COBALT(III) COMPLEXES OF THE TETRADENTATE MACROCYCLE 2, 12-DIMETHYL-3, 7, 11, 17-TETRAAZABICYCLO(11.3.1)HEPTADECA-1(17), 2, 11, 13, 15-PENTAENE

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COBALT(III) COMPLEXES OF THE TETRADENTATE MACROCYCLE 2, 12-DIMETHYL-3, 7, 11, 17-TETRAAZABI-CYCLO(11.3.1)HEPTADECA-1(17), 2, 11, 13, 15-PENTAENE [1]

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A series of cobalt(III) complexes of 2,12-dimethyl-3,7,11,17-tetraazabicyclo(11.3.1)heptadeca-1(17),2,11,13,15-pentaene, CR, has been prepared. In addition to materials of common compositions and structures, the series includes a diiodo complex, a complex containing a bidentate nitrate ligand, an NO$^-$ derivative, and one in which ethylenediamine acts as a monodentate ligand with a dangling, unprotonated primary amine group.

INTRODUCTION

Complexes of metal ions with synthetic macrocyclic ligands are of great interest, in part because of the many natural systems to which they are analogous, e.g. the porphyrins and cobaltamins. The ligands are also of theoretical interest since they are capable of furnishing an environment of controlled geometry and ligand field strength. The work of Curtis and coworkers produced the first of many new synthetic tetraaza macrocyclic ligands, especially with the hexamethyl tetraazacyclotetradecadienes. These have been followed by cyclam,[4] cyclen,[5] aminobenzaldehyde trimers and tetramers,[6] the bicylic condensation products of 2,6-diacetylpyridine[7] and various polyamines. For a recent review see Reference 8.

In the work presented here, complexes of the tetradentate, macrocyclic ligand 2,12-dimethyl-3,7,11,17-tetraazabicyclo(11.3.1)heptadeca 1(17),2,11,13,15-pentaene (abbreviated CR, structure I), with cobalt(III) have been prepared.

I
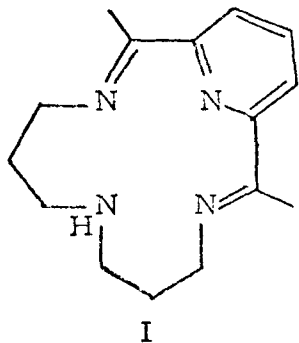
The spectral, solution and magnetic properties of these compounds have been investigated. It has been shown that CR will stabilize cobalt—carbon bonds for both univalent and trivalent cobalt.[9,10] The complexes of this ligand (CR) with nickel and copper have been discussed earlier.[11,12]

RESULTS AND DISCUSSION

Four classes of cobalt(III) complexes have been prepared: $[\text{Co(CR)}X_2]X \cdot n\text{H}_2\text{O}$, with X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, or ClO$_4^-$ and n = 1,1,0,5/2, and 3, respectively; $[\text{Co(CR)}X_2]\text{ClO}_4$ with X = NO$_2^-$, N$_3^-$, NCS$^-$, or CN$^-$; $[\text{Co(CR)(AA)}]X_m \cdot n\text{H}_2\text{O}$ with AA = oxalate, acetylacetonate, or ethylenediamine, X = ClO$_4^-$, NO$_3^-$, or Br$^-$, m = 1, 2, or 3, and n = 0 or 1; and $[\text{Co(CR)}X(\text{NO})]\text{B(C}_6\text{H}_5)_4$ with X = I$^-$, Br$^-$, or NCS$^-$. Three general methods have been used in the preparation of these compounds: *in situ* synthesis of the macrocyclic ligand in the presence of a cobalt(II) salt followed by air oxidation of the metal ion, metathetical replacement of the unidentate ligands Br$^-$ or OH$_2$ on cobalt(III) and the action of nitric oxide on Co(CR)$X_2 \cdot$ H$_2$O. All are low-spin, six-coordinate complexes of cobalt(III). The electronic spectra of the compounds with *trans* geometries have been interpreted by using the Wentworth and Piper model for tetragonal cobalt(III) complexes.[13]

Syntheses

Products of the composition Co(CR)$X_3 \cdot n\text{H}_2\text{O}$ have been prepared by a route dependent on *in situ*

TABLE I
Molar conductances of the cobalt(III) complexes, $Co(CR)X_2 \, Y_m$

X_2	Y_m	CH₃OH	H₂O	CH₃NO₂	DMF
			Solvent		
I_2	I	90.3	249 (456[a])		
Br_2	Br	81.1	430	97.2	
Cl_2	Cl	87.5	421	81.7	
$Br(en)/2$	Br_2	153	242		
$OH_2(NO_3)$	$(NO_3)_2$	166	465		179
$(OH_2)_2$	$(ClO_4)_3$		441	244	223
$(N_3)_2$	ClO_4	96.2			
$(NCS)_2$	ClO_4	117			
$I(NO)$	$B(C_6H_5)_4$			68.8	
$Br(NO)$	$B(C_6H_5)_4$			71.3	
$NCS(NO)$	$B(C_6H_5)_4$			65.3	
$(NO_2)_2$	ClO_4	95.3			
$(CN)_2$	ClO_4		86.5		
acac	$(ClO_4)_2$	166			
ox	ClO_4		96.1		
ox	NO_3	87.8			

[a] 1.18×10^{-4} molar, all other concentrations are approximately 10^{-3} molar.

synthesis of the CR ligand by condensation of 2,6-diacetylpyridine and 3,3'-diaminodipropylamine in the presence of an appropriate cobalt(II) salt, for $X = Cl^-$, Br^-, and NO_3^-. After the condensation was judged to be complete, the solution was acidified with HX and aerated to oxidize the cobalt. The products were obtained by reducing the volume of the solution in order to induce crystallization. These compounds have all been purified by recrystallization from water. For $X = ClO_4^-$ the previously isolated cobalt(II) complex, $Co(CR)OH_2(ClO_4)_2$,[14] was oxidized by a stream of air.

