

Preparation, Properties, and Crystal Structure of a Novel Series of Macrocyclic Organocobalt Complexes

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The organocobalt complexes $[(H_2O)([14]aneN_4)CoR](ClO_4)_2$ (R = primary alkyl, substituted primary alkyl, and benzyl; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) were prepared photochemically from the corresponding alkylcobaloximes and the cobalt(II) macrocycle. The complexes were characterized by elemental analysis, 1H NMR spectroscopy, a crystal structure determination for R = ethyl, and UV-visible spectroscopy. The ethyl complex, $[(H_2O)([14]aneN_4)CoC_2H_5](ClO_4)_2 \cdot H_2O$, crystallizes in the monoclinic crystal system, space group $P2_1/n$, with four molecules in a unit cell of dimensions $a = 8.901$ (11) Å, $b = 12.254$ (21) Å, $c = 19.637$ (15) Å, and $\beta = 91.76$ (22)°. The data refined to a final value of the weighted R factor of 0.083 based on 1242 independent observations. The complex is hexacoordinated, with the ethyl group and a coordinated molecule of water as axial ligands. All of the complexes are photosensitive and readily decompose to cobalt(II) and carbon-centered radicals when irradiated with visible light. Air-stable acidic aqueous solutions of the alkyl complexes show no sign of decomposition in hours when kept in the dark. The hydroxymethyl complex, prepared by a modified Fenton reaction, is air-sensitive, and the benzyl complex undergoes rapid homolysis of the cobalt-carbon bond.

Introduction

The discovery that coenzyme B_{12} contains a σ cobalt-carbon bond¹ has triggered intense research in the area of organocobalt chemistry. A large number of new organocobalt complexes containing *unsaturated* macrocyclic ligands has been synthesized and characterized.² Complexes with *saturated* macrocycles are, however, still quite rare. In fact, we were able to find only two examples in the literature.³

Prior to the work of Roche and Endicott³ the saturated macrocyclic ligands were thought to impose too much instability on the Co-C bond for such complexes to exist. For example, Busch⁴ lists $Co([14]aneN_4)Cl_2$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) under complexes that "do not form Co-C bonds". The point of view reflected in this classification may have discouraged other synthetic efforts. Green et al.⁵ have presented molecular orbital arguments to rationalize the apparent failure of the cobalt complexes with nonconjugated N_4 -macrocyclic ligands to form Co-C bonds. The predicted effect of the macrocycle saturation is obviously less severe⁶ than originally thought, however, since Endicott and co-workers did succeed³ in the preparation of the two methyl complexes $(H_2O)([14]aneN_4)CoCH_3^{2+}$ and $(H_2O)(Me_6[14]aneN_4)CH_3^{2+}$ ($Me_6[14]aneN_4$ = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). Their attempts to prepare the higher alkyl analogues were, however, unsuccessful.

We now report the preparation of a series of $(H_2O)([14]aneN_4)CoR^{2+}$ complexes, where R = primary alkyl, substituted primary alkyl, and benzyl. The complexes were isolated as solid perchlorates or hexafluorophosphates and characterized by elemental analysis, UV-visible and 1H NMR spectroscopy, and, for R = ethyl, by X-ray crystallography. We particularly wish to emphasize the stability of the primary alkyl compounds (the benzyl and secondary alkyl complexes decompose in solution), a feature that might seem surprising considering earlier statements.⁴ The lack of a suitable method for preparation and not inherent instability is apparently the reason for the situation.

Experimental Section

Syntheses. The organocobalt complexes were prepared by photolyzing acidic aqueous suspensions of appropriate organocobaloximes⁷ in the

presence of $Co([14]aneN_4)(H_2O)_n^{2+}$ ($n = 1$ or 2),⁸ hereafter $(H_2O)LCO^{2+}$. A typical procedure is given below for the methyl complex.

