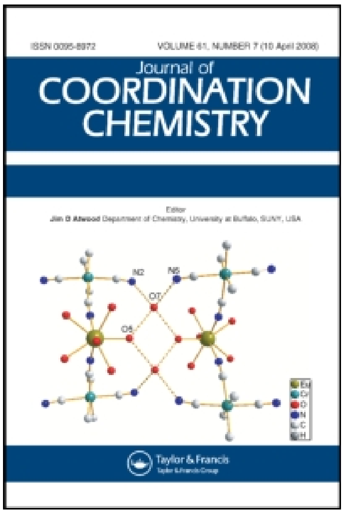

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AXIAL COORDINATION IN COBALT(II) COMPLEXES OF TWO SYNTHETIC MACROCYCLIC LIGANDS CONTAINING THE BIDENTATE α-DIIMINE GROUP

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In order to elucidate the nature of axial coordination in synthetic macrocyclic complexes of cobalt(II), we have synthesized two new series of such complexes, containing the macrocycles $\mathrm{Me_4}$[14]1,3,8,10-tetraene$\mathrm{N_4}$ and $\mathrm{Me_2}$[14]1,3-diene$\mathrm{N_4}$, by direct isolation of the Co(II) complexes from the condensation reaction mixtures. The complexes are formally five-coordinate in the solid state, but exhibit a tendency toward six-coordination in the presence of potential axial ligands, as demonstrated by electronic spectral and electron paramagnetic resonance studies. The Co(tetraene$\mathrm{N_4}$)$^{+2}$ and Co(diene$\mathrm{N_4}$)$^{+2}$ species are compared with the previously studied Co($\mathrm{Me_6}$[14]4,11-diene$\mathrm{N_4}$)$^{+2}$ moiety with respect to axial coordination. It is concluded that the presence of methyl substituents on the six-membered chelate rings of the latter complex have a marked effect on its tendency to coordinate axial ligands.

INTRODUCTION

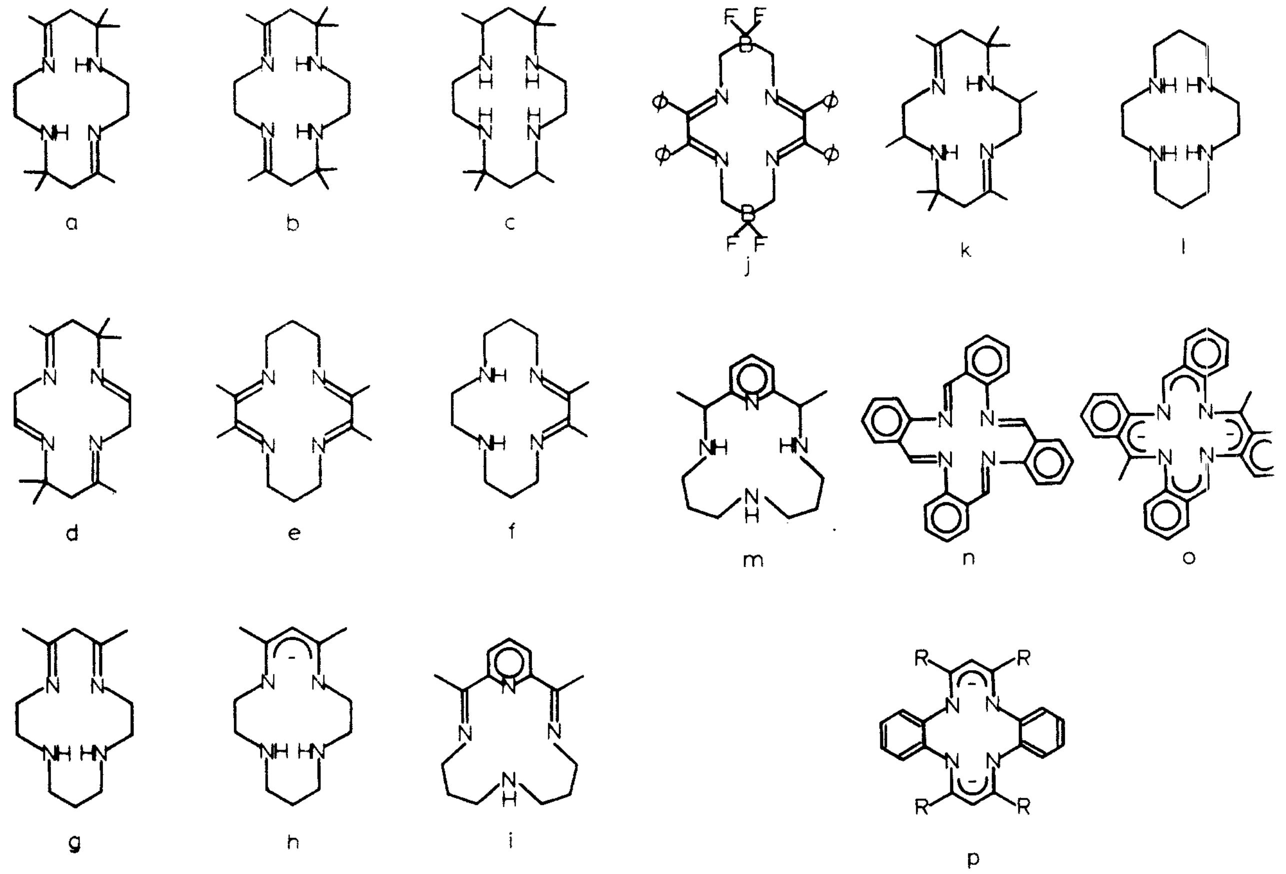
The use of synthetic macrocyclic ligands to provide a greater understanding of the metal-ligand interaction in bio-inorganic chemistry has recently been described in detail.[1,2] Cobalt complexes of such ligands are of interest with respect to their abilities to reversibly bind molecular oxygen[3-6] and to form cobalt-carbon bonds.[7-11]

At the present time, cobalt(III) complexes with several tetradentate, nitrogen-donor macrocyclic ligands are known,[12-21,28] and many of the analogous complexes with Co(II) have also been described.[22-34] Non-porphyrin synthetic macrocyclic ligands whose complexes with Co(II) have been studied are shown in I. The complexes with ligands Ia,[6,35] Ie, Ij, In, and Io[32] reversibly bind molecular oxygen, while those containing the ligands Ia,[7,8] Ie,[9,11] and Ii[9,10] react to form cobalt-carbon bonds, and are thus analogs of Vitamin B_{12}.

The cobalt(II) complexes of the ligands, I, are predominantly low spin, with the macrocycle encircling the cobalt(II) ion in square planar fashion and the additional ligand(s) occupying the axial position(s). The low spin d^7 configuration for Co(II) has, until recently, been found only in complexes containing sulfur or phosphorus donor atoms,[36-41] the complexes with fully saturated, non-cyclic nitrogen donors being high spin[42-43] and five- or six-coordinate.[43,44]

The extent of axial coordination in cobalt(II) complexes containing synthetic macrocyclic ligands is a matter of some uncertainty. In the course of their investigations of the outer sphere electron transfer reactions of $\mathrm{Co^{II,III}(N_4)}$ ($\mathrm{N_4}$ = a tetradentate nitrogen donor macrocyclic ligand) complexes, Endicott and co-workers have repeatedly addressed the problem. They have classified[45] low spin cobalt(II) complexes into two categories, based on coordination geometry: (a) 5-coordinate, for which the prototype is $\mathrm{Co(CN)_5}^{-3}$;[46,47] (b) tetragonally (or axially)-distorted 6-coordinate for which Co($\mathrm{Me_4}$[14]1,3,8,10-tetraene$\mathrm{N_4}$)$\mathrm{(H_2O)_2}^{+2}$ [31,48-49] might be considered the prototype. The classification has been based on, and applies to, solid state structural determinations, and many examples of each type have been found (for type (a), see 29,46–47, 50–53, for type (b), see 31,48–49,54–55). Although the interpretation of X-ray structural data in terms of 5- or 6-coordination is often clear, there are examples in which occupation of the 6th coordination position is a matter of opinion. For instance, the complex [Co($\mathrm{Me_6}$[14]4,7-diene$\mathrm{N_4}$)$\mathrm{(H_2O)}$]$\mathrm{(PF_6)_2}$ adopts a crystal structure[26] in which the axial Co–O bond length is 2.283(9) Å, with a fluorine of one $\mathrm{PF_6}^-$ anion "occupying" the second axial site at a distance of 2.559 Å. Although Endicott and co-workers include this in the 6-coordinate category,[31] we choose to place it in the 5-coordinate category.

The nature of the low spin Co(II) complexes in solution is less clear, since the axial sites are labile.



