vincingly.[23] However, when bridging ligand transfer does not obtain, then the alternate outer-sphere pathway is at least plausible.[24]

Registry No. $CoEDTA^-$, 15136-66-0; $Co(EDTA)Cl^{2-}$, 23467-31-4; $Co(EDTA)OH_2{}^-$, 24340-68-9; $Fe(CN)_6{}^{4-}$, 13408-63-4; $Co-EDTA^{2-}$, 14931-83-0; $Fe(CN)_6{}^{3-}$, 13408-62-3.

(24) There is one requirement that must be fulfilled for the alternate interpretation (mechanism B) to be physically meaningful. The product of the equilibrium constant for binuclear complex formation and the parameter commonly interpreted as the dissociation of the binuclear complex must be $<10^{10}$ M^{-1} sec^{-1}, the upper limit for a diffusion-controlled reaction.

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Saturated Macrocyclic (N_4) Complexes of Cobalt(III) Containing Cobalt-Alkyl Bonds. Preparation and Properties[1]

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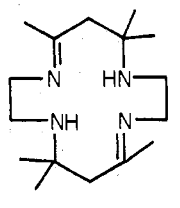
A photochemical approach to the preparation of $Co^{III}(N_4)YR$ complexes has been devised where (N_4) is some saturated or partly saturated quadridentate macrocyclic nitrogen donor ligand, R is an alkide or alkenide ligand, and Y is some ligand such as H_2O, NCS^-, etc. The photoredox decompositions of $Co(NH_3)_5O_2CR^{2+}$ complexes in acidic aqueous solutions were used for sources of ·R radicals; when photolyses were performed in the presence of $Co^{II}(N_4)$ complexes, the radical-cobalt(II) reactions were found to be rapid and reasonably efficient. Complexes have been prepared with (N_4) = a cyclic tetramine or a cyclic diimine–diamine, and R = CH_3 or C_2H_3. Side reactions and other problems of the preparative method are mentioned. The product $Co^{III}(N_4)YR$ complexes are very stable coordination complexes. Some apparently five-coordinate $Co(N_4)CH_3{}^{2+}$ complexes have been prepared and partially characterized. Although CH_3^- seems to be a good ligand with relatively high crystal field strength in the complexes with saturated equatorial (N_4) ligands, the absorption spectra of $Co^{III}(N_4)(OH_2)CH_3$ complexes with relatively unsaturated (N_4) ligand systems exhibit features which are not well understood.

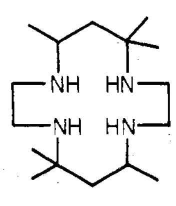
Introduction

Since the discovery[2] that the stable, natural product, coenzyme B_{12}, is a cobalt(III) complex containing a σ-bonded alkyl ligand, there has been considerable interest in the preparation and study of analogous synthetic complexes.[3] One point of interest in these studies has been the elucidation of the conditions which result in "stabilization" of cobalt(III)-alkyl moieties. Prior to the present study all the known complexes containing stable cobalt(III)-alkyl bonds contained highly unsaturated ligands (*e.g.*, corrin, bis(dimethylglyoxime), cyanide, etc.) cis to the organic ligand. The relative ease of preparation of such unsaturated cobalt-alkyl complexes compared to the numerous failures to prepare cobalt-alkyl complexes containing only saturated ligands, led to a belief that unsaturation of the equatorial ligand systems (with perhaps a concomitant enhancement of metal-ligand bond strength), was a necessary prerequisite to the formation of stable cobalt(III)-alkyl complexes.[3,4] In this report we describe the preparation and characterization of the first cobalt(III)-alkyl complexes with saturated equatorial ligand systems.

Experimental Section

The acetato-, phenylacetato-, and acrylatopentaamminecobalt(III) complexes were prepared as perchlorate salts by standard procedures.[5] The $Co^{II}(N_4)$[6,7] complexes with N_4 = $Me_6[14]dieneN_4$,[8] $Me_6[14]aneN_4$,[8] and $Me_4[14]tetraeneN_4$[9,10] were prepared as described previously and isolated as the $(CoCl_4)^{2-}$ salts.


$Me_6[14]dieneN_4$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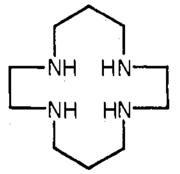
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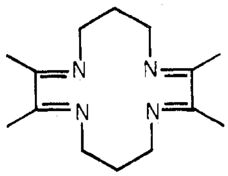
$Me_4[14]tetraeneN_4$

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(1) (a) Partial support of this research by the Public Health Service (Research Grant AM 14341) is gratefully acknowledged. (b) Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973; see Abstracts, No. INOR 80.

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(6) Abbreviations for macrocyclic ligands are based on suggestions by Busch and coworkers.[7] In this study we use $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, $Me_6[14]dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, $Me_6[14]aneN_4$ = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane.

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The [14]aneN_4 ligand was prepared by a published procedure.[11] The [Co([14]aneN_4)]($CoCl_4$) complex was prepared by a procedure similar to that used for the Me_6[14]aneN_4 complex. The isolated Co(II) complex was stored under N_2, a precaution required by the facile reaction of this complex with O_2 in the solid state.

