan. Intensities of four standard reflections varied less than 5% during the data collection. Extinction and absorption corrections were not applied. Standard deviations for I were assigned according to the formula $\sigma(I) = [P + (B_1 + B_2)\Delta(2\theta) + (0.05I)^2]^{1/2}$ where P is the gross intensity, B_1 and B_2 are the background counts, $\Delta(2\theta)$ is the scan length, and I is the net intensity. Of

Table I. Electronic Spectra of Macrocyclic Cobalt(II) Complexes in Aqueous Halide Solutions

	Absorption maximum,[a] μm^{-1} (ϵ)		
Compound/solvent	$^2A_1 \rightarrow {}^2B_1$	$^2A_1 \rightarrow {}^2B_2$	$Co^{II} \rightarrow {}^*\pi(N_4)$[b]
Co^{II}([14]tetraeneN_4)			
H_2O	1.04 (55.3)	*c*	1.84 (3.40×10^3), 2.74 (1.22×10^3)
1 M NaCl	1.02 (51.8)	*c*	1.84 (3.44×10^3), 2.71 (1.77×10^3)
1 M NaBr	0.96 (49.9)	*c*	1.82 (3.78×10^3), 2.68 (1.13×10^3)
Co^{II}(Me_6[14]4,11-dieneN_4)			
H_2O	1.33 (2.5)	2.26 (1.18×10^2)	3.02 (2.3×10^3), 3.45 (sh)
1 M NaCl	1.32 (2.0)	2.26 (1.05×10^2)	3.00 (2.2×10^3), 3.64 (sh)
1 M NaBr	1.32 (2.5)	2.26 (1.17×10^2)	2.94 (2.4×10^3), 3.64 (sh)

[a] Assignments based on ref 51 and W. C. Lin, *Inorg. Chem.*, **15**, 1114 (1976). [b] Charge transfer to ligand (CTTL). [c] Transition obscured by CTTL transition.

the 2668 independent reflections examined, 1442 had $I > 2.5\sigma(I)$ and were used in the solution and refinement of the structure.

The presence of two molecules in the space group $P2_1/c$ requires that the cobalt resides on an inversion center. A Fourier synthesis allowed placement of the remaining non-hydrogen atoms. Isotropic least-squares refinement of these atomic parameters resulted in discrepancy factors of $R = 0.112$ and $R_w = 0.139$. The hydrogen atoms were then located from a difference Fourier synthesis. Two cycles of anisotropic least-squares refinement, with fixed contributions from the hydrogen atoms with thermal parameters of 5.0 Å^2 and anomalous scattering factors included for the cobalt, produced $R = 0.068$, $R_w = 0.074$, an error-of-fit = 2.01, and a maximum residual electron density of 0.59 e/Å^3. Variation of occupancy factors of the oxygen atoms and the fluorine atoms showed 100% occupancy and indicated no sign of disorder. Atomic parameters are given in Table SII.[34]

[Co([14]tetraeneN_4)(OH_2)$_2$](ClO_4)$_2$. A preliminary report of this structure may be found in ref 15b. A single crystal of dimensions 0.10 × 0.10 × 0.15 mm was mounted on glass fiber with clear epoxy cement. The x-ray study was carried out on the previously described Syntex diffractometer. Rotation and axial photographs and the counter data were uniquely consistent with the space group $P2_1/c$. Final lattice constants were obtained from least-squares refinement of 15 reflections (λ 0.710 69 Å). The crystal data are: $a = 6.939$ (5), $b = 14.542$ (9), $c = 11.581$ (12) Å; $\beta = 94.64$ (7)°; $\rho_{(\text{flotation})} = 1.54$, $\rho_{(\text{calcd})} = 1.54$ g cm^{-3}; $Z = 2$; $\mu = 10.41$ cm^{-1}. Intensity data for $\sin \theta/\lambda < 0.538$ were collected by the θ-2θ scan technique. Each reflection was scanned from $2\theta(K\alpha_1) - 1.0°$ to $2\theta(K\alpha_2) + 1.0°$ at 2°/min with backgrounds measured at both ends of the scans for a total time equal to the scan time. The intensities of three standard reflections varied less than 4% from their means thoughout the data collection. Standard deviations were assigned as for Co([14]aneN_4)(ClO_4)$_2$. Extinction and absorption corrections were not applied. Of 2668 independent reflections examined, 496 had $I > 3\sigma(I)$ and were used in the solution and refinement of the structure.

The presence of two molecules in the space group $P2_1/c$ requires that the cobalt resides on an inversion center. A difference Fourier synthesis phased with the metal position revealed the chlorine, the non-hydrogen atoms of the macrocyclic ligand, and the axial oxygens clearly. Four poorly defined peaks about the chlorine position were taken for the oxygen positions of the perchlorate groups. Isotropic least-squares refinement converged to $R = 0.125$ and $R_w = 0.141$ with B's for the perchlorate oxygens from 15 to 30 Å^2. A model in which the perchlorate showed twofold disorder of 40° about one of the threefold axes resulted in reasonable Cl-O distances and in thermal parameters less than 10 Å^2 for all oxygen atoms with $R = 0.088$ and $R_w = 0.089$.

The hydrogen atoms were then located from a difference synthesis and included at fixed positions with isotropic thermal parameters of 5.0 Å^2. Final refinement with anisotropic thermal parameters for the cobalt, chlorine, and ligated oxygen converged with $R = 0.077$, $R_w = 0.076$, an error-of-fit = 1.61, and a maximum residual electron density of 0.39 e/Å^3. Atomic parameters are given in Table SIII.[34] Comparisons of calculated and observed structure factors for all three structures are included as Tables SIV, SV, and SVI in the supplementary material.

Results

A. General. except for the Co^{II}([14]aneN_4) species, aqueous perchloric acid solutions of the cobalt(II) complexes are not very oxygen sensitive and are handled with ease. In the presence of potential axial bases other than water, especially halides, all the cobalt(II) complexes became very air sensitive. The presence of potential axial ligands in aqueous solution does not greatly alter the cobalt(II) absorption spectra (see Table I). The magnetic moments of the cobalt(II) complexes are in the range $2.3 \geqslant \mu_{\text{eff}} \geqslant 1.8$ μ_B. The higher values were determined from bulk susceptibilities of the solid perchlorate salts and the lower values from apparent susceptibilities in solution determined by the Evans[35] method.[36,37]

B. Electron Paramagnetic Resonance Studies. The isotropic EPR spectrum of a low spin cobalt(II) complex is expected to be composed of eight lines since the electronic spin of ½ is split by the $^7\!/_2$ nuclear spin of the cobalt center. However, the complexes employed in this study do not have symmetry higher than C_{2h}, and thus, in the solid state or in frozen solutions, should exhibit anisotropic splitting into g_x, g_y, and g_z components. Since we are focusing on the axial interactions, we have treated the microsymmetry of the low spin cobalt(II) complexes as approximately D_{4h} or C_{4v} and have presumed $g_x \sim g_y = g_\perp$;[37] the axial component may be identified as $g_\parallel$.[37-39] Splitting factors, hyperfine constants, and superhyperfine constants from the EPR spectra of the several cobalt(II) complexes are summarized in Tables II and SVII[34] and Figures 2, 3, and S1-S3.[34]

The $A_\parallel$ and $g_\parallel$ values can be calculated with precision from the EPR spectrum; the method of Walker[40] was used for this purpose. The values of $g_\perp$ and $A_\perp$ depend on a number of factors and can be calculated only approximately. A computer simulation was also done to verify some of the results obtained[41,42] (see Figure S3[34]).