Three of these compounds ($X = Cl^-$, NO_3^-, ClO_4^-) were very soluble in water and alcohols. For example, if sodium perchlorate was added in an attempt to induce crystallization of $Co(CR)(ClO_4)_3 \cdot 3H_2O$ from aqueous solution, the sodium perchlorate crystallized before the desired product. Some of these compounds aquate very readily as evidenced by the molar conductivities of 10^{-3} molar aqueous solutions, Table 1. The shifting of the first band in the electronic spectrum to higher energy also indicated that the bromo complex was aquated at this concentration. However the aquo complexes could not be

isolated with chloride, bromide, or nitrate anions. As the aqueous solutions were concentrated, the dichloro, dibromo, and nitratoaquo complexes eventually crystallized.

The second general method of preparation involved metathetical replacement of the coordinated bromide ions of $Co(CR)Br_3 \cdot H_2O$, or of the coordinated water of $Co(CR)(ClO_4)_3 \cdot 3H_2O$. In this way, $Co(CR)I_3$, $Co(CR)X_2ClO_4$, $Co(CR)(ox)Y$, $Co(CR)acac(ClO_4)_2$, and $Co(CR)(en)Br_3 \cdot H_2O$ ($X = NO_2^-$, N_3^-, NCS^-, CN^-; $ox = C_2O_4^{2-}$; $Y = ClO_4^-$, NO_3^-; acac — acetylacetonate ion; en — ethylenediamine) were prepared by reaction of the appropriate ligand with a methanol solution of one of the starting materials. Water or aqueous methanol was used as the solvent only when the salt of the desired ligand was not sufficiently soluble in methanol to allow reaction in a homogeneous medium. These metatheses were quite rapid as indicated by almost immediate color changes from the green or brown color of the initial complex to the color of the product. Upon addition of sodium perchlorate in the same solvent, concentrating and/or cooling the solution, the products crystallized. These perchlorate salts were generally only sparingly soluble in the common polar solvents.

Of the products prepared by metathetical reactions, the iodo and ethylenediamine (see section on Conductances) complexes are unusual. Relatively few diiodo cobalt(III) complexes have been reported. Nyholm prepared diamagnetic $[Co(das)_2I_2]I$ (das = o-phenylenebis(dimethylarsine)) by metathesis from $Co(das)_2Cl_3$ with lithium iodide and by air oxidation of $Co(das)_2I_2$ in the presence of hydroiodic acid.[15]

In 1940, Ablov reported the preparation of $[Co(DH_2)(DH)I_2]$ (DH_2 = dimethylglyoxime and DH = its mononegative anion), a dark green crystalline solid which becomes dark brown when ground into a powder.[16] The compound is a rather strong acid in aqueous solution and readily undergoes aquation to the iodoaquocomplex.[17]

The nitrosyl derivatives were prepared by the reaction of nitric oxide with an alcoholic solution of $Co(CR)X_2 \cdot nH_2O$ ($X = Br^-$, I^-, NCS^-; with $n = 1, 0, 0$ respectively). This reaction proceeded smoothly and rapidly under nitrogen at room temperature and produced a dark cherry-red solution. The products, $[Co(CR)X(NO)]B(C_6H_5)_4$, were isolated as microcrystalline solids by the addition of a methanol solution of sodium tetraphenylborate(III) to the reaction mixture. The usual smaller anions did not induce crystallization.

If an aqueous solution of $Co(CR)Br_3 \cdot H_2O$ was made strongly alkaline, it turned brown and subsequent acidification and volume reduction did not produce the bromo complex. Solids isolated from such solutions exhibited an infrared absorption band of varying intensity at about 1695 cm^{-1}. This is the region where 2,6-diacetylpyridine has a very strong carbonyl absorption and hydrolysis of the ligand was inferred. This sensitivity to base hydrolysis prevented the isolation of the dihydroxo complex and its use in making complexes of other unidentate or bidentate ligands.

Infrared Spectra

The infrared spectra of cobalt(III) compounds are rather similar to each other and to those of the cobalt(II) compounds.[14] A number of the products contained uncoordinated lattice water. These include: $[Co(CR)Br_2]Br \cdot H_2O$, $[Co(CR)Cl_2]Cl \cdot H_2O$, $[Co(CR)ox]NO_3 \cdot H_2O$, $[Co(CR)(OH_2)_2](ClO_4)_3 \cdot H_2O$, $[Co(CR)OH_2(NO_3)](NO_3)_2 \cdot {}^3/_2 H_2O$ and $[Co(CR)NO_3](NO_3)_2 \cdot \frac{1}{2}H_2O$. In the first three of these compounds, the OH stretching bands are resolved. This occurrence of two distinct OH stretching vibrations is undoubtedly due to the fixed position of water molecule in the crystal, as in $Ni(CR)Br_2 \cdot H_2O$.[18]

The NH stretching frequencies vary from 3135 to 3280 cm^{-1} and average 3187 cm^{-1} in these cobalt(III) compounds and cannot be correlated with the donor or hydrogen-bonding characteristics of the non-macrocyclic ligands. Except in $[Co(CR)(N_3)_2](ClO_4)$ and $[Co(CR)(OH_2)_2](ClO_4)_3 \cdot H_2O$, the band assigned to the NH stretching mode of the secondary amine is a rather sharp singlet. In the two exceptional cases the NH stretching band is split by 53 and 80 cm^{-1}, respectively. Since there is only one secondary amine in this macrocyclic ligand, this splitting must be caused by nonequivalent sites in the unit cell. Unfortunately, neither compound is soluble enough in a solvent that is transparent in this region to permit recording the solution infrared spectra. The $N{\equiv}N$ stretching band of the azido complex is also split (2033 and 2003 cm^{-1}) with the lower energy band having the greater intensity, in accord with the observations mentioned on the NH stretching bands.