The cobalt(III)-alkyl complexes were prepared by the photolysis of the carboxylatopentaamminecobalt(III) complexes, using a low-pressure Hg lamp ($I_0 \approx 3 \times 10^{-3}$ einstein $l.^{-1}$ min^{-1} at 254 nm) in the presence of the appropriate $Co^{II}(N_4)$ complex. In a typical preparation approximately 1×10^{-3} mol of [$Co(N_4)$]($CoCl_4$) was dissolved in 200 ml of a 5×10^{-2} *M* HCl solution which had been deaerated for 1 hr. A threefold excess of the carboxylatopentaamminecobalt(III) complex was then added and the solution was irradiated for 2 hr in a nitrogen atmosphere in a Vycor tube. The solution volume was then reduced to ~30 ml, $HClO_4$ was added, the solution was cooled, and the impure solid was removed by filtration. This solid residue was purified in a semidarkened room by recrystallization from 10^{-2} *M* $HClO_4$ at 50–60°. Continuous and flash photolysis apparatus are described elsewhere.[12]

Most of the preparative reactions were run in HCl solution. However, under these conditions appreciable quantities of $Co(N_4)Cl_2^+$ formed in cases that $(N_4) = Me_6$[14]aneN_4 or [14]aneN_4. This problem was sufficiently serious with (N_4) = [14]aneN_4 that we ran most of our preparative reactions on a reduced scale in $HClO_4$ solutions.

The various derivatives of the alkyl and alkenyl complexes were prepared by metathasis in methanol of [$Co(N_4)OH_2R$]$(ClO_4)_2$ salts with the potassium salt of the desired anionic ligand. Excess $KClO_4$ was removed by filtration after the volume had been reduced; the complex was precipitated from the filtrate by the addition of ether. The cyanide and thiocyanate complexes, which are stable in aqueous solution in the presence of excess anion, could be precipitated by the addition of perchlorate to such aqueous solutions. *Caution*! Although we encountered no such problems in this research, perchlorate salts of metal complexes do tend to be explosive.

The isolation of the [Co([14]aneN_4)(OH_2)CH_3]$(ClO_4)_2$ salt was more difficult than that of the other complexes due to its solubility in perchlorate media. The solution was reduced to a minimum volume, $HClO_4$ added, and the solid filtered off. The solid was then washed with methanol until the color of the remaining solid corresponded to that of the acetatopentaamminecobalt(III) complex. The methanol was evaporated and the residue was stirred in acetone (to remove NH_4ClO_4). The acetone slurry was filtered and the solid was recrystallized by adding small amounts of $NaClO_4$ to the solution of the solid in a minimum amount of water.

Visible and ultraviolet spectra were determined using a Cary Model 14 spectrophotometer; pmr spectra were determined on Varian T-60 or JOELCO 100 spectrometers. TMS reference solutions were placed in a tube concentric with the sample tube for the chemical shift determinations. Voltametric determinations were made using the Chemtrix SSP-2 and procedures described elsewhere.[9]

Results and Discussion

A. Synthesis of Cobalt(III)–Carbanion Complexes.

1. General Chemical Considerations. The preparation of cobalt-alkyl complexes by means of the reaction of a cobalt(I) or a cobalt(II) complex with an alkyl halide has been exploited extensively for cobalt complexes containing highly unsaturated equatorial ligand systems.[3] Unfortunately the analogous approaches have not proved useful for complexes containing saturated (N_4) ligand systems.[3,8] In devising a preparative route we have made use of the following information: (1) the $Co^{II}(N_4)$ complexes are generally low spin[13,14] in solution; (2) the $Co^{II}(N_4)$ complexes were known to interact only weakly with axial ligands[15] and very recently have been shown to be axially distorted;[16] (3) strongly oxidizing radicals react with $Co^{II}(N_4)$ complexes at nearly diffusion-controlled rates;[17] (4) an approximate thermodynamic argument suggests that the alkyl radicals are strong oxidants in acidic aqueous solutions;[18] and (5) alkyl radicals have been shown to add to the dimethylglyoximate, cobalamine, and cyanocobalt(II) analogs.[3e,19] Since the axially distorted cobalt(II) complexes should be extremely labile in the axial positions, it seemed likely that (1) should

$$Co(N_4)(OH_2)_2^{2+} + \cdot R \rightarrow Co(N_4)(OH_2)R^{2+} + H_2O \qquad (1)$$

compete effectively with normal bimolecular radical decay modes.

As radical sources we chose the photoredox decompositions of $Co(NH_3)_5O_2CR^{2+}$ complexes (eq 2), since these

$$Co(NH_5)_5O_2CR^{2+} + h\nu \xrightarrow[H^+]{} Co^{2+} + 5NH_4^+ + CO_2 + \cdot R \qquad (2)$$

reactions proceed cleanly and without bulk solution radical-Co^{2+} recombination reactions.[20] In some preliminary studies we flash photolyzed $Co(NH_3)_5O_2CCH_3^{2+}$ in solutions which were 0.1 *M* in HCl or HBr; in the former experiments no transient was observed while in the latter we observed the Br_2^- radical. This confirmed that the $\cdot CH_3$ radical was a strong oxidant in acidic aqueous solution (for $\cdot Cl + e^- \rightleftharpoons Cl^-$, SRP = 2.6 V;[17] for $\cdot Br + e^- \rightleftharpoons Br^-$, SRP = 2.06 V;[21] see also discussion of aqueous radical reactions in ref 17). In additional flash photolyses of $Co(NH_3)_5O_2CCH_3^{2+}$ in $HClO_4$ solutions containing $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$, we found that the cobalt(II) complex was oxidized with a specific second-order rate constant of 7×10^8 M^{-1} sec^{-1}; since the $\cdot CH_3$ oxidation of $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$ proceeds by coordinative capture of the radical, this implies[22] a very large ($k \simeq 10^9$ sec^{-1}) axial water exchange rate constant for the cobalt(II) complex.