C. Pulse Radiolysis Studies. In order to study the axial lability of various cobalt(II) complexes we generated the species of interest by means of the very rapid ($k > 10^{10}$ M^{-1} s^{-1}) solvated electron reductions of the appropriate cobalt(III) complexes.[12,43] With the concentrations of complexes used, $>10^{-4}$ M, the reduction reactions were over in a time shorter than the time resolution of kinetic conductivity (~2 μs). Formation of charged species on irradiation of aqueous solutions results in a transient change in conductivity after the pulse which is determined, at our dose levels, by $\Lambda(e_{aq}^-) = 180$ Ω^{-1} mol^{-1} cm^2 and $\Lambda(H_3O)^+ = 350$ Ω^{-1} mol^{-1} cm^2, i.e., $\Delta = (530 \pm 53)$ Ω^{-1} mol^{-1} cm^2. When an efficient electron acceptor is present, the conductivity contribution due to e_{eq}^- will not be detected by the conductivity technique. The exact level of the remaining conductivity will depend on the nature of the elec-

Table II. Analysis of EPR Parameters for $Co^{II}(N_4)$ Systems[a] for Which $g_\perp \sim g_x \sim g_y$

(N_4)	Medium	$g_\parallel$	$g_\perp$	C_1	C_2	$E(^2A_1 \rightarrow {}^4B_1)$, μm^{-1}	$E(^2A_1 \rightarrow {}^2B_1)$, μm^{-1}	$A_\parallel$[b]	$-A_\perp$[b]	P[b]	$-K$[b]
[14]tetraeneN_4	50% pyridine	2.020	2.27	0.0454	0.109	0.37	0.88	85.0	10	226	22
	CH_3NO_2	2.012	2.23	0.0386	0.0842	0.48	1.04	97.7	10	210	13
	H_2O	2.016	2.25	0.0420	0.0974	0.41	0.95 (10.4)[c]	97.7	10	224	11
	1 M $NaNO_2$	2.017	2.23	0.0385	0.0978	0.41	1.04	86	10	191	7
	1 M NaCl	2.017	2.23	0.0385	0.0978	0.41	1.04 (10.2)[c]	108.3	11	235	6
[14]tetraeneoximatoN_4	50% pyridine	2.018	2.24	0.0401	0.1013	0.40	1.00	89.5	9	202	8
	CH_3NO_2	2.013	2.22	0.0368	0.0859	0.47	1.09	104.8	10	219	3
	H_2O	2.016	2.24	0.0402	0.0963	0.42	1.00	112.0	10	248	8
[14]aneN_4	50% pyridine	2.033	2.30	0.0500	0.138	0.23	0.80	97.8	10	277	5
	CH_3NO_2	2.030	2.26	0.0429	0.129	0.31	0.93	86.2	10	235	22
	H_2O	2.021	2.28	0.0472	0.113	0.35	0.85	122.7	10	308	1

[a] Analysis based on ref 47: $g_\parallel = 2.0023 + 2C_3^2 - 3C_1^2$; $g_\perp = 2.0023 + {}^2/_3 C_3^2 - 6C_1^2 + 6C_1$; $\sim A_\parallel = K + (P/7)[4 - 4C_3 - 6C_1 + (2/9)C_3^2 + 15C_1^2]$; $A_\perp = K + (P/7)[-2 + 45C_1 + 2C_3 + (4/3)C_3^3 - (57/2)C_1{}^2]$ where $C_1 = \lambda/E(^2A_1 \rightarrow {}^2B_1)$, $C_3 = \lambda/E(^2A_1 \rightarrow {}^4B_1)$, $P = 2\beta_e\beta_m\gamma_{Co}\langle 3d_{z^2}|r^{-3}|3d_{z^2}\rangle$, λ = spin orbit coupling constant of cobalt $\simeq 0.04\ \mu m^{-1}$ and β_e and β_m are electronic and nuclear magnetons. [b] In units of $10^{-4}\ cm^{-1}$. [c] Observed $^2A_1 \rightarrow {}^2B_1$ transition (Table I).

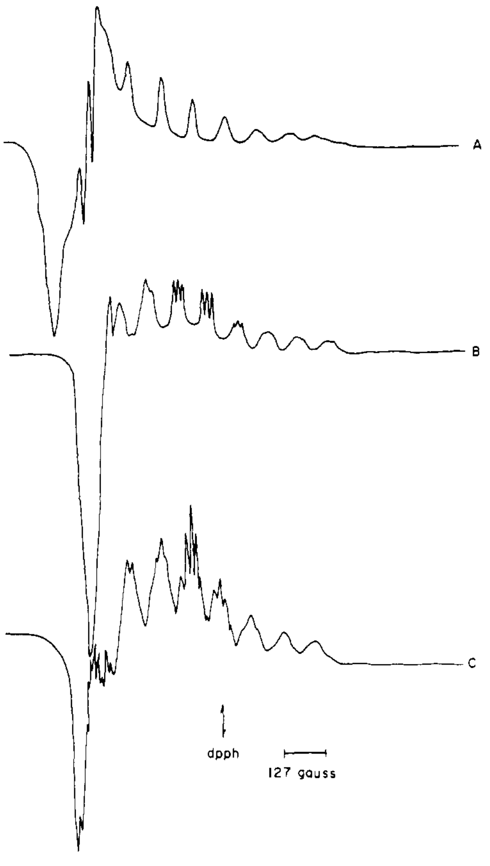


Figure 2. EPR spectra of low spin cobalt(II) complexes in 50% pyridine-water solutions (77 K): A, $Co([14]aneN_4)(ClO_4)_2$; B, $[Co([14]tetraeneN_4)(OH_2)_2](ClO_4)_2$; C, $[Co([14]tetraeneoximatoN_4)(OH_2)_2]ClO_4$.

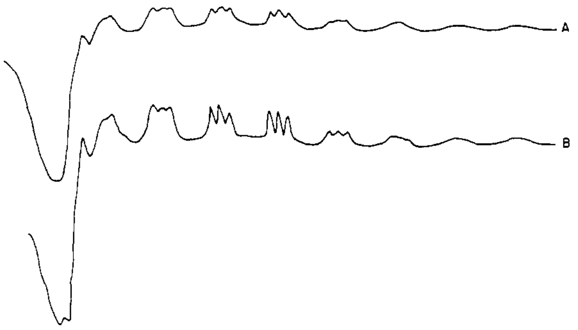


Figure 3. EPR spectra of $[Co([14]tetraeneN_4)(OH_2)_2](ClO_4)_2ClO_4$ (upper curve) and in 50% pyridine-D_2O (lower curve); [complex] = 10^{-3} M in both cases.