Conductances in nonaqueous solvents indicate that one of the nitrate ions is coordinated in $Co(CR)(NO_3)_3 \cdot \frac{5}{2}H_2O$. This immediately raises the question of whether the nitrate ion is unidentate or bidentate. Infrared spectra in Nujol and hexachlorobutadiene mulls show bands at 1478 cm^{-1}, sh; 1464 sh, ~1421 sh, 1416 vs, b, 1300 vs, b; 1274 s.

These bands are assigned to ionic and unidentate nitrate.[19] The infrared spectrum of a sample pressed into a KBr pellet shows a very strong band at 1380 cm^{-1} and the pellet turns from brown to green during the scanning time, indicating only the presence of ionic nitrate and the formation of the dibromo complex. Obviously the bromide ion displaces the coordinated nitrate and water.
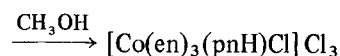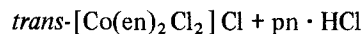
Upon heating at 100°C *in vacuo*, the nitrato complex undergoes a 6.69 ± 0.17% weight loss. This agrees very well with the theoretical value of 6.69% for the loss of two moles of water. Infrared spectra of Nujol mulls of the dried product indicated the presence of a small amount of water. Most noticeable however, is the appearance of a very strong band at 1523 cm^{-1}. Whimp and Curtis report a band at 1515 cm^{-1} for [Co(d,l-Me$_6$[14]aneN$_4$)NO$_3$]-(NO$_3$)$_2$.[20] If the Nujol mull of [Co(CR)NO$_3$]-(NO$_3$)$_2 \cdot \frac{1}{2}$H$_2$O is exposed to moist air, the 1523 cm^{-1} band decreases in intensity and eventually disappears completely as water is absorbed by the solid. The water absorption is shown by the enhanced intensity of the OH stretching band. Consequently, the compound Co(CR)(NO$_3$)$_3 \cdot \frac{5}{2}$H$_2$O is formulated as [Co(CR)(OH$_2$)(NO$_3$)](NO$_3$)$_2 \cdot \frac{3}{2}$H$_2$O. Dehydration appears to yield the complex of bidentate nitrate, [Co(CR)(NO$_3$)]$^{2+}$ rather than the bis-nitrate derivative.

The nitrosyl complexes [Co(CR)X(NO)]-B(C$_6$H$_5$)$_4$, are characterized by a very intense infrared band at 1658 cm^{-1} (X = Br$^-$) or 1665 cm^{-1} X = I$^-$ or NCS$^-$). In the thiocyanato case, the 1665 cm^{-1} band has a greater absorbance than does the thiocyanate band at 2095 cm^{-1}. These frequencies are in the range reported for similar cobalt nitrosyl complexes. For example, Earnshaw[21] reports a series of complexes, formed by the reaction of NO with cobalt(II) salicylaldimines, with NO stretching frequencies in the range from 1614 to 1696 cm^{-1}. Jackson[22] reports compounds formulated as [Co(ethylenimine)$_4$NO]X_2, which are diamagnetic and have NO stretching frequencies in the range from 1630 to 1850 cm^{-1}. Dichlorobis(triethylphosphine)-cobalt(II) forms complexes with NO which exhibit stretching frequencies in the range from 1646 to 1744 cm^{-1} in hexane solution.[23] In a series of compounds formulated as [CoX(NO)(en)$_2$]ClO$_4$ with X = Cl$^-$, Br$^-$, I$^-$, and NO$_3^-$, Feltham and Nyholm[24] report NO stretching frequencies in 1611, 1640, 1654 and 1643 cm^{-1}, respectively, and conclude that this is a consistent with a double bond between nitrogen and oxygen in NO$^-$.

Conductances

Conductances were calculated from the resistances of approximately 10^{-3} molar solutions in several solvents (Table I). All of the Co(CR)$X_3 \cdot n$H$_2$O compounds (X = halogen) are uni-univalent electrolytes in methanol. For X = NO$_3^-$, the conductance is typical of a di-univalent electrolyte in methanol and DMF, indicating that one of the nitrate ions is coordinated in these solvents; whereas, the substance is a tri-univalent electrolyte in water, indicating complete aquation. The Co(CR)X_2ClO$_4$ and the [CO(CR)X(NO)]B(C$_6$H$_5$)$_4$ compounds and [Co(CR)ox]Y are all uni-univalent electrolytes in at least one of the solvents methanol, DMF, and nitromethane. The conductance of the cyano complex, [Co(CR)(CN)$_2$]ClO$_4$, has been determined only for an aqueous solution due to its very limited solubility in other solvents. It is a uni-univalent electrolyte. Only [Co(CR)acac](ClO$_4$)$_2$, Co(CR)(en)Br$_3 \cdot$ H$_2$O and [Co(CR)OH$_2$(NO$_3$)]-(NO$_3$)$_2 \cdot \frac{3}{2}$H$_2$O are di-univalent electrolytes in methanol.

The ethylenediamine complex is also a di-univalent electrolyte in water. This rather suprising result implies that one of the bromide ions is tenaciously coordinated. Assuming a coordination number of six, this can be true only if the ethylenediamine is functioning as a unidentate ligand with a dangling NH$_2$ group. This is related to, but different from the complex of uni-dentate propylenediamine (pn) reported by Alexander and prepared by the reaction:[25]

$$\textit{trans-}[\text{Co(en)}_2\text{Cl}_2]\text{Cl} + \text{pn} \cdot \text{HCl}$$

$$\xrightarrow{\text{CH}_3\text{OH}} [\text{Co(en)}_3(\text{pnH})\text{Cl}]\text{Cl}_3$$

In this case, the one nitrogen atom of the diamine was protonated before reaction with the *trans*-dichlorobis(ethylenediamine)cobalt(III) ion. the product is assigned a cis geometry on the basis of the great similarity of its electronic spectrum to the spectrum of [Co(en)$_2$(NH$_3$)Cl]Cl$_2$.[25] In contrast, the compound reported here apparently has a dangling unprotonated amine group. This conclusion is supported by the preparation of the hydrobromide salt of the dangling amine. This is accomplished by addition of a slight excess of hydrobromic acid to a methanol solution of the bromoethylenediamine complex. New features of the spectrum of the isolated [Co(CR)(enH)Br]Br$_3 \cdot$ H$_2$O are a strong, broad band at 2915 cm^{-1} and a strong, sharp band at

