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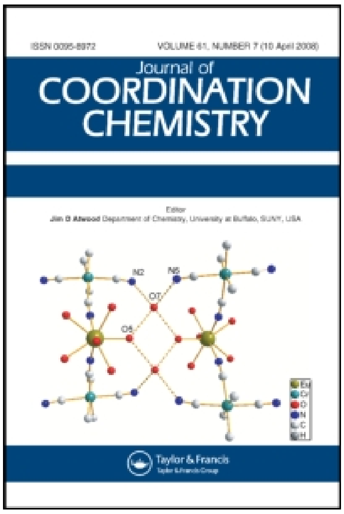

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FIVE-COORDINATE COBALT(II) COMPLEXES OF MACROCYCLIC LIGANDS — A NEW REVERSIBLE OXYGEN CARRYING SYSTEM

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FIVE-COORDINATE COBALT(II) COMPLEXES OF MACROCYCLIC LIGANDS — A NEW REVERSIBLE OXYGEN CARRYING SYSTEM

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We report the synthesis and characterization of cobalt(II) complexes with two macrocyclic Schiff base ligands, 5,7,7,12,14,14-hexamethyl-1,4,8,11,-tetraazacyclotetradeca-4,11-diene(Me_6 [14] 4,11-dieneN_4) and 5,7,7,12,14,-14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene(Me_6 [14] 4,14-dieneN_4), containing a large variety of axial ligands. The complexes are low spin and predominantly five-coordinate, the d–d electronic spectra and electron paramagnetic resonance (epr) spectra being consistent with a square pyramidal ligand environment. The complex [Co(Me_6 [14] 4,11-dieneN_4)] $(ClO_4)_2$ functions as a reversible oxygen carrier in several solvents and in the presence of several Lewis bases. Formation of the oxygen adduct in N,N-dimethylformamide (DMF) has been studied spectrophotometrically and by means of epr.

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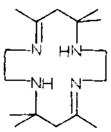
INTRODUCTION

Cobalt(II) complexes containing synthetic macrocyclic ligands[1–10] are of interest because of their potential biological significance, both with regard to their ability to reversibly bind molecular oxygen and their ability to form cobalt-carbon bonds. To date, cobalt(II) complexes containing the synthetic macrocyclic ligands of structures I–X have been described.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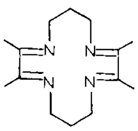
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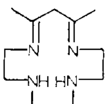
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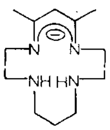
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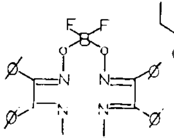
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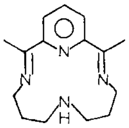
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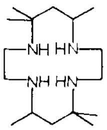
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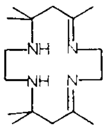
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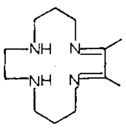
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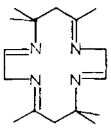
(X)

The complexes with ligands II and V have been reported to reversibly bind molecular oxygen, whereas those of ligands I,[13] II,[14,16] and VI[14,15] form Co-carbon bonds via nucleophilic pathways and may therefore be considered as analogs of vitamin B_{12}.

The Co(II) complexes of all of the ligands listed have the low spin, electronic configuration and many exhibit a coordination number of five. This is in contrast to the cobalt(II) complexes of fully saturated, noncyclic nitrogen donors, which are usually high spin[17,18] and very often six-coordinate. In fact, prior to the advent of synthetic macrocyclic ligands, relatively few low spin, four- or five-coordinate cobalt(II) complexes were known. Many of those that had been prepared contained sulfur or phosphorous among the donor atoms.[19–24]

This paper reports the preparation and characterization of a number of low spin, five-coordinate cobalt(II) complexes of the tetradentate macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, abbreviated (Me_6 [14] 4,11-dieneN_4, structure I), and 5,7,7,12,-12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,-14-diene,(Me_6 [14] 4,14-dieneN_4, structure VIII). Although preparations of cobalt(II) complexes of these macrocycles have been previously reported, we have developed improved preparative procedures; and, in addition, have examined the effects of axial

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ligands on the complexes by both electronic spectral and epr techniques. We have found that Co(Me$_6$ [14]-4,11-dieneN$_4$)$^{+2}$ reversibly binds molecular oxygen in various solvents and in the presence of several Lewis bases. The oxygen adduct has been characterized spectroscopically.

RESULTS AND DISCUSSION

The complexes reported herein are of two types: [Co(Me$_6$ [14] dieneN$_4$)Y] (ClO$_4$)$_2$, where Y is a neutral molecule, and [Co(Me$_6$ [14] dieneN$_4$)X]-(ClO$_4$), where X is an anion. Complexes in which Y = H_2O, C_5H_5N, $H_2NCH_2CH_2NH_2$, and CH_3CN, and X = Cl$^-$, Br$^-$, I$^-$, CN$^-$, and BH_4^- have been prepared and are all low spin and five coordinate. In addition, a dimeric oxalate complex containing folded macrocyclic rings and high spin cobalt(II) ions has been synthesized. The complexes have been characterized by means of their infrared spectra, solid state magnetic moments, conductance and solid state electronic spectra, and frozen solution epr spectra.

Syntheses and General Properties

The direct condensation of ethylenediamine with acetone utilizing the template action of Ni(II) and Cu(II) ions to form macrocyclic complexes was discovered some time ago.[25] However, attempts to carry out these condensations with other metal ions have often been less successful.[22] It is significant that Endicott and Sadasivan[1] report that a small yield of a macrocyclic product containing cobalt(II) was obtained, apparently, with some difficulty.

We have found that the condensation of ethylenediamine and acetone, utilizing the template action of cobalt(II) ions, proceeds very slowly, requiring almost ten days for substantial conversion. The process yields the complexes of two noninterconvertible isomeric macrocycles. This reaction is not so simple nor does it proceed as smoothly as the condensation of ethylenediamine and acetone in the presence of the perchlorate salts of nickel(II) and copper(II), for the following reasons: (1) The reaction must be carried out in an inert atmosphere to prevent oxidation of the cobalt(II) in intermediates to cobalt(III). (2) Moisture must be rigorously excluded to prevent the precipitation of hydroxo-species. (3) The desired macrocyclic complexes are very soluble in acetone and the separation of the desired complexes from the products of side reactions is more difficult than with the copper and nickel systems, where the macrocyclic complexes precipitate as they form. The products frequently consist of mixtures containing the isomers of [Co(Me$_6$ [14] dieneN$_4$)-ClO$_4$] ClO$_4$, as well as a dimer of the formula [(Me$_6$ [14] dieneN$_4$)CoNH$_2$CH$_2$CH$_2$NH$_2$Co-(Me$_6$ [14] dieneN$_4$)] (ClO$_4$)$_4$, which forms by further reaction with the excess ethylenediamine which is necessary to promote the desired process. The dimer reacts with acid to yield the desired complexes [Co(Me$_6$ [14] dieneN$_4$)ClO$_4$] ClO$_4$.

The two noninterconvertible isomers have similar solubilities, and are more difficult to separate by fractional crystallization than the corresponding Ni(II) and Cu(II) complexes. It is somewhat surprising that [Co(Me$_6$ [14] 4,14-dieneN$_4$)ClO$_4$]-ClO$_4$ contains coordinated perchlorate even when crystallized from water. Perchlorate anions generally form very weak bonds with transition metals and extraordinary measures are usually required to remove water and other possible ligands when perchlorate coordination is desired. However, this phenomenon has been previously observed with macrocyclic complexes of nickel which apparently contain two coordinated perchlorate anions, even when crystallized from water.[26]

The isomeric macrocycles reported here have been identified as the *cis* and *trans* dienes, Me$_6$ [14] 4,11-dieneN$_4$(structure I) and Me$_6$ [14] 4,-14-dieneN$_4$(structure VIII). Their identification was verified by preparing [Co(Me$_6$ [14] 4,11-dieneN$_4$)-ClO$_4$] ClO$_4$ and [Co(Me$_6$ [14] 4,14-dieneN$_4$)ClO$_4$]-ClO$_4$ from the previously synthesized ligand. The infrared spectra, electronic spectra, and X-ray powder diffraction patterns of the complexes prepared by the two methods were identical.