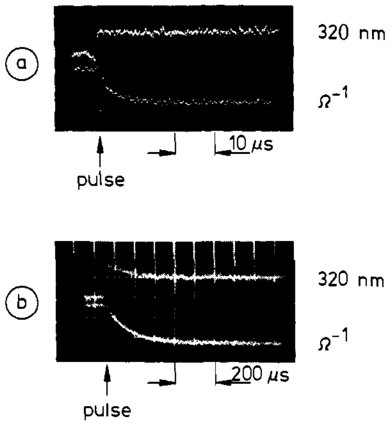


Figure 4. Changes of absorbance at 330 nm (upper curves of each pair) and conductivity (lower curves of each pair) which occur following the solvated electron reductions of $Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2{}^{3+}$ (a) and $Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)(CN)_2{}^+$ (b). The observed decay corresponds to a conductivity change $\Delta\Lambda = -244 \pm 20\ \Omega^{-1}$, compared to $\Delta\Lambda \cong -260$ estimated for eq 3-4. Note that conductivity and absorbance changes do occur during the pulse (eq 1) or the time resolution of our measurements (eq 2).

tron acceptor. For example, if one starts with a neutral solute, S, the overall conductivity change after the e_{aq}^- reaction will be $\Delta\Lambda = \Lambda(H_3O^+) + \Lambda(\cdot S^-)$; in case of a positively charged metal ion or a metal complex, it will be $\Delta\Lambda = (\Lambda H_3O^+) + \Lambda(M^{(n-1)+}) - \Lambda(M^{n+})$. For the cases of interest here, the exact values of Λ(metal complex) are not known and have to be approximated with those for species of similar charge and size. Those Λ values associated with a change in the charge of metal ions are much smaller than (H_3O^+); hence only a small error should result from these approximations.[11,12]

In order to ensure that the cobalt(III) substrates reacted completely with e_{aq}^- in competition with H_3O^+ ($k = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$),[43] we had to keep the pH > 4.0 in all studies and pH ~5 was most convenient. The pH was generally varied in the range 4.5-5.5, but the only pH dependent decays observed were those of the reduction products of $Co(Me_6[14]4,11\text{-}diene)(NO_2)_2{}^+$ (see Table III; Figure 4).

All the macrocyclic cobalt(II) complexes were found to be axially labile. The reactions observed can be described by eq 2-4 where, except for X = NO_2^-, protonation (eq 4)

Table III. Lifetimes for Axial Substitution in Some Low Spin Cobalt(II) Complexes

Cobalt(III) substrate	Initial decay[a] $\Delta\Lambda$, Ω mol^{-1} cm^{-1}	τ_1, s	Second decay[b] $\Delta\Delta\Lambda$, Ω mol^{-1} cm^{-1}	τ_2, s	Subsequent decays $\Delta\Delta\Lambda$, Ω mol^{-1} cm^{-1}	τ, s
$Co(Me_6[14]4,11\text{-diene}N_4)(NH_3)_2^{3+}$	0(0)	$\leqslant 1$	-244 ± 18 (-270)	20	None obsd	
$Co([14]\text{tetraene}N_4)(NH_3)_2^{3+}$	*c*		-260 ± 20 (-275)	$<3^c$	None obsd	
$Co(Me_6[14]4,11\text{-diene}N_4)(NO_2)_2^{+}$	380 (410)[d]	$\leqslant 1$	-76	3-6[e]	38	61[f]
$Co(Me_6[14]4,11\text{-diene}N_4)(CN)_2^{+}$	~0 (0)	$\leqslant 1$	-215 (-290)[g]	100 ± 10	None obsd	
$Co([14]\text{tetraene}N_4)(CN)_2^{+}$	100 (0)	$\leqslant 1$	-150 (-290)[g]	1.0×10^3	None obsd	
$Co(CN)_6^{3-}$	0 (0)	$\leqslant 1$	-80 (-270)[g]	84		39×10^3
$Co(CN)_5Cl^{3-}$	320 (410)[h]	$\leqslant 1$	-160 (320)[g]	93	-160	33×10^3

[a] This corresponds to the two step process: $Co^{III}(L_4)XY + e^- \rightarrow Co^{II}(L_4)XY$, k_e; H^+ . $co^{II}(L_4)XY \rightarrow Co^{II}(L_4)X + HY$, k_i; where $k_e > 10^{10}$ M^{-1} s^{-1}; the conductivity values are those after the pulse within the time resolution of the instrument (1×10^{-6} s) (values in parentheses are conductivities expected after these processes). [b] This corresponds to the loss of the second axial ligand; the difference in conductivity is indicated for this step only (values in parentheses are conductivity changes expected for this step only). [c] No decay resolved. The conductivity change corresponded to loss of both ligands in less than 3×10^{-6} s. [d] Calculated for $(Co^{II}(N_4)(NO_2)^+ + NO_2^- + H^+)$; $4.1 < pH < 5$. For $(Co^{II}(N_4) + 2NO_2^- + H^+)$ we would calculate $\Delta\Lambda = 530$. [e] τ_2 was inversely proportional to $[H^+]$ with $k_2 = 1.0 \times 10^{10}$ M^{-1} s^{-1} in the range $4.6 \leqslant pH \leqslant 5.0$. This could be the result of protonation of a small amount of NO_2^- (pK_a of $HNO_2 \simeq 3.35$). [f] Observed over the pH range 4.1-4.6. Possibly due to $Co^{II}(N_4)NO_2 \rightarrow Co^{II}(N_4) + NO_2^-$ (see notes *d* and *e*). [g] Decays are suppressed in the presence of O_2. [h] Estimated for $Co(CN)_5Cl^{3-} + e^- + H^+ \rightarrow Co(CN)_5^{3-} + Cl^- + H^+$.

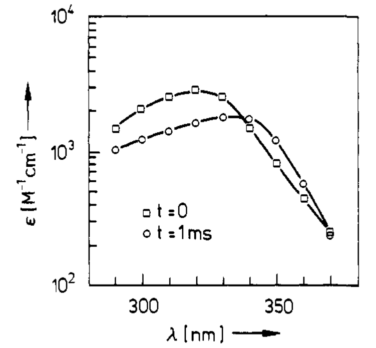
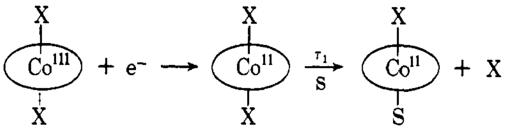
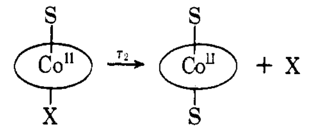


Figure 5. Absorption spectrum of a solution of 5×10^4 M $Co([14]\text{-}4,11\text{-diene})CN_2$ (oxygen free with 10^{-1} M *tert*-butyl alcohol) immediately after the pulse and 1 ms later.



$$\mathrm{X{-}Co^{III}{-}X} + e^- \longrightarrow \mathrm{X{-}Co^{II}{-}X} \xrightarrow[\mathrm{S}]{\tau_1} \mathrm{X{-}Co^{II}{-}S} + \mathrm{X} \qquad (2)$$



$$\mathrm{S{-}Co^{II}{-}X} \xrightarrow{\tau_2} \mathrm{S{-}Co^{II}{-}S} + \mathrm{X} \qquad (3)$$

$$X + H^+ \rightleftharpoons HX^+ \qquad (4)$$

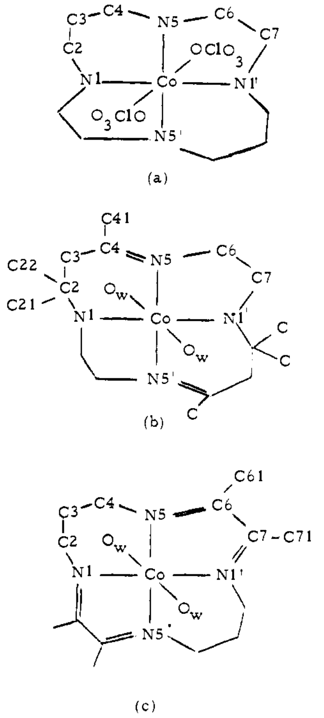


Figure 6. Atomic numbering for the three Co(II) macrocyclic complexes: (a) $Co([14]aneN_4)(ClO_4)_2$, (b) $[Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2](BF_4)_2$, (c) $[Co([14]\text{tetraene}N_4)(OH_2)_2](ClO_4)_2$.

undoubtedly occurs subsequent to the solvolysis steps (eq 2 and 3).