In an additional series of experiments which preceded the isolation of cobalt(III)-carbanion complexes, we examined the distribution of gaseous products resulting from irradiation of $Co(NH_3)_5O_2CCH_3^{2+}$ in the presence of $Co(N_4)^{2+}$ species. From gas chromatographic analysis of products resulting from irradiation of degassed, evacuated solutions we found that the sum, (moles of CH_4) + 2 × (moles of C_2H_6), was 3 times higher in the absence of $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$ than it was when photolyses were performed with $\sim 10^{-3}$ *M* $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$ present, for comparable amounts of photoredox decomposition of the $Co(NH_3)_5O_2CCH_3^{2+}$ substrate. The decrease in yield of gaseous products was almost exclusively in ethane; this sug-

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[17] S. D. Malone and J. F. Endicott, *J. Phys. Chem.*, 76, 2223 (1972).

[18] J. F. Endicott, manuscript in preparation. For example if one assumed similar solvation energies for $\cdot CH_3$ and CH_4 and that the principal contribution to the redox couple is enthalpic, then the standard reduction potential for this couple ($\cdot CH_3 + e^- + H^+ \rightleftharpoons CH_4$) is SRP ≈ 2.25 V.

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Table I. Analytical Data for $[Co(N_4)(X)R](ClO_4)_n$ Complexes

			% C		% H		% N		% Cl	
(N_4)	R	X	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[14]aneN_4	CH_3	H_2O	26.88	25.51	5.91	5.92	11.41	11.19	14.46	14.82
Me_6[14]aneN_4	CH_3	H_2O	35.5	35.19	7.15	7.14	9.75	9.51	12.3	11.41
Me_6[14]dieneN_4	CH_3	H_2O	35.7	35.24	6.48	6.74	9.80	9.77	12.4	11.60
Me_6[14]dieneN_4	CH_3	CN	43.4[a]	43.78	7.48	7.47	14.0	13.60	7.13	7.32
Me_6[14]dieneN_4	CH_3	SCN	42.2	42.17	6.90	6.75	13.7	12.88	6.94	6.72
Me_6[14]dieneN_4	C_2H_3	H_2O	37.1	35.07	6.35	6.19	9.61	9.61	12.2	12.47

[a] Calculated for $[Co(Me_6[14]dieneN_4)(CN)CH_3]ClO_4 \cdot H_2O$.

gests the possibility that a path for $\cdot CH_3$ oxidation of $Co^{II}(N_4)$ exists which does not involve the coordinative capture of the organic radical. When similar studies were performed with $Co(Me_6[14]aneN_4)(OH_2)_2^{2+}$ present in HCl solutions, we obtained significantly larger (by a factor of about 3.5) yields of methane than were obtained from identical photolyses of solutions of $Co(NH_3)_5O_2CCH_3^{2+}$ or from photolyses of $Co(NH_3)_5O_2CCH_3^{2+}$ in the presence of $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$. These observations may be related to the relatively small yields obtained in preparations of $Co([14]aneN_4)(OH_2)CH_3^{2+}$ and to the observation of some $Co(N_4)Cl_2^+$ (in chloride media) or $Co(N_4)(OH_2)_2^{3+}$ (in perchlorate media) in our preparative procedures for these complexes. That is, we believe that a serious complicating feature of our preparative method may be an "outer-sphere" oxidation of the type (3), which under some conditions and

$$\cdot CH_3 + H^+ + Co^{II}(N_4)X_2 \rightarrow CH_4 + Co^{III}(N_4)X_2 \qquad (3)$$

with some of the cobalt(II) substrates can compete effectively with (1). Although the pK_a of CH_4^+ is not known, the pK_a of CH_4 is certainly very large, so that CH_4^+ might be expected to be a weak or moderate acid and the competition between (1) and (3) which we seem to find in our acidic systems may represent a kinetic selectivity of the various cobalt(II) substrates for oxidation by $\cdot CH_3$ or CH_4^+.

We have found another, relatively minor, complicating side reaction in the photochemical preparations described in this report. Mass spectrometric analyses of the gaseous products of photoredox decomposition of $Co(NH_3)_5O_2CCH_3^{2+}$ in 0.1 *M* chloride solutions always indicated the presence of some (~5% compared to CO_2) CH_3Cl. The yield of CH_3Cl was found to be largely independent of the presence or absence of $Co^{II}(N_4)$ substrates; we would suggest that this species arises from reactions 4 and 5, analogous to reactions of halogen atoms (*e.g.*, see ref 17).

$$\cdot CH_3 + Cl^- \rightleftharpoons CH_3Cl^- \qquad (4)$$

$$CH_3Cl^- + Co(NH_3)_5O_2CCH_3^{2+} \xrightarrow[H^+]{} CH_3Cl + Co^{2+} + 5NH_4^+ + HO_2CCH_3 \qquad (5)$$

Since our major interest in the present report is to describe the preparation and characterization of a new family of organocobalt complexes, we have not attempted to investigate the above reactions in detail. We have presented these semiquantitative observations in this report because (1) it is apparent that the aqueous solution chemistry of at least the $\cdot CH_3$ radical is far more complex than we had suspected from the previous literature and (2) our preparations of $Co([14]aneN_4)(OH_2)CH_3^{2+}$ and a few other complexes have proved relatively inefficient. It seems quite likely that the evolution of more efficient preparative procedures[23] could be built around a more detailed knowledge of the aqueous solution chemistry of the organic radicals.