$1504 \, \mathrm{cm}^{-1}$, the latter with a shoulder on the high energy side. These compare well with bands in the infrared spectrum of the dihydrobromide salt of ethylenediamine which has a strong, broad band at $2910 \, \mathrm{cm}^{-1}$ and a strong band at $1502 \, \mathrm{cm}^{-1}$, the latter with a shoulder on the high energy side. The bands near $2900 \, \mathrm{cm}^{-1}$ are assigned to overlapping $-NH_3^+$ asymmetric and symmetric stretching vibrations, and the bands near $1500 \, \mathrm{cm}^{-1}$ are assigned to $-NH_3^+$ symmetric bendings.[26] The electronic spectra of the two bromoethylenediamine compounds, unprotonated and protonated, are practically identical. Apparently, either the flexible ethylenediamine molecule cannot force the CR ligand to fold or the hydrogen atoms of the amine interact so strongly with the macrocycle that the second end of the amine cannot coordinate.

On the other hand, the oxalate and acetylacetonate ions act as bidentate ligands. The elemental analyses indicate one oxalate or acetylacetonate ion per cobalt. The infrared spectrum of the oxalato complex exhibits strong and very strong bands at 1704, 1683, and $1670 \, \mathrm{cm}^{-1}$ $(\nu_{as}C=O)$, $1393 \, \mathrm{cm}^{-1}$ $(\nu_sC-O + \nu C-C)$, all of which are consistent with the oxalate ion acting as a bidentate ligand with five-membered chelate rings.[27] Likewise the infrared spectrum of the acetylacetonato complex is consistent with the presence of a bidentae ion: $1577 \, \mathrm{cm}^{-1}$ $(\nu C \cdots C)$, $1528 \, \mathrm{cm}^{-1}$ $(\nu C \cdots O)$, $1427 \, \mathrm{cm}^{-1}$ $(\nu C \cdots C + \delta C-H)$, $1372 \, \mathrm{cm}^{-1}$ $(\delta s \, CH_3)$ and $1284 \, \mathrm{cm}^{-1}$ $(\nu C \cdots C + \nu C-CH_3)$.[27] These ligands can act as bidentate donors only forcing the macrocycle to fold:

Since the two azo-methine linkages must be coplanar with the pyridine ring, folding can occur only by moving the secondary amine nitrogen atom out of this plane toward an axial site on cobalt ion. That such a process is possible is evident in the structure of $Ni(CR)Br_2 \cdot H_2O$.[18]

As noted above, the chloro, bromo, and nitrato complexes aquate rapidly in 10^{-3} molar aqueous solutions. However, the iodo complex does not aquate fully at this concentration. Its equilibrium molar conductance is $249 \, \mathrm{ohm}^{-1}$ at 10^{-3} molar. Upon dilution to 10^{-4} molar, the molar conductance rises to $465 \, \mathrm{ohm}^{-1}$, indicating complete aquation. This decreased tendency to aquate may be due to the smaller heat of hydration of the large iodide ion, 62.4 kcal/mole, compared to 72.7 and 80.9 kcal/mole for bromide and chlorine ions, respectively.[28] Ablov has reported that if an aqueous solution of $[Co(DH_2)(DH)I_2]$ is heated, fine brown crystals of $[Co(DH)_2(OH_2)I]$ separate from the solution.[29] Sychev, Ablov, and Zarinskii report specific rate constants for the aquation of $[Co(DH)_2(OH_2)X]$ with $X = Cl^-, Br^-, I^-$. The constants vary in the order $Cl^- > Br^- > I^-$ with the chloro complex aquating six times as fast as the iodide. In addition, studies with the iodo complex were carried out at $35°$ and the others at $25°C$. Thus, both thermodynamic and kinetic factors would appear to favour incomplete aquation of $[Co(CR)I_2]I$.
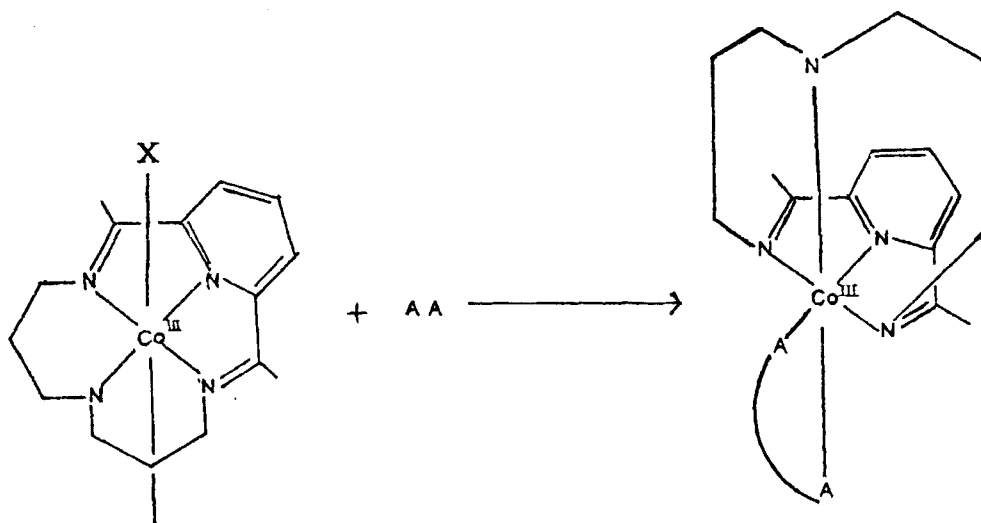
Electronic Spectra

Tetragonal cobalt(III) electronic spectra are commonly characterized by three bands in the visible and near ultraviolet regions, the first two being due to the splitting of the first excited state of the hypothetical parent octahedral complex.[13] However, if the ligand field strength of the axial donors is nearly the same as that of the in-plane ligands, only two bands are observed. If the macrocyclic ligand is folded so that the two remaining sites are *cis* to each other, the predicted splitting of the first octahedral band is one half that of the *trans* case with the same non-macrocyclic ligands. This splitting has not been observed among *cis* isomers of diacidotetramines in general.

