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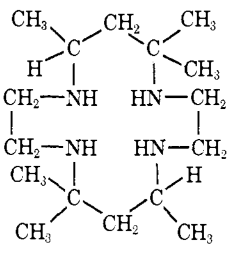
A Photochemical Synthesis of Amine Complexes Containing Cobalt(III)–Alkyl Bonds[1]

Sir:

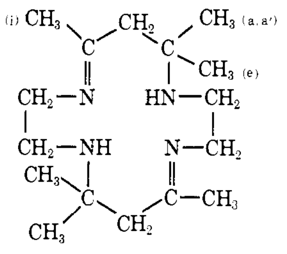
Since the discovery that coenzyme B_{12} contains a cobalt(III)–carbon bond,[2] there has been considerable interest in the preparation and properties of simpler inorganic analogs.[3] To date, inorganic complexes have been prepared containing a variety of unsaturated (generally Schiff-base) ligands in the coordination positions cis to the bound alkyl.[3] Since such complexes have become so commonplace and since previous attempts to prepare cobalt(III)–alkyl complexes containing only saturated ligand systems have failed, several authors have made theoretical or quasi-theoretical suggestions to account for the "instability" of the cobalt(III)–alkyl bond in complexes containing only saturated ligands.[3,4]

With this report we call attention to the first preparation of a cobalt(III)–alkyl complex containing only saturated ligands. We do not find these compounds to be particularly unstable, consistent with Chatt's suggestion that CH_3^- should have a large crystal field strength and that metal–alkyl decomposition depends on the rate of solvolysis;[5] but these compounds are relatively difficult to prepare.

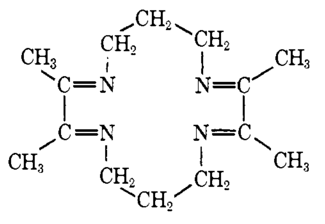
Whereas $Co([14]\text{-}4,11\text{-diene}N_4)(OH_2)CH_3^{2+}$ and $Co([14]aneN_4)(OH_2)CH_3^{2+}$ have not been isolated from the reaction of the cobalt(I) complexes with CH_3I,[4c,6] the $Co^{III}([14]tetraeneN_4)XCH_3$ complexes are relatively easily prepared[4c] by this route.[7] On the other hand, all the corresponding $Co^{III}(N_4)$ complexes are oxidized at nearly diffusion-controlled rates with the dihalide radical anions, Cl_2^-, Br_2^-, and I_2^-.[8] Since it seemed likely that the $\cdot CH_3/Co^{II}(N_4)$ reactions might be relatively slow,[9] we have employed the photochemical decomposition of $Co(NH_3)_5O_2CCH_3^{2+}$ to provide a convenient source of methyl radicals[10] at sufficiently low concentrations (the photostationary state $[\cdot CH_3] \approx 10^{-8}$ *M* under our conditions) that the $\cdot CH_3/Co^{II}(N_4)$ reactions ($[Co^{III}(N_4)] \simeq 10^{-3}$ *M*) could compete effectively with radical–radical combination ($k_2 \simeq 10^{10}$ $M^{-1}\,sec^{-1}$).



[14]aneN$_4$



[14]-4,11-dieneN$_4$



[14]tetraeneN$_4$

$$Co(NH_3)_5O_2CCH_3^{2+} + h\nu \xrightarrow[H^+]{} Co^{2+} + 5NH_4^+ + CO_2 + \cdot CH_3$$

$$\cdot CH_3 + Co^{II}(N_4) \xrightarrow[H_2O]{} Co(N_4)(OH_2)CH_3^{2+} \qquad (1)$$

$$2\cdot CH_3 \longrightarrow C_2H_6 \qquad (2)$$

By monitoring changes in the charge transfer to ligand absorbancies of the cobalt(II) complexes in flash photolysis studies, we have found that $k_1 \simeq 7 \times 10^8$ $M^{-1}\,sec^{-1}$ when N_4 = [14]-4,11-dieneN$_4$ and $k_1 \simeq 1 \times 10^8$ $M^{-1}\,sec^{-1}$ when N_4 = [14]tetraeneN$_4$.