Scheme I

a. Me$_6$ [14] 4,11-dieneN$_4$;
b. Me$_6$ [14] 4,14-dieneN$_4$;
c. Me$_6$ [14] aneN$_4$;
d. Me$_6$ [14] 1,4,8,11-tetraeneN$_4$;
e. Me$_4$ [14] 1,3,8,10-tetraeneN$_4$;
f. Me$_2$ [14] 1,3-dieneN$_4$;
g. Me$_2$ [14] 4,7-dieneN$_4$;
h. Me$_2$ [14] 4,7-dienoN$_4$;
i. [14] pentaeneN$_4$;

j. ϕ_4 [14] teteneoximatoN$_4$;
k. Me$_8$ [14] 4,11-dieneN$_4$;
l. [14] aneN$_4$;
m. [14] trieneN$_4$;
n. TAAB;
o. Me$_2$ TAAB;
p. R$_4$ [14] hexaenatoN$_4$, R = CH$_3$, R = H

Depending upon such factors as solvent, available axial ligands, and temperature, a given Co^{II}(N$_4$) moiety may be either five- or six-coordinate in solution, and in fact may be five-coordinate in solution even though it is six-coordinate in the solid state,[6,26] and vice versa. The extent of coordination in solution has most often been deduced from epr spectra of frozen solutions,[3,4,6,28,33,34,57-66] although electronic spectral and conductivity data have been used as well.[6] The latter method has been employed primarily for complexes of the type [Co(N$_4$)X] Y, where X = halide and Y = ClO$_4^-$, PF$_6^-$, BF$_4^-$, or Bϕ_4^-, and is admittedly risky, since the observance of 1:1 electrolyte behavior (i.e., the halide remains coordinated) does not rule out coordination by solvent in the second axial position. Electron paramagnetic resonance provides the most direct indication of the extent of axial coordination in solution, but only in cases where the axial ligands contain a donor atom with nuclear spin. It is very seldom possible to observe isotropic epr spectra for fluid solutions containing Co(II) complexes at room temperature, since electron spin relaxation times are generally short. Therefore, spin Hamiltonian parameters are obtained from the anisotropic spectra of frozen solutions, usually measured at 77°K. These spectra reflect the extent of axial coordination at the temperature at which freezing occurs. The freezing point of the solvent and the rate of freezing of the sample are therefore important factors. While a given complex may exhibit five-coordination in a high-melting solvent such as water, it may well exhibit six-coordination in a low-melting solvent such as acetone or methanol. A change in the equilibrium constant for formation of the 6-coordinate species over a 90° temperature interval is expected if ΔH for the process is favorable, and could give rise to a shift from 5- to 6-coordination. Thus the extent of axial coordination as inferred from frozen solution epr spectra is not necessarily the same as at room temperature. For a given solvent, it is possible to compare the axial interaction of various $Co^{II}(N_4)$ species with a given axial ligand, or the interaction of one $Co^{II}(N_4)$ species with several potential axial ligands, with some reliability using frozen solution epr spectra. However, extrapolations to room temperature are dangerous.

In an attempt to clarify the picture of axial ligation in low-spin $Co^{II}(N_4)$ species, we have undertaken the synthesis and investigation of two series of such complexes containing a variety of axial ligands. The two macrocyclic ligands involved are 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene(Ie, abbreviated tetraeneN_4), and 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene (If, abbreviated dieneN_4). Although some Co(II) complexes with these macrocycles have been previously synthesized and studied,[14,26,30,67-69] the range of axial ligands investigated has been limited. In addition, previous methods have almost all involved synthesis of Co(III) complexes, followed by reduction to the Co(II) complex using Cr^{+2}. We present methods for the direct isolation of the Co(II) complexes from the condensation reaction mixture, by precipitation with tetraphenylborate anion. Many of the complexes are five-coordinate when so prepared. In addition, we present a novel synthesis of the six-coordinate compound, $[\bar{C}o(tetraeneN_4)(CH_3CN)_2](B\phi_4)_2$, using ethanol to reduce the diaquo cobalt(III) complex. (The potent oxidizing ability of $Co(tetraeneN_4)^{+3}$ has been previously noted,[70-71] as has the tendency for ethanol to reduce macrocyclic complexes of Co(III).[72]) This material can be synthesized in very pure form by this method and can be used as a starting material to prepare the other complexes reported herein. Molar conductivities, magnetic moments, electronic spectra, and electron paramagnetic resonance spectra of the two series of complexes have been measured and used to analyze the axial bonding situation. Low solid state magnetic moments for some of the stoichiometrically-five-coordinate complexes are discussed in terms of metal-metal interactions through halide bridges.

Finally, some interesting oxidation reactions are described.

RESULTS AND DISCUSSION

The cobalt(II) complexes of the ligands, tetraeneN_4, Ie, and dieneN_4, If, have been prepared by condensation of biacetyl with the primary amine functions of 1,3-diaminopropane and N,N-*bis* (3-aminopropyl)-1,2-diaminoethane (referred to as 3,2,3), respectively, in the presence of cobalt(II). As described earlier,[12] this type of condensation reaction of biacetyl is critically dependent upon conditions, the macrocycles being successfully synthesized in isolable quantities only when the reactions are performed in

TABLE I
Analytical data for the complexes

Complex	Found C	H	N	Hal	Calcd. C	H	N	Hal
$[Co(tetraeneN_4)Cl]B\phi_4$	68.7	6.6	8.8	5.4	68.9	6.6	8.5	5.3
$[Co(tetraeneN_4)Br]B\phi_4$	64.8	6.3	7.7	11.1	64.6	6.2	7.9	11.3
$[Co(tetraeneN_4)I]B\phi_4$	60.2	5.8	7.4	16.8	60.6	5.9	7.4	16.9
$[Co(tetraeneN_4)(H_2O)](B\phi_4)_2$	77.0	7.0	5.7		77.3	6.9	5.8	
$[Co(tetraeneN_4)(CH_3CN)_2](B\phi_4)_2$	77.0	6.84	8.19		77.1	6.86	8.18	
$Co(tetraeneN_4)(NCS)_2$	37.0	4.7	15.9	12.2(S)	36.7	4.6	16.1	12.2(S)
$[Co(dieneN_4)Cl]B\phi_4$	67.6	7.0	8.7	5.4	67.8	6.9	8.8	5.6
$[Co(dieneN_4)Br]B\phi_4$	63.9	6.7	8.2	11.6	63.4	6.4	8.2	11.7
$[Co(dieneN_4)I]B\phi_4$	59.5	6.1	7.7	15.9	59.2	6.0	7.7	16.1
$[Co(dieneN_4)(H_2O)_2](B\phi_4)_2 \cdot 2H_2O$	72.3	7.2	5.7		72.5	7.3	5.6	

the presence of a suitable quantity of acid. The best yields of these complexes were rather low (5–15%, on cobalt(II)), and we succeeded in isolating them from the reaction mixtures only as the insoluble tetraphenylborate salts.

The condensation of biacetyl with these two amines in the presence of hydrohalic acid and Co(II) leads to complexes containing the corresponding halide ligand, as shown by analysis (see Table I). The thiocyanate derivative, Co(tetraeneN_4) $(NCS)_2$, was synthesized by allowing the condensation of the monohydroperchlorate of 1,7-diaminopropane and biacetyl to proceed in the presence of anhydrous cobalt(II) thiocyanate and sodium acetate. By this procedure a much higher yield of the macrocyclic complex (~42%) was obtained.

When the tetraeneN_4 formation reaction was performed in the absence of coordinating anion (i.e., by use of perchloric, instead of hydrohalic, acid and cobalt(II) acetate) the aquocomplex was isolated. This same material has been prepared in aqueous solution using chromous ion to reduce the cobalt(III) derivative [Co(tetraeneN_4)Br_2] Br.[30] The complex [Co(tetraeneN_4) $(CH_3CN)_2$] $(B\phi_4)_2$ has been synthesized in a novel way from [Co(tetraeneN_4) $(H_2O)_2$] $(PF_6)_3$ using ethanol as the reductant.[70] Very pure, crystalline samples of the complex were obtained by this route, which has the advantage of avoiding Cr^{+3} contamination.