The electronic spectra of the $Co^{III}(CR)X_2{}^{n+}$ derivatives are summarized in Table II. In general, the first observable band is assigned to the $^1E^a \leftarrow {}^1A_1$ transition of the tetragonally distorted *trans* diacido complexes. It would be tempting to assign the second band to the $^1A_2 \leftarrow {}^1A_1$ transition and the third band to a transition to the $^1B_2$ and/or $^1E^b$ states. A number of inconsistencies argue against this set of assignments. Such assignments ascribe a Dq^{xy} of about 2550 cm^{-1} to CR in its cobalt(III) complexes, a value closer to that of ethylenediamine than to those of other ligands having high degrees of unsaturation.[30] Further, the values one calculates by this route for the Dq^z parameters for the axial ligands are distressingly high.[31] Finally the chemistry of the Co—CR system most nearly resembles that of the tetraimine ligand 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (Me$_4$[14] 1,3,8,10teteneN$_4$).[30] The similarities are extreme involving related electrochemical properties[31] and the striking and shared, ability to form cobalt—carbon bonds by nucleophilic mechanisms.[9,10] An alternate interpretation of the spectra accords with these constraining relationships.

We concede that the position and assignment of the second spectral band are both highly uncertain. Consequently a spectrochemical parameter is derived from the first spectral band, retaining its assignment to the transition $^1E^a \leftarrow {}^1A_1$. To do this the values of the spectrochemical parameters Dq^z are assumed to correspond to those observed in closely related structures. Using $Dq_{Br}^z Br = 1280$ cm^{-1}, $Dq_{Cl}^z = 1460$ cm^{-1}, and the Racah parameter $C = 3800$ cm^{-1} we estimate Dq^{xy} to be approximately 2820 cm^{-1} for the ligand CR, from the relationship

$$Dq^{xy} = {}^1{}_5(\nu_E + C) - Dq^z$$

This is an extremely crude treatment and the figure must be viewed as both approximate and tentative.

The large molar extinction coefficient (10,000) of the second band of the iodo complex deserves mention. For comparison, $[Co(das)_2 I_2]I$ and $[Co(DH_2)(DH)I_2]$ were prepared by the methods of Nyholm[15] and Ablov,[16] respectively, and their electronic spectra were recorded. The second band is at $20,830$ cm^{-1} ($\epsilon = 4664$) in the diarsine complex and at $21,930$ cm^{-1} ($\epsilon = 7614$) in the dimethylglyoxime complex. In addition, it should be noted that Ochiai's $[Co(meso\text{-}CRH)ICl]^+$ complex has a molar extinction coefficient of 1100 for the ν_2 band. This is much larger than that observed for the ν_A band of any other $[Co(meso\text{-}CRH)X_2]^{n+}$ complex.[32] In the same connection, the molar extinction coefficient of the second band of $[Co(NH_3)_5 I]^{2+}$ is 2690.[33] In 10^{-3} molar aqueous solution where conductance data indicate that the complex should be formulated as $[Co(CR)(OH_2)I]^{2+}$ the ν_2 band has a molar extinction coefficient of 2060.

From these examples, it is apparent that coordination of iodide ions to cobalt(III) results in a very intense absorption band. The large values may be in part due to the reducing nature of the iodide ion or they may be due to 'intensity stealing' from the even more intense third band ($\epsilon = 17,700$ in the $[Co(CR)I_2]I$ case).

Since en and CR have similar Dq values (2530 and 2820 cm^{-1}, respectively), a nearly 'octahedral spectrum' should be observed if the ethylenediamine in $Co(CR)(en)Br_3 \cdot H_2O$ were functioning as a bidentate ligand. Appearance of a low energy band indicates that the axial field is weaker than the in-plane field. This is consistent with the presence of a dangling, unidentate ethylenediamine ligand with a coordinated bromide ion in the *trans* position, as noted earlier.

The solution and solid state spectra of the nitrosyl complexes are similar, but exceptions are noted. The low energy band ν_1 observed in the solid state spectrum of $[Co(CR)Br(NO)]^+$ is *not* seen in nitromethane solution. The ν_2 band is of low intensity in the nearly saturated solution, so the less intense ν_1 band is just not evident. The reflectance spectrum has two weak bands at 8700 and $12,600$ cm^{-1} in addition to the bands given in Table II. From the energy level diagram for octahedral d^6 ions, it seems probable that the lowest energy transitions are spin-forbidden. The low relative intensities are consistent with this assignment. Feltham and Nyholm assigned two low intensity bands at 9000 and $13,5000$ cm^{-1} in the spectrum of *trans*-$[CoCl(NO)(en)_2]Cl$ to spin-forbidden transitions.