Characterization of the Complexes

The cobalt(II) complexes of the Me$_6$ [14] 4,11-diene-N$_4$ ligand are formulated as being low spin and five-coordinate with square pyramidal geometry. This formulation is suggested from: (1) the observation that the infrared spectrum of the anhydrous perchlorate complex contains absorptions indicating the presence of both free and coordinated perchlorate anions and the absence of any absorptions due to water or other hydroxylic solvents; (2) the infrared spectra of the monohydrate complexes indicate the presence of only uncoordinated perchlorate; (3) complexes can be readily synthesized in which one of the perchlorate ions is replaced by another anion (usually halide); (4) the solution

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conductivities of the [Co(Me_6 [14] 4,11-dieneN_4)-X] ClO_4 complexes are typical of those found for 1:1 electrolytes; (5) the magnetic moments are in the range from 1.9 to 2.15 B.M., and the electronic spectra can best be interpreted by assuming a five-coordinate, square pyramidal ligand arrangement; and (6) the epr spectra of frozen solutions of the complexes in the presence of excesses of various nitrogen-donor Lewis bases show superhyperfine splitting by only one nitrogen.

Analytical data for the complexes are given in Table I. The complexes are all crystalline solids and stable, to varying degrees, toward aerial oxidation in the solid state. Co(Me_6 [14] 4,11-dieneN_4)$(ClO_4)_2$ and corresponding Me_6 [14] 4,14-dieneN_4 derivative are stable in the solid state for at least a year under normal laboratory conditions. Although [Co(Me_6-[14] 4,11-dieneN_4)H_2O] $(ClO_4)_2$ shows a tendency to dehydrate to form the anhydrous compound it exhibits relatively little tendency to oxidize to the Co(III) species. This complex can easily be dehydrated by heating *in vacuo* at 100°C for 24 hrs. The weight loss, 3.25%, corresponds to the loss of one molecule of water and is accompanied by the removal from the infrared spectrum of the intense O–H stretching and weak deformation absorptions at 3,400 and 1,630 cm^{-1}, respectively. If either [Co(Me_6 [14] 4,11-dieneN_4)ClO_4] ClO_4 or [Co(Me_6 [14] 4,11-dieneN_4)H_2O] $(ClO_4)_2$ is recrystallized from methanol, a molecule of methanol occupies the fifth coordination site; however, under normal laboratory conditions, the crystals effloresce.

In contrast to the stability of [Co(Me_6 [14] 4,-11-dieneN_4)ClO_4] ClO_4 and [Co(Me_6 [14] 4,-11-dieneN_4)H_2O] $(ClO_4)_2$, the halo complexes decompose within a few months, the acetonitrile complex, within a few days; and the cyanide complex darkens and decomposes within minutes in the presence of air.

All of the complexes, with the exception of the oxalato derivative, are soluble in polar solvents. They are sparingly soluble in alcohols, but very soluble in acetonitrile and nitromethane. In solution, the rate at which the complexes oxidize depends on the solvent, anions present, and pH. For solutions in aqueous hydrohalic acids, the cobalt oxidizes to the *trans*-dihalo–cobalt(III) complex in about one hour. Neutral aqueous, alcoholic, and nitromethane solutions show little change in the visible and ultraviolet portions of their spectrum during an hour. Although the perchlorato, chloro, and bromo complexes can be prepared in the atmosphere without appreciable oxidation to Co(III) species, the preparation of the borohydride, cyanide, and iodide complexes requires rigorous exclusion of oxygen. Even under nitrogen, the addition of excess cyanide to Co(Me_6 [14] 4,11-dieneN_4)$(ClO_4)_2$ in practical grade nitromethane leads to immediate oxidation to yellow [Co(Me_6 [14] 4,11-dieneN_4)$(CN)_2$] ClO_4 complex.

The borohydride complex, [Co(Me_6 [14] 4,-

TABLE I
Analytical data for the complexes

Complex	Calcd.			Found			Halogen	
	C	H	N	C	H	N	Calcd.	Found
[Co(Me_6[14]4, 11-dieneN_4)ClO_4]ClO_4	35.7	5.99	10.41	36.3	6.21	10.4	13.17	13.1
[Co(Me_6[14]4, 11-dieneN_4)H_2O]$(ClO_4)_2$	34.54	6.16	10.07	34.8	6.65	10.4	12.15	13.1
[Co(Me_6[14]4, 14-dieneN_4)ClO_4]ClO_4	35.7	5.99	10.41	35.5	5.04	10.5	13.17	13.1
[Co(Me_6[14]4, 11-dieneN_4)Cl]ClO_4	40.52	6.80	11.81	40.4	6.70	12.0	14.95	15.0
[Co(Me_6[14]4, 11-dieneN_4)Br]ClO_4	37.04	6.22	10.80	36.9	6.12	11.0	Br	
							15.41	15.2
							Cl	
							6.8	6.9
[Co(Me_6[14]4, 11-dieneN_4)I]ClO_4	33.97	5.70	9.90	33.9	5.73	9.75	Cl	
							6.3	6.8
							I	
							22.43	22.5
[{Co(Me_6[14]4, 11-dieneN_4)}$_2$CN]$(ClO_4)_3$	39.51	6.43	12.57	39.2	6.22	12.5	10.60	10.5
[Co(Me_6[14]4, 11-dieneN_4)BH_4]ClO_4	42.36	8.00	12.35	40.7	7.61	11.1	7.81	7.60
[Co(Me_6[14]4, 11-dieneN_4)C_5H_5N]$(ClO_4)_2$	40.85	6.04	11.34	40.4	5.82	11.3	11.5	11.6
[{Co(Me_6[14]4, 11-dieneN_4)}$_2$$(NH_2CH_2)_2$]$(ClO_4)_4$	35.93	6.38	12.32	35.1	6.26	12.4	12.48	12.5
[Co(Me_6[14]4, 11-dieneN_4)CH_3CN]$(ClO_4)_2$	37.32	6.09	12.1	38.0	6.57	11.6	12.24	11.0
[{Co(Me_6[14]4, 11-dieneN_4)}$_2$$C_2O_4$]$(ClO_4)_2$	42.29	6.68	11.60	41.1	6.72	11.8	7.34	7.5

11-dieneN$_4$)BH$_4$]ClO$_4$, was first isolated while attempting to reduce Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ to a Co(I) species with sodium borohydride in ethanol. Rather than the deep blue-green color of Co(I), which forms with some other Co(II) macrocyclic complexes,[15] a tan precipitate formed. The borohydride ligand dissociates with solvent substitution in hydroxylic solvents. Extensive reaction of excess sodium borohydride with Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ results in the hydrogenation of the imine linkages. The resultant complex has no absorption in the 1,660 cm^{-1} region of the infrared spectrum, thus indicating the presence of a fully saturated ligand. The cobalt in these complexes can be reduced to the univalent state with sodium amalgam yielding intense blue-green solutions which are highly air sensitive.

Molar conductivities for some of the complexes are given in Table II. The value found for Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ in nitromethane indicates complete replacement of coordinated perchlorate by solvent. The graph of $\Lambda_0 - \Lambda_e$ versus the square root of concentration is linear with slope of 461, which falls in the range expected for di-univalent electrolytes.[27] On the other hand, the halo complexes, [Co(Me$_6$[14]4,11-dieneN$_4$)X]ClO$_4$, exhibit molar conductivities in nitromethane which are characteristic of one-to-one electrolytes ($\Lambda \cong 100$). This is consistent with pentacoordination in the solid state with the halide molecules remaining bound in solution, but does not preclude occupation of the second axial site by a solvent molecule. Halide coordination is also supported by the results of a conductometric titration of [Co(Me$_6$[14]4,11-dieneN$_4$)](ClO$_4$)$_2$, with tetraethylammonium chloride in nitromethane, which gave an end point at one equivalent of chloride ion.

TABLE II
Molar conductances of some five-coordinate cobalt(II) compounds[a]

Compound	Λ_M(in CH$_3$NO$_2$)
[Co(Me$_6$[14]4, 11-dieneN$_4$)Cl]ClO$_4$	95
[Co(Me$_6$[14]4, 11-dieneN$_4$)Br]ClO$_4$	97
[Co(Me$_6$[14]4, 11-dieneN$_4$)I]ClO$_4$	101
[Co(Me$_6$[14]4, 11-dieneN$_4$)](ClO$_4$)$_2$	195

[a] Concentrations were in the range from 0.98×10^{-3} to 1.1×10^{-3} M.