$[(H_2O)LCOCH_3](PF_6)_2$. A 1.74-mL aliquot of 0.576 M $Co(ClO_4)_2$ (1 mmol) was added to 100 mL of a deaerated aqueous solution of 200 mg (1 mmol) of $[14]aneN_4$ (Strem) in a 200-mL Erlenmeyer flask. The solution was stirred for 10 min until the formation of $(H_2O)LCO^{2+}$ was complete. At this point 1 mL of 5 M $HClO_4$ was added, followed by 380 mg (1 mmol) of $(py)(dmgH)_2CoCH_3$.⁷ The stirred suspension was cooled to 0 °C and irradiated by use of a 300-W sun lamp until all the organocobaloxime was consumed. The solid $dmgH_2$ produced was removed by filtration and the yellow filtrate loaded onto a column of Sephadex SP-C25. The column was rinsed with 0.01 M $HClO_4$ and the desired complex eluted with a solution containing 0.4 M $LiClO_4$ + 0.1 M $HClO_4$. The solid $[(H_2O)LCOCH_3](PF_6)_2$ precipitated upon addition of $NaPF_6$. The product was recrystallized twice from warm water and dried in a dessicator overnight. Yield: 100 mg (20%). Anal. Calcd: C, 22.7; H, 4.98; N, 9.62. Found: C, 22.7; H, 5.27; N, 9.35.

Other complexes were prepared by the same procedure from appropriate organocobaloximes, except that saturated $NaClO_4$ was used to precipitate the solid perchlorate salts. The benzyl complex is air-sensitive, and all the manipulations were performed in an argon atmosphere.

Solutions of the hydroxymethyl complex were prepared by oxidizing 0.02 M $(H_2O)LCO^{2+}$ by H_2O_2 (0.01 M) in the presence of 1 M methanol, as described earlier for the pentaquo chromium complex,⁹ and purified by ion exchange.

All the complexes prepared in this work are photosensitive. Irradiation with visible light results in the formation of $(H_2O)LCO^{2+}$ and the carbon-centered radical as observed earlier for the methyl complex.¹⁰

Measurements. UV-visible spectra were recorded by use of a Perkin-Elmer diode array and Cary 219 spectrophotometers. A Nicolet NT-300 instrument was used to record the 1H NMR spectrum of $(H_2O)LCOC_2H_5^{2+}$ in D_2O .

The crystallographic data¹¹ are summarized in Table I. The crystal system and orientation matrix were obtained by use of an automatic indexing program.¹² The position of the cobalt atom was found by the heavy-atom method. The rest of the non-hydrogen atoms were found by use of the direct-methods program DIRDIF.¹³ Positional and anisotropic

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Table I. Crystallographic Data for $\text{CoC}_{12}\text{H}_{27}\text{N}_4\text{O}_9\text{Cl}_2\cdot\text{H}_2\text{O}$

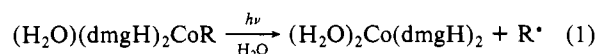
empirical formula	$\text{CoC}_{12}\text{H}_{27}\text{N}_4\text{O}_9\text{Cl}_2\cdot\text{H}_2\text{O}$
Z, molecules/unit cell	4
fw	519.22
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.901 (11)
b, Å	12.254 (21)
c, Å	19.637 (15)
β , deg	91.76 (22)
V, Å ³	2140.8 (49)
cryst size, mm	0.30 × 0.30 × 0.4
cryst color	orange
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	11.03 (empirical cor applied) ^a
ρ_{calc} , g/cm ³	1.61
temp, °C	-20
diffractometer	Syntax P2 ₁
monochromator	graphite cryst
reflcn measd	hkl, hkl̄ (2 octants)
radiation	Mo K α ($\lambda = 0.71069$ Å)
scan rate	ω -scan
scan rate	variable (min. 2.0°/min, max 15.0°/min)
std reflcn	1 measd every 75 reflcn; no significant decay obsd
secondary extinctn param ^b	0.279×10^{-4}
no. of reflcn colld	3751
no. of indep obsd reflcn	1242 ($I > 3\sigma_I$)
max 2 θ , deg	55
min. 2 θ , deg	2
max no. of params refined	209
no. of indep atoms	54
R ^c	0.082
R _w ^c	0.083
R _i ^d	0.057

^a An empirical absorption correction was carried out by use of diffractometer ϕ -scan data and the program ABSN (Karcher, B. A. Ph.D. Dissertation, Iowa State University, 1981). ^b Isotropic parameter applied onto F_c based on: Coppens, P.; Hamilton, W. C. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1970**, *A26*, 71. A polarization factor in the case of a monochromator in the diffracted beam was used. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F)$. ^d Consistency factor for averaging equivalent reflections.