For $Co(Me_6[14]4,11\text{-diene}N_4)(NO_2)_2^+$ it would be very hard to distinguish between release of one ($\Delta\Lambda \simeq 400$ Ω^{-1}) or both ($\Delta\Lambda \simeq 500$ Ω^{-1})NO_2^- ligands following reduction with e_{aq}^-. We observed three conductivity changes with this complex: (a) the initial rise in conductivity ($\Delta\Lambda = 380$ Ω^{-1}; $\tau < 10^{-6}$s); (b) a small, rapid decrease ($\Delta\Lambda = -76$ Ω^{-1}; $\tau \sim 3$-6 μs); and (c) a very small, slow increase of conductivity ($\Delta\Lambda \simeq 38$ Ω^{-1}; $\tau \sim 42$ μs). That the initial rise in conductivity is less than 400 Ω^{-1} (or 500 Ω^{-1}) is verylikely due to a contribution of ($e_{aq}^- + H^+$) in these solutions of relatively high acidity. Thus it is possible that both axial ligands were aquated in less than 10^{-6} s. The short term decay (b) is probably a contribution of ($H^+ + NO_2^-$; $k \sim 10^{10}$ M^{-1} s^{-1}; pK_a (HNO_2) = 3.35[44]). The long term conductivity rise (c) could be due to an instrumental artifact, but can be used to set an upper limit of 42 μs on the lifetime of NO_2^- in the cobalt(II) coordination sphere.

All the cyanocobalt(II) complexes are powerful reducing agents[44-46] which react very rapidly with dioxygen. For each of the cyano complexes, $[O_2] = 10^{-5}$ M was more than sufficient to supress all transient decays of conductivity. The $Co^{II}(N_4)CN^+$ species were found to have absorption spectra different from the $Co^{II}(N_4)$ final products (e.g., Figure 5).

We have found that the first solvolysis reaction is more rapid than the second so that $\tau_1 < \tau_2$ (e.g., Figure 4). For the second step (τ_2) ammine and nitro ligands are significantly more labile

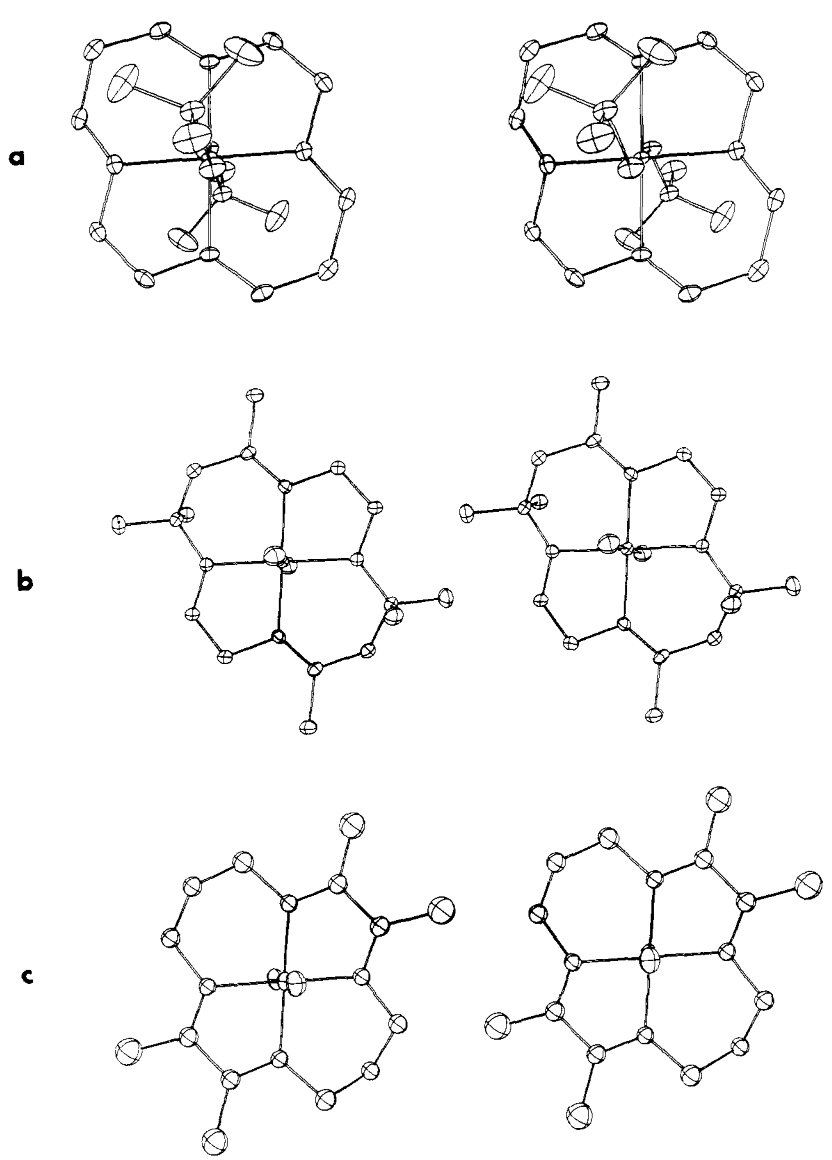


Figure 7. Stereoscopic views of the molecular units of the three Co(II) macrocyclic complexes with 20% probability thermal ellipsoids: (a) Co([14]aneN_4)$(ClO_4)_2$, (b) [Co(Me_6[14]4,11-dieneN_4)$(OH_2)_2$]$(BF_4)_2$, (c) [Co([14]tetraeneN_4)$(OH_2)_2$]$(ClO_4)_2$.

than cyano ligands. In each low spin cobalt(II) complex there are demonstrated to be two, presumably axial, very labile coordination positions.

D. Descriptions of Structures. The labeling used for the three cobalt(II) macrocyclic complexes studied crystallographically is given in Figure 6. Stereoscopic views of the three molecular units with 20% thermal ellipsoids are presented in Figure 7. Important distances and angles for the three compounds appear in Table IV. Packing diagrams are included as Figures S4-S6 in the supplementary material.

All three of the complexes studied comprise six-coordinate low-spin cobalt(II) coordinated to four nitrogenous donor sites of the macrocycle and to two axial ligands. The cobalt(II) ion, in all cases, resides at a crystallographic center of inversion; thus all compounds have crystallographic molecular symmetry $\bar{1}$ with the cobalt(II) ion centered in the equatorial plane. The equatorial Co-N bonds vary from 1.89 to 1.98 Å whereas the axial Co-O bonds vary from 2.29 to 2.48 Å. This elongation results from the presence of the unpaired electron in the d_{z^2} orbital of cobalt(II) and is of the mode commonly observed for Jahn-Teller distorted complexes.