Magnetic Properties

The magnetic moments of the complexes, corrected for diamagnetism, are listed in Table III. Low spin electronic configurations ($S = 1/2$) are indicated for all the complexes with the exception of the oxalato derivative. The moments are generally in the range 1.9 to 2.1 B.M., and are consistent with values reported for low spin penta- and hexacoordinated cobalt(II)[4,28] but are lower than those generally reported for presumed square planar cobalt(II).[19,23,29,30] The observed values and trends, that is, higher moments for the halo-complexes (Cl > Br > I) and lower moments for nitrogen donors in the axial sites, closely parallel the moments observed for the five-coordinate cobalt(II) complexes containing the macrocyclic ligand, CR.[4] The cyanide complex, ([Co(Me$_6$[14]4,11-dieneN$_4$)]$_2$-CN)(ClO$_4$)$_3$, has an appreciably low moment, 1.50 B.M. This lower magnetic moment is most probably the result of antiferromagnetic coupling between cobalt(II) atoms connected by a cyanide bridge. The oxalato-complex [{Co(Me$_6$[14]4,11-dieneN$_4$}$_2$(C$_2$O$_4$)](ClO$_4$)$_2$ has $\mu_{eff} = 4.84$, which is in the range generally found for high spin ($S = 3/2$), six-coordinate cobalt(II) complexes.[31]

TABLE III
Magnetic moments of the new complexes

Complex	μ_{eff}, B.M.
[Co(Me$_6$[14]4, 11-dieneN$_4$)ClO$_4$]ClO$_4$	2.14
[Co(Me$_6$[14]4, 11-dieneN$_4$)H$_2$O](ClO$_4$)$_2$	2.13
[Co(Me$_6$[14]4, 11-dieneN$_4$)Cl]ClO$_4$	2.10
[Co(Me$_6$[14]4, 11-dieneN$_4$)Br]ClO$_4$	2.04
[Co(Me$_6$[14]4, 11-dieneN$_4$)I]ClO$_4$	2.02
[Co(Me$_6$[14]4, 11-dieneN$_4$)(CN)$_{1/2}$]ClO$_4$	1.50
[Co(Me$_6$[14]4, 11-dieneN$_4$)BH$_4$]ClO$_4$	1.98
[Co(Me$_6$[14]4, 11-dieneN$_4$)C$_5$H$_5$N](ClO$_4$)$_2$	1.92
[Co(Me$_6$[14]4, 11-dieneN$_4$)(NH$_2$CH$_2$CH$_2$NH$_2$)$_{1/2}$](ClO$_4$)$_2$	2.02
[Co(Me$_6$[14]4, 11-dieneN$_4$)CH$_3$CN](ClO$_4$)$_2$	1.98
[Co(Me$_6$[14]4, 14-dieneN$_4$)ClO$_4$]ClO$_4$	2.10
[{Co(Me$_6$[14]4, 11-dieneN$_4$)}$_2$C$_2$O$_4$](ClO$_4$)$_2$ · H$_2$O	4.84

Infrared Spectra

The infrared spectra of all of the complexes contain, as common features, a strong sharp N–H stretching absorption near 3,250 cm^{-1}, an intense sharp absorption attributable to the C = N stretching mode near 1,650 cm^{-1}, and intense absorptions due to the perchlorate anion near 1,100 and 630 cm^{-1} (Table IV).

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TABLE IV
Selected frequencies from the infrared absorption spectra of the new complexes

Complex	N-H Stretch	C=N Stretch	ClO$_4$	Additional Frequencies
[Co(Me$_6$[14]4,11-dieneN$_4$)ClO$_4$]ClO$_4$	3220	1667	1135,1100,1065 630,622	
[Co(Me$_6$[14]4,11-dieneN$_4$)H$_2$O](ClO$_4$)$_2$	3220	1665	1100,625	
[Co(Me$_6$[14]4,14-dieneN$_4$)ClO$_4$]ClO$_4$	3225	1655	1100,1050,1000, 623(sh),625	
[Co(Me$_6$[14]4,11-dieneN$_4$)Cl]ClO$_4$	3236	1661	1100,624	
[Co(Me$_6$[14]4,11-dieneN$_4$)Br]ClO$_4$	3225	1658	1100,625	
[Co(Me$_6$[14]4,11-dieneN$_4$)I]ClO$_4$	3236	1664	1100,625	
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$en](ClO$_4$)$_4$	3333,3284,3225	1653	1100,625	
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$CN](ClO$_4$)$_3$	3236,3174	1661	1100,623	2132(C≡N)
[Co(Me$_6$[14]4,11-dieneN$_4$)py](ClO$_4$)$_2$	3195,3135	1653	1100,623	(py modes) 1600, 1589,767,750,702
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$C$_2$O$_4$](ClO$_4$)$_2$ · H$_2$O	3279	1650[a]	1100,625	3610(H$_2$O)
[Co(Me$_6$[14]4,11-dieneN$_4$)BH$_4$]ClO$_4$	3255	1665	1100,625	(BH$_4$)2398,2370, 2100,2174,2012, 2079,1972
[Co(Me$_6$[14]4,11-dieneN$_4$)CH$_3$CN](ClO$_4$)$_2$	3236	1665	1100,625	2314,2283(CH$_3$CN)

[a]This band due to C=N and $-CO_2^-$.

Anhydrous Co(Me$_6$ [14] 4,11-dieneN$_4$)(ClO$_4$)$_2$ exhibits bands at 1,135, and 1,065 cm^{-1}, indicative of coordinated perchlorate species,[32] in addition to bands at 1,100 and 630 cm^{-1} indicating "free" perchlorate. Similarly, [Co(Me$_6$ [14] -dieneN$_4$)-ClO$_4$] ClO$_4$ contains no infrared absorptions which could be attributed to water whereas the ClO$_4^-$ bands in the infrared spectrum indicated the presence of both coordinated and free perchlorate anions. Those bands attributable to coordinated perchlorate are absent from the spectrum of the aquo complex, [Co(Me$_6$ [14] 4,11-dieneN$_4$)H$_2$O] (ClO$_4$)$_2$, and from the spectra of the complexes where one perchlorate group has been replaced by other neutral addends. The oxalato complex has a very strong band at 1,650 cm^{-1} in which the $-CO_2^-$asymmetric absorption overlays that of the imino function. This single band, attributable to the oxalate grouping suggests a symmetrical bridging structure of the type proposed by Curtis for the corresponding nickel(II) complexes.[33]

The infrared spectrum of the borohydride complex, [Co(Me$_6$ [14] 4,11-dieneN$_4$)BH$_4$] ClO$_4$, has absorptions in the 2,200–2,400 cm^{-1} region, which are characteristic of terminal B–H absorptions, and a second set of bands in the 1,900–2,200 cm^{-1} region, typical of B–H bonds weakened by multicenter interaction.[34] The infrared spectrum of this complex is very similar to that reported by Curtis[35] for some nickel(II) borohydride complexes of the fully hydrogenated ligand, Me$_6$ [14] aneN$_4$.

d–d Spectra

The d–d electronic spectra of the complexes are best interpreted assuming a five-coordinate, square pyramidal, donor atom configuration about a low spin d^7 metal ion. The energy level diagram used for

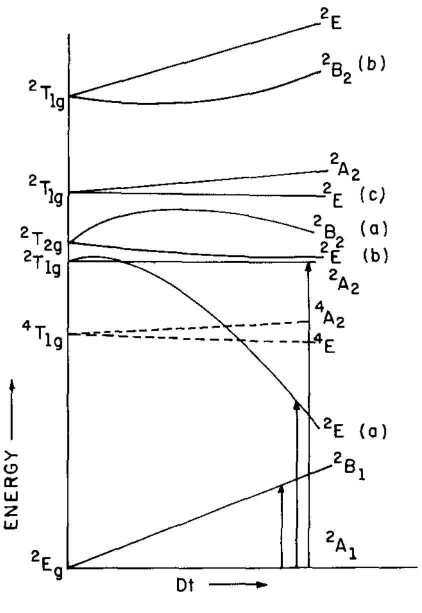

FIGURE 1 Schematic energy level giagram for a low spin d^7 system in a square-pyramidal ligand environment (after Allen and Warren, Ref. 37).

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the tentative band assignments is shown schematically in Figure 1 and is taken from those derived by other workers.[36,37] The absorption maxima and molar extinction coefficients of the complexes are listed in Table V. Representative solid state and solution spectra are shown in Figures 2 and 3. The spectra obtained under these different conditions are sufficiently similar to offer considerable support to the suggestion that the complexes are five-coordinate.

