$[HFe(CO)_4]^-$, 18716-80-8; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9.

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A Spectrochemical and Electrochemical Study of Complexes of Cobalt with Macrocyclic Ligands Having Various Degrees of Unsaturation

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Spectrochemical and electrochemical studies have been carried out on a series of macrocyclic complexes of cobalt, which vary in the nature and degree of ligand unsaturation. The complexes are of the type $[Co(MAC)(CH_3CN)_2]^{3+}$ where MAC represents a series of 14-membered macrocycles varying in their degree and position of ligand unsaturation and substitution. Spectral analysis of the cobalt(III) complexes provides an evaluation of the variation of the ligand field strength as a function of position and degree of ligand unsaturation for macrocycles of the same ring size and donor atoms. The half-wave potentials for the Co^{II}/Co^{I} couple vary in a predictable manner related to ligand unsaturation, while the Co^{III}/Co^{II} couple is insensitive to these structural variations.

Introduction

Macrocyclic complexes of cobalt(III) have been the subject of several studies concerning various aspects of stereochemistry, electrochemistry, and electronic structure.[1-4] Stereochemical considerations have led to a better understanding of such factors as ring size effects, steric interactions, the inflexibility of unsaturated structures toward folding, and the energetics and consequences of possible chelate ring conformations. In the case of cobalt, electronic relationships have received scant attention, so that the effect of varying the position and extent of ligand unsaturation in the macrocyclic ring on such parameters as ligand field strength and the oxidation state stability of the cobalt complexes is poorly documented. Electrochemical studies on macrocyclic complexes of nickel(II)[5-7] and iron(II)[8] have shed considerable light on the chemistry of such systems, including the stabilization of unusual metal oxidation states, the ease of oxidation or reduction of the central metal ion with respect to macrocyclic ring size and the degree and position of ligand unsaturation, and the reactivity of the ligand as a function of the site of electron donating or withdrawing substituents.

The availability of a substantial series of complexes of cobalt(III) with macrocyclic ligands (Figure 1) allows an extension of our studies to this metal system. The complexes present a unique opportunity to study and correlate the significant changes in spectroscopic and redox properties which occur as a result of changing ligand structural parameters. The complexes reported here all involve coordination of 14-membered tetradentate macrocyclic ligands in a square-planar fashion, with coordinating CH_3CN groups present in the axial sites. The use of acetonitrile in the coordination sphere, and as solvent in our investigations, overcomes the problems associated with solvolysis reactions when other coordinated species, such as Cl^- or Br^-, are used.

Results and Discussion

Synthesis of the New Complexes. The series of 14-membered macrocyclic cobalt(III) complexes containing coordi-

Table I. Conductances and Elemental Analyses of the $[Co(MAC)(CH_3CN)_2](ClO_4)_3$ Complexes

Macrocycle	Λ_M[a]	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
$Me_2[14]$py-dieneN_4	398	32.69	32.84	4.01	3.94	12.04	12.08
$Me_2[14]$py-aneN_4	386	32.55	32.45	4.57	4.54	11.99	11.68
$Me_4[14]$1,3,8,10-tetraeneN_4	411	31.42	31.38	4.36	4.29	12.22	12.19
$Me_2[14]$1,3-dieneN_4	380	29.00	29.25	4.53	4.56	12.68	12.81
$Me_6[14]$1,4,8,11-tetraeneN_4	343	33.55	33.68	4.75	4.70	11.74	11.53
$Me_6[14]$4,11-dieneN_4	369	33.41	33.14	5.29	5.12	11.69	12.00
$Me_6[14]$4,14-dieneN_4	370	33.41	33.52	5.29	5.19	11.69	12.00
$Me_4[14]$1,8-dieneN_4	410	31.33	31.26	4.64	4.69	12.18	12.22
$Me_2[14]$1-eneN_4	375	28.90	28.81	4.82	4.70	12.64	12.54
$Me_2[14]$aneN_4	361	28.81	28.71	5.10	4.81	12.61	12.61
$Me_6[14]$aneN_4	384	33.22	33.16	5.81	5.79	11.61	11.70

[a] Approximately 5×10^{-4} M solutions; units Ω^{-1} cm^2 mol^{-1}.

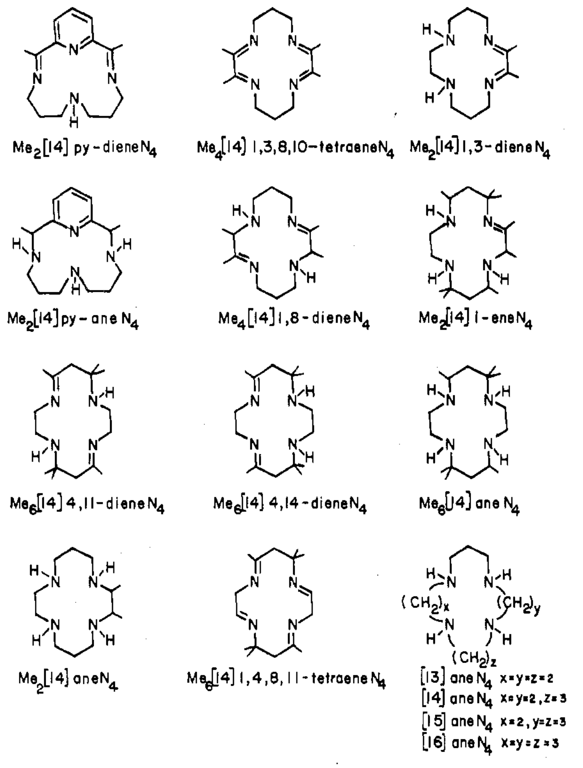

Figure 1. Macrocyclic ligands in complexes of cobalt. An explanation of the abbreviations used can be found in ref 23 and 24.