More detailed examination of the coordination geometries shows the Co-N(sp^2) distances range from 1.89 to 1.94 Å, whereas the Co-N(sp^3) distances range from 1.97 to 1.98 Å. The angles about the cobalt(II) ions are comparable to those found in other N_4-macrocyclic complexes; the N-Co-N angles in the five-membered rings are in the range 83-86° and those in the six-membered rings are in the range 94-97°. The bond distances and angles in the macrocyclic backbone are normal with average distances of C—C, 1.51 Å, C—N, 1.49 Å, and C=N, 1.29 Å and expected variations for single bonds involving sp^2 and sp^3 atoms.

The ligand conformations found are those which are stereochemically favored. Maximum deviations of the torsion angles from the strain-free values are 11° ([14]aneN_4), 17° (Me_6-[14]4,11-dieneN_4), and 9° ([14]tetraeneN_4). In all cases this strain appears about the methylene carbon in the six-membered rings.

Discussion

While the major issues of concern in this paper require consideration of evidence from each of the three lines of experimental evidence reported, there are some important points to be considered regarding each line of investigation before entering into the general discussion.

A. Structural Studies. All three of the cobalt(II) complexes for which we have determined molecular structures were tetragonally distorted six coordinate. That we have been unable

Table IV. Important Distances and Angles[a]

	Co([14]aneN$_4$)-(ClO$_4$)$_2$	[Co(Me$_6$[14]4,-11-dieneN$_4$)-(OH$_2$)$_2$](BF$_4$)$_2$	[Co([14]-tetraeneN$_4$)-(OH$_2$)$_2$]-(ClO$_4$)$_2$
N1-C2	1.493 (6)	1.506 (8)	1.47 (2)
C2-C3	1.509 (7)	1.545 (9)	1.54 (2)
C3-C4	1.509 (8)	1.495 (10)	1.53 (2)
C4-N5	1.494 (6)	1.285 (8)	1.50 (2)
N5-C6	1.486 (6)	1.485 (8)	1.30 (2)
C6-C7	1.499 (7)	1.545 (9)	1.46 (2)
C7-N1′	1.489 (6)	1.469 (8)	1.29 (2)
N1-C2-C3	111.0 (4)	105.6 (5)	111 (1)
C2-C3-C4	114.7 (4)	118.1 (5)	112 (2)
C3-C4-N5	111.7 (4)	120.7 (6)	109 (2)
C4-N5-C6	110.9 (4)	119.2 (6)	117 (2)
N5-C6-C7	107.2 (4)	105.6 (5)	114 (1)
C6-C7-N1′	107.1 (4)	106.4 (5)	114 (1)
C7-N1′C2′	109.9 (4)	114.0 (5)	122 (2)
C4-C41		1.511 (9)	
C2-C21		1.536 (9)	
C2-C22		1.514 (9)	
C6-C61			1.53 (2)
C7-C71			1.55 (2)
Co-N1	1.982 (4)	1.968 (5)	1.891 (14)
Co-N2	1.978 (4)	1.936 (5)	1.904 (15)
Co-O$_w$		2.482 (5)	2.289 (15)
Co-O1	2.409 (3)		
Co-N1-C2	118.6 (3)	120.6 (4)	123 (1)
Co-N1-C7	107.9 (3)	107.4 (4)	114 (1)
Co-N5-C4	117.6 (3)	128.7 (5)	128 (1)
Co-N5-C6	108.1 (3)	112.1 (4)	115 (1)
N1-Co-N5	94.1 (2)	94.6 (2)	97 (1)
N1-Co-N5	85.9 (2)	85.4 (2)	83 (1)
N1-Co-O$_w$		96.9 (2)	87 (1)
N5-Co-O$_w$		92.5 (2)	91 (1)
N1-Co-O1	85.5 (2)		
N5-Co-O1	92.0 (2)		
Cl-O1	1.446 (3)		1.31 (4)
Cl-O2	1.416 (5)		1.37 (4)
Cl-O3	1.411 (4)		1.41 (4)
Cl-O4	1.420 (5)		1.44 (4)
Cl-O2*			1.56 (4)
Cl-O3*			1.49 (4)
Cl-O4*			1.36 (4)
B-F1		1.327 (9)	
B-F2		1.328 (8)	
B-F3		1.270 (10)	
B-F4		1.353 (9)	
Co-OO-Cl	126.7 (2)		

[a] The primed atoms are related to unprimed atoms by the inversion center at the Co(II) ion.

to obtain a [Co([14]aneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$ complex in recrystallizations from aqueous ethanol is consistent with very weak Co$^{\rm II}$-OH$_2$ bonding. That there is some axial bonding is manifested in the weak Co$^{\rm II}$-O-ClO$_3$ bonding interactions. It is clear from the structural determination that Co([14]aneN$_4$)(ClO$_4$)$_2$ is six coordinate; in contrast EPR and infrared data have been cited as evidence that Co([14]tetraeneN$_4$)(ClO$_4$)$_2$ is five coordinate.[21]

In fact the various structural studies have demonstrated a considerable variability of the weak axial bonding interactions in low spin cobalt(II) complexes. We have at one limit the centrosymmetric, tetragonal, six-coordinate complexes reported here, in which the axial bonding interactions apparently increase in strength with increased unsaturation in the equatorial (N$_4$) ligand. An intermediate example is [Co([14]-4,7-dieneN$_4$)(OH$_2$)PF$_6$]PF$_6$ which contains two nonequivalent axial ligands.[14] In that complex, the *average* axial bond length is close to that of [Co([14]4,11-dieneN$_4$)(OH$_2$)$_2$](ClO$_4$)$_2$, but Co$^{\rm II}$-OH$_2$ < Co$^{\rm II}$-F-PF$_5$, suggesting that substitutin of the weaker axial base PF$_6^-$ for H$_2$O has resulted in a strengthening of the remaining Co$^{\rm II}$-OH$_2$ bond. This effect has been seen in porphyrin complexes, where the bond to a single axial base (imidazole) has been found to be much shorter than the axial bonds when two axial bases (piperidine) are present (see Table V). If one carries this point of view a step further, introduction of a sufficiently strongly bonded axial base could be expected to greatly reduce or eliminate the acceptor properties of the trans-axial position. Such behavior seems to occur for the cyanide and phenylisocyanide complexes of cobalt(II).[13] In these complexes bonding to the axial cyanide apparently weakens the trans-bonding interaction. Furthermore, the longer axial than equatorial Co$^{\rm II}$-CN distance in Co(CN)$_5^{3-}$ suggests that one ought to expect some variability of the strengths of the Co$^{\rm II}$-CN axial interactions, although the range of bond lengths (and energies) observed may well be smaller than for aquo ligands.