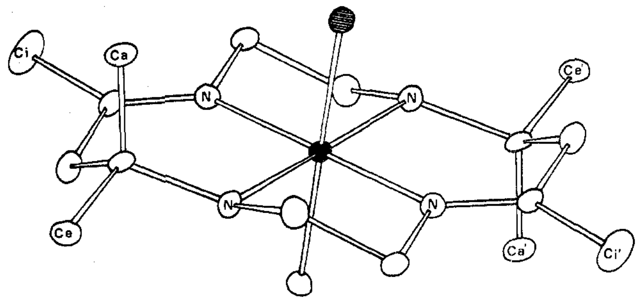

Figure 1. Structure of $Co(N\text{-}meso\text{-}Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$, based on the structure of $Co(N\text{-}meso\text{-}Me_6[14]dieneN_4)(NH_3)_2^{3+}$ in ref 17. Note that the "axial" methyls, Ca and Ca', are in different environments.

2. **Synthetic Studies.** In general photolyses were performed until at least 50% of the $Co(NH_3)_5O_2CR^{2+}$ substrate had been decomposed. For R = CH_3 and with $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$ and $Co^{II}(Me_6[14]aneN_4)$, the yields ran around 40%, based on the initial $[Co(N_4)(OH_2)_2^{2+}]$; with $Co^{II}([14]aneN_4)$ substrates the yields of methylaquocobalt(III) products never exceeded 10%. For R = $CHCH_2$, the yield of $[Co(Me_6[14]dieneN_4)(OH_2)CHCH_2](ClO_4)_2$ was only about 20%. We were unable to isolate $[Co(Me_6[14]dieneN_4)(OH_2)R](ClO_4)_2$ products from synthetic attempts with R = CF_3, $CH_2C_6H_5$, or CH_2CH_3, although observed spectral changes were consistent with the formation of some of the desired product in the latter case.

Analytical data for the successful preparations are presented in Table I.

3. **Attempts to Prepare Other Saturated Cobalt(III)–Carbanion Complexes.** Since the $Co^{III}(N_4)(X)R$ complexes which we have prepared have tended to be relatively stable, there is no obvious reason that the analogous $Co^{III}(NH_3)_4(X)R$ or $Co^{III}(en)_2(X)R$ complexes should not be stable. However, we have been unsuccessful in our attempts to prepare such complexes. Since the reactions with labile cobalt(II) complexes had to be performed in basic media, we were unable to use the photoredox decomposition of $Co(NH_3)_5O_2CCH_3^{2+}$ as a methyl radical source. Our attempts included photolyses of $Co^{III}(DMG)_2(py)CH_3$[24] and methylcobalamin in the presence of cobalt(II) in aqueous ammoniacal and liquid ammonia solutions.

4. **Preparation and Separation of Configurational Isomers.** Since $Co(Me_6[14]dieneN_4)(OH_2)_2^{2+}$ is prepared as predominantly the centrosymmetric isomer,[16] the methylaquocobalt(III) derivative formed from the species in acidic solution is expected to have the same ligand isomer configuration (see Figure 1). This expectation has been confirmed by the pmr spectrum of the product (Figure 1 of ref 25). This isomer is stable in acidic solution (pH <3). In basic solution

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[23] Recent work (D. J. Halko and J. F. Endicott, work in progress) has shown that Goedkin's method may be used to obtain much better yields of the alkyl complexes reported in this paper: V. L. Goedkin, S.-M. Peng, and Y. Park, *J. Amer. Chem. Soc.*, 96, 284 (1974).

[24] DMG = dimethylglyoximate.

[25] T. S. Roche and J. F. Endicott, *J. Amer. Chem. Soc.*, 94, 8622 (1972).

Table II. Visible-Ultraviolet Absorption Spectra of *trans*-$Co^{III}(N_4)XY$ Complexes[a]

(N_4)	X	Y	Metal ion spectra: λ_{max}, nm (ϵ)		
[14]aneN_4	CH_3^-	H_2O	478 (81)	367 (104)	
Me_6[14]aneN_4	CH_3^-	H_2O	498 (74)	384 (33)	225 (2×10^4)
	H_2O	H_2O	565 (36)	449 (sh)	257 (4×10^3)
N-meso-Me_6[14]dieneN_4	CH_3^-	H_2O	470 (228)	376 (404)	286 (2.98×10^3), 235 sh, 208 (2.3×10^4)
	CH_3^-	NCS^-	458 (273)	367 (393)	286 sh
	$C_2H_3^-$	H_2O	455 (164)	362 (382)	270 (1130), 215 (2.1×10^4)
N-d,l-Me_6[14]dieneN_4	CH_3^-	H_2O	468 (300)	371 (298)	280 (2.86×10^3), 237 sh, 208 (1.9×10^4)
	CH_3^-	NCS^-	448 (208)	358 (449)	286 sh
	CH_3^-	CN^-	427 (91)	335 (sh)	
Me_6[14]dieneN_4	H_2O	H_2O	582 (27)	431 sh	
	NCS^-	NCS^-	514 (320)	340 (3100)	
	CN^-	CN^-	410 (90)		
Me_4[14]tetraeneN_4	CH_3^-	H_2O	485 (2200)	421 (1400)	
	CH_3	NCS^-	458 (1570)	420 (1620)	338 (5500)
	H_2O	H_2O	575 sh, 505 (54), 425 sh		
	NCS^-	NCS^-	510 (215)		

[a] All spectra in acidic solutions (pH <3; perchlorate media or excess Y) except for the cyano complexes (pH 5-7) and thiocyanato complexes (pH <3 and 1 *M* NaSCN).