Reduction of [Co(dieneN_4)Cl_2] ClO_4 by chromous chloride in water produces the aquo-cobalt(II) complex ion. On the addition of $NaB\phi_4$, this is precipitated as a pink material whose analysis (Table I) corresponds to the composition Co(dieneN_4) $(H_2O)_n$ $(B\phi_4)_2$(n = 3 to 4). The infrared spectrum has three bands in the ν(O–H) region at 3600, 3540, and 3470 cm^{-1}, a single ν(N–H) band at 3225 cm^{-1} and a very strong band corresponding to δ(O–H) at 1620 cm^{-1}. In a dry atmosphere at 35°C, the complex changes color slightly to orange-pink, with a weight loss corresponding to one water molecule, and the ir spectrum changes as follows. The two high energy ν(O–H) bands disappear, the ν(N–H) band splits into a doublet at 3212 and 3175 cm^{-1}, and the δ(O–H) band loses nearly half its intensity. In a wet atmosphere, these changes are reversed. Thus, the additional, weakly-held, water molecule probably enters into hydrogen-bonding with one of the secondary amine protons of the macrocycle. Such interaction is unusual, but has been observed before in nickel(II) complexes of the macrocycles [14]pentaeneN_4 and Me_6 [14]4,11-dieneN_4,[73] as well as in a recently synthesized cobalt(II) complex.[29]

Oxidation Reactions

All of the complexes are air-stable in the solid state, but air causes solutions to rapidly turn dark brown in color. This color change, possibly due to formation of μ-peroxobridged dimers containing Co(III), is quite common for polyamine complexes of Co(II).[32c,70] These reactions were not pursued further. In acid solution, rapid quantitative oxidation by air occurs to yield the *trans*-diacido cobalt(III) complexes reported earlier.[12]

Oxidation of the cobalt ion can also be achieved by use of other oxidizing agents. For example, NO_2-free NO causes a rapid color change of an acetone or acetonitrile solution of [Co(tetraeneN_4)X] $B\phi_4$ (X=Cl or Br) from red-purple to yellowish-brown. Addition of water initiates crystallization of [Co(tetraeneN_4)X(NO)] $B\phi_4$. In both cases, ν(N–O) may be observed as a very strong, sharp band at 1690 cm^{-1}, within the range 1600–1800 cm^{-1} reported for several series[75-78] of similar cobalt nitrosyl complexes. Upon shaking the nitrosyl complex in an acetonitrile/water mixture, the red complex [Co(tetraeneN_4) $(CH_3CN)_2$] $(B\phi_4)_3$ is formed, accompanied by total loss of NO (by infrared). The same *bis*-acetonitrile complex is generated quantitatively upon the addition of the versatile oxidizing agent $NOBF_4$ to the cobalt(II) complexes in acetonitrile.

As we shall demonstrate below, the five-coordinate complexes (i.e., those with axial halide) exhibit square pyramidal geometry, having a $^2A_1$ electronic ground state arising from a single electron in the d_z2 orbital of Co(II). Since this orbital is directed through the vacant coordination site, the complexes may be thought of as free-radicals. Indeed the tetraeneN_4 derivatives react directly with alkyl halides (R–X), suffering oxidative addition by one of the fragments of the homolysis of the C–X bond. Thus, one mole of [Co(tetraeneN_4)X] BPh_4 is half converted to the alkyl complex [RCo(tetraeneN_4)X] BPh_4, the other half becoming [Co(tetraeneN_4)X_2] BPh_4. We have described these oxidation reactions and their products in greater detail in a paper[11] concerned directly with the cobalt-carbon bond.

Infrared Spectra

The infrared spectra of both series of complexes imply, by the absence of carbonyl C=O and primary amine N–H stretching bands, that condensation to form the cyclic ligands has occurred. The spectra of the tetraeneN_4 complexes are essentially identical with the exception of bands assignable to monodentate ligands or to anions. The spectra are also similar to those of the corresponding Ni(II) and Co(III) derivatives, the most important features being a broad, weak C=N stretching vibration around 1610 cm^{-1} and a very sharp band of medium intensity at 1215 cm^{-1} which we earlier[12] assigned to a coupled vibration of the α-diimine fragment. The spectra of the cobalt(II) complexes of dieneN$_4$ are likewise similar to each other and to those of the corresponding Ni(II) and Co(III) complexes. Here, the salient features are a single secondary amine N–H stretching vibration around 3190 cm^{-1}, a very broad, weak absorption in the C=N stretching region around 1600 cm^{-1} and the sharp α-diimine band of medium intensity at 1190 cm^{-1}. As detailed above, the aquo complex crystallizes with weakly bound water in its structure. This affects the N–H stretching modes of the ligand considerably.

Conductivity Studies

Table II shows molar conductivity data for 10^{-3} to 10^{-4} M solutions of the complexes in nitromethane at room temperature. Complexes of the type [Co(macrocycle)X]$B\phi_4$ (X=halide) display standard 1:1 electrolyte behavior, while the aquo and acetonitrile complexes are 2:1 electrolytes. In all cases, approximately standard behavior was observed for concentrations between 10^{-3} and 10^{-5}M, dissociation effects becoming noticeable at the lowest concentrations. We therefore conclude that the halide ligands remain coordinated in nitromethane down to a concentration of 10^{-5}M. Whether or not the complexes are five- or six-coordinate is not determinable by conductivity measurements, since coordination of a solvent molecule in the second axial site would not affect the results.

In acetonitrile, molar conductance measurements showed that some dissociation of the halide complexes occurred at concentrations of 10^{-4}M and below. In agreement with these results, the complex [Co(tetraeneN$_4$)($CH_3CN)_2$]$(B\phi_4)_2$ may be obtained upon repeated recrystallization of any of the complexes from acetonitrile in the presence of excess $NaB\phi_4$(ν(C≡N) = 2295 cm^{-1} (w) and 2280 cm^{-1} (w)). There are concomitant changes in the electronic spectra of the complexes in this solvent, although both types of measurement imply that dissociation is not totally complete, even at 10^{-5}M. EPR spectra of frozen acetonitrile solutions of the complexes indicate complete displacement of axial halide by CH_3CN at the freezing point of acetonitrile (−45.7°C) for concentrations as high as 10^{-3}M. Moreover, the spectra indicate that both axial sites are occupied (*vide infra*). Apparently the 60° temperature change increases the equilibrium constant for acetonitrile binding more rapidly than that for halide binding, implying a larger enthalpy of interaction between the cobalt complexes and acetonitrile.

Magnetic Properties

The effective magnetic moments of the complexes are collected in Table III. They indicate the low spin d^7 configuration in all cases. The moments of the tetraeneN$_4$ complexes are slightly higher than the spin-only values for one unpaired electron, as are those for the large majority of low-spin pentacoordinate cobalt(II) compounds containing macrocyclic ligands.[16,25,28,29]

We shall argue that the electronic ground state for the complexes under discussion here is an orbital singlet ($^2A_1$), so no orbital contribution to the moment is expected. The slightly high values of the moments presumably result either from the presence of a high-spin impurity or from second-order spin-orbit coupling interactions.

TABLE II
Molar conductances of the complexes

Complex	Solvent	Concentration (molar)	Ω_M (cm^2/ohmmole)	Electrolyte Type
[Co(tetraeneN$_4$)Cl] BPh_4	CH_3NO_2	8.1×10^{-4}	67	1:1
	CH_3CN	3.1×10^{-4}	105	1:1
[Co(tetraeneN$_4$)Br] BPh_4	CH_3NO_2	7.9×10^{-4}	69	1:1
[Co(tetraeneN$_4$)I] BPh_4	CH_3NO_2	8.3×10^{-4}	71	1:1
[Co(tetraeneN$_4$)($CH_3CN)_2$] $(B\phi_4)_2$	CH_3NO_2	8.0×10^{-4}	143	2:1
[Co(dieneN$_4$)Cl] BPh_4	CH_3NO_2	3.0×10^{-4}	82	1:1
[Co(dieneN$_4$)Br] BPh_4	CH_3NO_2	6.9×10^{-4}	70	1:1
[Co(dieneN$_4$)I] BPh_4	CH_3NO_2	4.0×10^{-4}	65	1:1

TABLE III
Room temperature magnetic moments for Co(II) complexes of tetraeneN_4 and dieneN_4

Compound	μ_{eff} (B.M.)	Method and Medium
[Co(tetraeneN_4)Cl] BPh_4	2.22	Faraday, solid
[Co(tetraeneN_4)Br] BPh_4	2.03	Faraday, solid
[Co(tetraeneN_4)I] BPh_4	1.98	Faraday, solid
[Co(dieneN_4)Cl] BPh_4	1.5	Faraday, solid
[Co(dieneN_4)Cl] BPh_4	2.02	NMR, 7×10^{-3}M sol'n in CH_3NO_2
[Co(dieneN_4)Br] BPh_4	1.1	Faraday, solid
[Co(dieneN_4)Br] BPh_4	1.88	NMR, 5.6×10^{-3}M sol'n in CH_3NO_2
[Co(dieneN_4)$(H_2O)_2$] $(BPh_4)_2 \cdot 2H_2O$	1.98	Gouy, solid
[Co(dieneN_4)$(H_2O)_2$] $(BPh_4)_2 \cdot 2H_2O$	1.96	NMR 10^{-3}M sol'n in CH_3NO_2