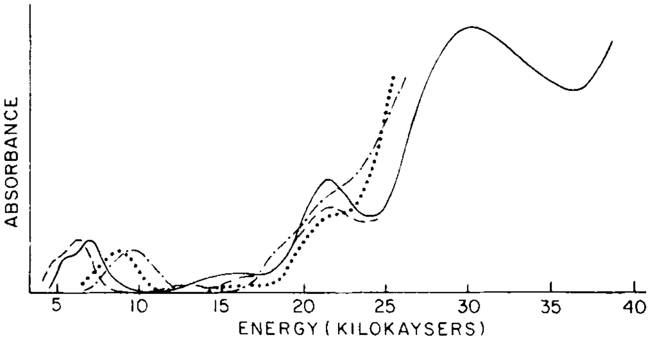

FIGURE 2 Solid state d–d electronic spectra for some representative five-coordinate cobalt(II) complexes.
(a) — · — [{Co(Me$_6$ [14]4,11-dieneN$_4$)}$_2$C$_2$H$_8$N$_2$](ClO$_4$)$_2$
(b) – – – [Co(Me$_6$ [14]4,11-dieneN$_4$)Br]ClO$_4$
(c) .... [{Co(Me$_6$ [14]4,11-dieneN$_4$)}$_2$CN](ClO$_4$)$_3$
(d) ——— [Co(Me$_6$ [14]4,11-dieneN$_4$)BH$_4$](ClO$_4$)

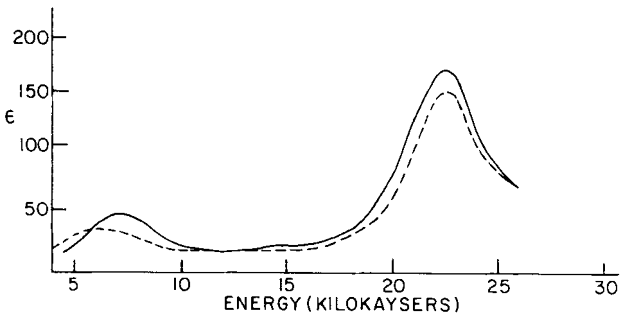

FIGURE 3 d–d Electronic Spectra of
(a) ——— [Co(Me$_6$ [14]4,14-dieneN$_4$)ClO$_4$](ClO$_4$)
(b) – – – – [Co(Me$_6$ [14]4,14-dieneN$_4$)(CH$_3$CN)](ClO$_4$)$_2$

The d–d electronic spectra of these cobalt(II) complexes are characterized by three areas of absorption. There generally exists a very broad absorption (ϵ_{max} = 20 to 80) in the 4,000–10,000 cm^{-1} region, one or two very weak bands in the 13,000 to 17,000 cm^{-1} region (ϵ_{max} = 1 to 2),

TABLE V
d–d Electronic spectra of the cobalt(II) complexes[a]

Complex	Absorption Maxima[b]
[Co(Me$_6$[14]4,11-dieneN$_4$)H$_2$O](ClO$_4$)$_2$[c]	5.90(32.5), 13.5(2), 22.4(80), 30.7(2090).
[Co(Me$_6$[14]4,11-dieneN$_4$)ClO$_4$]ClO$_4$[d]	5.90(20.3), 13.2(1), 22.2(103)
[Co(Me$_6$[14]4,14-dieneN$_4$)ClO$_4$]ClO$_4$[d]	5.21(sh), 6.67(21.5), 22.7(150)
[Co(Me$_6$[14]4,14-dieneN$_4$)CH$_3$CN](ClO$_4$)$_2$[e]	5.4(sh), 7.15(37), 14.7(4), 22.7(170)
[Co(Me$_6$[14]4,11-dieneN$_4$)Cl]ClO$_4$[d]	5.10(27.6), 6.25(41.5), 22.3(95)
[Co(Me$_6$[14]4,11-dieneN$_4$)Cl](ClO$_4$)[g]	5.15(sh), 6.50, 22.30
[Co(Me$_6$[14]4,11-dieneN$_4$)Br]ClO$_4$[d]	5.00(40.5), 5.85(52.5), 13.0(2), 21.8(100)
[Co(Me$_6$[14]4,11-dieneN$_4$)Br]ClO$_4$[g]	5.00(sh), 6.29, 13.0, 17.6, 21.8
[Co(Me$_6$[14]4,11-dieneN$_4$)I]ClO$_4$[d]	5.63(48.5), 12.72(2), 23.8(sh)
[Co(Me$_6$[14]4,11-dieneN$_4$)I]ClO$_4$[g]	6.10, 23.8(sh)
[Co(Me$_6$[14]4,11-dieneN$_4$)C$_5$H$_5$N](ClO$_4$)$_2$[d,f]	7.35(54.5), 22.2(137)
[Co(Me$_6$[14]4,11-dieneN$_4$)C$_5$H$_5$N)(ClO$_4$)$_2$[g]	6.0(sh), 7.50, 16.6(sh), 22.0
[Co(Me$_6$[14]4,11-dieneN$_4$)BH$_4$]ClO$_4$[g]	5.40, 9.76, 18.5(sh), 22.5
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$C$_2$H$_8$N$_2$](ClO$_4$)$_4$[g]	5.70(sh), 7.21, 15.6(sh), 21.5
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$CN](ClO$_4$)$_3$[g]	8.90, 18.2(sh), 22.2
[Co(Me$_6$[14]4,11-dieneN$_4$)Br]$_2$CoBr$_4$[g]	~6.25, 13.7, 14.31, 15.0, 15.7, 22.7
[{Co(Me$_6$[14]4,11-dieneN$_4$)}$_2$C$_2$O$_4$](ClO$_4$)$_2$[g]	9.61, 20.4

[a] Maxima are in kilokaysers; numbers in parentheses are extinction coefficients.

[b] Abbreviations: sh = shoulder.

[c] Aqueous solution.

[d] Nitromethane solution.

[e] Acetonitrile solution.

[f] 10% excess pyridine added to prevent partial solvation of axial sites.

[g] Solid state spectra.

an absorption in the visible near 22,400 cm^{-1}, and, when not covered by charge transfer bands, an intense absorption near 33,000 cm^{-1} ($\epsilon_{max} = 2,000$).

The maxima and contours of the low energy near-infrared bands are quite dependent on the nature of the axial ligand. For some complexes, such as the one containing pyridine, $[Co(Me_6[14]4,11\text{-diene}N_4)C_5H_5N](ClO_4)_2$, this region contains two definite absorptions (at 6,000 and 7,500 cm^{-1}). The halo-complexes generally have a low energy shoulder in this region, while those complexes containing oxygen donor atoms in the axial position have a single, but very broad absorption, in this vicinity which becomes asymmetric at liquid nitrogen temperatures.

The absorption in the visible portion of the spectrum consists of a single symmetrically shaped band near 22,500 cm^{-1}, the position of which is independent of the nature of the axial ligand, within experimental error.

For the aquo, methanol, and acetonitrile complexes, there is a band near 33,000 cm^{-1} ($\epsilon \cong 2,000$) that is presumed to be associated with the imine functions since $Ni(Me_6[14]4,11\text{-diene}N_4)^{2+}$(38) and $Fe(Me_6[14]4,11\text{-diene}N_4)^{2+}$(39) have absorptions of the same intensity in the same region of the spectrum which vanish on hydrogenation of the imine functions. This absorption is obscured by more intense charge transfer bands for those cobalt(II) complexes having coordinated halides.

The small number of observed d–d bands compared with the large number predicted for this system does not permit a detailed analysis of the spectra. Furthermore, absorptions appearing in the low energy region (4,000–10,000 cm^{-1}) are broad and overlap considerably making it difficult to locate the band maxima accurately. However, a tentative assignment has been made on the basis of the energy level diagram in Figure 1.

The lowest energy absorption, generally observed as a shoulder in the spectra between 5,000 to 7,000 cm^{-1}, is assigned to the $^2A_1 \rightarrow {}^2B_1(d_{z^2} \rightarrow d_{x^2-y^2})$ transition. As the field strength of the axial ligand is increased, the energy of this band is expected to decrease because the "tetragonality" is decreased. (The substitution of various ligands in the axial site affects the values of both Dq^2 and Dt (the degree of tetragonality). Increasing the ligand field of the axial group has the effect of decreasing the tetragonality of the system.) From the standpoint of a 1-electron orbital picture, the energy separation between the z^2 orbital and the x^2-y^2 orbital is decreased.