nated CH_3CN groups was prepared by reaction of silver perchlorate with the appropriate dihalo derivative in acetonitrile solution. The ligands $Me_2[14]$py-dieneN_4,[9,10] $Me_4[14]$1,3,8,10-tetraeneN_4,[11] and $Me_2[14]$1,3-dieneN_4[11] were prepared directly on cobalt by template reactions. $Me_6[14]$4,14-dieneN_4,[12,13] $Me_2[14]$aneN_4,[14] and *ms*-$Me_2[14]$py-aneN_4[15,16] were prepared on nickel and removed with cyanide, while $Me_6[14]$1,4,8,11-tetraeneN_4 was prepared on iron and removed with 1,10-phenanthroline.[17,18] $Me_6[14]$4,11-dieneN_4[19] and *ms*-$Me_6[14]$aneN_4[20] were prepared as free ligands. The complexes of $Me_4[14]$1,8-dieneN_4 and $Me_2[14]$1-eneN_4 were prepared in the form of their cobalt complexes by hydrogenation of the dichloro complexes of $Me_4[14]$1,3,8,10-tetraeneN_4 and $Me_2[14]$1,3-dieneN_4, respectively, in methanol, using hypophosphorous acid.[21] The free organic ligands were combined with cobalt(II) acetate or perchlorate under an inert atmosphere followed by addition of halo acids to produce, upon oxidation, the respective cobalt(III)–dihalo complex. Analytical data for the bisacetonitrile complexes are given in Table I. The complexes are diamagnetic and six-coordinate and behave as 1:3 electrolytes in acetonitrile solution (Table I).[22,23]

Infrared Spectra. In general, the IR spectra of these CH_3CN complexes are similar to those of their respective dihalo–perchlorate precursor derivatives. The materials are anhydrous and show characteristic N–H absorptions (except for $Me_4[14]$1,3,8,10-tetraeneN_4 and $Me_6[14]$1,4,8,11-tetraeneN_4) at ca. 3200 cm^{-1}. Intensity varies depending upon the number of such functions present. One or two sharp bands of variable intensity occur for the symmetric and asymmetric C═N vibrations (except for $Me_6[14]$aneN_4 and $Me_2[14]$aneN_4) between 1670 and 1570 cm^{-1}. The complexes of $Me_4[14]$1,3,8,10-tetraeneN_4 and $Me_2[14]$1,3-dieneN_4 containing α-diimine functions are also characterized by a strong sharp band at ca. 1210 cm^{-1}, which has previously been assigned to the –N═CC═N– linkage.[11] All complexes show a sharp doublet or broad singlet in the 2290–2350-cm^{-1} region of the infrared range which is assignable to the C≡N of the coordinated CH_3CN groups. There are no adjacent bands at lower energy to suggest the presence of uncoordinated CH_3CN groups[24] so that the complexes must have the desired formulation. The perchlorate anions show broad absorptions in the 1100- and 620-cm^{-1} region.

Electronic Spectra. Wentworth and Piper[25] have demonstrated the utility of crystal field theory in analyzing tetragonal splittings of the spectroscopically accessible $^1T_1$ state of cobalt(III) complexes. Since the splittings may be expressed in terms of the ligand field strengths of the macrocycle, Dq^{xy}, and of the axial ligand, Dq^z, the electronic spectra of complexes of the type $[Co(amine)_4X_2]^+$ have been subjected to extensive studies. An analysis of the absorption spectra of the macrocyclic complexes reported here demonstrates the effect of ligand unsaturation on Dq^{xy} and the interrelationship that exists between Dq^{xy} and Dq^z.

The crystal field model for tetragonally distorted d^6 metal complexes suggests that the splitting of the low-energy d–d transition ($^1T_{1g}$ in O_h symmetry) into its two components, $^1E_g{}^a \leftarrow {}^1A_{1g}$ and $^1A_{2g} \leftarrow {}^1A_{1g}$, upon lowering of the symmetry to D_{4h}, will be observed if the in-plane and axial ligands have significantly different ligand field strengths. If no splitting is observed or if the high-energy component is obscured by a charge-transfer band, simple approximations do not provide a consistent means of evaluating the desired spectral parameters. For example, the practice of using a common value of Dq^z for a series of related compounds in the calculation of Dq^{xy} is basically unsound[11,26] since Dq^z varies, as we will indicate, with the environment of the ligand system.

The frequencies of maximum absorption and extinction coefficients for the observed electronic transitions are presented in Table II. In general, the spectra exhibit three low-intensity absorptions in the visible and near-ultraviolet spectral region which are characteristic of *trans*-$[Co(amine)_4X_2]^{n+}$ complexes.[25] The site symmetry of the cobalt atom is rigorously lower than D_{4h} since the ligand field strengths of the four in-plane nitrogen functions are not, in general, equivalent. For

Table II. Electronic Spectral Data[a] and Calculated Gaussian Components for the $[Co(MAC)(CH_3CN)_2](ClO_4)_3$ Complexes