B. Pulse Radiolysis Studies of Axial Lability. The cobalt(II) complexes examined in this study are all very labile in their axial coordination positions. The cyano complexes of cobalt(II) may be the most interesting systems investigated radiolytically. The solid state crystal structure of pentacyanocobaltate(II) shows that the axial cobalt-cyanide bond is about 0.2 Å longer than the equatorial cobalt-cyanide bonds.[13] This structural manifestation of the weakness of the axial bond has its kinetic counterpart in a ~300-fold difference in lability. In other words, the pulse radiolysis and hydrolysis of these complexes may be described by eq 5-8 where $\tau_1 < 10^{-6}$ s, $\tau_2 = (88 \pm 5) \times 10^{-6}$ s, and $\tau_3 = (3.6 \pm 0.3) \times 10^{-2}$ s. It should be noted that the total hydrolysis of Co^{2+} has been found to require times of the order of seconds[10] (we have written eq 5-8 with the usual understanding that solvent molecules will fill vacant coordination sites). In fact pentacyanocobaltate(II) appears remarkably similar to the Co$^{\rm II}$(N$_4$)CN complexes. Since the difference in charge ought to manifest itself in a longer lifetime (τ_2) as observed for Co$^{\rm II}$([14]tetraeneN$_4$)CN, the fortuitously similar values of τ_2 observed for Co(CN)$_5^{3-}$ and Co$^{\rm II}$(Me$_6$[14]-4,11-dieneN$_4$)CN probably reflect the difference in charge superimposed on the labilizing effect of the geminal methyl groups. This labilizing influence in the Co$^{\rm III}$(Me$_6$[14]4,11-dieneN$_4$)X$_2$ complexes has been estimated to contribute a factor of the order of 10^2 in the hydrolysis rate constants.[26f,47]

$$\mathrm{Co(CN)_5X^{3-} + e^- \rightarrow Co(CN)_5X^{4-} \xrightarrow{\tau_1} Co(CN)_5{}^{3-} + X^-} \quad (5)$$

$$\mathrm{Co(CN)_5{}^{3-} \xrightarrow[H^+]{\tau_2} Co(CN)_4{}^{2-} + HCN} \quad (6)$$

$$\mathrm{Co(CN)_4{}^{2-} \xrightarrow[H^+]{\tau_3} Co(CN)_3{}^{-} + HCN} \quad (7)$$

$$\mathrm{Co(CN)_3{}^{-} \rightarrow etc. \rightarrow Co^{2+}} \quad (8)$$

It was unexpected that the metal to ligand charge transfer transitions in the Co$^{\rm II}$(N$_4$)CN complexes should occur at higher energy than the similar transitions in the Co$^{\rm II}$(N$_4$) complexes (Figure 5), since the dicyano complexes are far more powerful reducing agents than their aquo analogues[26c] and the charge transfer transition energy should parallel the redox thermodynamics.[48-50] This feature is interpreted in section D, below.

C. EPR Studies. We have found superhyperfine interactions depending on the axial bases (e.g., Figures 2-3, Table SVII), with a medium dependent resolution of the superhyperfine

Table V. Average Coordination Parameters in Selected Low-Spin Co(II) Complexes

	Equatorial	Axial	Displacement of Co(II) from equatorial plane	Ref.
$Co([14]aneN_4)(ClO_4)_2$	4N at 1.98 Å	2 perchlorates at 2.41 Å	0.0	*a*
$Co(Me_6[14]4,11\text{-}dieneN_4)H_2O)_2(BF_4)_2$	2N at 1.92 2N at 1.98	2 waters at 2.48	0.0	*a*
$Co([14]tetraeneN_4)(H_2O)_2(ClO_4)_2$	4N at 1.90	2 waters at 2.29	0.0	*a*
Pip_2CoTPP[b]	4N at 1.99	2 piperidines at 2.44	0.0	17
Co(1-MeIm)OEP[c]	4N at 1.96	1 imidazole at 2.15	0.16 Toward imidazole	16
$[Co([14]4,7\text{-}dieneN_4)H_2O](PF_6)_2$	2N at 1.92	1 water at 2.28	0.02	14
	2N at 1.99	1 PF_6^{-1} anion at 2.56	0.16	
$[Co(CNC_6H_5)_5]ClO_4^+$	4C at 1.84	1 perchlorate at 2.59 1C at 1.95	Toward phenyl isocyanide	13d
$Co(CN)_5^{3-}$	4C at 1.89	1C at 2.01	0.25 Å Toward cyanide	13e

[a] This work. [b] Bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II). [c] 2,3,7,8,12,13,17,18-Octaethylporphinatobis(3-methylpyridine)cobalt(II).

interactions (e.g., Figure 3). We do not find any obvious correlation of any of the EPR parameters with the strength of the axial base, nor do our data imply in any simple way that any particular $Co^{II}(N_4)$ moiety is consistently either five coordinate or six coordinate. As qualitative examples note that we found that nitromethane (presumably a Co–O bond) as well as pyridine could result in nitrogen superhyperfine splittings (similar observations are noted in ref 21); for some complexes these were equally well resolved; yet it may be presumed that only pyridine binds to the cobalt through nitrogen. Further, solutions of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ in pyridine provided evidence for interaction of a single axial base (i.e., three components of the nitrogen superhyperfine splitting), this same complex in 1 M $NaNO_2$ provided some evidence for interactions with two axial bases (i.e., five components of the nitrogen superhyperfine splitting (Figure S1)); yet NO_2^- has proved to be an extremely labile ligand in $Co^{II}(N_4)(NO_2)_2$ complexes generated in fluid solution.

On a more quantitative level, it has been proposed[23] that among porphyrin complexes the energy of the $^2B_1$ excited state or the sign of the isotropic Fermi contact interaction can be systematically correlated with the type of axial bonding. Although the complexes studied here are only very approximately of D_{4h} or C_{4v} symmetry, the application of the simplified forms of McGarvey's treatment[51] are instructive.

For $Co^{II}([14]tetraeneN_4)$ in water and in 1 M HCl, the simplified McGarvey treatment gives the $^2A_1 \rightarrow {}^2B_1$ transition energy as 0.95 and 1.04 μm^{-1}, respectively, while these transitions are observed to occur at 1.04 and 1.02 μm^{-1} in the respective fluid solutions. This is rather good agreement and suggests that this approach has semiquantitative validity for the $Co^{II}([14]tetraeneN_4)$ systems, probably because g_x and g_y are not too dissimilar. In contrast the predicted energies of the $^2A_1 \rightarrow {}^2B_1$ transition in $Co^{II}(Me_6[14]diengN_4)$ systems are 0.4-0.6 μm^{-1} smaller than those observed, no doubt because the differences between g_x and g_y are larger for this complex.

Application of the approximate McGarvey treatment to the several $Co^{II}([14]tetraeneN_4)$, $Co^{II}([14]aneN_4)$, and $Co^{II}([14]tetraeneoximatoN_4)$ systems studied in this paper, predicts that the $^2A_1 \rightarrow {}^2B_1$ energies for these complexes should range from 0.8 to 1.1 μm^{-1} (Table II). The values observed for the $^2A_1 \rightarrow {}^2B_1$ transition in $Co^{II}(Me_6[14]dieneN_4)$ systems are all about 1.3 μm^{-1} (Table I). These energies are somewhat larger than those attributed to five-coordinate porphyrin complexes, and, if the correlation were applicable here, would be more consistent with six-coordinate species.