The next absorption is assigned to the $^2A_1 \rightarrow {}^2E(a)$ transition (xz, yz → z^2), this assignment being confirmed by the epr results (*vide infra*). The energy of this transition is expected to increase with increasing field strength of the axial ligand in agreement with our observation. The order of increasing ligand field strength, based on the position of this band is $I^- < Br^- < Cl^- < CH_3CN \sim en < py < CN^- < BH_4^-$, which generally agrees well with the established spectrochemical series. It has not been possible to place either H_2O or ClO_4^- in this series since the $^2A_1 \rightarrow {}^2E$ bands for these complexes were broad, flat-topped, and unresolvable. The relative positions in the spectrochemical series of borohydride and cyanide are interesting. The position of cyanide is lower than expected, presumably because it is acting as a bridging ligand. Very few borohydride complexes of the divalent first row transition metals are known, although they are well known among elements in low oxidation states.[40] Those reported by Curtis[25] for a series of Ni(II) complexes of the fully hydrogenated ligands ($Me_6[14]aneN_4$) yield high spin complexes. In the series of five-coordinate complexes reported here, the absorption assigned to the $^2A_1 \rightarrow {}^2E$ transition for the borohydride complex is about fifteen percent higher in energy than that for any other complex. This indicates that borohydride anion is among the strongest of ligands. The apparent strong interaction between $Co(Me_6[14]4,11\text{-diene}N_4)^{+2}$ and borohydride is probably a result of the interaction of two hydrogen atoms through chelation of the borohydride moiety. The similarity of the infrared spectrum of the borohydride entity in this complex to those of complexes in which chelation has been confirmed by X-ray studies[40] supports this conclusion, although other modes of coordination are known.[41]

The absorption centered near 22,800 cm^{-1} may be assigned to either the $^2A_1 \rightarrow {}^2E(b)$ or $^2A_1 \rightarrow {}^2A_2$ transition. Both of the transitions are expected to be relatively insensitive to the nature of the axial ligand (neglecting π bonding), and the two transitions should be very close together in energy. The very weak transitions ($\epsilon_{max} = 1–2$) in the 13,000 to 17,000 cm^{-1} portion of the spectrum are probably associated with the $^2A_2 \rightarrow {}^4A_2$ and $^2A_2 \rightarrow {}^1E$ transitions. The spectra of the solid $Co(Me_6[14]4,14\text{-diene}N_4)(ClO_4)_2$ and $[Co(Me_6[14]4,14\text{-diene}N_4)(CH_3CN)](ClO_4)_2$ complexes, as well as nitromethane solutions of $Co(Me_6[14]4,14\text{-diene}N_4)(ClO_4)_2$ containing a tenfold excess of tetraethylammonium halide, are similar to those of the analogous $Me_6[14]4,11\text{-diene}N_4$ complexes. The ν_{max} values for the absorptions are close to those of the $Me_6[14]4,11\text{-diene}N_4$ complexes, but the intensities of the low energy

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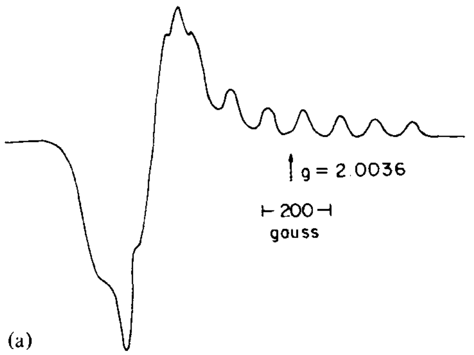
bands are considerably smaller, while the intensities of the band at 22,400 cm^{-1} are approximately the same. It is concluded that coordination number, geometry and spin state for the complexes of the isomeric ligands are the same.

It is significant that these complexes exhibit electronic spectra compatible with the energy level diagrams for square pyramidal geometry. Five-coordinate Co(II) complexes containing the 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene ligand have distinctly different spectra, and are most compatible with a trigonal bipyramidal geometry.[4] Also, whereas these complexes are all five-coordinate, with the exception of the oxalato-complex, those prepared using the saturated ligand 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane exhibit five and six coordination.[3]



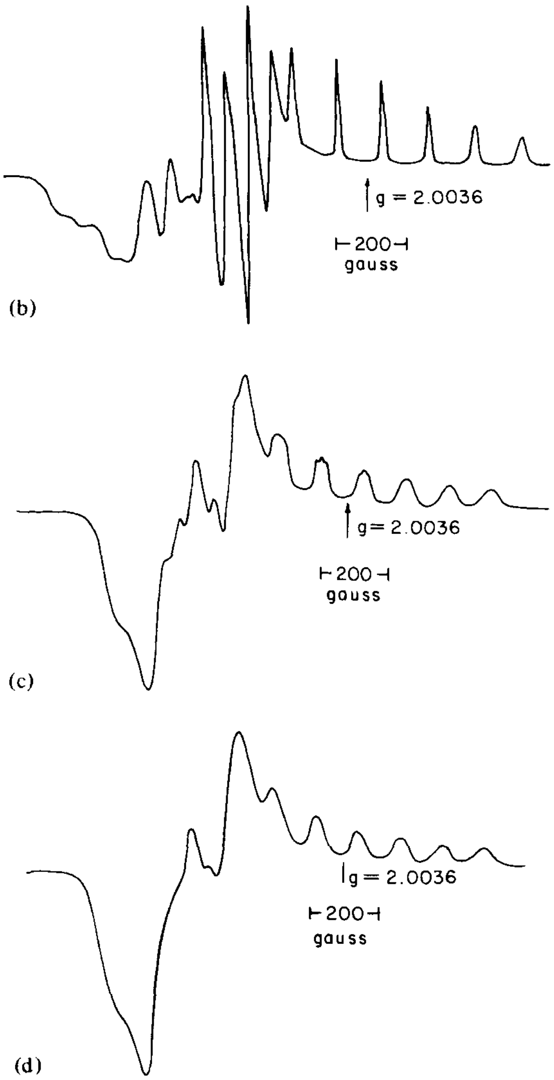


FIGURE 4 EPR Spectra of
(a) Co(Me$_6$[14]4,11-dieneN$_4$)(Imid)$^{+2}$ in MeNO$_2$
(b) Co(Me$_6$[14]4.11-dieneN$_4$)(ClO$_4$)$_2$ in DMF
(c) Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ in MeNO$_2$
(d) Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ in CH$_3$CN

TABLE VI
EPR spectral data for the cobalt(II) complexes

Complex	Solvent	$g_\parallel$	$g_\perp$	$A_\parallel^{Co}$, cm^{-1} (x 10^4)	$A_\perp^{Co}$, cm^{-1} (x 10^4)	$^2A \to {}^2E$, (cm^{-1})	$-k^2\lambda$, (cm^{-1})
Co(Me$_6$[14]4, 11-dieneN$_4$)(C$_3$H$_4$N$_2$)$^{+2(a)}$	MeNO$_2$	2.0137	2.36	98			
Co(Me$_6$[14]4, 11-dieneN$_4$)(C$_5$H$_5$N)$^{+2(b)}$	CH$_3$CN	2.0149	2.38			7.35	466
Co(Me$_6$[14]4, 11-dieneN$_4$)$^{+2}$	DMF	2.0160	2.43	125			
Co(Me$_6$[14]4, 11-dieneN$_4$)$^{+2}$	MeNO$_2$	2.0145	2.43	117			
Co(Me$_6$[14]4, 11-dieneN$_4$)(CH$_3$CN)$^{+2}$	CH$_3$CN	2.0158	2.44	114.1		~7.15^c	519
Co(Me$_6$[14]4, 11-dieneN$_4$)Cl$^+$	MeNO$_2$	2.0155	2.45	125	50,73	6.25	469
Co(Me$_6$[14]4, 11-dieneN$_4$)Br$^+$	MeNO$_2$	2.0159	2.47	125	70,81	5.85	458
Co(Me$_6$[14]4, 11-dieneN$_4$)(imid)O$_2$$^{+2}$	DMF	2.0843	2.007, 1.999	20.2	12.5, 12.4		

^{a}C$_3$H$_4$N$_2$ = imidazole.
^{b}C$_5$H$_5$N = pyridine.
^{c}Assumed from the value measured for Co(Me$_6$[14]4, 14-dieneN$_4$)(CH$_3$CN)$^{+2}$.