Macrocycle	Obsd spectra[b] λ_{max}, cm^{-1} × 10^3	Calcd Gaussian components[c]	
		λ_{max}, cm^{-1} × 10^3	Half-bandwidth,[d] cm^{-1} × 10^3
$Me_2[14]$py-dieneN_4	22.5 (434)	22.4 (388)	1.55
	28.6 sh	28.7 (591)	1.19
	30.5 (1510)	30.4 (552)	0.99
		65.3	12.03
$Me_2[14]$py-aneN_4	22.0 (348)	21.8 (331)	1.67
	27.0 sh	27.3 (266)	2.69
		44.0	5.10
$Me_4[14]$1,3,8,10-tetraeneN_4	22.2 sh	20.8 (82)	2.84
	25.4 (159)	25.8 (137)	2.86
	29.4 sh	30.4 (294)	2.09
		43.9	5.06
$Me_2[14]$1,3-dieneN_4	21.3 (120)	20.6 (106)	2.12
	23.6 (125)	24.1 (94)	1.91
	27.8 sh	28.1 (80)	1.63
		43.3	6.20
$Me_6[14]$4,11-dieneN_4	21.3 (58)	20.6 (47)	1.58
	24.1 (82)	24.0 (72)	1.71
	27.0 sh	27.2 (31)	1.52
		47.4	6.14
$Me_6[14]$4,14-dieneN_4	20.8 (68)	20.3 (62)	1.32
	23.5 (114)	23.4 (107)	1.50
	26.2 sh	26.5 (42)	1.39
		55.3	7.28
$Me_4[14]$1,8-dieneN_4	21.3 (100)	19.9 (72)	1.93
	23.4 (144)	23.5 (128)	1.95
	29.4 sh	29.6 (236)	2.79
		43.9	4.47
$Me_2[14]$1-eneN_4	20.8 sh	20.7 (90)	2.25
	22.7 (150)	23.4 (69)	1.43
	27.7 (sh	26.7 (67)	2.06
		44.2	6.14
$Me_2[14]$aneN_4	21.3 sh	21.1 (129)	3.14
	22.7 (150)	23.3 (41)	1.42
	27.0 sh	26.7 (102)	1.79
		44.4	5.15
$Me_6[14]$aneN_4	21.3 (121)	20.3 (64)	1.96
		22.2 (74)	1.86
	26.3 sh	25.8 (66)	1.44
		42.6	4.80

[a] In acetonitrile solution. [b] Molar extinction coefficients in parentheses. [c] The calculated Gaussian band at highest energy (>4.00 μm^{-1}) in no way represents the spectra in the ultraviolet region but serves only to account for the tail of the charge transfer in the region of best fit, as shown in Figures 2 and 3. [d] Half-bandwidth calculated at half band height.

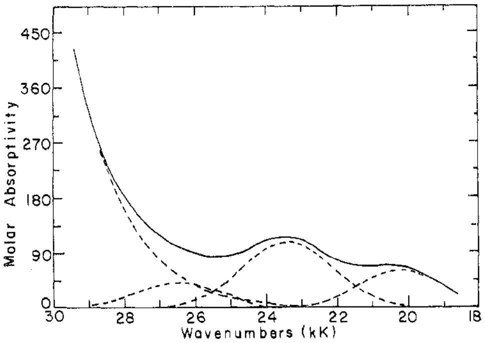

Figure 2. Electronic spectrum (solid line) of $[Co(Me_6[14]4,14\text{-diene}N_4)(CH_3CN)_2](ClO_4)_3$ in acetonitrile solution and the calculated Gaussian bands (broken lines) of the observed spectral curve. (1 μm^{-1} = 10 kK.)

Table III. Calculated Electronic Spectral Parameters (cm^{-1}) for the $[Co(MAC)(CH_3CN)_2](ClO_4)_3$ Complexes

Macrocycle	ν_E, cm^{-1} × 10^3	ν_A, cm^{-1} × 10^3	*Dt*	Dq^{xy}	Dq^z
$Me_4[14]$1,3,8,10-tetraeneN_4	20.8	25.8	571	2960	1960
$Me_6[14]$1,4,8,11-tetraeneN_4	21.3	25.6	491	2940	2080
$Me_2[14]$1,3-dieneN_4	20.6	24.1	400	2790	2090
$Me_6[14]$4,11-dieneN_4	20.6	24.0	389	2780	2100
$Me_4[14]$1,8-dieneN_4	19.9	23.5	411	2730	2010
$Me_6[14]$4,14-dieneN_4	20.3	23.4	354	2720	2100
$Me_2[14]$1-eneN_4	20.7	23.4	309	2720	2180
$Me_2[14]$aneN_4	21.1	23.3	251	2710	2270
$Me_6[14]$aneN_4	20.3	22.2	217	2600	2220

the purpose of analysis, the site symmetry of the cobalt atom is considered to be D_{4h}. The spectrum of $[Co(Me_6[14]4,14\text{-diene}N_4)(CH_3CN)_2](ClO_4)_3$, shown in Figure 2, is typical of the spectra observed for the complexes in that a broad ill-resolved d–d absorption, clearly containing two envelopes, is observed in the visible region. The second d–d transition is observed in most cases as a shoulder on the intense charge-transfer absorption. Since the resolution of the lower energy absorption into its two components is critical to the calculation of the spectral parameters, Dq^{xy} and Dq^z, the spectra were subjected to four-band Gaussian analysis in the 1.8–3.3-μm^{-1} region. The calculated band maxima, half-bandwidth at band half-height and the band intensities of the Gaussian components are shown in Table II. It should be pointed out that the calculated Gaussian band at highest energy (i.e., above 4.0 μm^{-1}) in no way represents the absorption spectrum in the ultraviolet region but serves only to account for the tail of the charge-transfer band in the region of best fit. Figure 2 shows the Gaussian components calculated for the spectrum of $[Co(Me_6[14]4,14\text{-diene}N_4)(CH_3CN)_2](ClO_4)_3$. In all cases the agreement between the observed curve and the curve resulting on combination of the Gaussian components is excellent. Use of the calculated band maxima for the absorptions assigned to the ν_E and ν_A transitions leads to values of *Dt*, Dq^{xy}, and Dq^z (Table III), according to the equations

$$\nu_A = 10Dq^{xy} - C \tag{1}$$

$$Dt = (4/35)(10Dq^{xy} - \nu_E - C) \tag{2}$$

and

$$Dq^z = Dq^{xy} - (7/4)Dt \tag{3}$$

where *Dt* is a measure of the splitting between ν_E and ν_A. The electronic repulsion parameter, *C*, is taken to be 3800 cm^{-1}.