TABLE II
Electronic spectra of Co(CR)$^{3+}$ derivatives

Compound	$\nu_1 (cm^{-1})$	$\nu_2 (cm^{-1})$	$\nu_3 (cm^{-1})$
Co(CR)I$_3$[a]	14,700	20,600	28,500
Co(CR)Br$_3 \cdot$H$_2$O[a]	16,570	20,600	25,300
Co(CR)Cl$_3 \cdot$H$_2$O[a]	17,670	21,600	25,000
Co(CR)(en)Br$_3 \cdot$H$_2$O[a]	17,200	20,800	25,600
Co(CR)(enH)Br$_4 \cdot$H$_2$O[a]	17,100	20,900	25,500
Co(CR)(NO$_3$)$_3 \cdot$⁵/₂H$_2$O[a]		21,700	e
Co(CR)(ClO$_4$)$_3 \cdot$3H$_2$O[b]	17,900	22,000	26,000
Co(CR)(N$_3$)$_2$ClO$_4$[a]	18,500	f	28,100
Co(CR)(NCS)$_2$ClO$_4$[a]	19,000	24,000	28,200
Co(CR)I(NO)B(C$_6$H$_5$)$_4$[c]	17,100	21,100	e
Co(CR)Br(NO)B(C$_6$H$_5$)$_4$[d]	17,700	21,600	26,300
Co(CR)NCS(NO)B(C$_6$H$_5$)$_4$[c]	19,150	21,300	e
Co(CR)(NO$_2$)$_2$ClO$_4$[a]		21,500[g]	27,250
Co(CR)(CN)$_2$ClO$_4$[b]		22,100	28,500 32,000
Co(CR)acac(ClO$_4$)$_2$[a]		19,080[h]	26,700
Co(CR)ox(ClO$_4$)[b]		20,100[h]	26,500
Co(CR)ox(NO$_3$)[a]		20,600[h]	26,000

[a]In methanol.
[b]In water.
[c]Nujol transmittance spectrum.
[d]Reflectance spectrum.
[e]Obscured by charge transfer band.
[f]Masked by intense ν_E and ν_A bands.
[g]Average of ν_E and ν_A bands.
[h]cis Complex.

Magnetic Properties

The Faraday method was used to determine the susceptibility of $[Co(CR)Cl_2]Cl \cdot H_2O$ and an effective magnetic moment of 0.62 ± 0.00 B.M. was found. This is consistent with the value expected for a low-spin d^6 ion.

Reactions with Reducing Agents

It has been reported by Endicott that zinc or borohydride ion reduces the metal ion in $[Co^{III}(1,7\text{-}CT)X_2]^{n+}$ to cobalt(II) with one exception. When the cyano derivative was reduced with BH_4^- the insoluble $[Co(meso\text{-}7,[14]CTH)(CN)_2] \cdot ClO_4 \cdot H_2O$ precipitated from the reaction mixture,[34] indicating ligand hydrogenation rather than metal ion reduction.

Hydrogenation with platinum oxide catalyst was tried with aqueous solutions of $[Co(CR)Br_2]Br \cdot H_2O$ and $[Co(CR)(CN)_2]ClO_4$. There was no apparent uptake of hydrogen in the Parr apparatus and the recovered materials were identical with the starting compounds. In contrast to these results, the ligand in the cobalt(II) bromo complex reduces smoothly in methanol or aqueous methanol.[14]

The metal ion in $[Co(CR)Br_2]Br \cdot H_2O$ can be reduced by several reagents. If an excess of aqueous tin(II) chloride is added to an aqueous solution of the bromo complex, the brownigh-green solution becomes red. The electronic spectrum exhibits bands at $14,550\ cm^{-1}$ ($\epsilon = 207$); $\sim16,600$ sh; $\sim18,600$ sh; $\sim20,400$ sh; $21,700$ (1570); and $27,200$ (1200). The solution cannot be made concentrated enough to see any band(s) in the near infrared, but the spectrum in the visible region is essentially the same as the spectrum of $[Co(CR)OH_2](ClO_4)_2$ in methanol solution and of $[Co(CR)Br]BrH_2O$ in water,[14] indicating that the cobalt has been reduced to the plus two state and is probably present as $[Co(CR)OH_2]^{2+}$. Similar results are obtained with hydrazine hydrate.

EXPERIMENTAL

Materials

Anhydrous cobalt(III) bromide and thiocyanate were obtained from City Chemical Company, 2,6-diacetylpyridine from Aldrich Chemical Company and Columbia Organic Chemicals and 3,3'-diaminodipropylamine from Matheson, Coleman and Bell. The diacetylpyridine was recrystallized from hot ethanol before use.

Physical Measurements

Visible, near infrared and ultraviolet spectra were obtained with a Cary Model 14 Recording Spectrophotometer. Spectra of solid samples were run on Njuol mulls impregnated on filter paper or with a Cary Model 1411 Reflectance Attachment, using magnesium carbonate as a blank. A Perkin-Elmer Model 337 Recording Spectrophotometer was used to obtain all infrared spectra. Infrared spectra were run on potassium bromide pellets and Nujol and hexachlorobutadiene mulls.

The electrical resistances of solutions of the compounds were measured using an industrial instruments RC 16B Conductivity Bridge and a conductance cell with platinum electrodes and a cell constant of $2.116\ cm^{-1}$. Conductances were determined at $25°C$ at 1000 cps for approximately 10^{-3} molar solutions.

A Faraday magnetic susceptibility balance equipped with a Cahn Gram electrobalance and a Varian 4 in. electromagnet fitted with specially shaped pole pieces was used to determine the susceptibilities. All of the measured susceptibilities were corrected for diamagnetism. From Pascal's constants a value of -162.7×10^{-6} cgs units was calculated for the magnetic susceptibility of the macrocyclic ligand.

Analyses

Elemental analyses for carbon, hydrogen, and nitrogen were performed in this laboratory, using an F + M Model 185 Carbon, Hydrogen, Nitrogen Analyzer, and by Galbraith Laboratories, Inc. All analyses for other elements were by Galbraith Laboratories, Inc.

$Co(CR)Br_3 \cdot H_2O$ The preparation of this product was similar to that of $Co(CR)Br_2 \cdot H_2O$.[14] Diacetylpyridine (16.3 g, 0.10 mole) was dissolved in 150 ml of hot ethanol. One hundred ml of water was added and dissolved in the hot mixed solvent. The solution was held at $65-75°C$ and stirred as 3,3'-diaminodipropylamine (13.1 g, 0.10 mole) was added. The solution became cloudy on addition of the amine. Four ml of glacial acetic acid was added to clarify the solution and it was heated at $65-75°C$ for about five hours. At this time, the condensation was judged to be complete and concentrated hydrobromic acid (0.11 mole) was added. The solution was aerated for about six hours. At this point the solution was green and some light green crystals may have formed. The volume was reduced on the rotary evaporator and the solid collected. The crude produce was recrystallized

by dissolving it in warm water, filtering the solution and cooling in the refrigerator. The small, light green crystals were collected, washed with ethanol, and dried. Yield, 70%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4Br_3 \cdot H_2O$: C, 31.33; H, 4.21; N, 9.74. Found: C, 31.50; H, 4.51; N, 9.81.