The moments for solid samples of the chloro- and bromo-complexes of dieneN_4, on the other hand, are significantly lower than the spin-only value, whereas the aquo complex [Co(dieneN_4) $(H_2O)_2$] $(B\phi_4)_2 \cdot 2H_2O$ behaves normally. In nitromethane solution all three dieneN_4 complexes have moments near 2.0 B.M. These results indicate significant spin-spin interaction in the solid state for the halo derivatives, which is destroyed in solution (i.e., at concentrations below 10^{-2}M in CH_3NO_2). These derivatives display behavior analogous to that of the complexes (Co[14]pentaeneN_4)Br)Y (Y = ClO_4^-, PF_6^-, $B\phi_4^-$) and the chloro and bromo cobalt(II) complexes of the ligand, TAAB (In).[79]

Assuming that the halide complexes reported here have square pyramidal symmetry, the two most likely mechanisms for this kind of spin-coupling are (a) direct coupling of two spins on adjacent cobalt ions via formation of a Co--Co σ-bond, and (b) spin superexchange through a bridging ligand, giving rise to linear polymers or oligomers consisting of Co(macrocycle) groups linked by halide ligands. There are well-substantiated examples of both of these mechanisms in complexes of transition metals.

There are at least two complexes in which the presence of a Co--Co bond has been demonstrated in the solid state. These are potassium pentacyanocobalt(II),[80] which has an effective magnetic moment of 0.35 B.M. at room temperature, and $[Co(CNCH_3)_5]_2$ $(ClO_4)_4$, which is diamagnetic in the solid state.[81,82] In solution the metal-metal bonded pairs of octahedral units separate into monomers having room temperature magnetic susceptibilities corresponding to one unpaired electron.

Obviously, such bonding interactions are possible in the complexes under discussion herein. However, we see no reason why the formation of Co--Co bonds should be limited to macrocyclic complexes containing halide ligands, as seems to be the case for all three systems in which reduced magnetic moments have been observed (the non-halide-containing complexes of [14]pentaeneN_4 and TAAB do not have anomalously low magnetic moments). We therefore suggest that a superexchange mechanism is responsible for partial spin-pairing in these systems. There are numerous examples of this phenomenon, exemplified by the halo- and oxo-bridged complexes of iron[83-84] and the many examples of dimeric copper complexes.[85-87] For the complexes under discussion here, there is some tendency for the cobalt ions to become coordinatively saturated (*vide infra*) so that interaction of the 6th coordination site with the axial halide of a neighboring cobalt ion is quite possible. Such bridging would allow coupling between pairs of Co ions and could account for the low solid state magnetic moments. A related situation occurs for Co(salen),[88] which also shows evidence of metal-metal interaction, albeit at much lower temperatures than is the case here.

Electronic Spectra

The maxima and intensities of resolved electronic spectral bands and of shoulders on resolved peaks are collected in Table IV. In general, the spectra consist of one area of weak absorption in the infrared region (λ_{max}, 6–9 kK; $\epsilon < 50$), a complex absorption area in the low energy part of the visible region (λ_{max}, 15–22 kK; $1000 < \epsilon < 2000$) and more intense bands in the ultraviolet region above 28 kK. We found it difficult to obtain spectra of sufficient quality on solid samples to allow satisfactory assignment of λ_{max} values to the shoulders observed, or in some cases even to determine with assurance the number of such shoulders. Therefore, Table IV lists

TABLE IV
Electronic spectral data for the complexes[a]

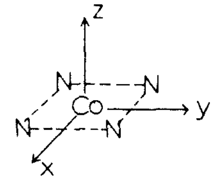
Complex	Medium	IR region	Visible region	UV region
$[\mathrm{Co(tetraeneN_4)Cl}]\mathrm{B}\phi_4$	CH_3NO_2	6.9(52)	21.8(1600)	
	Nujol	7.5	17.0(sh) 18.5	28.5
	CH_3CN	7.0(<10)	14.9(sh) 19.3(sh) 20.0(700)	31.0(2300)
$[\mathrm{Co(tetraeneN_4)Br}]\mathrm{B}\phi_4$	CH_3NO_2	6.7(2.5)	19.5(2000) 21.8(sh)	
	Nujol	7.7	14.3(sh) 17.0(sh) 18.2	
	CH_3CN	6.5(15)	15.5(sh) 18.9(1700) 25.2(sh)	33.0(5500)
$[\mathrm{Co(tetraeneN_4)I}]\mathrm{B}\phi_4$	CH_3NO_2	6.5	21.7 25.3(sh)	
	Nujol	7.5	16.4 ~20	28.6
$[\mathrm{Co(tetraeneN_4)(H_2O)}](\mathrm{B}\phi_4)_2$	Nujol	7.2	10.5(sh) 18.5	28.5
$[\mathrm{Co(tetraeneN_4)(CH_3CN)_2}](\mathrm{B}\phi_4)_2$	CH_3NO_2	8.65(210)	20.4(2641) 22.2(sh)	
$[\mathrm{Co(dieneN_4)Cl}]\mathrm{B}\phi_4$	CH_3NO_2	7.2(7)	14.3(sh) 15.4(sh) 20.8	
	Nujol	8-9(sh)	16.5 18.5 20(sh)	33
$[\mathrm{Co(dieneN_4)Br}]\mathrm{B}\phi_4$	CH_3NO_2	6.9(5)	16.2(sh) 19.0(1200)	
	Nujol	8.4(sh)	14.7(sh) 18.9	~28
$[\mathrm{Co(dieneN_4)I}]\mathrm{B}\phi_4$	CH_3NO_2	6.6(10)	16.7(sh) 21.2(3800)	
$[\mathrm{Co(dieneN_4)(H_2O)_2}](\mathrm{B}\phi_4)_2 \cdot 2H_2O$	CH_3NO_2	8.5	15.6(sh) 21.6(sh)	

[a] Band positions are reported in kilokaysers, with molar extinction coefficients (in parentheses) in M^{-1} cm^{-1}.

only those bands which were reproducibly and clearly discernible. The solution spectra were more clearly resolved than were spectra of solid samples.

Table IV indicates that while there is a qualitative similarity between the spectra of the complexes in different environments, in that the major regions of absorption are the same, there are significant differences between the spectra of the species in a noncoordinating solvent (CH_3NO_2), in the solid state and in a potentially coordinating solvent (CH_3CN). This is the case for complexes of both the ligands, tetraeneN$_4$ and dieneN$_4$, and certain general trends in behavior are evident. First, in the latter two media, shoulders appear to the low energy side of the main bands in the visible region. This may imply that in nitromethane the cobalt ions are separated and pentacoordinate, while in the solid state and in acetonitrile solution there are interactions with other species via the 6th coordination position (i.e., another cobalt ion and solvent, respectively). Second, the shifts observed for the band in the IR region as a function of medium indicate differing extents of axial interaction in the various media. As shown below, the position of this band is strongly dependent on the degree of tetragonality in low spin complexes of cobalt(II) and can be used, in conjunction with epr data, to analyze axial interactions.

There have been several recent ligand field treatments of low-spin d^7 systems with four-fold (D_{4h},C_{4v})[89-93] and two-fold (D_{2h},C_{2v})[94-96] symmetries, all aimed at establishing ground state electronic configurations in complexes of this type.



II

Based on the coordinate system given in II, three ground state configurations have been proposed, depending on the complexes being considered:

$|(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{z^2})\rangle$

($^2A_1$ in D_{4h}, C_{4v}, and C_{2v}; ^2A in D_{2h});

$|(\overset{+}{xy})(\overset{-}{xy})(x^2 \overset{+}{-} y^2)\rangle$

($^2B_2$ in D_{4h} and C_{4v}; ^2A in D_{2h}; $^2A_1$ in C_{2v});

and $|(\overset{+}{xy})(\overset{-}{xy})(\overset{+}{v}z)\rangle$

(^2E in D_{4h} and C_{4v}; $^2B_2$ in D_{2h}; $^2B_1$ in C_{2v}),

written in the three-hole formalism. We will discuss the first configuration ($^2A_1$ ground state), since our epr results indicate the unpaired electron to be in a molecular orbital with a large contribution from the d_{z^2} orbital of cobalt.