The spectrum of $[Co(Me_6[14]aneN_4)(CH_3CN)_2]^{3+}$ is of interest since no splitting between the ν_E and ν_A bands is observed. This is also the case for the analogous low-spin ion(II) complex, $[Fe(Me_6[14]aneN_4)(CH_3CN)_2]^{2+}$.[24] This implies that the field experienced by cobalt(III) and iron(II) is accidently close to O_h symmetry and that the value of Dq^{xy} for $Me_6[14]aneN_4$ is the lowest for this series of macrocycles. Circular dichroism studies indicate that the first band envelope in the absorption spectrum of the iron(II) complex is not strictly degenerate but is composed of two energy levels that are in close proximity.[27] Indeed, Gaussian analysis of the low-energy band in the spectrum of $[Co(Me_6[14]aneN_4)(CH_3CN)_2]^{3+}$ gives a good fit for two components at 2.03 and 2.12 μm^{-1}.

The calculated spectral parameters based on the Gaussian analysis are given in Table III. The overall pattern revealed by these results supports earlier observations[11,26] that the field strength, Dq^{xy}, of the macrocyclic ligand increases steadily as the extent of unsaturation increases and that the values of *Dt* are greatest for the strongest in-plane ligands. Values of Dq^{xy} range from 2600 cm^{-1} ($Dq^{xy}(NH_3)$ – 2500)[25] to ~3000 cm^{-1}

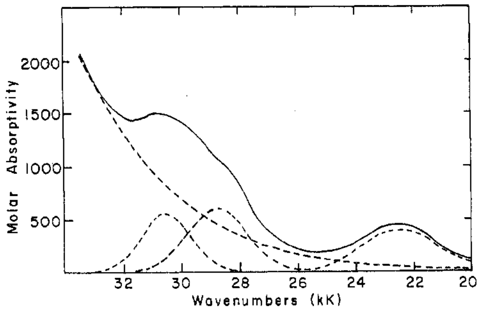

Figure 3. Electronic spectrum (solid line) of [Co(Me$_2$[14]-pydieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$ in acetonitrile solution and the calculated Gaussian bands (broken lines) of the observed spectral curve. (1 μm^{-1} = 10 kK.)

(compare Dq^{xy}(NO$_2^-$) ~ 3200 cm^{-1})[25] and it is apparent that saturated amine nitrogens interact less strongly with the cobalt(III) center than do imine nitrogens.

The magnitude of the values for Dq^{xy} calculated here are some 100–200 cm^{-1} higher than those calculated for the analogous dihalo–perchlorate complexes. This difference can be rationalized in part by the fact that only one d–d transition (the ν_E band) was clearly observed for the dihalo complexes, necessitating the use of assumed values for Dq^z, Cl = 1460, Br = 1277 cm^{-1}. This assumption implies that Dq^z is independent of Dq^{xy}, while in fact, Dq^z is related in an inverse manner to Dq^{xy}. The calculated values of Dq^{xy} for the dihalo complexes[11,26] are therefore likely to be low, especially for the ligands of greatest ligand field strengths, since Dq^z decreases as Dq^{xy} increases (Table III).

The ordering of the ligands, with respect to ligand field strengths is the same, however, for the acetonitrile complexes and the dihalo complexes. The order parallels the degree of ligand unsaturation, bis-α-diimine $\geq$ four isolated imines > α-diimine $\approx$ *trans*-diimines (six-membered rings) > *trans*-diimines (five-membered rings) $\approx$ *cis*-diimines (six-membered rings) $\approx$ one imine > amines. The distinction between α-diimine linkages and corresponding sets of isolated imines is sufficiently small that the difference is of questionable chemical significance.

The spectra of a series of high-spin tetragonally distorted nickel(II) complexes[28,29] of the type [Ni(MAC)(NCS)$_2$] have previously been analyzed. The ligand field strengths of the macrocycles were found to decrease in the order Me$_2$[14]-py-dieneN$_4$ > Me$_4$[14]1,3,8,10-tetraeneN$_4$ > Me$_2$[14]1,3-dieneN$_4$ $\approx$ Me$_6$[14]4,11-dieneN$_4$ > Me$_2$[14]aneN$_4$ > Me$_6$-[14]aneN$_2$ $\approx$ Me$_2$[14]py-aneN$_4$. This is the same order as is observed for the cobalt(III) complexes, with the exception that the ligand Me$_2$[14]py-aneN$_4$ appears to be the weakest macrocycle on nickel(II). The spectra of only three low-spin six-coordinate iron(II) complexes containing macrocyclic ligands have been found suitable for analysis.[17,23,24] Although unusually high values of Dq^{xy} were calculated (~2200 cm^{-1}), the ligand field strengths decreased in the order Me$_6$[14]-1,4,8,11-tetraeneN$_4$ > Me$_6$[14]4,11-dieneN$_4$ > Me$_6$[14]aneN$_4$. It is apparent from these observations, that the trends in the macrocyclic ligand field strengths are generally the same, whether we consider the cobalt(III), nickel(II), or iron(II) complexes. A similar ordering of the macrocyclic ligands is reflected in the Co(II)/Co(I) reduction couples. This aspect will be discussed further in other parts of this paper.

The spectra of the complexes of Me$_2$[14]py-dieneN$_4$ and Me$_2$[14]py-aneN$_4$ deserve further consideration. Recent studies have shown that there is some uncertainty in correctly interpreting the spectra of cobalt(III) and nickel(II) complexes of these ligands.[29] The observed spectrum of [Co(Me$_2$-[14]py-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$ (Figure 3) can be readily resolved into three Gaussian components. The assignment of the bands at 2.24 and 2.87 μm^{-1} to the ν_E and ν_A transitions leads to values of 720, 3250, and 1990 cm^{-1} for Dt, Dq^{xy}, and Dq^z, respectively. These results support earlier data which suggested that Me$_2$[14]py-dieneN$_4$ has a greater field strength than Me$_4$[14]1,3,8,10-tetraeneN$_4$,[11] although the difference in Dq^{xy} values was significantly smaller than that calculated here. The values of Dt and Dq^z, based on these band assignments, are in full agreement with the trends in Table III. In the case of [Co(Me$_2$[14]py-aneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, however, assgnment of the bands at 2.18 and 2.73 μm^{-1} to the ν_E and ν_A transitions leads to the improbable results that Me$_2$[14]py-aneN$_4$ is also a stronger ligand than Me$_4$[14]-1,3,8,10-tetraeneN$_4$. Here the values calculated for Dt, Dq^{xy}, and Dq^z are 629, 3110, and 2010 cm^{-1}, respectively. Previous results[11] suggest that the pyridine nitrogen atom has a similar strengthening effect on the field produced by these ligands as that of the α-diimine moiety in Me$_4$[14]1,3,8,10-tetraeneN$_4$ and in Me$_2$[14]1,3-dieneN$_4$. Hence the ligand field strengths of Me$_2$[14]py-aneN$_4$ and Me$_2$[14]1,3-dieneN$_4$ should be very similar and less than those of Me$_2$[14]py-dieneN$_4$ and Me$_4$[14]1,3,8,10-tetraeneN$_4$.