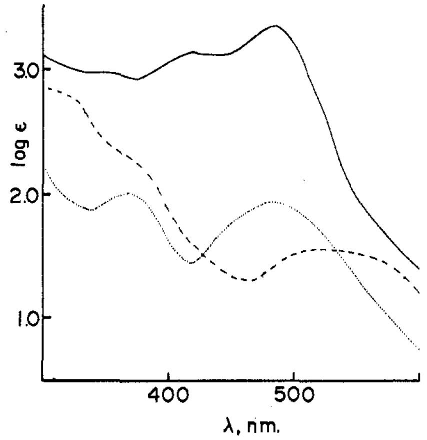

Figure 2. Absorption spectra of $Co^{III}(N_4)LX$ complexes and the anomalous absorptivity of $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$: top curve, $Co(Me_4[14]tetraeneN_4)(OH_2)CH_3^{2+}$ in 10^{-2} *M* $HClO_4$; dashed curve, $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ in 0.1 *M* $HClO_4$; dotted curve, $Co([14]aneN_4)(OH_2)CH_3^{2+}$ in 10^{-2} *M* $HClO_4$.

the *N*-meso and *N-d,l* configurational isomers equilibrate, presumably by means of inversion of coordinated amido groups. The *N-d,l* isomer is readily isolated by separation of $[Co(N\text{-}d,l\text{-}Me_6[14]dieneN_4)(CN)CH_3]ClO_4$ following addition of a small stoichiometric excess of NaCN to a methanolic solution of $Co(N\text{-}meso\text{-}Me_6[14]dieneN_4)(OH_2)CH_3^{2+}$; addition of a $HClO_4$ solution to the cyano derivative produces the aquo complex.

We have not been able to achieve a separation of configurational isomers by similar treatment of $Co(Me_6[14]aneN_4)(OH_2)CH_3^{2+}$.

B. Physical Properties. 1. Absorption Spectra. Absorption spectra of the complexes we have studied are summarized in Table II; spectra of a few $Co^{III}(N_4)X_2$ complexes are included in Table II to facilitate comparisons. Comparison of metal ion spectra in Table II indicates that the carbanion ligands have an intermediate position in the spectrochemical series; *i.e.*, apparent crystal field strengths increase in the order $H_2O < NCS^- < CH_3^- < C_2H_3^- < CN^-$. For the methyl ligand, our estimates of Dq[26] run around 2700 cm^{-1}. Similar orders have been observed in the less saturated analogs.[4e] However it must be observed that our estimates of Dq are based on the *assumption* that the crystal field strength of H_2O is the same in the alkyl as in, for example, diaquo complexes. Since the Co^{III}-OH_2 bond appears to be relatively long in some of the alkylated complexes[27] it would be more appropriate to assume a reduced value of Dq for H_2O which would result in a larger value of Dq for the alkyl. Our values of Dq would therefore be better regarded as lower limits than as reasonable approximations.

For the complexes with only saturated ligands the intensities of the d-d transitions have values characteristic of somewhat asymmetric cobalt(III) complexes and no low-energy (*i.e.*, with $\bar{\nu} < 40$ kK) charge-transfer transitions are observed; however the charge-transfer transitions do seem to be unusually broad in these complexes. Certainly there is no spectroscopic evidence that the coordinated alkyls should be considered as strongly reducing ligands; on the basis of the ultraviolet spectra of these complexes, CH_3^- would seem to be less "reducing" (more correctly, to have a higher optical electronegativity[28]) than Br^-.

There is a very definite trend of increasing intensity of the "metal-centered" electronic transitions with increasing unsaturation of the (N_4) ligand (Figure 2 and Table II). Although the assignment of transitions in the $Co^{III}(Me_4[14]tetraeneN_4)(X)CH_3$ complexes must be regarded as equivocal at present, we would point out that the lowest energy transition observed in these complexes occurs at about the energy predicted using a simple crystal field model[26] and that the unusually high intensity suggests a relaxation of the Laporte selection rule. Since the symmetry and "covalency" should be very similar for the $Co^{III}(Me_4[14]tetraeneN_4)(X)CH_3$ and $Co^{III}([14]aneN_4)(X)CH_3$ complexes, we cannot agree with Busch and coworkers[29] that these are the factors responsible for the enhanced intensities of metal-centered transitions in the cobalt(III)-alkyl complexes containing unsaturated equatorial ligand systems.

2. H Nmr Spectra. Some features of the nmr spectra of these complexes have been discussed in the preliminary communication of this work.[25] Of some interest are variations in the chemical shifts of the coordinated organic ligand and we have compared such data for several complexes in Table III. The frequency at which resonance of the methyl group is observed seems more sensitive to variations of the local

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(26) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965).

(27) The Co-OH_2 bond length in $[Co([14]aneN_4)(OH_2)CH_3](ClO_4)_2$ is about 2.13 Å, compared with "normal" Co^{III}-OH_2 bond lengths of 1.94-1.98 Å: M. D. Glick, W. Butler, and J. F. Endicott, work in progress.