In the preparative experiments $[Co(NH_3)_5O_2CCH_3^{2+}] \simeq 2[Co^{II}(N_4)]$, irradiations were performed at 254 nm, using a low-pressure mercury lamp, in a nitrogen atmosphere and in acidic ($[HClO_4] \simeq 0.1$ *M*) solutions. Preparative solutions were photolyzed until the acetato complex was completely destroyed. The photolyte was then concentrated about fivefold by distillation and the [*trans*-$Co(N_4)(OH_2)CH_3](ClO_4)_2$ products were precipitated by addition of concentrated $HClO_4$.[11] The complexes were recrystallized from 0.01 *M* $HClO_4$ at about 60° (yield ~50%).

The $Co^{II}([14]\text{-}4,11\text{-diene}N_4)$ complexes which we employed were most likely to be predominately of the N-meso isomer of the ligand.[12] Since our preparative reactions were run in acidic solution, we would expect the product $[Co([14]\text{-}4,11\text{-diene}N_4)(OH_2)CH_3](ClO_4)_2$ to be predominately this isomer and this assignment is confirmed by the pmr spectra (Figure 1) since only two of the geminal methyls are pairwise coupled; the axial methyl groups (CH_3(a) and CH_3(a′)) experience different local fields owing to the asymmetry along the axis perpendicular to the Co–N$_4$ plane. We have also prepared the Co(N-*dl*-[14]-4,11-dieneN$_4$)$(OH_2)CH_3^{2+}$ complex in isomerically pure form by first preparing the $[Co([14]\text{-}4,11\text{-diene}N_4)(CN)CH_3]ClO_4$ salt from $Co([14]\text{-}4,11\text{-diene}N_4)(OH_2)CH_3^{2+}$ in methanol solu-

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(1) Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged.

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(11) Analytical data for recrystallized samples were as follows. (a) Calcd for $[Co([14]\text{-}4,11\text{-diene}N_4)(OH_2)CH_3](ClO_4)_2$: C, 35.7; H, 6.48; N, 9.80; Cl, 12.4. Found: C, 35.2; H, 6.74; N, 9.77; Cl, 11.6. (b) Calcd for $[Co([14]aneN_4)(OH_2)CH_3](ClO_4)_2$: C, 35.5; H, 7.14; N, 9.75; Cl, 12.34. Found: C, 35.2; H, 7.14; N, 9.51; Cl, 11.41.

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tion. The aquo derivative is obtained as a perchlorate salt by acidification of an aqueous solution of the cyano complex. The pmr spectrum of [Co([14]-4,11-dieneN_4)(OH_2)CH_3^{2+} shows a pairwise matching of the three types of methyl groups as expected; the axial geminal methyl groups are no doubt on the Co–OH_2 side of this molecule.

When [Co(N-*dl*-[14]-4,11-dieneN_4)(OH_2)CH_3](ClO_4)$_2$ is heated to about 40° in a vacuum oven, the orange solid becomes deep blue and remains blue in a water-free atmosphere; the original salt is regenerated without decomposition in a humid atmosphere. The blue compound exhibits a temperature-dependent magnetic moment and may be five-coordinate. We are investigating this behavior further.

The pmr spectrum of Co([14]aneN_4)(OH_2)CH_3^{2+} is more complex due to the similarity in chemical shifts of the ligand methyl groups (Figure 1). The Co–CH_3 singlet is located at 2.13 ppm *vs.* TMS in this complex compared with 1.90 and 1.63 ppm, respectively, for the Co–CH_3 resonance in the N-*meso* and N-*dl* isomers of Co([14]-4,11-dieneN_4)(OH_2)CH_3^{2+}.

In these complexes CH_3^- appears to be a strong field ligand ($Dq \sim 2500$ cm^{-1}). The ligand field absorption bands increase markedly in intensity as the unsaturation of the cyclic ligand increases, in contrast to the behavior of diammine[13] and other simple cobalt(III) derivatives[14,15] with these same cyclic ligands: for Co([14]aneN_4)(OH_2)CH_3^{2+}, λ_{max} 495 nm (ϵ 70) and 383 (135); for Co(N-*meso*-[14]-4,11-dieneN_4)(OH_2)CH_3^{2+}, λ_{max} 465 nm (ϵ 235) and 375 (405); for Co(N-*dl*-[14]-4,11-dieneN_4)(OH_2)CH_3^{2+}, λ_{max} 465 nm (ϵ 300) and 372 (286); for Co([14]tetraeneN_4)(CH_3)Cl^+, λ_{max} 570 nm (ϵ 140)[15] and 500 (2300).[15] However, it is not evident that these spectral changes are to be associated with changes in stability.