This anomaly for Me$_2$[14]py-aneN$_4$ and in part for Me$_2$-[14]py-dieneN$_4$ could result from incorrectly assigning the band in the 2.7–2.9-μm^{-1} region to the ν_A transition. The remaining complexes have, in general, a d–d transition in this region, assignable to a mixed E + B envelope of the $^1T_{1g}$ and $^1T_{2g}$ states in O_h symmetry. It is entirely possible that both the ν_E and ν_A transitions are obscured by the relatively intense band (ϵ ~300–400) which occurs near 2.20 μm^{-1} in the spectra of these complexes. The intensity of this band suggests that it is not entirely d–d in nature.

The values of Dq^z(CH$_3$CN) generally increase with decreasing values of Dq^{xy}, and represent the first extended range (1960–2770 cm^{-1}) of ligand field strengths reported for coordinated CH$_3$CN groups. The average value of Dq^z(CH$_3$CN) is 2110 cm^{-1} placing acetonitrile between ammonia (Dq^z ~2500 cm^{-1})[25] and water (Dq^z ~1900 cm^{-1})[25] in the spectrochemical series for Co^{3+}.

A point of interest for these results lies in the values of Dq^z for the complexes of Me$_2$[14]aneN$_4$ and of Me$_6$[14]aneN$_4$. The latter ligand, being the weaker of the two, may be expected to produce a higher value of Dq^z in the complex than that observed for the Me$_2$[14]aneN$_4$ system. The reverse result is probably due in part to the number and orientation of axial methyl groups present on the ligands. Me$_6$[14]aneN$_4$, having an axial methyl group on each of the six-membered chelate rings, interacts more strongly with monodentate ligands occupying the axial coordination sites than does Me$_2$[14]aneN$_4$, having either one (meso isomer) or no (racemic isomer) axial methyl group on the five-membered chelate ring. Conformational analyses[30,31] predict greater axial methyl/axial ligand interactions for six-membered chelate rings than for five-membered chelate rings in octahedral complexes and such interactions have been confirmed experimentally. For cobalt(III) complexes, axial ligand hydrolysis rates are markedly affected by the presence of axial methyl groups.[32,33] Also, NMR studies have been used to correlate the chemical shifts observed for axial and equatorial methyl groups with changes in the ligand field strengths, Dq^z, for a variety of axial ligands.[34] Similar spectral studies have been conducted with high-spin, six-coordinated Ni^{2+} complexes.[29]

This study is limited to a series of complexes containing 14-membered cyclic ligands. Changes in Co^{III}–N distances resulting from the decrease in ring size that accompanies the introduction of unsaturated linkages (Co—N=C ~ 1.92 Å in Me$_4$[14]1,3,8,10-tetraeneN$_4$,[35] Co—N=C ~ 1.92 Å and Co—NH—C ~ 1.99 Å in Me$_6$[14]4,11-dieneN$_4$)[36] provide one possible rationalization for the variation of Dq^{xy} values.

Table IV. Voltammetry of the $[Co(MAC)(CH_3CN)_2](ClO_4)_3$ Complexes in Acetonitrile Solution[a]

Macrocycle	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V	$E_{1/2}(3)$, V	Σn[b]
$Me_2[14]$py-dieneN_4	+0.17	−0.86	−1.84	3
$Me_4[14]$1,3,8,10-tetraeneN_4	+0.12	−0.72	−1.61	3
$Me_2[14]$1,3-dieneN_4	+0.05	−1.17		2
$Me_6[14]$1,4,8,11-tetraeneN_4	+0.13	−1.32		2
$Me_6[14]$4,11-dieneN_4	+0.13	−1.69		2
$Me_6[14]$4,14-dieneN_4	+0.13	−1.69		2
$Me_2[14]$py-aneN_4	+0.11	−1.72		2
$Me_4[14]$1,8-dieneN_4	+0.00	−1.74		2
$Me_2[14]$1-eneN_4	+0.08	−1.86		2
$Me_2[14]$aneN_4	−0.09	−2.03		2
$Me_6[14]$aneN_4	+0.08	−2.21		2

[a] All potentials measured with a rotating platinum electrode vs. Ag/Ag^+ (0.1 M) reference electrode using tetraethylammonium perchlorate (0.05 M) as background electrolyte. [b] Total number of electrons involved in the reduction of each complex.

Strong π-electron interactions between the metal ion and the donor nitrogen atoms in the 14-membered cyclic ligands provide a second possibility and the rehybridization of the nitrogen lone pair, that accompanies conversion of an amine into an imine, should produce substantial alterations in the ligand field, as well. A macrocyclic ring size effect has been clearly demonstrated for a series of complexes of the type $[Co([13–16]aneN_4)Cl_2]^+$ containing fully saturated, unsubstituted cyclic ligands of variable ring size (Figure 1).[3] Variations of the value of Dq^{xy} (~2750 cm^{-1} for [13]aneN_4 and ~2250 cm^{-1} for [16]aneN_4) were correlated with calculated ideal Co–N bond lengths and ligand strain energies. The results demonstrated that the 14-membered macrocycle provides the best fit for Co(III) (i.e., minimum strain energy) and that smaller or larger ring sizes reflect the variation from the best fit by changes in Dq^{xy}. These changes are generated by enhanced strain energy which produces either a compression of the metal–donor bond or a dilation of that bond.