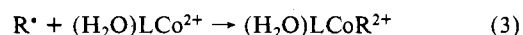
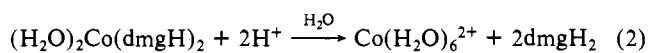
thermal parameters were refined by a combination of block matrix and full matrix in the program ALLS.¹⁴ The hydrogen positions were calculated by assuming ideal geometries with the C-H bond distance set to 1.0 Å. Both the perchlorate groups showed disorder; for one of the groups, the disorder could be modeled.

Results and Discussion

The preparation of the organocobalt complexes is based on the known photochemistry of organocobaloximes (eq 1).^{2,15-18}



Photohomolysis yields carbon-centered radicals and $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$. The latter decomposes in acidic aqueous solution to Co^{2+} and dmgH_2 (eq 2).¹⁹ The rapidity of the demetalation at



high $[\text{H}^+]$ minimizes recapture of R^\bullet by $(\text{H}_2\text{O})_2\text{Co}(\text{dmgH})_2$ and allows capture of the radical by $(\text{H}_2\text{O})\text{LCo}^{2+}$ (eq 3)³ to give the organocobalt complex. The photochemical steps and the capture

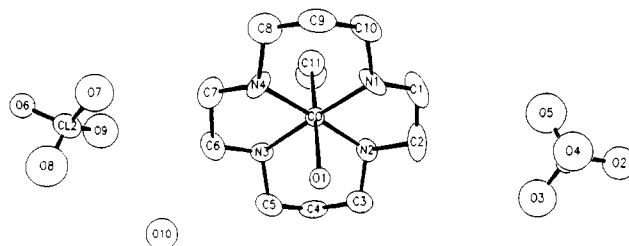


Figure 1. ORTEP drawing of the molecular structure of $[(\text{H}_2\text{O})([14]\text{-aneN}_4)\text{CoC}_2\text{H}_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$. Hydrogen atoms are not included. The thermal ellipsoids are drawn at 50% probability.

Table II. Selected Bond Distances (Å) for $[(\text{H}_2\text{O})([14]\text{-aneN}_4)\text{CoC}_2\text{H}_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$

Co-O1	2.20 (1)	Co-N1	2.00 (2)
Co-N2	1.98 (1)	Co-N3	1.98 (1)
Co-N4	1.98 (1)	Co-Cl1	1.99 (2)

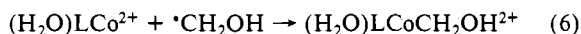
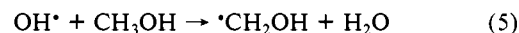
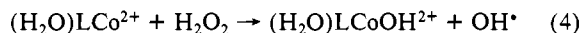
Table III. Selected Bond Angles (deg) for $[(\text{H}_2\text{O})([14]\text{-aneN}_4)\text{CoC}_2\text{H}_3](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$

O1-Co-N1	84.9 (0.5)	O1-Co-N2	90.7 (0.5)
O1-Co-N3	92.5 (0.5)	O1-Co-N4	85.9 (0.5)
O1-Co-Cl1	175.7 (0.7)	N1-Co-N2	86.7 (0.6)
N1-Co-N3	177.3 (0.6)	N1-Co-N4	93.7 (0.6)
N1-Co-Cl1	91.9 (0.8)	N2-Co-N3	92.9 (0.6)
N2-Co-N4	176.5 (0.6)	N2-Co-Cl1	92.1 (0.7)
N3-Co-N4	86.6 (0.6)	N3-Co-Cl1	90.8 (0.7)
N4-Co-Cl1	91.3 (0.7)	Co-N1-C1	106.4 (1.2)
Co-N1-C10	119.9 (1.2)	Co-N2-C3	116.2 (1.2)
Co-N2-C2	106.2 (1.1)	Co-N3-C5	118.3 (1.1)
Co-N3-C6	106.7 (1.0)	Co-N4-C8	119.1 (1.2)
Co-N4-C7	108.2 (1.1)	Co-Cl1-Cl2	122.3 (1.6)