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EPR Spectra

Electron paramagnetic resonance spectral data for some of the complexes are given in Table VI, and some representative spectra are pictured in Figure 4. In all cases, measurements were performed at 77°K on frozen solutions. The spectra were not computer fit, so the values of g and A^{Co} corresponding to the perpendicular branches of the spectra are not known with great precision. In general, the spectra are consistent with axial or rhombic symmetry, having perpendicular branches with values of g ranging between 2.35 and 2.47 and parallel branches at $g_{\parallel} \cong 2.02$, split into eight lines due to hyperfine interaction with the Co nucleus (I = 7/2). The values of $A_{\parallel}^{Co}$ for the complexes lie in the range 97–125 x 10^{-4} cm^{-1}. For nitrogen donor axial ligands, (eg., pyridine and imidazole, Figure 4a) superhyperfine splitting of some of the hyperfine components was observed. Only three lines were observed in all cases, substantiating our conclusion that five-coordination is preferred for these complexes. Further, the superhyperfine structure indicates that the unpaired electron is located in a molecular orbital containing a substantial contribution from the cobalt d_{z^2} orbital, and therefore supports the use of the energy level diagram in Figure 1 for interpretation of the electronic spectra.

The epr spectrum of $Co(Me_6[14]4,11\text{-diene}N_4)(ClO_4)_2$ in nitromethane is characteristic of nearly axial symmetry and shows three-line superhyperfine structure in the hyperfine components of the parallel branch. This unexpected phenomenon has been previously observed in our laboratories for the complexes $Co(Me_4[14]1,3,8,10\text{-tetraene}N_4)^{+2}$(10) and $Co(Me_6[14]1,4,8,11\text{-tetraene}N_4)^{+2}$(7) in CH_3NO_2, and has been attributed to axial coordination of either the solvent or some nitrogen-donor impurity in the solvent. An additional possibility is weak interaction with the tetraalkylammonium cation of the electrolyte which is added to improve superhyperfine resolution, although this seems unlikely.

The spectrum of $Co(Me_6[14]4,11\text{-diene}N_4)^{+2}$ in DMF, Figure 4(b), shows good resolution of the hyperfine coupling in both the parallel and perpendicular branches of the spectrum. The sharp singlets in the parallel branch indicate that DMF coordinates through the oxygen atom, rather than through the nitrogen atom.

In general, the epr spectra shown in Figure 4 are consistent with near-axial symmetry and, therefore, correspond to the Hamiltonian in equation (1):[44]

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

Values of A^{Co} for the Br^- and Cl^- complexes are quite large. This is consistent with the negative charge on these ligands, which repels the d_{z^2} electron of Co and causes it to be localized to a larger extent on the metal. The positions of these ligands in the spectrochemical series is also consistent with a large cobalt hyperfine interaction.

The epr data support the assignments of the bands in the ir region of the electronic spectra for this series of complexes. Equation (2) shows the relationship between the value of $g_{\perp}$, the free ion spin-orbit coupling constant, λ (-515 cm^{-1} for low spin Co(II)), and the energy of the $^2A \rightarrow {}^2E$ transition in cm^{-1} for a complex of axial symmetry.[45]

$$g_{\perp} = 2 - \frac{6\lambda k^2}{\Delta E(^2A \rightarrow {}^2E)} \qquad (2)$$

k^2 is the orbital reduction factor and gives a measure of the extent of electron delocalization onto the axial ligand.[46,47] From the values of $g_{\perp}$ reported in Table 6 and the energy of the band assigned to $^2A \rightarrow {}^2E$ transition, also included in Table 6, we compute the values of $k^2\lambda$ in the last column of the table. All of the values calculated are quite similar except that for the CH_3CN adduct, which is too high. This may reflect the uncertainty involved in measuring the positions of the maxima for the broad low-energy electronic spectral bands in this case. The values of $k^2\lambda$ for the $Co(Me_6[14]4,11\text{-diene}N_4)^{+2}$ complexes are substantially larger than those which we reported for two series of complexes containing the cations $Co(Me_4[14]1,3,8,10\text{-tetraene}N_4)^{+2}$ and $Co(Me_2[14]1,3\text{-diene}N_4)^{+2}$.[10] This indicates a smaller delocalization of electron density onto the axial ligand for the complexes reported herein. All other factors being equal, we would expect similar delocalization for $Co(Me_2[14]1,3\text{-diene}N_4)^{+2}$ and $Co(Me_6[14]4,11\text{-diene}N_4)^{+2}$ since both macrocyclic rings contain the same amount of unsaturation and have similar ligand field strengths.[48] The evident decreased axial interaction in the case of the $Co(Me_6[14]4,11\text{-diene}N_4)^{+2}$ complexes is possibly due to the presence of six methyl substituents on the six-membered chelate rings. These rings are flexible and will assume conformations which will place two of the methyl substituents in positions which interfere with axial coordination of ligands. Therefore, the axial interaction will be weaker in these

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complexes than in the Me_4 [14] 1,3,8,10-tetraeneN_4 and Me_2 [14] 1,3-dieneN_4 complexes, where the methyl substituents are forced to lie in the plane of the macrocycle. Steric interaction with substituent methyl groups may also partially explain the reduced tendency for six-coordination in the case of the Co(Me_6 [14] 4,11-dieneN_4)$^{+2}$ complexes. The question of steric versus electronic effects in the axial coordination sites of these complexes has recently been discussed.[49-50]

Reversible Oxygenation

When a solution of Co(Me_6 [14] 4,11-dieneN_4)(ClO_4)$_2$ in DMF is exposed to air or oxygen at temperatures ⩽ 0°C, it undergoes a color change from yellow-orange to dark red. The color reverts to yellow-orange when oxygen is purged from the system or when the solution is warmed above 0°C. The deep red color which is generated in the presence of oxygen is due to an intense absorption band which grows into the visible region at ~520 nm. The epr spectrum of a frozen oxygenated solution is very similar to those reported for cobalt adducts with molecular oxygen in which one mole of oxygen is present per mole of cobalt.[8,51-54] We therefore conclude that the electronic and electron paramagnetic resonance spectral changes which result from oxygenation of Co(Me_6 [14]-4,11-dieneN_4)$^{+2}$ are due to formation of a monomeric oxygen adduct in which oxygen is reversibly bound. A typical oxygen adduct epr spectrum is shown in Figure 5.

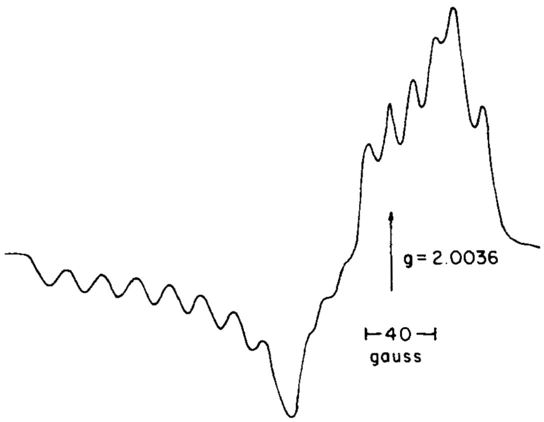


FIGURE 5 EPR spectrum of Co(Me_6 [14] 4,11-dieneN_4)(Imid)(O_2)$^{+2}$ in DMF

We have attempted to measure thermodynamic parameters for the oxygenation of Co(Me_6 [14] 4,11-dieneN_4)$^{+2}$ in DMF by monitoring the 520 nm electronic absorption band as a function of temperature and oxygen pressure. At each temperature, a series of spectra were recorded for various oxygen pressures between 0 and 760 mm/Hg. From the measured absorbance changes at 520 nm and the known oxygen pressures, we attempted to calculate K, the equilibrium constant for oxygen adduct formation, and ΔG, the difference between the molar extinction coefficient of the oxygen adduct and the unoxygenated Co(Me_6 [14] 4,11-dieneN_4)$^{+2}$ at 520 nm, at each temperature using equation (3).[55]

$$\frac{1}{K} = \frac{[M]_0 P_{O_2}}{\Delta A} \Delta\epsilon - P_{O_2} \qquad (3)$$

Here, $[M]_0$ = the total concentration of cobalt species in solution; $\Delta A = A_{obs} - A_0$ (the difference between the observed absorbance and the absorbance in the absence of oxygen at 520 nm); P_{O_2} is the partial pressure of oxygen above the solution; and a one centimeter optical path length has been used. For each ordered pair (P_{O_2}, ΔA), at a given temperature, one equation of the form of equation (3) results. Thus if, for example, five oxygen pressures are used at a given temperature, five simultaneous equations result, one for each (P_{O_2}, ΔA) pair. Since there are only two unknowns, ΔE and K, to be calculated for each temperature, the system is overdetermined if more than two oxygen pressures are used. In our example, there are 10 ways to combine the five equations in pairs, and solution of each pair gives values for ΔE and K. These values can then be averaged to obtain the "best" ΔE and K for the temperature at which the data was obtained. If an ordered pair (P_{O_2}, ΔA) is in error, this becomes obvious from solution of the equations, since all pairs of simultaneous equations which involve the equation resulting from the erroneous data (P_{O_2}, ΔA) will give ΔE and K values which deviate substantially from the norm. The errant (P_{O_2}, ΔA) can then be eliminated from consideration.