The fact that Dq^{xy} is essentially the same for conjugated and nonconjugated tetraimines (compare values for $Me_4[14]$1,3,8,10-tetraeneN_4 and $Me_6[14]$1,4,8,11-tetraeneN_4) and diimines ($Me_2[14]$1,3-dieneN_4 vs. $Me_6[14]$4,11-dieneN_4) suggests that π back-bonding is not the major source of the enhancement in Dq^{xy} that accompanies the replacement of amines by imines. If the effect were mainly the result of a decrease in the *effective ring size*, then the complexes *trans*-$Co(L)(CH_3CN)_2{}^{3+}$ with the various [14]dieneN_4 ligands would be expected to exhibit electrochemical behavior analogous to that of the [13]aneN_4 since they share the same approximate value of Dq^{xy}. This clearly is not the case (compare Table III, vide infra, with ref 3). These considerations suggest that the alteration in the character of the metal–nitrogen σ bond makes a major contribution to the enhanced ligand field strengths of unsaturated ligands.

Electrochemical Behavior of the Complexes. The electrochemical data for the series of cobalt complexes are presented in Table IV, and the voltammetric behavior of $[Co(Me_2[14]py\text{-}dieneN_4)(CH_3CN)_2]^{3+}$ at the rotating platinum electrode is shown in Figure 4. For the 14-membered macrocyclic ligand derivatives containing coordinated CH_3CN molecules, at least two well-defined one-electron reduction processes, corresponding to the formation of species formally containing Co(II) and Co(I), are observed. The complexes with the more highly unsaturated ligands display further redox activity, producing formally zerovalent complexes. The stabilization of unusual oxidation states of the central metal ion is one of the more pronounced characteristics of cyclic ligand systems. Such behavior has been documented previously for series of nickel[5] and iron complexes,[8] and to some extent for cobalt,[11] leading to the isolation of such complexes as $[CH_3Co^{I}(1,3,8,10\text{-tetraene}N_4)]^0$,[37] $[Ni^{III}(Me_2[14]aneN_4)]^{3+}$,[38] and $[HFe^{I}(1,3,8,10\text{-tetraene}N_4)(CH_3CN)]^0$.[39]

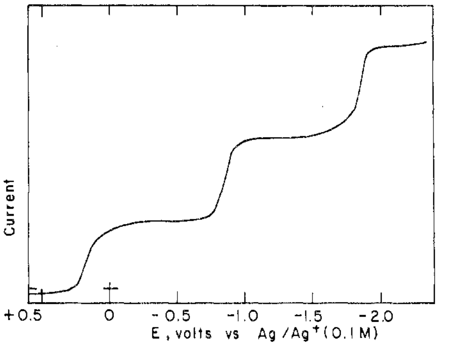

Figure 4. The current–potential curve for ~10^{-3} M $[Co(Me_2[14]py\text{-}dieneN_4)(CH_3CN)_2](ClO_4)_3$ at the rpe (600 rpm) in acetonitrile solution using Ag/Ag^+ (0.1 M) reference electrode and tetraethylammonium perchlorate (0.05 M) as background electrolyte.

In general the Co(III) → Co(II) reductions for all of these complexes are quasi-reversible when examined by cyclic voltammetry at moderate potential scan rates (0.03–0.3 V/s). This results in peak potential separations which are larger than the expected value of ~60 mV for a reversible one-electron redox couple. In addition, the anodic and cathodic peak current segments of the cyclic voltammograms lack the characteristic "sharpness" of a reversible electrode process. Nevertheless, the waves have much better definition at the platinum electrode than is apparent from the previously published curves of the isolated examples of $Co^{II}Me_6[14]aneN_4$ and $Co^{II}Me_6[14]4,11\text{-diene}N_4$.[41] It is apparent that the Co(III)–Co(II) redox process proceeds, although not ideally, at least relatively smoothly at the electrode surface. This may be due in part to the use of coordinated solvent molecules in the starting materials in the present study and to the low-spin configuration expected for these Co(II) complexes on the basis of the relatively strong field provided by the four donor atoms of the cyclic ligand. Such a configuration would permit a minimal change in the metal–nitrogen distances accompanying the Co(III) → Co(II) reduction. Indeed, x-ray crystallographic analysis of the Co(III) and Co(II) complexes of $Me_4[14]$1,3,8,10-tetraeneN_4 and of $Me_6[14]$4,11-dieneN_4 shows a deviation of ≤0.02 Å in the Co–N distances for each set of complexes.[35,36] As well, the cobalt(II) complexes of $Me_2[14]$py-dieneN_4, $Me_4[14]$1,3,8,10-tetraeneN_4,[35,42] $Me_2[14]$1,3-dieneN_4,[42] $Me_6[14]$4,11-dieneN_4,[35,43] $Me_6[14]$4,14-dieneN_4,[43] $Me_6[14]$1,4,8,11-tetraeneN_4,[18] and *ms*-$Me_6[14]$aneN_4[40,44] have been found to be low spin with weakly to moderately coordinating axial ligands in the solid state and in solution.