Both Co([14]aneN_4)(OH_2)CH_3^{2+} and Co([14]-4,11-dieneN_4)(OH_2)CH_3^{2+} are reasonably stable in acidic aqueous solutions, and CH_4 (determined chromatographically) is a product of the Cr^{2+} reduction of both complexes.

$$Co(N_4)(OH_2)CH_3^{2+} + Cr^{2+} + H^+ \longrightarrow Co(N_4)^{2+} + Cr^{3+} + CH_4$$

Both complexes undergo some redox decomposition when their ligand field absorption bands are irradiated; the primary redox yields for irradiations in the low-energy ligand field bands appear to be less than 0.1.[16]

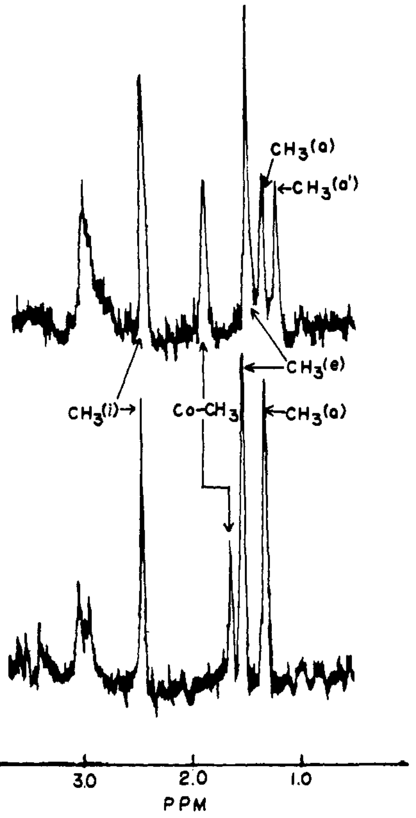

Figure 1. Upper spectrum for Co(N-*meso*-[14]-4,11-dieneN_4)(OH_2)CH_3^+; lower spectrum for Co(N-*dl*-[14]-4,11-dieneN_4)(OH_2)CH_3^+. External TMS used as reference.

$$e^- + CH_3I \longrightarrow \cdot CH_3 + I^- \qquad (3)$$

It has been observed that cobalt(III)–alkyls may be prepared from reactions of cobalt(I)[3] or cobalt(II)[17] with alkyl halides. Taking CH_3I as an example and using literature values for the C–I bond energy,[18] and the I·/I$^-$ standard reduction potential,[8a,19] one can estimate a standard reduction potential of about −1 V for (3). The cobalt(II) complexes employed in this study are all weak reducing agents (SRP for Co(N_4)(OH_2)$_2^{3+,2+}$ is about 0.56 V[20,21]) so direct formation of alkyl radicals from reactions of CH_3X with Co(N_4)$^{2+}$ is not observable. On the other hand, all the Co(N_4)$^+$ complexes are powerful reducing agents (SRP estimated as −0.48,[22] −0.7,[6,23] and −1.0 V,[6,23] respectively, for N_4 = [14]tetraeneN_4, [14]-4,11-dieneN_4, and [14]aneN_4). Thus, in the competition between reaction paths 4 or 5 and 1, the latter path is thermodynamically unfavorable for Co([14]tetraeneN_4)$^+$.

$$Co(N_4)^+ + CH_3I \longrightarrow Co(N_4)(CH_3)I^+ \qquad (4)$$

$$Co(N_4)^+ + CH_3I \longrightarrow Co(N_4)^{2+} + \cdot CH_3 + I^- \qquad (5)$$

In contrast (5) is the observed reaction mode[6] for Co([14]aneN_4)$^+$ (reactions are generally run in nonaqueous solvents which scavenge for ·CH_3) even though the products of (4) are necessarily more stable than the products of (5).

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[15] D. H. Busch, private communication.

[16] For a discussion of the similar photoinertness of related cobalt–methyl complexes, see G. N. Schrauzer, L. P. Lee, and J. W. Silbert, *J. Amer. Chem. Soc.*, **92**, 2997 (1970).

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