All of the treatments of the $^2A_1$ ground state predict an electronic transition which should be strongly related to the degree of tetragonality in the complex. The transition involves the d_{xz} and d_{z^2} orbitals and is characterized as $^2A_1 \rightarrow {}^2E$ in D_{4h} and C_{4v} symmetries; as $^2A_1 \rightarrow {}^2B_2$ in D_{2h} symmetry; and as $^2A_1 \rightarrow {}^2B_1$ in C_{2v} symmetry. In the latter two cases, the degeneracy of d_{xz} and d_{yz} has been removed by the reduction in symmetry. Based upon available data, this transition is expected to fall somewhere in the range 2–17 kK. The low end of this range is associated with square planar complexes, and the high end, with complexes of low tetragonality. For instance, the transition occurs at 2.5 kK in Co(acac)$_2$(–)pn,[95] a square planar species in solution, and as high as 9.8 kK in the Co(Me$_6$[14]4,11-dieneN$_4$)X$^{+1,2}$ complexes which we have reported.[6] In the Co(tetraeneN$_4$)$^{+2}$ and Co(dieneN$_4$)$^{+2}$ complexes, the band in the IR region of the spectrum is sensitive to axial environment, as shown in Table IV. Following the treatment of McGarvey[96] (*vide infra*), we calculate that for a complex for which $g_\perp \simeq 2.3$ and $g_\parallel \simeq 2.020$, a band should appear in the neighborhood of 10 kK (assuming no reduction in the one-electron spin-orbit coupling constant of 0.515 kK). This is close to the observed energies for the IR bands, and with a suitable reduction in the spin-orbit coupling constant, the agreement is even better. We therefore assign the bands in the 6–9 kK region of the spectra to the $^2A_1 \rightarrow {}^2E$ transition (D_{4h} or C_{4v} symmetry is assumed, since only one g value is resolved in the perpendicular region of the epr spectra). There are at least three transitions which are expected to fall at lower energy than this, namely, those to the $^2B_1$ state arising from splitting of the $^2E_g(O_h)$ multiplet in tetragonal symmetry, and to the ^4E and $^4A_2$ states arising from splitting of $^4T_{1g}(O_h)$. The latter two bands are not observed, since they are multiplicity-forbidden. The transition to $^2B_1$, on the other hand, should be of reasonable intensity but is not observed. There are two possible explanations for this: either the band is too low in energy to be observed; or it lies very closely in energy to the $^2A_1 \rightarrow {}^2E$ transition, which appears as a very broad, weak band. The latter interpretation is probably more reasonable since if the tetragonality is great enough, the energies of the $^2B_1$ and ^2E excited states can be quite close (see Figure 1 of ref. 89 and Figure 4 of reference 90). It may be that over the limited range of axial field strengths available (I^- to CH_3CN), these bands are never distinguished. In further support of our assignment of the IR band, Table IV shows that in nitromethane solution, both series of complexes exhibit an increase in the energy of the infrared band as the axial ligand field strength increases ($I^- < Br^- < Cl^- < H_2O$). This should be the case if the band corresponds to the $^2A_1 \rightarrow {}^2E$ transition. Further, throughout both series of complexes, the IR band for the complex [Co(tetraeneN$_4$)X]$^+$ is lower in energy than the equivalent band in [Co(dieneN$_4$)X]$^+$ for the same axial ligand X in CH_3NO_2 solution. This is in keeping with a reduction in energy of the $^2A_1 \rightarrow {}^2E$ transition as the tetragonality of the complex becomes greater. Finally, the infrared bands in the spectra of solid state samples are generally to rather higher energy than the corresponding bands observed in solution spectra, indicating that the overall tetragonality of the

TABLE V
EPR spectral data

Complex	Medium	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{Co}$(cm^{-1}) x 10^4	$A_{\perp}^{Co}$(cm^{-1}) x 10^4	$A_{\parallel}^{axial}$ (cm^{-1}) x 10^4	C_1	ξ_{eff}, kK	C_3	Δ(4E) kK	K(cm^{-1}) x 10^4	P(cm^{-1}) x 10^4
Co(tetraeneN$_4$)Cl$^+$	CH$_3$NO$_2$	–	2.292	–	–	–	.050	.348	.062	5.64		
Co(tetraeneN$_4$)Br$^+$	CH$_3$NO$_2$	~2.0	2.304	–	107.6	18.5	.053	.352	.065	5.42		
Co(tetraeneN$_4$)I$^+$	CH$_3$NO$_2$	~1.877	2.339	110	131	–	.067	.434	negative			
Co(tetraeneN$_4$)-(CH$_3$CN)$_2^{+2}$	CH$_3$CN	2.020	2.300	92.4	⩽15	14.4	.051	.439	.113	3.89	1.4	194
	powder	2.024	2.311	83.6	–	–						
Co(tetraeneN$_4$)-(acetone)$^{+2}$	acetone	2.022	2.307	98.2	22.9	–	.052	–	.118	–	7.6	194.6
Co(tetraeneN$_4$)Cl$_2$	acetone	2.045	2.287 2.183	–	–	–						
Co(tetraeneN$_4$)Br$_2$	acetone	2.057	2.272 2.180	–	–	–						
Co(dieneN$_4$)-(CH$_3$CN)$_2^{+2}$	CH$_3$CN	2.023	2.309	90.7	⩽26	–	.052	–	.120	–	12.7	168
	acetone	2.024	2.312	91.7	⩽26	–	.053	–	.123	–	9.4	175
Co(dieneN$_4$)-(acetone)$^{+2}$	acetone	2.024	2.335	101.1	57.8	–	.057	–	.125	–	43.9	125
Co(dieneN$_4$)Cl$^+$	CH$_3$NO$_2$	2.023	2.315	94.4	⩽43.2	–	.053	.384	.121	3.18		
Co(dieneN$_4$)Br$^+$	CH$_3$NO$_2$	–	2.331	–	95	–	.058	.397	.071	5.59		
Co(dieneN$_4$)I$^+$	CH$_3$NO$_2$	–	2.364	–	102.6	–	.064	.420	.078	5.36		

complexes is reduced as a result of interactions via the 6th coordination site.

The high intensities of the bands in the 14–22 kK region make it unlikely that they arise from *d–d* transitions (comparable bands in the Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$ complexes have $\epsilon \sim 100$). They are probably assignable to charge transfer transitions involving the α-diimine groups and most likely obscure the ligand field transitions to the $^2A_2$, ^2E, and $^2B_2$ excited states.

Epr Spectra

EPR spectra for the complexes were obtained in the same media in which electronic spectra were measured: acetonitrile solution, nitromethane solution, and in the solid state. In addition, spectra were recorded in acetone solvent, in which the complexes are quite soluble. In all cases, measurements were performed at 77°K on frozen solutions or directly on powders. Data are presented in Table V.

Acetonitrile solution. – Frozen acetonitrile solution epr spectra of Co(tetraeneN$_4$)X$^+$ (X = Cl$^-$, Br$^-$, I$^-$) and Co(tetraeneN$_4$)X$_2^{2+}$ (X = H$_2$O, CH$_3$CN) are identical regardless of the original axial ligand. A typical spectrum is shown in Figure 1. The spectrum is consistent with displacement of the original axial ligand by solvent, with a second solvent molecule occupying the 6th coordination position.

Similarly the epr spectra of Co(dieneN$_4$)Cl$^+$ and Co(dieneN$_4$)Br$^+$ in frozen acetonitrile or in acetone containing 10% acetonitrile indicate two axial acetonitriles.

Acetone solution. – Again, Co(tetraeneN$_4$)X$^+$ (X = Cl$^-$, Br$^-$) and Co(tetraeneN$_4$)X$_2^{+2}$ (X = H$_2$O, CH$_3$CN) all gave the same spectrum in frozen acetone, regardless of the original axial ligand, in the absence of excess axial ligand. The spectrum, shown in Figure 2, is presumably that of the acetone adduct of Co(tetraeneN$_4$)$^{2+}$. The iodo complex produced no spectrum in acetone.

To obtain spectra characteristic of the mono-halo complexes, Co(tetraeneN$_4$)X$^+$, we attempted *in situ* generation of the species by addition of excess NMe$_4$Cl, N(pentyl)$_4$Br, or Nbu$_4$I to acetone solutions of Co(tetraeneN$_4$) (CH$_3$CN)$_2$(BØ$_4$)$_2$. The technique was successful for the bromo and iodo complexes, but attempts to generate the chloro complex in acetone by this method resulted in the formation of a pale-violet solid, probably Co(tetraeneN$_4$)Cl$_2$. The epr spectrum of an acetone suspension of this solid, shown in Figure 3, indicates rhombic symmetry.