(28) C. K. Jorgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, New York, N. Y., 1969, Chapter 7.

(29) E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 3201 (1969).

Table III. Comparison of Methide ($Co^{III}-CH_3^-$) Chemical Shifts in $CH_3Co^{III}(N_4)L$ Complexes

(N_4)	L	Conditions and medium[a]	σ,[b] ppm
[14]aneN_4	D_2O	D_2O-D^+	1.78
Me_6[14]aneN_4	D_2O	D_2O-D^+	2.14
		D_2O-OD^-	1.89
		CD_3OD-D^+	1.99
		CD_3OD-OD^-	1.58
	NCS^-	CD_3OD-D^+	1.88
	CN^-	CD_3OD-CN^-	1.89
N-meso-Me_6[14]dieneN_4	D_2O	D_2O-D^+	1.90
		D_2O-D^+, NaCl[c]	1.93
		D_2O-OD^-	1.96
N-d,l-Me_6[14]dieneN_4	D_2O	D_2O-D^+	1.63
		D_2O-OD^-	1.67
	CN^-	D_2O-CN^-	1.62
Me_4[14]tetraeneN_4	D_2O	D_2O-D^+	1.42
		D_2O-OD^-	0.77
Corrin	D_2O		−0.24[d]
Tetrasulfanatophthalocyanine	D_2O		−6.1[e]

[a] Concentrations of solute species 0.1 *M* except as indicated. Perchlorate or sodium counterions except as indicated. [b] Relative to external TMS. [c] 1 *M* in NaCl. [d] H. A. O. Hill, B. E. Mann, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc. A*, 564 (1968). [e] P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc. A*, 90 (1968).

environment (*e.g.*, water *vs.* methanol solvent or *N*-meso *vs.* *N-d,l*(N_4) configurational isomers) than to the nature of the trans ligand in the saturated complexes. On the other hand a comparison of the methyl frequency in these complexes with those complexes containing highly unsaturated (N_4) ligands does indicate that a significant upfield shift (Table III) does result from the anisotropic deshielding of the (N_4) π electrons.

We have found that the splitting pattern of the (N_4) ligand methyl groups is nearly identical for Co(*N-meso*-Me_6[14]-dieneN_4)$(OH_2)C_2H_3^{2+}$ and Co(*N-meso*-Me_6[14]dieneN_4)-$(OH_2)CH_3^{2+}$. Unfortunately the low solubility of the complex, the relatively low intensities expected for the components of the $C_2H_3^-$ ligand, and the probable coincidence of these resonances with some of the methylene and methyl (imine) resonances of the (N_4) ligand prevented us from detecting resonances of the organocobalt moiety in the former complex.

The $Co^{III}-CH_3$ resonances of the Me_6[14]aneN_4 and Me_4[14]tetraeneN_4 complexes were shifted surprisingly far upfield in basic solution. These shifts may indicate some chemical reactivity (*e.g.*, variations in configurational isomers or reactions of imine methyl groups, respectively), but we have not further investigated the behavior of these complexes in basic solutions.

3. Infrared Spectra. Discussions of the infrared spectra of complexes containing the macrocyclic (N_4) ligands may be found in the literature.[9,30,31] The $\nu_{C\equiv N}$ stretching frequencies observed in the saturated $Co^{III}(N_4)(CN)R$ complexes exhibit no trend which can be associated with a strong ground-state trans effect of the axial ligand.[32] In fact these frequencies appear to be more sensitive to variations in crystal packing forces, as evidenced by changes in frequency which occur in changing the counterion, than to the nature of the trans ligand. On the other hand structural data do indicate a "strong ground-state trans effect" among aquo complexes.[27] (See Table IV for ir frequencies of selected ligands.)

Table IV. Infrared Frequencies of Selected Ligands[a] in Organocobalt Complexes

Complex	$\nu_{C=C}$, cm^{-1}	$\nu_{C\equiv N}$, cm^{-1}
[Co(Me_6[14]dieneN_4)(OH_2)*C_2H_3*]$(ClO_4)_2$	1570	
[Co(Me_6[14]dieneN_4)(OH_2)*C_2H_3*]Cl_2	1560	
[Co(Me_6[14]dieneN_4)(*CN*)*C_2H_3*]ClO_4	1574	2123
[Co(Me_6[14]dieneN_4)(*CN*)*C_2H_3*]CN	1560	2115
[Co(Me_6[14]dieneN_4)(*CN*)CH_3]ClO_4		2123
[Co(Me_6[14]dieneN_4)$(CN)_2$]ClO_4		2120
[Co(Me_6[14]aneN_4)(*CN*)CH_3]ClO_4		2115
[Co(Me_6[14]aneN_4)$(CN)_2$]ClO_4		2130
Methylcyanocob(III)alamin		2088[b]
Dicyanocob(III)alamin		2119[b]

[a] Frequencies quoted for italic ligands. All were sharp intense absorption bands. [b] Table 6.3 of ref 3c, p 88.