The average Fermi contact interaction, fitted to the approximate McGarvey equations, is very sensitive to errors in other parameters but has an average value of $K \sim (-10 \pm 7) \times 10^{-4}$ cm^{-1} for complexes with nearly axial spectra. This is more consistent with five coordination than six coordination according to the correlation proposed for porphyrin complexes.[23] Thus the correlations proposed[23] for porphyrins do not provide a consistent basis for the discussion of axial interactions in the cobalt(II) complexes we have studied.

The $Co^{II}([14]py(diene)N_4)$ system is rather interesting. The absorption spectra and bulk magnetic properties have been cited as evidence[31] that this complex is trigonal bipyramidal. Such a geometry would give rise to a $^2B_1$ ground state. As a consequence one would infer $g_\parallel > g_\perp$, contrary to observation (see Table SVII, Figure S2).[34] The apparent d_{z^2} ground state is compatible with a tetragonal geometry, similar to the other low spin cobalt(II) complexes considered here, with relatively larger difference between g_x and g_y. Actually the absorption spectra of $Co^{II}([14]py(diene)N_4)$ complexes are not qualitatively different from spectra of $Co^{II}([14]tetraeneN_4)$ complexes.

The increased resolution obtained for $Co^{II}([14]tetraeneN_4)$ in 50% pyridine D_2O (Figure 3) is suggestive of axial interaction with both water and pyridine.

D. General Discussion. The substitutional lability of cobalt(III) complexes containing macrocyclic ligands has been demonstrated by other workers to increase with (1) increasing unsaturation of the equatorial ligand;[27f,52,53] (2) alkyl substitution into the equatorial ligand;[7,47,52-55] and (3) the nature of the trans ligand.[7,27f,47,52-56] However, most of these labilizing effects in cobalt(III) complexes are kinetic effects and are not correlated with large changes in the ground state bond lengths (an exception occurs in complexes with cobalt-carbon bonds in which the labile Co–X bond in the trans position is appreciably lengthened[56]). The cobalt(II) complexes investigated in this study are clearly several orders of magnitude more labile in their axial positions than are their cobalt(III) analogues. Even with the increase in lability, a range of substitutional behavior has been found for these complexes. In contrast to the cobalt(III) analogues, the cobalt(II) complexes exhibit a large range of axial bond lengths. Despite this important contrast, aspects of our studies suggest that features important in the substitutional chemistry of cobalt(III) have their counterparts in the substitutional chemistry of low spin cobalt(II), but these are present in the latter only as perturbations on the dominating weakness of the axial bonding interactions. For example, steric effects may play a role in the relative rates of replacement of axial cyanide ligands by water, while equatorial ligand unsaturation may be a feature in the relative labilities of axial NH_3.[55] Such relatively small variations aside, both axial positions in the low spin cobalt(II) complexes are labile. Axial cyanide is somewhat less labile than axial ammonia which in turn is roughly comparable to or a bit less labile than axial NO_2^-. These observations are consistent with relatively weak axial bonding in which the more basic ligand forms the stronger bond, and with a wide range of axial bonding interactions. That the cobalt-axial ligand bonding interaction is found to be increased at the expense of the bonding interaction in the trans position suggests a strong synergistic trans-influence in these low spin d^7 systems. The weakness of the bonding interaction and the inferred parallels between bond strength and basicity suggest that a simple three-center σ-bonding model might provide insight into the axial bonding in these complexes.

A simple three-center bonding scheme which combines axial ligand σ-orbitals (χ_X and χ_L) with symmetric metal acceptor orbitals (χ_M) results in bonding (ψ_B), nonbonding, (ψ_{NB}), and antibonding (ψ_{AB}) wave functions as in eq 9–11.

$$\psi_B = a_1\chi_X + a_2\chi_M + a_3\chi_L \tag{9}$$

$$\psi_{NB} \simeq b_1\chi_X + b_2\chi_L \tag{10}$$

$$\psi_{AB} \simeq c_1\chi_X - c_2\chi_M + c_3\chi_L \tag{11}$$

The energy of the axial bonding orbital for a tetragonally distorted six-coordinate complex with identical axial ligands may be expressed as eq 12,[57]

$$E_{BMO} \simeq \frac{(\alpha_1 - 4\beta S)}{(1 - 2S^2)}\left[1 + \frac{2\beta^2(1 - 2S^2)}{(\alpha_1 - 4\beta S)^2}\right] \tag{12}$$

while the energy of the antibonding orbital may be expressed as eq 13.[57]

$$E_{ABMO} \simeq -\frac{2\beta^2}{\alpha_1 - 4\beta S} \tag{13}$$

For a weak donor-acceptor interaction in a five-electron system, the odd electron will be in an antibonding orbital with a great deal of $d_{z^2}(\chi_M)$ character, as is found for the low spin cobalt(II) complexes. In the simplest case, as the bonding component to one axial ligand (e.g., M–X) is strengthened, the trans-bonding component (e.g., M–L) will be weakened. The antibonding wave function (eq 11) will have a node between M and X and between M and L; strengthening the M–X bond will have the effect of placing more of the antibonding electron density in the M–L region than in the M–X region. Since the unpaired electron of the low spin cobalt(II) complexes is in an antibonding orbital, there is a greater probability that this electron density will be nearer the more weakly bonding of an axially nonequivalent pair of ligands. Consequently the observation of ligand superhyperfine splitting in a low spin d^7 system is not an adequate criterion for strong metal–ligand bonding. If the M–X bond is much stronger than the M–L bond, and neglecting overlap, eq 12 and 13 become

$$E'_{BMO} \sim \left\{\alpha_1\left[1 + \frac{(\beta')^2}{{\alpha_1}^2}\right] + \frac{\delta^2}{\alpha_2}\left[1 + \frac{1}{\gamma}\right]\right\}$$

and

$$E'_{ABMO} \sim -\left[\frac{(\beta')^2}{\alpha_1} + \frac{\delta^2}{\alpha_2\gamma}\right]$$

where $\gamma^2 \simeq (1 + \beta^2/\alpha_1\alpha_2)$. For $|\delta^2/\alpha_2| \ll |(\beta')^2/\alpha_1|$, $E'_{ABMO} < E_{ABMO}$ when $\beta' < \beta\sqrt{2}$. Thus a shift of the metal to ligand charge transfer absorption ($\psi_{ABMO} \rightarrow {}^*\pi(N_4)$) to higher energy for $Co^{II}(N_4)CN$ as compared to $Co^{II}(N_4)(OH_2)_2$ is consistent with weak axial bonding interactions and with Co^{II}–CN^- being stronger than Co^{II}–OH_2. Thus the spectroscopic, kinetic, and structural evidence are in accord with one relatively strong and one very weak axial bond when the low spin cobalt(II) complex contains an axial cyanide. In systems where no suitable sixth ligand is available similar reasoning would lead one to expect a strengthening of the bond to even a weak axial base and a further decrease in energy of the d_{z^2} orbital. This appears to be the case for $Co([14]tetraeneN_4)X^+$ (X = Cl, Br) complexes in noncomplexing media.[24]

Some current approaches to the theory of the trans-influence[58] and to bonding in pentacoordinate complexes[59] implicate a contribution of an antisymmetric metal orbital (e.g., p_z) in addition to the symmetric orbital component considered above. This approach will result in two bonding orbitals and a more complex combination of orbital contributions than we have used in eq 9–13. However, the qualitative points made above are not significantly altered. At this time, the inclusion of additional metal-orbital (i.e., p_z) contributions in the description of the weak axial bonding of low spin d^7 systems may not be much more useful than the three-center, three-orbital approach considered above.