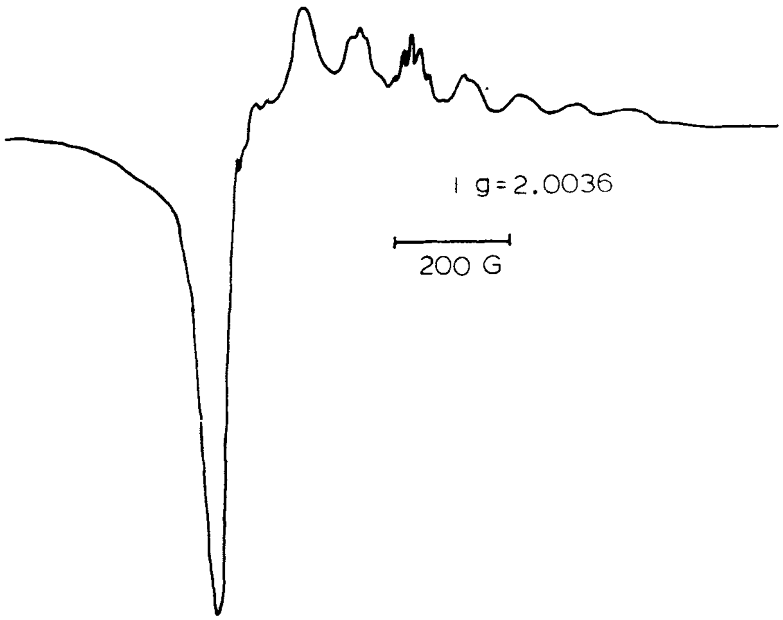


FIGURE 1 Frozen solution EPR spectrum of Co(tetraeneN$_4$)Cl$^+$, Co(tetraeneN$_4$)Br$^+$, Co(tetraeneN$_4$)I$^+$, Co(tetraeneN$_4$)(H$_2$O)$^{+2}$, or Co(tetraeneN$_4$)(CH$_3$CN)$_2^{2+}$ in CH$_3$CN.

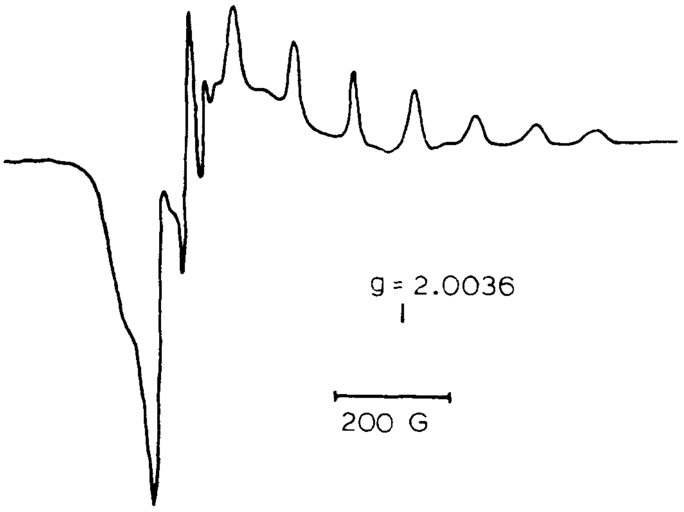


FIGURE 2 Frozen solution epr spectrum of Co(tetraeneN$_4$)Cl$^+$ Co(tetraeneN$_4$)Br$^+$, or Co(tetraeneN$_4$)(H$_2$O)$^+$ in acetone.

Similarly, addition of a large excess of N(pentyl)$_4$Br to a concentrated acetone solution of Co(tetraeneN$_4$)(CH$_3$CN)$_2$(BØ$_4$)$_2$ resulted in a violet precipitate similar to that formed in the presence of excess Cl$^-$. The epr spectrum of the solid, presumably Co(tetraeneN$_4$)Br$_2$, suspended in frozen acetone was similar to that of the dichloro complex.

Finally, the spectra of Co(dieneN$_4$)X$^+$(X = Cl$^-$, Br$^-$) in frozen acetone were very similar. The spectra of the I$^-$ and H$_2$O complexes were not observed. All data obtained from frozen acetone solution of the complexes is included in Table V.

Nitromethane solution. – The chloro and aquo complexes of Co(tetraeneN$_4$)$^{2+}$ gave identical spectra in frozen nitromethane. The spectra show three-line superhyperfine structure in the hyperfine components

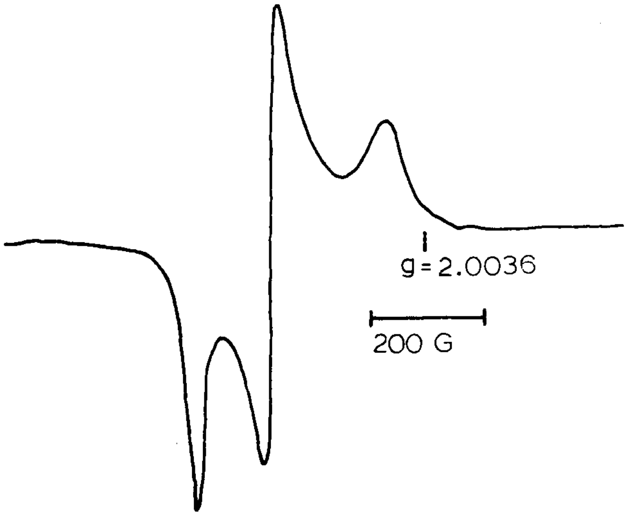


FIGURE 3 epr spectrum of Co(tetraeneN_4)Cl_2 – solid suspended in frozen acetone.

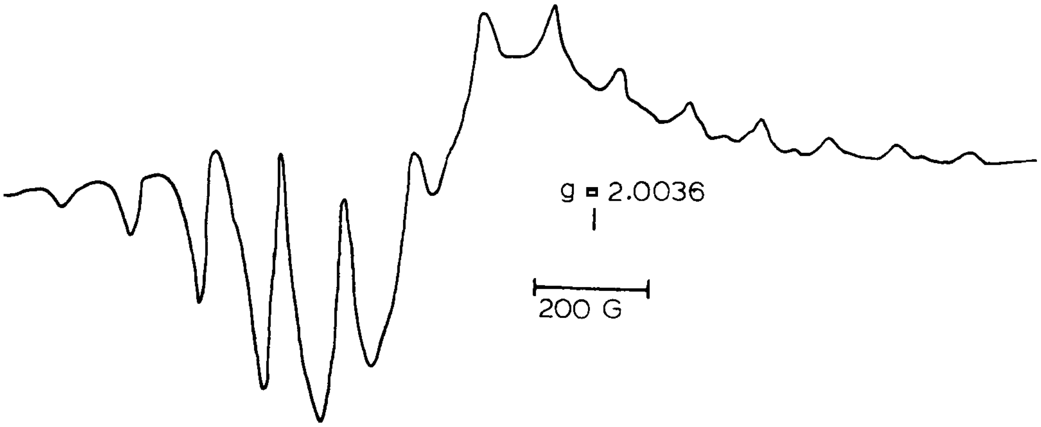


FIGURE 4 Frozen solution epr spectrum of Co(tetraeneN_4)I^+ in CH_3NO_2.

of the parallel branch, due either to coordination of nitromethane or a nitrogen-donor solvent impurity.[6,28] The bromide complex gives a different spectrum with a broad perpendicular branch and a parallel branch showing eight-line hyperfine structure with four-line superhyperfine structure, expected for one axial Br^-, superimposed. The iodo complex gave no spectrum in frozen nitromethane.

As in acetone solvent, the mono-halo complexes could be generated *in situ* by addition of tetraalkyl ammonium halide to nitromethane solutions of Co(tetraeneN_4)$(CH_3CN)_2(B\phi_4)_2$ (e.g., see Figure 4.)

Finally, spectra of the Co(dieneN_4)$^{2+}$ derivatives could be obtained in frozen nitromethane in the presence of an excess of the appropriate halide (Figure 5). Spin Hamiltonian parameters obtained from frozen nitromethane solutions of all the complexes are included in Table V.

Powder spectra' – With a few exceptions, attempts to obtain spectra of powders of the complexes were unsuccessful, yielding only broad unresolved signals of low intensity. An exception is [Co(tetraeneN_4)$(CH_3CN)_2$]$(B\phi_4)_2$, which yielded a fairly strong and well-resolved spectrum. The spin Hamiltonian parameters are collected in Table V.