Several factors limit the accuracy of our results: (1) our means of temperature regulation was rather crude, resulting in substantial temperature fluctuations during a set of runs at varying pressures. Consequently, the observed absorbances incorporate considerable uncertainty; (2) we were unable to work at oxygen pressures higher than 1 atmosphere, which restricted the range of absorbance changes that we observed;[56] (3) the construction of our oxygenation cell is such as to allow only slow equilibrium between the solution and the atmosphere over it. Thus additional uncertainty is introduced into our

TABLE VII

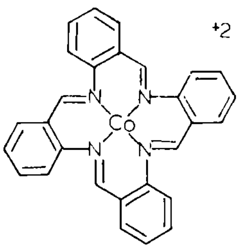
Equilibrium data for the reaction with O_2

Temp, °K	Number of Data Points (P_{O_2}, ΔA) Used	K, mm^{-1}(x 10^2)	Δε
211	8	1.55	853
214	4	1.38	858
219	8	.726	811
224	4	.490	817
226	9	.301	781
230	4	.200	619
236	8	.155	617
243	6	.090	604
243	4	.062	540

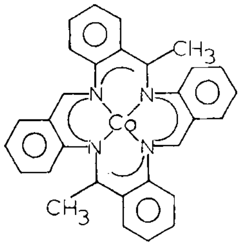
absorbance values. We therefore regard our equilibrium constants as approximations for the true values. Similarly, values of ΔH and ΔS for oxygenation obtained from a suitable Van't Hoff plot involve substantial uncertainties.

Values of K and Δε obtained from our experiments are reported in Table VII. Error limits on these quantities are at least ± 20%. The slope of a plot of ln K vs 1/T gives ΔH ≅ 10 kcal/mole and ΔS ≅ −55 e.u.. Those values are similar in magnitude to those reported by other workers.[56],[57] However, inaccuracy prevents comparison with values for other systems.

A recent report[8] indicates that there is considerable information regarding the extent of electron transfer from Co(II) to O_2 in the magnitude of the anisotropy in the cobalt hyperfine coupling constant obtained from the epr spectrum. The extent of electron transfer should be closely related not only to the ligand field strengths of groups coordinated to cobalt(II) but also to the redox properties of the complex. We are therefore in the process of studying the reversible oxygenation of Co(Me_6 [14] 4,11-dieneN_4)$^{+2}$ in the presence of a wide variety of Lewis bases and in several solvents in order to examine the extent of electron transfer as a function of axial ligand field strength and redox potential. In addition to Co(Me_6 [14] 4,11-dieneN_4)$^{+2}$, we have observed that several other complexes of cobalt(II) with macrocyclic ligands (eg., structures VII and XI–XII) form monomeric oxygen adducts in solution. There is a considerable variation of in-plane ligand field strength in this series of complexes, which should be reflected in the extent of electron transfer to bound O_2. These complexes are also under study in our laboratories.



(XI)



XII

CONCLUSIONS

The five-coordinate cobalt(II) complexes of the Me_6 [14] dieneN_4 ligands reported herein further illustrate the ability of macrocyclic ligands to induce spin pairing in the d^7 system as a result of strong in-plane ligand fields. With these ligand systems, as well as with many of those mentioned in the Introduction, the electronic, thermodynamic, and steric requirements of the cobalt(II) ion are fulfilled by coordination of a fifth ligand in one of the two available axial sites. The limited tendency to coordinate a sixth ligand is probably due both to the electronic repulsions arising from the single unpaired electron in the d_{z^2} orbital of the Co(II) ion and to the steric effect expected from axial methyl substituents on the carbons of the six-membered chelate rings of the macrocycle. That both factors are important is evidenced by the fact that complexes of Me_6 [14] 4,11-dieneN_4 with Co(III)[1] and Fe(II)[39] (both low spin d^6 systems) are six-coordinate, as are some complexes of Co(Me_4 [14] 1,3,8,10-tetraeneN_4)$^{+2}$.(10) In the case of Co(III) and Fe(II), electronic repulsions are certainly less significant than for Co(II), since the d_{z^2} orbital is empty. Steric effects due to the axial methyl groups have been documented in both cases. However, in the case of Co(Me_4 [14] 1,3,8,10-tetraeneN_4)$^{2+}$ in which substituent methyl groups are forced to be in the plane of the macrocycle, six-coordination can occur despite the presence of electron–electron repulsion. Therefore both factors must be considered. In the case of the oxalato complex, where the macrocycle has been

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forced to fold, ligand field effects are lessened and the cobalt ion assumes a high spin configuration. The energies of the d–d absorption bands for this complex are typical of those found for octahedral Co(II) coordinated to four nitrogen and two oxygen donors.[58]

The electronic spectra of the complexes have been tentatively assigned, with assignment of the $^2A \rightarrow ^2E$ transition in the ir region of the spectrum being supported by epr results. The energy of this transition is dependent on the donor strength of the axial ligand and allows us to tentatively place the borohydride anion at the strong-field extremity of the spectrochemical series. Finally, we have found that $Co(Me_6[14]4,11\text{-}dieneN_4)^+$ serves as a reversible oxygen binder in DMF and have characterized the oxygen adduct spectroscopically.

It should be noted that our formulation of the complexes discussed here as five-coordinate may seem inconsistent with the report by Endicott and co-workers of six-coordinate Co(II) adducts with their ligands.[5,49–50] They have provided X-ray structural data for a diaquo complex of $Co(Me_6[14]4,11\text{-}dieneN_4)^{+2}$.(49) The results summarized here demonstrate the existence of five-coordinate species as well. The most likely explanation for these combined results is that both coordination numbers are reasonably stable, and the formation of one or other depends on synthetic procedures and the axial ligands that are available. In the case of our monohalide complexes, conductance data reveals convincingly that the halides remain coordinated in solution; but the data do *not* rule out solvent coordination in the second axial site. The electronic spectra measured both in solution and in the solid state are sufficiently similar, however, to strongly suggest the absence of solvent coordination for these species. It is also reasonable to assume that, if six-coordination were strongly preferred, it should occur in the presence of strong nitrogen donor ligands, such as pyridine and imidazole. However, our epr results indicate coordination of only a single nitrogen donor in an axial site in the presence of these ligands. The certainty that five-coordinate structures do occur *with ligands* of this class is provided by a recent crystal structure on a mono-aquo complex of Co(II) – $([14]dieneN_4)$.[9] Although a fluoride from a PF_6^- anion is associated with the second axial site in this species in the solid state, the distance is so long that the bonding nature of the interaction is a matter worthy of some debate.

EXPERIMENTAL

Physical Measurements

Visible, near infrared, and ultraviolet spectra were obtained using a Cary Model 14 Recording Spectrophotometer. Spectra of solid samples were run with Nujol mulls impregnated on filter paper. Low (variable) temperature solution spectra were obtained using a special cell which allowed the solution to be exposed to oxygen or nitrogen (at any pressure between 1 and 760 mm/Hg) or to vacuum. Temperature was regulated by adjusting the flow of cooled N_2 gas through the dewar in which the cell was suspended. Temperature was measured using a copper-constantin thermocouple wired to a Digitek millovoltimeter. Temperature could be maintained constant to within ± 2°C. All samples for epr measurement were prepared under a dry nitrogen atmosphere in a glove bag or a Vacuum Atmospheres glove box. Infrared spectra were obtained on a Perkin-Elmer Model 337 Recording Spectrophotometer using Nujol and hexachlorobutadiene mulls and polystyrene as a calibrant. Solution conductivities were measured using an Industrial Instruments RC16B Conductivity Bridge at 25°C and 1000 cps on approximately 10^{-3} molar solutions. Magnetic susceptibilities of solid samples were determined at room temperature by the Faraday method on a system equipped with a Cahn Gram Electrobalance. Mercury(II) tetrathiocyanatocobaltate(II) was used as a calibrant and diamagnetic corrections were applied to all measurements. X-ray powder patterns were obtained from selected samples using Cu K_a radiation. Electron paramagnetic resonance 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 with tetraalkylammonium salt added to improve resolution of superhyperfine structure.