Co(CR)Cl$_3$ · H$_2$O   The preparation of this product was similar to that of $Co(CR)Br_3 \cdot H_2O$ with the following exceptions: $CoCl_2 \cdot 6H_2O$ was used instead of $CoBr_2$ and hydrochloric acid was added instead of hydrobromic acid. The crude green product was recrystallized twice from a warm saturated aqueous solution with cold ($<0°C$) ethanol. Yield, 35%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4Cl_3 \cdot H_2O$: C, 40.79; H, 5.02; H, 12.69. Found: C, 40.60; H, 5.37; N, 12.80.

Co(CR)(NO$_3$)$_3$·$\frac{5}{2}$H$_2$O   The preparation of this product was similar to that of $Co(CR)Br_3 \cdot H_2O$ with the following exceptions: $Co(NO_3)_2 \cdot 6H_2O$ was used instead of $CoBr_2$ and nitric acid was used to acidify the solution when the condensation was judged to be complete. The volume of the solution was then greatly reduced and the solution set aside. Crystals of the brown product formed after several days. The crude product was recrystallized by dissolving it in warm water to make a very concentrated solution and allowing the solution to stand at room temperature for several days. The product was collected, washed with a small amount of *cold* water and dried, *in vacuo*, over P_4O_{10}. Yield, 45%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4(NO_3)_3 \cdot \frac{5}{2}H_2O$: C, 32.85; H, 4.93; N, 17.88. Found: C, 32.70; H, 4.95; N, 17.90.

Co(CR)(NO$_3$)$_3$·$\frac{1}{2}$H$_2$O   This product was prepared from the preceding one by heating at 100°C *in vacuo* for two hours. Anal. calcd. for loss of $2H_2O$: 6.69%. Found: 6.69 ± 0.17%.

Co(CR)(ClO$_4$)$_3$ · 3H$_2$O   One   gram   of $Co(CR)(ClO_4)_2 \cdot H_2O^{14}$ was suspended in 25 ml of water in which it was only slightly soluble. One ml of 70% perchloric acid was diluted with a few ml of water and added to the suspension. Air was bubbled through the suspension with stirring for 15 hours. The solid slowly dissolved as the reaction proceeded to form a clear red-brown solution. After reducing the volume to about 10 ml by blowing air over the surface, the solution was set aside for several days. Dark brown crystals slowly formed. If the cobalt(II) compound was dissolved in acetone which had been acidified with perchloric acid, the oxidation was much more rapid. The product was collected and

washed with a very small amount of cold water. Strong heating of the solid compound on a hot plate caused it to flash with a smokeless flame. Yield, 60%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4(ClO_4)_3 \cdot 3H_2O$: C, 26.90; H, 4.21; N, 8.37; Co, 9.04. Found: C, 26.80; H, 4.18; N, 8.39; Co, 9.46.

Co(CR)I$_3$ $Co(CR)Br_3 \cdot H_2O$ (0.5 g) was dissolved in methanol and 1.5 g of sodium iodide dissolved in methanol was added. The solution was acidified with a few drops of concentrated hydro-iodic acid. The color of the solution rapidly changed from green to dark red and dark red-brown crystals were deposited on cooling. The product, which was sparingly soluble in water and methanol was collected and washed with ethanol. Yield, 95%. *Anol.* Calcd. for $CoC_{15}H_{22}N_4I_3$: C, 25.81; H, 3.18; N, 8.03; I, 54.54. Found: C, 25.90; H, 2.96; N, 7.91; I, 54.21.

Co(CR)(NO$_2$)$_2$ClO$_4$ To a solution of $Co(CR)Br_3 \cdot H_2O$ (0.5 g) in cool methanol was added a cool solution of 1.2 g of sodium nitrite in methanol. The color of the solution immediately changed from green to orange. A concentrated solution of sodium perchlorate (0.3 g) dissolved in methanol was added and the solution placed in the refrigerator overnight. Small bronze crystals formed, were collected, washed with methanol, and dried.

The product was moderately soluble in methanol. Yield, 68%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4(NO_2)_2ClO_4$: C, 35.41; H, 4.36; N, 16.52. Found: C, 35.4; H, 4.36; N, 16.52. Found: C, 35.4; H, 4.43; N, 16.7.

Co(CR)(N$_3$)$_2$ClO$_4$ The preparation of this product was similar to that of $Co(CR)(NO_2)_2ClO_4$ with the following exceptions: An aqueous solution of sodium azide (0.7 g) was added to the $Co(CR)Br_3 \cdot H_2O$ in warm methanol. The solution became red immediately. The fairly large dark red needles which formed on cooling after addition of $NaClO_4$ were sparingly soluble in methanol. Yield, 69%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4(N_3)_2ClO_4$: C, 36.1; H, 4.50; N, 28.0. Found: C, 36.2; H, 4.37; N, 27.8.

Co(CR)(CN)$_2$ClO$_4$ The preparation of this compound was similar to that of $Co(CR)(NO_2)_2ClO_4$ with the following exceptions: The reaction of $Co(CR)Br_3 \cdot H_2O$ (0.5 g) with sodium cyanide (0.10 g) was carried out in warm water. The solution changed from green to yellow-brown immediately upon addition of the sodium cyanide. Yellow cubic crystals formed on cooling. Yield, 69%. *Anal.* Calcd. for $CoC_{15}H_{22}N_4(CN)_2ClO_4$: C, 43.58; H, 4.73; N, 17.94. Found: C, 43.9; H, 4.58; N, 18.0.