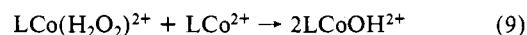
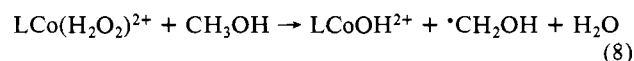
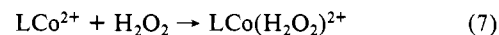
of the radical are quite efficient, yielding nearly quantitative amounts of $(\text{H}_2\text{O})\text{LCoR}^{2+}$ in solution. Significant losses occur later in the purification and isolation stages.

In the original preparation of the methyl complex, the radical was generated by photolysis of $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3^{2+}$.³ The low yields of the methyl complex and the inability to prepare complexes with other alkyl groups may be related to the low absorption coefficients of $(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3^{2+}$ relative to those of the product organocobalt complex and the ready photolysis of the latter.¹⁰ The yields were better in a preparation using methylhydrazine as a methylating agent for $(\text{H}_2\text{O})\text{LCo}^{2+}$.^{10b}

The hydroxymethyl complex was prepared by the reaction of $(\text{H}_2\text{O})\text{LCo}^{2+}$ with H_2O_2 in the presence of methanol.^{9,20} The reaction scheme is possibly given by eq 4-6, although the very



low yields of the hydroxymethyl complex indicate that other reactions occur as well. An alternative mechanism is shown in eq 7-9 followed by reaction 6. The latter mechanism is based



on the recently advanced idea of the involvement of the metal- H_2O_2 complexes in the reactions of reduced metals with H_2O_2 .²¹ The low yields of the organometallic complex are consistent with the unfavorable competition between reactions 8 and 9. Further experiments with this complex are in progress.

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Table IV. Atom Coordinates ($\times 10^4$)^a and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$)^b for $[(\text{H}_2\text{O})([14]\text{aneN}_4)\text{CoC}_2\text{H}_5](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

atom	x	y	z	U_{eq}
Co	4717 (3)	2971 (2)	6418 (1)	26 (1)
N1	3687 (19)	3793 (12)	7149 (8)	45 (10)
N2	6087 (19)	2403 (11)	4149 (7)	40 (9)
N3	5684 (17)	2096 (11)	5705 (6)	37 (8)
N4	3279 (17)	3457 (13)	5692 (7)	37 (9)
C1	4710 (25)	3789 (19)	7740 (10)	57 (14)
C2	5359 (25)	2681 (20)	7818 (10)	60 (14)
C3	6415 (25)	1237 (15)	7127 (11)	49 (13)
C4	7204 (27)	920 (14)	6464 (11)	55 (14)
C5	6097 (25)	935 (15)	5865 (10)	49 (13)
C6	4615 (20)	2100 (16)	5086 (9)	45 (12)
C7	3939 (23)	3217 (16)	5023 (9)	50 (13)
C8	2642 (25)	4588 (17)	5723 (11)	62 (15)
C9	1909 (25)	4775 (15)	6406 (12)	60 (14)
C10	3007 (25)	4834 (16)	6998 (10)	50 (14)
C11	4820 (7)	2733 (5)	9828 (3)	64 (4)
C12	5114 (7)	2192 (4)	2971 (3)	55 (3)

^aThe estimated standard deviations in the parentheses are for the least significant digit. ^b $U_{\text{eq}} = 1/3 \sum U_{ij} a_i^* a_j^* a_{ij} \times 10^3$, where the temperature factors are defined as $\exp(-2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij})$.