Materials

All metal salts were of reagent grade and used without further purification. Organic solvents were of reagent grade and dried with molecular sieves for several weeks before using.

Preparation of $Co(Me_6[14]4,14\text{-}dieneN_4)(ClO_4)_2$ *and* $Co(Me_6[14]4,11\text{-}dieneN_4)(ClO_4)_2$. One-tenth mole (42.1 g) of $Co(ClO_4)_2 \cdot 6C_2H_5OH$ (prepared by the reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with triethylorthoformate) and three-tenths mole (20 g) of ethylenediamine were dissolved in 300 ml of acetone under nitrogen. The flask and contents were purged with nitrogen, stoppered tightly, and allowed to stand for one week. The initial pink color of the solution gradually turned orange-brown (three to four hours). After standing for one week, ethyl ether was added to the solution (under nitrogen) until it became slightly turbid, and the solution was then set aside for several more days. A small crop of orange and yellow crystals formed. The solution was decanted from these crystals and more ether was added to this solution, resulting in the formation of a thick viscous dark brown oil. The supernatant liquid was poured off and discarded while the residue was redissolved in acetone-ethanol mixture. Recrystallization yielded an olive-brown microcrystalline solid.

A slurry of 8.8 mmole (5 g) of the above compound was neutralized by the addition of 9 mmole of perchloric acid in methanol. The olive-colored solid immediately dissolved to give a yellow-orange solution. The solution was concentrated by evaporation, and crystallization was induced with a small amount of water. The yellow-orange solid was filtered, and recrystallized from methanol. The compound thus obtained was combined with the crystals which first precipitated from the condensation reaction. These were then fractionally crystallized under nitrogen from methanol to yield noninterconvertible isomers, the *cis*(4,14)diene complex being slightly more insoluble and separating from the solution first.

Alternate Preparation of Co(Me$_6$[14]4,14-dieneN$_4$)(ClO$_4$)$_2$ and Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$. Because of the time and effort required to prepare and separate the two isomers which result from the in situ condensation of acetone and ethylenediamine, a more expedient route to the preparation of the two complexes individually was preferred.

Co(Me$_6$[14]4,14-dieneN$_4$)(ClO$_4$)$_2$ is most easily prepared by the method of Love and Powell[2] by removing the ligand from the analogous nickel complex, which can be prepared in much higher yield with less difficulty. A four to one molar ratio of a cyanide salt to nickel complex was stirred together in anhydrous ethanol for several hours. The nickel cyanide complex and potassium perchlorate were removed by filtration and a molar equivalent of Co(ClO$_4$)$_2$·6C$_2$H$_5$OH was added to the filtrate under nitrogen. The solution immediately turned orange, and concentration by evaporation yielded a yellow-orange crystalline complex. The complex was filtered, washed with ethanol, and dried under vacuum.

Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$·CH$_3$OH. This complex is most easily prepared by the reaction of Co(CH$_3$CO$_2$)$_2$·4H$_2$O with the dihydroperchlorate of the ligand. The macrocyclic Schiff base dihydrogen perchlorate was readily prepared by the reaction of ethylenediamine hydroperchlorate and acetone as described by Curtis.[59] Equimolar quantities of cobalt acetate 4-hydrate and the ligand dihydroperchlorate were stirred together as a slurry, under nitrogen, and refluxed until the solids dissolved and the solution was dark-brown. The flask were stoppered and chilled overnight. The deep orange crystals that separated from solution were filtered, washed with ethanol, and dried *in vacuo* for one hour. The anhydrous material can be obtained by prolonged exposure to dry atmosphere or by placing the compound under vacuum. The aquo complex, Co(Me$_6$[14]4,11-dieneN$_4$)(H$_2$O)(ClO$_4$)$_2$, is obtained by recrystallization from water.

[Co(Me$_6$[14]4,11-dieneN$_4$)Cl](ClO$_4$). One gram (2.1 mm) of Co(Me$_6$[14]4,11-dieneN$_4$)(H$_2$O)(ClO$_4$)$_2$ was dissolved in 20 ml of methanol. One-fourth gram (8 mm) of lithium chloride, dissolved in methanol, was added to the solution. The solution was flushed with nitrogen the flask was stoppered and chilled for several hours to induce crystallization. The brown crystalline precipitate was filtered, washed with ethanol, and dried *in vacuo.*

[Co(Me$_6$[14]4,11-dieneN$_4$)Br](ClO$_4$). This complex was prepared in the same manner as the chloro derivative, using lithium bromide in place of lithium chloride.

[Co(Me$_6$[14]4,11-dieneN$_4$)I](ClO$_4$). This complex was also prepared in the same manner as the chloro complex, but using sodium iodide in place of lithium chloride. A large excess of sodium iodide must be avoided, and the solution is much more sensitive to air than are the solutions of the chloro- and bromo-complexes.

[Co(Me$_6$[14]4,11-dieneN$_4$)C$_5$H$_5$N](ClO$_4$)$_2$ One gram of Co(Me$_6$[14]4,11-dieneN$_4$)(ClO$_4$)$_2$ was dissolved in 20 ml of methanol and two ml of pyridine was added. Concentration and chilling of the solution yielded an olive colored crystalline precipitate which was filtered, washed with ethanol, and dried *in vacuo.*

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[Co(Me$_6$[14]4,11-dieneN$_4$)BH$_4$](ClO$_4$). One gram of Co(Me$_6$ [14] 4,11-dieneN$_4$)(ClO$_4$)$_2$ was dispersed in 30 ml of ethanol and 0.7 g (1.85 mmole) of tetraphenylarsonium tetrahydroborate (prepared by mixing equimolar quantities of tetraphenylarsonium chloride and sodium tetrahydroborate in water and filtering the insoluble tetraphenylarsonium tetrahydroborate) added under nitrogen. The cobalt complex goes into solution and tetraphenylarsonium perchlorate precipitates. The tetraphenylarsonium perchlorate was filtered under nitrogen and lithium perchlorate (0.185 g) was added to precipitate this complex. The light brown precipitate was filtered under nitrogen, washed with ethanol, and dried under vacuum.

[Co(Me$_6$[14]4,11-dieneN$_4$)CH$_3$CN](ClO$_4$)$_2$. One gram of Co(Me$_6$ [14] 4,11-dieneN$_4$)(ClO$_4$)$_2$ was dissolved in 10 ml of a 50:50 methanol-acetonitrile mixture. Ethyl ether was added dropwise until the solution became slightly turbid. The solution was flushed with nitrogen, stoppered and set aside for 24 hours. The large crystals which formed were filtered from the solution, washed with ethanol and dried under vacuum.

[Co(Me$_6$[14]4,11-dieneN$_4$)$_2$(C$_2$O$_4$)](ClO$_4$)$_2$·H$_2$O One gram of Co(Me$_6$ [14] 4,11-dieneN$_4$)(ClO$_4$)$_2$ was dissolved in 30 ml of water and 0.12 g of potassium oxalate was added. The solution was flushed with nitrogen, stoppered, and chilled in a refrigerator overnight. The bright red-pink crystals were filtered from the solution, washed with ethanol, and dried under reduced pressure.

It should be pointed out that similar five-coordinate cationic species can be prepared by starting with the ligand dihydrohalide salts, rather than the ligand dihydroperchlorate. However, the tetrahalo cobaltate species form and serve as the counter ions. The electronic spectra of these complexes are then cluttered with the intense d–d transitions of the tetrahedral CoX$_4$$^{-2}$ species, both in the visible and the infrared portions of the spectrum. Similarly, the magnetic moments then contain contributions from both the low spin, five-coordinate cationic species, as well as from the high spin tetrahedral anions.

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