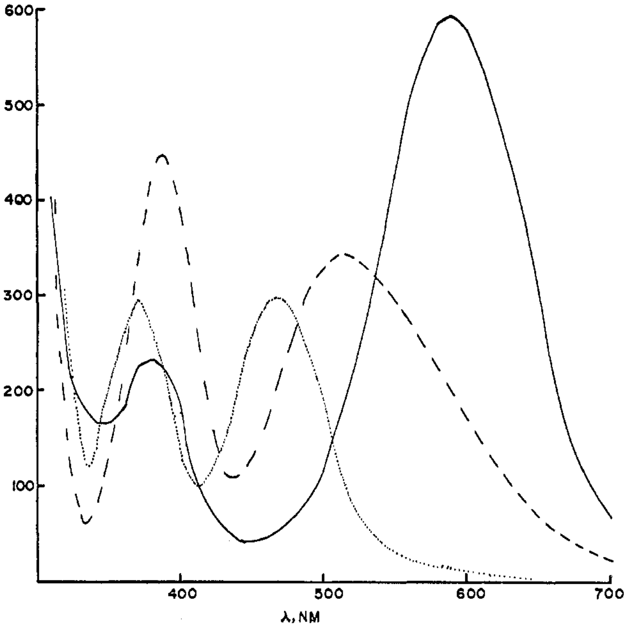

Figure 3. Spectra of presumed five-coordinate species: solid curve, Co(*N-d,l*-Me_6[14]dieneN_4)$OH_2CH_3^{2+}$ in concentrated H_2SO_4; dashed curve, Co(*N-meso*-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ in concentrated H_2SO_4. Spectrum of Co(*N-d,l*-Me_6[14]dieneN_4)$(OH_2)CH_3^{2+}$ in 10^{-2} *M* $HClO_4$ (dotted curve) is included for comparison.

C. Chemical Properties. We have found the relatively saturated cobalt(III)-alkyl complexes to be reasonably tractable materials. They appear to be well behaved in acidic and basic solutions, are not noticeably air or light sensitive under normal laboratory conditions. They are appreciably easier to handle than $Co(NH_3)_5I^{2+}$ and far less photosensitive than $Co(NH_3)_5NO_2^{2+}$ or $Co(NH_3)_5N_3^{2+}$.[33] On the other hand these compounds do have some unusual chemical properties, some of which are discussed below.

Upon drying [Co(*N-d,l*-Me_6[14]dieneN_4)$(OH_2)CH_3$]-$(ClO_4)_2$ in a vacuum oven at −50°, the color of the complex changed from orange to blue. This blue color persisted indefinitely in an anhydrous atmosphere.

Our earlier report[25] of a temperature-dependent paramagnetism of this blue complex is incorrect. However an impurity does exist (or is easily formed) in the compound which results in an esr spectrum typical of a Co(II) species. This impurity is present to the extent of <1%, and the blue compound is not significantly paramagnetic at room or liquid nitrogen temperature.

The blue compound dissolves in water, DMF, and alcohols

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(30) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(31) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 6, 770 (1967).

(32) Reference 3c, p 88.

(33) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

to regenerate the spectrum of the aquo complex.

The *N-d,l* complex, either as the blue solid or the orange species, is soluble and stable in 70% $HClO_4$ and concentrated H_2SO_4. Only the blue species is detectable in these solvents (Figure 3). The nmr spectrum of the complex in concentrated H_2SO_4 is similar to that of the *N-d,l* complex in D_2O although broadened by viscosity effects. The meso complex is insoluble in $HClO_4$ but dissolves in H_2SO_4 giving the spectrum indicated in Figure 3. The conversion between blue and orange species appears to be completely reversible, the solutions in concentrated H_2SO_4 and concentrated $HClO_4$ appear to obey Beer's law, and we believe the blue species is a five-coordinate cobalt(III) complex.

We have found that the $Co^{III}(N_4)(L)CH_3$ complexes are reduced at only very negative potentials. The cyclic voltammograms of $Co^{III}(Me_6[14]dieneN_4)(L)CH_3$ in acetonitrile were irreversible in that they exhibited no anodic wave; this may be due to rapid solvolysis of the axially distorted $Co^{II}(N_4)(L)CH_3$ products. Values of the half-wave potential (in CH_3CN *vs.* sce) were found to be $E_{1/2} = -1.3, -1.4$, and -1.8 V for $L = H_2O$, NCS^-, and CN^-, respectively.