Co(CR)ox(ClO₄) The preparation of this product was similar to that of Co(CR)(CN)₂ClO₄ with the following exceptions: The addition of sodium oxalate in a 1:1 molar ratio to Co(CR)Br₃·H₂O resulted in a red solution. Red-orange rod shaped crystals formed as the product was only sparingly soluble in water. Yield, 95%. *Anal.* Calcd. for CoC₁₅H₂₂N₄ (C₂O₄)ClO₄: C, 40.47; H, 4.40; N, 11.1. Found: C, 40.8; H, 4.41; N, 11.9.

Co(CR)ox(NO₃)·H₂O The preparation of this product was similar to that of the perchlorate salt with the following exceptions: Co(CR)(NO₃)₃· ⁵⁄₂H₂O was used instead of the corresponding bromide and no sodium perchlorate was added. The volume of the solution was reduced slowly by blowing air over the surface and the product came out as a microcrystalline pink solid. This salt of the oxalato complex was moderately soluble in water and sparingly soluble in methanol. Yield: 50%. *Anal.* Calcd. for CoC₁₅H₂₂N₄(C₂O₄)NO₃· H₂O: C, 42.1; H, 4.98; N, 14.43. Found: C, 42.4; H, 5.06; N, 14.7.

Co(CR)acac(ClO₄)₂ The preparation of this compound was similar to that of Co(CR)ox(ClO₄) with the following exceptions: An excess of 2,4-pentanedione was added to a solution of Co(CR)Br₃· H₂O in methanol. The solution was made slightly alkaline with 1.0 N sodium hydroxide, at which point the color of the solution was red. An approximately stoichiometric amount of sodium perchlorate in methanol solution was added. Three volumes of *l*-porpanol were added to the methanol solution and the mixture was allowed to stand overnight. The dark red crystals which formed were collected, washed with *l*-propanol and dried. *Anal.* Calcd. for CoC₁₅H₂₂N₄(C₅H₇O₂)(ClO₄)₂: C, 39.0; H, 4.75; N, 9.10. Found: C, 38.9; H, 4.45; N, 8.99.

Co(CR)(NCS)₂ClO₄ The preparation of this product was similar to that of Co(CR)(NO₂)₂ClO₄ with the following exceptions: About 0.2 g of sodium thiocyanate was dissolved in methanol and added to the methanol solution of Co(CR)Br₃· H₂O (0.5 g). The volume of the brown product solution was reduced on the rotary evaporator to induce crystallization. The crude brown product was recrystallized from water. Yield, 30%. *Anal.* Calcd. for CoC₁₅H₂₂N₄(NCS)₂ClO₄: C, 38.33; H, 4.16; N, 15.84; S, 12.0. Found: C, 38.40; H, 4.07; N, 15.47; S, 11.5.

This product was also prepared by adding potassium thiocyanate in methanol to Co(CR)-

(ClO₄)₃· 3H₂O in ethanol. The precipitated potassium perchlorate was removed by filtration and the solution was evaporated slowly to induce crystallization of the product. Yield, 50%. *Anal.* Found: C, 38.5; H, 4.27; N, 15.7.

Co(CR)(en)Br₃· H₂O To Co(CR)Br₃· H₂O (1.0 g) dissolved in warm methanol, 0.20 ml of ethylenediamine was added (neat) with stirring. The solution turned brown immediately. Small brown crystals formed on cooling overnight in the refrigerator. The product was collected, washed with ethanol and dried. Yield, 60%.*Anal.* Calcd. for CoC₁₅H₂₂N₄ (C₂H₈N₂)Br₃· H₂O: C, 32.2; H, 5.08; N, 13.2. Found: C, 32.4; H, 5.03; N, 13.2.

Co(CR)(enH⁺)Br₄·H₂O To a warm methanol solution of Co(CR)enBr₃· H₂O (0.1 g), a slight excess of hydrobromic acid was added. The solution was concentrated on the rotary evaporator to obtain a dark brown microcrystalline solid. The collected product is washed with ethanol and dried. Yield, 90%. *Anal.* Calcd. for CoC₁₅H₂₂N₄(C₂H₉N₂)Br₄· H₂O: C, 28.5; H, 4.64; N, 11.7. Found: C, 28.7; H, 4.85; N, 11.4.

Co(CR)Br(NO)B(C₆H₅)₄ Nitric oxide (Matheson) was bubbled through an ethanol solution of Co(CR)Br₂· H₂O (1.0 g). The solution became deep cherry red within five minutes. Of the anions tried, only B(C₆H₅)₄⁻ in methanol induced crystallization of the product. It separated as a finely divided light brown solid. The product was collected, washed with methanol and dried. Yield, 90%. *Anal.* Calcd. for CoC₁₅H₂₂N₄Br(NO)B(C₆H₅)₄: C, 62.75; H, 5.67; N, 9.38; Br, 10.71. Found, C, 63.1; H, 5.67; N, 9.23; Br, 10.68.

Co(CR)I(NO)B(C₆H₅)₄ The preparation of this product was similar to that of the preceding one with the following exceptions: Methanol was used as the solvent for the Co(CR)I₂ starting material and the product was dark brown. Yield, 90%. si,Anal. Calcd. for CoC₁₅H₂₂N₄I(NO)B(C₆H₅)₄: C, 59.0; H, 5.34; N, 8.83; I, 16.00. Found: C, 60.2; H, 5.59; N, 9.00; I, 15.82.

Co(CR)NCS(NO)B(C₆H₅)₄ The preparation of this product was similar to that of the preceding one with the following exceptions: Co(CR)(NCS)₂ was used as the starting material and the product was maroon in color. Yield, 90%. *Anal.* Calcd. for CoC₁₅N₂₂N₄ (NCS)(NO)B(C₆H₅)₄. C, 66.2; H, 5.84; N, 9.66; S, 4.42. Found: C, 67.7; H, 6.15; N, 9.72; S, 3.94.

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