Discussion of epr results. – In general, the epr spectra for the complexes are consistent with axial symmetry, corresponding to the Hamiltonian in equation 1.[97]

$$H = g_{\parallel}\beta H_z\tilde{S}_z + g_{\perp}\beta(H_x\tilde{S}_x + H_y\tilde{S}_y) + A_{\parallel}\tilde{I}_z\tilde{S}_z + A_{\perp}(\tilde{I}_x\tilde{S}_x + \tilde{I}_y\tilde{S}_y) \tag{1}$$

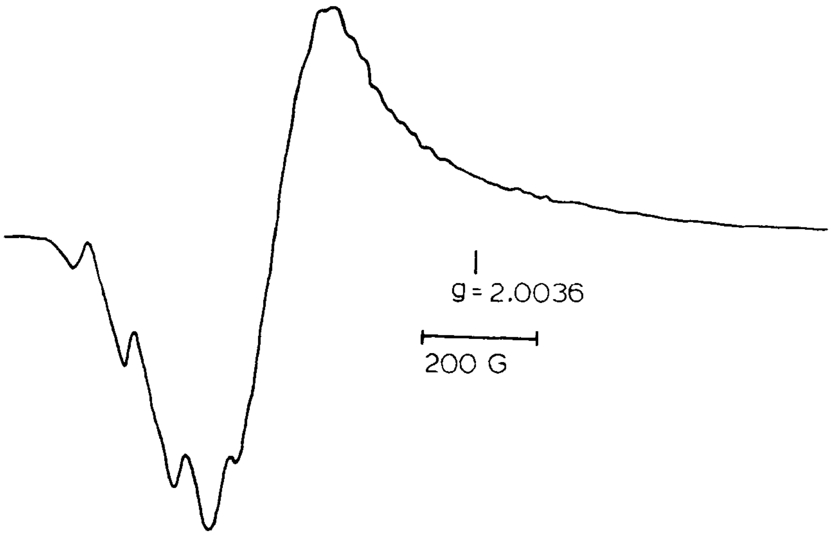


FIGURE 5 Frozen solution epr spectrum of Co(dieneN$_4$)Br$^+$ in CH$_3$NO$_2$.

As mentioned in the section dealing with the electronic spectra, the epr data support the assignment of the near IR band in these spectra to the $^2A_1 \rightarrow {}^2E$ transition (for D_{4h} or C_{4v} symmetry). This follows from the following equations, appropriate to axial (four-fold) symmetry:[96]

$$g_{\parallel} = 2.0023 + 2c_3^2 - 3c_1^2 \tag{2a}$$

$$g_{\perp} = 2.0023 + \tfrac{2}{3}c_3^2 - 6c_1^2 + 6c_1 \tag{2b}$$

$$A_{\parallel} = K + P(\tfrac{4}{7} - \tfrac{4}{7}c_3 - \tfrac{6}{7}c_1 + \tfrac{2}{63}c_3^2 + \tfrac{15}{7}c_1^2) \tag{2c}$$

$$A_{\perp} = P(-\tfrac{2}{7} + \tfrac{45}{7}c_1 + \tfrac{2}{7}c_3 + \tfrac{4}{21}c_3^2 - \tfrac{57}{14}c_1^2) + K \tag{2d}$$

The parameters c_1 and c_3 are defined as follows:

$$c_1 = \frac{\xi}{\Delta(^2E)}$$

$$c_3 = \frac{\xi}{\Delta(^4E)},$$

where $\Delta(^2E)$ is the energy of the transition $^2A_1 \rightarrow {}^2E$ and ξ is the one-electron spin-orbit coupling constant. K is the isotropic Fermi contact interaction, and P is $2.0023\beta g_N \beta_N \langle 1/r^3 \rangle$ ($\langle 1/r^3 \rangle$ = the average value of r^{-3} for the d_{z^2} orbital, where r is the distance between the unpaired electron and the cobalt nucleus). Defining $\Delta g_{\parallel} = g_{\parallel} - 2.0023$ and $\Delta g_{\perp} = g_{\perp} - 2.0023$, equation (3) may be derived from (2a) and (2b):

$$5c_1^2 - 6c_1 + \Delta g_{\perp} - \frac{\Delta g_{\parallel}}{3} = 0. \tag{3}$$

This equation may be readily solved for c_1, which may be used in equation (2a) to calculate c_3. The resulting values of c_1 and c_3 are then used in equations (2c) and (2d) to calculate K and P. For typical values of $\Delta g_{\perp}$ and $\Delta g_{\parallel}$ of .307 and .021, c_1 is .0523 (the other root of equation (3) results in an unreasonably low value for the energy of the $^2A_1 \rightarrow {}^2E$ transition), which, when combined with the definition of c_1, gives $\Delta E(^2A_1 \rightarrow {}^2E) = 9.8$ kK for $\xi = 0.515$ kK (the free-ion value). This is quite close to the energies of the near IR bands and leads us to assign this band to the $^2A_1 \rightarrow {}^2E$ transition. Reversing the calculation, effective values of ξ, ξ_{eff}, may be calculated from the observed energies of the $^2A_1 \rightarrow {}^2E$ transition. These values are shown in Table V for the various complexes. They indicate a reduction of ~30% from the free ion value for the Cl$^-$ and Br$^-$ complexes of Co(tetraeneN$_4$)$^{+2}$, and thus represent a substantial amount of electron delocalization.

Interestingly, the epr spectra of the halide derivatives show increasing values of $A_{\perp}^{\text{Co}}$ in order of decreasing ligand field strength (i.e., $(A_{\perp}^{\text{Co}})_{\text{Cl}^-} < (A_{\perp}^{\text{Co}})_{\text{Br}^-} < (A_{\perp}^{\text{Co}})_{\text{I}^-}$). This follows from equations (2c) and (2d), and can be seen easily if these two equations are written in their more common forms:

$$A_{\parallel} = K + P(\tfrac{4}{7} - \tfrac{1}{7}\Delta g_{\perp}) \tag{4a}$$

$$A_{\perp} = K + P(-\tfrac{2}{7} + \tfrac{15}{14}\Delta g_{\perp}) \tag{4b}$$

These equations result from equations (2a) – (2d) if quartet state coefficients and terms higher than the first power in the c's are ignored. Taking the difference of (4a) and (4b), we find

$$A_{\parallel} - A_{\perp} = P(\tfrac{6}{7} - \tfrac{17}{14}\Delta g_{\perp}). \tag{5}$$

From (5) it can be seen that as $\Delta g_\perp$ increases (that is, as axial ligand field strength decreases), $A_\| - A_\perp$ should decrease. This is exactly what our spectra reveal and the trend confirms the expected variation in axial interaction with donor strength.

In general, the delocalization of electron density onto the axial ligands in the Co(tetraeneN$_4$)$^{+2}$ and Co(dieneN$_4$)$^{+2}$ complexes is greater than that found for the Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$ complexes.[6] We expect similar axial interactions for complexes in which the macrocyclic rings contain similar amounts of unsaturation, other factors being equal. Thus it must be explained why the delocalization is greater for the Co(dieneN$_4$)$^{+2}$ than for the Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$ complexes. The explanation lies in the presence of the methyl substituents on the 6-membered chelate rings of the latter complexes.[6,48-49] These chelate rings are flexible and will adopt conformations in which the methyl substituents interfere with the axial positions. The interaction with axial ligands in these complexes is therefore somewhat weaker. Although there are methyl substituents present on the five-membered chelate rings in Co(tetraeneN$_4$)$^{+2}$ and Co(dieneN$_4$)$^{+2}$, these are constrained to lie in the plane of the macrocycle and will not interfere significantly with the axial positions.

As detailed above, we have observed an increased tendency for 6-coordination in Co(tetraeneN$_4$)$^{+2}$ and Co(dieneN$_4$)$^{+2}$ over that for Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$. For example, the frozen solution epr spectrum of Co(Me$_6$ [14] 4,11-dieneN$_4$) (ClO$_4$)$_2$ in acetonitrile indicates that only one acetonitrile molecule is axially coordinated. This too, can be attributed to the presence of the methyl substituents in these complexes. Coordination in one axial site is expected to increase the interference of the methyl substituents with the other axial site, thus making coordination at that site less likely. Further support for this explanation comes from the magnetic susceptibility data. The solid state magnetic moments for the Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$ and Co(Me$_6$ [14] 1,4,8,11-tetraeneN$_4$)$^{+2}$ complexes show no reduction from the solution values, indicating minimal metal-metal interaction in the solid state.[6,28] These complexes are apparently prevented sterically from achieving strong six-coordination in the solid state, and their magnetic moments are therefore normal.