The variation of the Co(III)/Co(II) redox potential for this series of complexes containing axially coordinated CH_3CN molecules spans the relatively small range of 0.26 V. This is consistent with the electron being added to the d_{z^2} antibonding metal orbital with the result that the potential is insensitive to the in-plane ligand. Since the axial ligands in this series are invariant, the electron affinity of the receptor orbital for the several complexes remains relatively constant. The same effect is observed for a series of complexes of the type $Co^{III}L(H_2O)_2$ where L = $Me_4[14]$1,3,8,10-tetraeneN_4, $Me_6[14]$4,11-dieneN_4, and $Me_6[14]$aneN_4, for which measured values of the standard potential, $E°$, for the Co(III)/Co(II) couple (aqueous) are ~0.55 V.[45] Complementary studies by Endicott et al.[40] have shown that for a series of cobalt(III) complexes containing a constant macrocyclic ligand and a variety of axial ligands large differences are observed for the potential of the Co(III)/Co(II) redox couple. These differences are systematically related to the ligand field strengths of the predominantly σ-donor axial ligands. This type of relationship, however satisfying, must be viewed with caution. For example, the relatively anodic potentials for the Co(III) $\rightarrow$ Co(II) redox process for our series of acetonitrile complexes, would imply, according to previously published data,[40] that CH_3CN exerts a weaker ligand field than Br^-, clearly an erroneous conclusion. It is obvious that electrostatic effects must also be considered and that the correlation between potential and ligand field strength of the axial ligand is restricted to species of the same charge type.

It is perhaps instructive, at this point, to note that the Co(III)/Co(II) redox couples, for a brief series of macrocyclic complexes of the type $Co^{III}(MAC)(NO_2)_2$,[11] display a considerable sensitivity toward variations in the degree of unsaturation of the in-plane macrocycle, a sensitivity not found for the analogous CH_3CN complexes. It is assumed that since the NO_2^- group is a stronger ligand than the macrocycles, the electron is added to the $d_{x^2-y^2}$ orbital, thus facilitating the reduction process for those unsaturated ligand complexes in which extensive delocalization of the d electrons occurs. The effect of metal ligand π bonding on redox processes is, however, more clearly demonstrated when the Co(II)/Co(I) potentials are considered.

The results clearly show that the Co(II)–Co(I) reduction process for the CH_3CN complexes is responsive to the extent and type of unsaturation present in the cyclic ligand (Table IV). Progressive amounts of ligand unsaturation cause an anodic shift in the measured $E_{1/2}$ values. For example, $E_{1/2}{}^{\text{II-I}}$ for the Me_6[14]aneN_4, Me_6[14]4,11-dieneN_4, and Me_6-[14]1,4,8,11-tetraeneN_4 complexes are −2.21, −1.69, and −1.32 V, respectively. As is the case for the analogous nickel complexes,[5] these values reflect the increasing stability of the lower valent state (Co(I), Ni(II)) with respect to the higher valent state, with increasing ligand unsaturation. The presence of an α-diimine linkage significantly increases the magnitude of this shift and imparts further reversibility to the electrode reaction. The mild potentials required indicate that structures containing this moiety form the most stable Co(I) complexes. A similar stabilization of low-valent oxidation states of nickel[5] and iron[8] by α-diimine linkages has been documented. The presence of axial methyl substituents in the six-membered macrocyclic chelate rings, however, makes the Co(II)–Co(I) reduction process more difficult. This is evident in the $E_{1/2}$ values for the Me_6[14]aneN_4 (containing two axial methyl groups) and Me_2[14]aneN_4 (no axial methyl groups on the six-membered rings) complexes, for which $E_{1/2}$ values are −2.21 and −2.03 V, respectively. The electronic spectral studies on the Co(III)–CH_3CN derivatives have indicated that Me_6[14]aneN_4 is a weaker ligand than is Me_2[14]aneN_4 due to axial methyl–axial ligand interactions. In view of the nonconstancy of the difference in half-wave potentials between the first two reductions for these CH_3CN complexes, it is likely that the same orbital, i.e., d_{z^2}, is not involved in both of these electron transfer processes. This is also implied by the work of Endicott et al.,[40] whose results show a relative insensitivity of the Co(II)/Co(I) redox potential toward the presence of different axial ligands in complexes containing the same macrocyclic ligand. Similar results were also obtained by Costa et al.[46] for the cobalt complexes of some linear tetradentate ligands.

The small influence of the d_{z^2} orbital on the formation of the Co(I) species may be rationalized on the basis of the assumption that a bond weakening occurs between the cobalt atom and the axial ligand in the reduced species. In the extreme case, a square-planar bonding environment results, a situation not at all uncommon for d^8 metal ions. In this case, d_{z^2} is no longer the lowest unoccupied orbital and the absence of an axial field dependence for $E_{1/2}$ is readily understood.

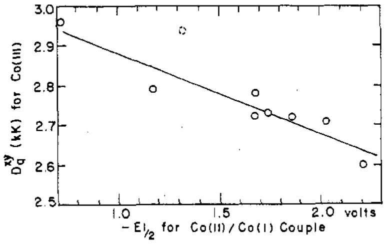

Figure 5. Correlation of $E_{1/2}$ for the Co^{II}/Co^{I} couple with $Dq^{xy}(Co^{III})$ for the *trans*-$Co(MAC)(CH_3CN)_2{}^{3+}$ complexes. (1 μm^{-1} = 10 kK.)

Thus, in view of the sharp dependence of $E_{1/2}$ for the Co(II)/Co(I) couple on the extent and type of ligand unsaturation, it is reasonable to assume that the lowest unoccupied molecular orbital in the more unsaturated derivatives contains a considerable amount of in-plane ligand character.