Registry No. $[Co([14]aneN_4)(H_2O)CH_3](ClO_4)_2$, 51240-13-2; $[Co(Me_6[14]aneN_4)(H_2O)CH_3](ClO_4)_2$, 40489-13-2; $[Co(Me_6[14]dieneN_4)(H_2O)CH_3](ClO_4)_2$, 51240-15-4; $[Co(Me_6[14]dieneN_4)(CN)CH_3]ClO_4$, 51240-17-6; $[Co(Me_6[14]dieneN_4)(SCN)CH_3]ClO_4$, 51240-19-8; $[Co(Me_6[14]dieneN_4)(H_2O)(C_2H_3)](ClO_4)_2$, 51240-21-2; $Co(NH_3)_5O_2CCH_3{}^{2+}$, 16632-78-3; $Co(NH_3)_5O_2CCHCH_2{}^{2+}$, 44982-34-5; $Co(Me_6[14]dieneN_4)(OH_2)_2{}^{2+}$, 38331-68-9; $Co(Me_6[14]aneN_4)(OH_2)_2{}^{2+}$, 39162-58-8; $Co([14]aneN_4)(CH_3)(H_2O)^{2+}$, 51240-12-1; $Co(Me_6[14]aneN_4)(CH_3)(H_2O)^{2+}$, 47247-32-5; Co(*N-meso*-$Me_6[14]dieneN_4)(CH_3)(H_2O)^{2+}$, 51240-22-3; Co(*N-meso*-$Me_6[14]dieneN_4)(CH_3)(NCS)^+$, 51240-23-4; Co(*N-meso*-$Me_6[14]dieneN_4)(C_2H_3)(H_2O)^{2+}$, 51240-24-5; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(H_2O)^{2+}$, 47247-33-6; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(NCS)^+$, 51240-25-6; Co(*N-d,l*-$Me_6[14]dieneN_4)(CH_3)(CN)^+$, 51240-26-7; $Co(Me_6[14]dieneN_4)(NCS)_2{}^+$, 47512-96-9; $Co(Me_6[14]dieneN_4)(CN)_2{}^+$, 17747-64-7; $Co(Me_4[14]tetraeneN_4)(CH_3)(H_2O)^{2+}$, 50600-07-2; $Co(Me_4[14]tetraeneN_4)(CH_3)(NCS)^+$, 51240-27-8; $Co(Me_4[14]tetraeneN_4)(H_2O)_2{}^{3+}$, 36452-48-9; $Co(Me_4[14]tetraeneN_4)(NCS)_2{}^+$, 51240-28-9; $[Co(Me_6[14]dieneN_4)(OH_2)C_2H_3]Cl_2$, 51240-29-0; $[Co(Me_6[14]dieneN_4)(CN)C_2H_3]ClO_4$, 51240-31-4; $[Co(Me_6[14]dieneN_4)(CN)C_2H_3]CN$, 51240-32-5; $[Co(Me_6[14]dieneN_4)(CN)_2]ClO_4$, 16247-32-8; $[Co(Me_6[14]aneN_4)(CN)(CH_3)]ClO_4$, 51240-34-7; $[Co(Me_6[14]aneN_4)(CN)_2]ClO_4$, 51268-46-3.

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Preparation of η-Cyclopentadienylcobalt(III) and η-Cyclopentadienylnickel(IV) Complexes of the η-7-$B_{10}CH_{11}{}^{3-}$ Carbollide Ligand

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Abstraction of bridging protons from $B_{10}CH_{13}{}^-$ with ethanolic KOH followed by addition of C_5H_6 and anhydrous $CoCl_2$ and subsequent oxidation produces a high yield of the $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$ ion. Abstraction of $N(CH_3)_3$ and bridging protons from $B_{10}H_{12}C[N(CH_3)_3]$ with sodium in THF followed by the addition of NaC_5H_5 and $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$ and subsequent oxidation gives a low yield of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$. Both metallocarboranes are isoelectronic and isostructural with the icosahedral two-carbon species $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_9C_2H_{11})$ and contain the metal atom bonded to a B_4C face. At 450° under high vacuum $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ rearranges to a mixture of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}2\text{-}B_{10}CH_{11})$ and $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}1\text{-}B_{10}CH_{11})$.

Introduction

We have recently reported[1] that cyclopentadienylcobalt complexes of the $B_7CH_8{}^{3-}$ ion are formed in the base degradation of orange $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}6,7\text{-}B_{10}C_2H_{12})$. Here we describe a direct route to cyclopentadienylcobalt(III) complexes of the known $B_{10}CH_{11}{}^{3-}$ carbollide ion,[2] the first reported member of the $B_nCH_{n+1}{}^{3-}$ series of anions. Anionic bis complexes of $B_{10}CH_{11}{}^{3-}$ with Cr, Mn, Fe, Ni, and Co have already been reported by Knoth, Todd, and coworkers.[2,3]

We have also recently reported[4] a neutral bimetallic species $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_7CH_8)Ni^{IV}(\eta\text{-}C_5H_5)$ formed by addition of a formal $[Ni^{IV}(\eta\text{-}C_5H_5)]^{3+}$ vertex to the reduced $[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_7CH_8)]^-$ complex. We now report the reconstruction of the icosahedron by the addition of $[Ni^{IV}(\eta\text{-}C_5H_5)]^{3+}$ and $[Co^{III}(\eta\text{-}C_5H_5)]^{2+}$ vertices to the $B_{10}CH_{11}{}^{3-}$ ion. $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})$ is the first known member of the $(\eta\text{-}C_5H_5)Ni^{IV}(B_nCH_{n+1})$ series of *neutral* monocarbon metalloboranes.

Results and Discussion

$[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}7\text{-}B_{10}CH_{11})]^-$. The use of cyclopentadienylcobalt carborane complexes has greatly simplified structural interpretations of spectra in the study of the reactions of metallocarborane cages.[5] Recently, an improved synthesis of icosahedral metallocarboranes such as $(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_9C_2H_{11})$ incorporating η-cyclopentadienyl ligands has been developed in this laboratory.[6] This improved method involves the simultaneous abstraction of protons from the $B_9C_2H_{12}{}^-$ ion and from cyclopentadiene by ethanolic potassium hydroxide in the presence of the metal salt. The same synthetic route (eq 1) was followed for the $B_{10}CH_{13}{}^-$ ion and the η-

$$3CoCl_2 + 2C_5H_6 + 2B_{10}CH_{13}{}^- + 6C_2H_5O^- \xrightarrow[C_2H_5OH]{KOH} 2[(\eta\text{-}C_5H_5)Co^{III}(\eta\text{-}B_{10}CH_{11})]^- + 6C_2H_5OH + Co^0 + 6Cl^- \quad (1)$$

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