Generally speaking, we expect the tendency for axial coordination to reflect the amount of electron density present on the cobalt(II) ion in the Co(macrocycle)$^{+2}$ moiety. Axial coordination should decrease with increasing electron density on the metal. It has been shown[21,98] that the macrocycle tetraeneN$_4$ generates a ligand field second only to that of [14] pentaeneN$_4$. We might expect, therefore, that it would place greater electron density on Co(II) than either dieneN$_4$ or Me$_6$ [14] 4,11-dieneN$_4$, and that the extent of axial interaction in the Co(tetraeneN$_4$)$^{+2}$ complexes should be the smallest of the three. This is contrary to observation. If it were true that the tetraeneN$_4$ macrocycle generates its strong ligand field solely through sigma effects, then our expectation would probably be realized. However, the large ligand field of tetraeneN$_4$ is due to a combination of σ donor and π acceptor abilities. It is not necessarily true that there is substantially more electron density on the metal in the Co(tetraeneN$_4$)$^{+2}$ complexes than in the Co(dieneN$_4$)$^{+2}$ and Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$ complexes. Thus Co(tetraeneN$_4$)$^{+2}$ willingly coordinates two axial ligands, whereas Co(Me$_6$ [14]-4,11-dieneN$_4$)$^{+2}$ does so only with reluctance.

Finally, whether the Co(tetraeneN$_4$)$^{+2}$ and Co(dieneN$_4$)$^{+2}$ complexes are isolated as five-coordinate or six-coordinate species may depend to some extent on conditions of the synthetic procedure. For instance, we have been able to prepare both [Co(tetraeneN$_4$)Cl] (Bϕ_4) and [Co(tetraeneN$_4$)Cl$_2$], depending upon which solvent is used and the conditions under which the halide is added. The same may be said of other Co^{II} (macrocycle) species. For instance, Endicott *et al.* claim a bis-pyridine adduct of Co(Me$_6$ [14] 4,11-dieneN$_4$)$^{+2}$,[26] whereas we have isolated a mono-pyridine adduct of the same species[6] which analyzes quite well. Tait and Busch[28] have prepared complexes of Co(Me$_6$ [14] 1,4,8,11-tetraeneN$_4$)$^{+2}$ that analyze excellently for only one axial ligand. Thus the question of five- or six-coordination in these complexes must be resolved by admitting to both possibilities.

EXPERIMENTAL SECTION

Materials

N,N'-bis(3-aminopropyl)-1,2-diaminoethane(3,2,3) was prepared from 1,3-diaminopropane and 1,2-dibromoethane.[10] All other materials were reagent grade.

Physical Measurements

Elemental analyses were performed by Chemalytics, Inc., and Galbraith Laboratories. Infrared spectra were recorded as nujol or halo-oil mulls or as KBr pellets on a Perkin-Elmer Model 337 spectrophotometer.

Magnetic susceptibilities on solid samples were determined by the Faraday method. Solution susceptibilities were determined by the nmr method[99] using the nitromethane proton peak.

Electronic spectra were recorded on a Cary Model 14R recording spectrophotometer. Solid samples were run as nujol mulls impregnated on filter paper, and solutions were prepared and transferred to quartz cells in a glove box under nitrogen.

EPR spectra were obtained using a Varian 4502 EPR spectrometer operating in the X-band at ~9.3 GHz. The spectrometer is equipped with a 100 KHz field modulator and control unit, a 6" magnet, and a V4531 Dual Cavity. Frequency was measured using a TS-488A/UP Echo Box from Aeromotive Equipment Corporation: g-Values were calculated from the position of the resonance with respect to that of DPPH ($g = 2.0036$). Samples were run as frozen solutions of the solvents acetone, acetonitrile, and nitromethane, with NBu_4BF_4 added to improve resolution of superhyperfine structure.

Syntheses

All reactions involving cobalt(II) were carried out in deoxygenated solvents under a blanket of nitrogen in a conventional manner. Samples for magnetic susceptibility measurements were prepared, and kept at all times in a glove box filled with highly purified nitrogen.

[Co(tetraeneN$_4$)Cl] Bϕ_4 – Method A: Hydrochloric acid (0.2 moles) was added slowly to a solution of 1,3-diaminopropane (0.2 moles) in methanol (600 ml). After the solution had cooled to ambient temperature, biacetyl (0.2 moles) was added slowly from a dropping funnel over a period of 30 min., with stirring, resulting in an orange or yellow-orange colored solution. Cobaltous acetate, $Co(CH_3CO_2)_2 \cdot 4H_2O$, (0.1 moles) was then added and the mixture stirred rapidly for a minimum of three hours. To the resulting deep red-purple, highly air-sensitive solution was added a solution of sodium tetraphenylborate in methanol. Usually, 30% of the required molar quantity was more than sufficient to precipitate all the product as a deep maroon powder. After the product had settled out, it was filtered, washed well with methanol until the washings were only pale maroon in color, and finally washed with ether and dried in vacuo at room temperature. Yield, *ca.* 15%.

[Co(tetraeneN$_4$)Cl] Bϕ_4 – Method B: To the yellow-orange solution resulting from adding biacetyl to 1,3-diaminopropane hydrochloride over a half-hour period, as in A, was added cobaltous chloride (0.1 moles) followed by sodium acetate (0.2 moles). The reaction time and workup procedure are then identical to those in A. Alternatively, perchloric acid can be used to make the amine salt when cobaltous chloride would be the source of cobalt and halide ligand.

[Co(tetraeneN$_4$)Br] Bϕ_4: This purple solid was prepared in an analogous fashion by either of methods A or B, using the corresponding bromide.

[Co(tetraeneN$_4$)I] Bϕ_4: Use of the corresponding iodide in method A above gave the deep brown solid product in an entirely corresponding way.

Co(tetraeneN$_4$)(NCS)$_2$: Perchloric acid (5.8 g of 70% aqueous solution) was cautiously added, dropwise, and with stirring, to a cooled solution of 1,3-diaminopropane (3g: 0.04 moles) in methanol (200 ml). This was followed by the slow, dropwise addition of biacetyl (.04 mol) over a half-hour period. Anhydrous cobaltous thiocyanate (0.02 moles) was added followed by sodium acetate (0.04 moles) and the mixture was stirred vigorously until crystallization of the product was complete (approx. 3 hours). The deep purple, almost black microcrystalline product was filtered, washed copiously with methanol, and dried. Yield, *ca.* 42%.

[Co(dieneN$_4$)X] Bϕ_4 (X = Cl, Br, I): Syntheses of these complexes were achieved, although with difficulty and often in very low yields, by a method essentially identical to A above with the following exceptions. First, a deficiency of cobaltous acetate was added so that the reaction mixture was not too basic; thus, for each mole of tetraamine hydrohalide and biacetyl, only half of a mole of cobaltous acetate was added. Secondly, when the reaction appeared to have finished (3–5 hrs) half of the solvent was removed *in vacuo*, the flask was refilled with nitrogen, and after the addition of $NaBPh_4$ the solution was cooled overnight in a refrigerator. The crystalline product thus obtained was filtered, washed in a nitrogen atmosphere, and dried *in vacuo*. Identical products could be made, but also in low yield, by use of CoX_2 and sodium acetate in the above procedure.

[Co(tetraeneN$_4$)(H$_2$O)] (Bϕ_4)$_2$ and [Co(dieneN$_4$)(H$_2$O)$_2$] (Bϕ_4)$_2$·nH$_2$O: A slurry of Co(tetraeneN$_4$)Br$_3$ or [Co(dieneN$_4$)Br$_2$]ClO$_4$ in a 50:50 mixture of methanol and water (20 ml) was degassed. Then an acidic solution of a twofold excess of chromous bromide (or chloride) prepared in the conventional way from the chromic salt and zinc/mercury amalgam was added dropwise. Immediately, the color changed to a deep maroon color and upon the addition of all the chromous solution, a clear solution was obtained. A concentrated solution of excess sodium tetraphenylborate in methanol was then added against a counter stream of nitrogen, causing the immediate formation of a fawn precipitate of the product, which was filtered and washed with water under a nitrogen atmosphere.

[Co(tetraeneN$_4$)(CH$_3$CN)$_2$] (Bϕ_4)$_2$: 2 g (.00257 mol) [Co(tetraeneN$_4$)(H$_2$O)$_2$] (PF$_6$)$_3$ was slurried with ~30 ml EtOH and 10 ml CH_3CN under N_2. The mixture was heated at reflux for 1 hr, during which time the color of the solution changed from rose-red to deep red-purple. At the end of this time, the mixture was filtered through cellite and an equal volume of acetonitrile was added to the filtrate. The volume was reduced by half, and acetonitrile (20 ml) again added. 1.76 g (.00514 mol) NaBϕ_4 dissolved in a minimum of acetonitrile was added slowly, resulting in the precipitation of a red-purple crystalline solid. This was collected by filtration, washed with ether, and dried *in vacuo*. The product was recrystallized from hot acetonitrile. Attempts to prepare Co(dieneN$_4$)$^{2+}$ by a similar procedure were unsuccessful.

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