As is the case for series of nickel,[5] and (to a more limited extent) iron[8] complexes, the effects of variations of half-wave potentials on the Co(II)–Co(I) couple can be discussed in terms of the additivity of ligand structural parameters.[5] The discussion refers to the Co(II) $\rightleftarrows$ Co(I) process and the Me_2[14]aneN_4 complex is used as the reference compound. As mentioned previously, the presence of unsaturation causes an increase (less negative) in the value of $E_{1/2}$; the presence of axial methyl groups causes a decrease in $E_{1/2}$. The following quantitative correlations between $E_{1/2}$ and structural parameters were calculated: (1) two axial methyl groups on six-membered chelate rings, −180 mV; (2) isolated imine, six-membered ring, +260 mV; (3) isolated imine, five-membered ring, 155 mV; (4) one α-diimine, +860 mV; and (5) pyridine ring, +310 mV. The validity of this process is shown by comparing the calculated $E_{1/2}$ values for the complexes of Me_2[14]1-eneN_4, Me_2[14]1,8-dieneN_4, Me_6-[14]1,4,8,11-tetraeneN_4, and Me_2[14]py-dieneN_4 with the observed values. Thus values of $E_{1/2}$ (calculated) are −1.87, −1.72, −1.38, and −0.86 V vs. $E_{1/2}$ (observed) of −1.86, −1.74, −1.32, and −0.86 V, respectively. It is apparent also from the data, that the effect of introducing a second α-diimine functional group into the cyclic ligand to produce Me_4[14]-1,3,8,10-tetraeneN_4, is approximately half of that produced by the first α-diimine group. Thus, despite the rather limited data on cobalt, the idea of additive contributions by structural features to half-wave potentials seems to apply. The values for the structural contributions are much larger for Co(II)/Co(I) than for Fe(II)/Fe(III) or Ni(II)/Ni(III) (e.g., α-diimine, +304 and +170 mV, respectively)[4] so that introduction of ligand unsaturation appears to stabilize the Co(I) state to a larger degree than is true for Fe(II) or Ni(II) when compared to their respective higher oxidation states.

Since conjugated diimine groups affect the value of $E_{1/2}$ for the Co^{2+}/Co^{+} couple differently from unconjugated imines any attempt to correlate the variations of this parameter with the ligand field strengths of these rings as estimated on the basis of the cobalt(III) spectrochemical parameters must be of limited validity since conjugation has little effect on Dq^{xy} for Co^{3+}. This is dramatized by the fact that Dq^{xy} for the bis-α-diimine derivative (Me_4[14]1,3,8,10-tetraeneN_4) at 2960 cm^{-1} lies very close to the value for the nonconjugated tetraimine (Me_6[14]1,4,8,11-tetraimineN_4) which is 2940 cm^{-1} while the corresponding $E_{1/2}$ values are quite different at −0.86 and −1.32 V, respectively. However, if the point corresponding to the Me_6[14]1,4,8,11-tetraimineN_4 complexes is ignored, the correlation between $Dq^{xy}(Co^{3+})$ and $E_{1/2}(Co^{2+}/Co^{+})$ is fair with a correlation coefficient (R^2) of 0.88. Thus, this approximate correlation reflects the general dependence of both parameters on the extent of unsaturation of the ligand, despite smaller differences in their sensitivities to such structural details as position of saturation (Figure 5).

Experimental Section

Physical Measurements. Visible and near-infrared absorption spectra were obtained on a Cary Model 14R recording spectrophotometer in acetonitrile and in Nujol mulls. Infrared spectra were obtained on a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls between KBr disks. The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. The measurements were determined at 25 °C at 1000 Hz on ca. 5×10^{-4} M solutions in dry acetonitrile. Analyses were determined by Chemalytics, Inc. Electrochemical measurements in high-purity spectroquality acetonitrile were carried out in a Vacuum Atmospheres Dri-Train with a nitrogen atmosphere as previously described.[6]

Preparation of Complexes. [Co(Me$_2$[14]py-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$. Co(Me$_2$[14]py-dieneN$_4$)Br$_3$ (1.15 g, 0.002 mol) was slurried in 50 mL of acetonitrile. To this solution, silver perchlorate (3 molar equiv) was added. The color of the solution changed slowly from green to bright orange-red. The solution was stirred on a warm water bath for 12 h, cooled to room temperature, and filtered to remove the precipitated silver bromide. The filtrate was taken to dryness on a rotary evaporator, the solid was redissolved in a minimum volume of warm acetonitrile, and the solution was filtered. This process was repeated several times before the final recrystallization from hot acetonitrile by the addition of ether. The orange crystals were washed with ethanol and dried in vacuo over P_4O_{10}, yield 80–90%.

All other complexes were prepared in an analogous manner, using the appropriate dihalo–perchlorate or dihalo–halide complex. The materials are all orange to yellow-orange in color. Yields were generally 70–80%.

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Registry No. [Co(Me$_2$[14]py-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-88-3; [Co(Me$_2$[14]py-aneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-90-7; [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-92-9; [Co(Me$_2$[14]1,3-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-86-1; [Co(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 57139-50-1; [Co(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-66-7; [Co(Me$_6$[14]4,14-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-68-9; [Co(Me$_4$[14]1,8-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-70-3; [Co(Me$_2$[14]1-eneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-72-5; [Co(Me$_2$[14]aneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-74-7; [Co(Me$_6$[14]aneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 63122-76-9; [Co(Me$_2$[14]py-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-83-8; [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-77-0; [Co(Me$_2$[14]1,3-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-78-1; [Co(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-79-2; [Co(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-80-5; [Co(Me$_6$[14]4,14-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-82-7; [Co(Me$_2$[14]py-aneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-84-9; [Co(Me$_4$[14]1,8-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-81-6; [Co(Me$_2$[14]1-eneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63148-40-3; [Co(Me$_2$[14]aneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-54-3; [Co(Me$_6$[14]aneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, 63122-60-1; [Co(Me$_2$[14]py-dieneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-61-2; [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-55-4; [Co(Me$_2$[14]1,3-dieneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-56-5; [Co(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63148-41-4; [Co(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63148-42-5; [Co(Me$_6$[14]4,14-dieneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63148-43-6; [Co(Me$_2$[14]py-aneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-62-3; [Co(Me$_4$[14]1,8-dieneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-57-6; [Co(Me$_2$[14]1-eneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-58-7; [Co(Me$_2$[14]aneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63122-59-8; [Co(Me$_6$[14]aneN$_4$)(CH$_3$CN)$_2$]$^{+}$, 63148-44-7; Co(Me$_2$[14]py-dieneN$_4$)(CH$_3$CN)$_2$, 63122-63-4; Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)(CH$_3$CN)$_2$, 63122-64-5; Co(Me$_2$[14]py-dieneN$_4$)Br$_3$, 63122-53-2.

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