Whatever the details of the model for axial bonding one might prefer, it is evident that the axial interactions in these complexes are not so easily categorized that one may dogmatically presume that all the complexes with a given equatorial ligand are either "five coordinate" or "six coordinate" in solution. Clearly for each metal-equatorial ligand system there is a range of axial interactions, and as one axial bond becomes stronger, the bond to the trans-position must become weaker. At some point it probably becomes useful to consider the system as "five-coordinate" in solution, at least in limited chemical contexts. This limit seems to be approached by complexes with cyanide or phenylisocyanide in an axial position and by several other systems in noncomplexing media. On the basis of the relative σ-donor ability of the ligand (as manifested in proton affinities),[60,61] one would expect axial bond strengths to increase in the order: $H_2O < CH_3CN < NH_3 < py \ll CN^-$. Thus the pyridine (and acetonitrile[21]) complexes are no doubt intermediate in their bonding interactions and it is not obvious that the observation of nitrogen superhyperfine in the EPR provides more information about the nature of the cobalt-pyridine bonding interaction than about the locus of electron density in the antibonding orbital. Certainly the interaction with electron density in a diffuse antibonding orbital would conveniently account for nitrogen superhyperfine structure observed in nitromethane media.

Much of our concern with the nature of low spin cobalt(II) species in aqueous solution originated in our attempts to document the contributions of ligand reorganizational barriers to the rates of electron transfer reactions.[15,25,27b,d,g,62] The aquo complexes we have investigated are six-coordinate in the solid state. A large number of oxidations of the $Me_6[14]4,11$-$dieneN_4$ and $[14]teteneN_4$ complexes of cobalt(II) in aqueous solution appear to be substitution limited with $k_{obsd} = K_{os}k_w$,[62b,63-65] and with K_{os} an "outer sphere" (or precursor) formation constant and $k_w \sim 10^9\ s^{-1}$. This is most consistent with the $Co(N_4)(OH_2)_2{}^{2+}$ formulation in solution and with the evidence and models discussed in the present report.

An unexpected inference from the present study is that replacement of one of a pair of axial water molecules by a more weakly bonding ligand should result in a shortening of the bond to the remaining water molecule. In the precursor complex for an inner sphere electron transfer reaction of a $Co(N_4)(OH_2)_2{}^{2+}$ substrate, one of the axial water molecules will be replaced by some very weakly basic ligand (e.g., MCl^{2+}), and consequently the bond to the remaining aquo ligand should shorten and the Franck–Condon barrier to the electron transfer process should be diminished.[66] Based on available structural data this shortening of the Co^{II}–OH_2 bond in the inner sphere precursor complex may be estimated to be in the range of

0.1–0.4 Å and could result in a reorganizational barrier which is 4–50 kJ/mol lower than that for outer sphere oxidation of the corresponding $Co(N_4)(OH_2)_2^{2+}$ complex. Thus the "role" of the bridging ligand may be somewhat less direct and more varied than has been commonly believed.[67]

Conclusions

The results of our investigations of axial interactions in low spin cobalt(II) complexes may be summarized as follows: (1) Low spin d^7 systems are axially labile. (2) Axial lability in these systems is correlated with an elongation of axial bond lengths found in x-ray structural studies. (3) Low temperature EPR studies indicate that the unpaired electron in these systems is in an axial orbital of significant d_{z^2} character. (4) The range of axial bonding interactions, including an apparent axial trans influence, is at least qualitatively described by a three-center, five-electron bonding model. (5) The inferred synergistic trans influence has significant implications for models of inner sphere electron transfer reactions.

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Supplementary Material Available: Atomic parameters, tabulated structure factors, tabulated EPR parameters, Figures S1–S6 (EPR spectra and packing diagrams), and Appendix I (variational treatment of three-center bonding) (36 pages). Ordering information is available on any current masthead page.

References and Notes

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Molecular Transforms: a Potential Tool for Structure-Activity Studies[1]

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Abstract: A chemical pattern recognition approach to the study of structure–activity relationships has been investigated. In this work, a generalized molecular transform function has been examined as a possible nonprejudicial structure encoding scheme. For the set of 114 tranquilizers and 72 sedatives used in this study, such a procedure is shown to be efficacious. These results are compared with those of a previous study, using substantially the same set of compounds, in which molecular fragment coding was used, and the present method is shown to be essentially as effective for the dichotomy of the tranquilizers and sedatives examined. Examination of the patterns generated suggests the possibility of extracting geometric "prototypes" for each activity class.

The objective of correlating molecular structure with chemical activity is one of the fundamental driving forces of chemical inquiry. In organic chemistry, structure–activity relationships have been successfully pursued by Hammett analysis, in the empirical domain, and by theoretical constructs, such as orbital symmetry rules.

In pharmacology, more elusive structure–activity relationships have also been pursued at both the empirical and the theoretical levels.[3] The complexity of metabolic processes virtually guarantees complexity in the relationship between the structure of a pharmacologic agent and the observable reaction of the recipient organism. Since the agent affects a system involving not one chemical reaction but several coupled reactions occurring in a physically heterogeneous medium, the relation between modifications in structure and the corresponding modifications in activity may well be obscure. It is in such situations, where the existence of a complex but genuine relationship is suspected, that the methods of pattern recognition can be most useful.

Chemical applications of pattern recognition have been extensively discussed in recent literature.[4] In pattern recognition analysis, a complex relationship within a group of patterns (representing chemical compounds, in the present case) is reduced to a readily understood measure such as nearness in a multidimensional space or to some other similarity measure based on multidimensional representation of the patterns. For reference, we contrast this approach with that of Hansch analysis and of Free–Wilson analysis, which typify two major avenues for current pharmacological structure–activity study.

One can view the search for structure–activity relationships very generally as a quest for functions of the form

$$\text{activity} = f(\text{molecular features})$$

Here, the definitions of the activity, of the functional relationship f (not necessarily an explicit analytic formula), and of the nature of the molecular features employed characterize any particular approach to the problem. In Hansch analysis, the biological activity is related to a dose level required to produce a standard effect; the function f is generally a polynomial of the second degree; and the molecular features are physicochemical data including octanol-water partition coefficients, Hammett-type ρ–σ electronic parameters, and, in some cases, a steric term.[5] The Free–Wilson method also defines activity on a quantitative scale of response, such as LD_{50}; here, the function f is a linear additive combination of "substituent contribution" terms; and the features themselves are simply the identities of the various substituents on some parent compound.[6] Both of these methods begin with a specific active structural nucleus, for which the magnitude of the activity can be modified by modifying various substituents. In contrast, the pattern recognition approach to structure–activity correlation takes the broader (and, perhaps, more naive) view that a diverse group of materials with similar *qualitative* biological activity may possess some common set of molecular characteristics which are responsible for the activity. In this case, the biological activity is defined as a qualitative type of action (for example, sedation, analgesia); the function f is a pattern discriminator capable of recognizing materials of a particular activity class; and the molecular features can be either physicochemical data or items from a predetermined list of descriptors, including fragment identities, molecular weight, topological features, and so forth. The first stage in such an analysis is to create a pattern classifier which can