X-ray Crystal Structure of $[(\text{H}_2\text{O})([14]\text{aneN}_4)\text{CoC}_2\text{H}_5](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. The structure of the complex is represented by the ORTEP drawing shown in Figure 1. The cobalt(III) ion is coordinated to the four nitrogen atoms of the macrocycle and to two axial ligands, an ethyl group, and a coordinated water molecule. The macrocyclic ligand adopts the stereochemically favored chair configuration with a coplanar arrangement of the four nitrogens. The cobalt atom is displaced towards the ethyl group by 0.05 Å. The complex contains an additional molecule of water hydrogen bonded to the coordinated water. The bond distances, bond angles, and positional and isotropic thermal parameters are given in Tables II–IV. The bond distances and angles in the macrocyclic ligand, as well as the Co–N bond distances and N–Co–N angles in the five- and six-membered rings are, within error, identical with those found in the parent Co(II) complex, $\text{Co}([14]\text{aneN}_4)(\text{ClO}_4)_2$.⁸ The Co–C bond length, 1.99 (2) Å, is “normal” for an ethylaquacobalt(III) complex,^{2,22,23} indicating that the effect of the macrocycle saturation on the Co–C bond dissociation energy, BDE, is perhaps quite moderate. An increase in the Co–C bond length would be expected for a complex with a BDE significantly smaller than that of the other ethylcobalt complexes.² In fact, the Co–C bond length is, within error, identical with that found in the methyl analogue, $(\text{H}_2\text{O})\text{Co}([14]\text{aneN}_4)\text{CH}_3^{2+}$ (1.99 Å). The Co–OH₂ distance (2.20 (1) Å) in $(\text{H}_2\text{O})\text{Co}([14]\text{aneN}_4)\text{C}_2\text{H}_5^{2+}$ is also comparable to that in the methyl analogue (2.16 Å)²⁴ but significantly longer than that in related $(\text{H}_2\text{O})_2\text{CoL}^{3+}$ complexes (1.91 Å).²⁵ The long Co–O bond is consistent with a strong trans effect of the alkyl group.^{2,24}

¹H NMR and UV–Visible Spectra. The ¹H NMR spectrum of $(\text{H}_2\text{O})\text{LCoC}_2\text{H}_5^{2+}$ in D₂O features a triplet (δ 0.333) and a quadruplet (δ 1.22) in a relative ratio of 3:2, clearly showing the presence of the ethyl group.

The visible spectra of all the alkyl complexes, Table V, exhibit two weakly allowed transitions of approximately equal intensity at $\lambda = 460\text{--}490$ nm and $\lambda = 360\text{--}380$ nm. The spectrum of the methyl complex agrees well with that reported previously.³ The low-energy band of the benzyl derivative is red shifted by ~30 nm compared to those of the alkyls. The second band is apparently obscured by the intense charge-transfer absorption with a maximum at $\lambda = 310$ nm. A similar effect of the benzyl group on

Table V. UV–Visible Spectral Data for $(\text{H}_2\text{O})([14]\text{aneN}_4)\text{CoR}^{2+}$

R	color ^a	λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	
		λ_1 (ϵ_1)	λ_2 (ϵ_2)
CH ₃	yellow-brown	476 (81)	368 (106)
		478 (81) ^b	367 (104) ^b
C ₂ H ₅	red-brown	490 (70.7)	381 (115)
C ₃ H ₇	red-brown	490 (67.9)	380 (110)
CH ₂ Cl	gold	468 (94.6)	357 (98.3)
CH ₂ Br	gold	470 (109)	358 (122)
CH ₂ OH ^c		470	360
CH ₂ OCH ₃	yellow	464 (77.6)	360 (95.3)
CH ₂ Ph	purple	512 (94)	

^aThe color of the perchlorate salts varies somewhat with the size of the crystals and the dryness of the sample. ^bReference 3b. ^cPrepared in solution only.

the UV–visible spectra of some organochromium²⁶ and organonickel²⁷ complexes has been observed earlier.

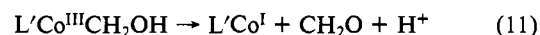
A detailed spectral analysis for $(\text{H}_2\text{O})\text{LCoCH}_3^{2+}$ in terms of a three-center bonding model has been published.¹⁰ The similarity of the spectral data in Table V indicates comparable orbital energy levels for all the alkyl complexes.

Reactivity. The complexes $[(\text{H}_2\text{O})\text{LCoCH}_3](\text{PF}_6)_2$ and $[(\text{H}_2\text{O})\text{LCoR}](\text{ClO}_4)_2$ (R = C₂H₅, C₃H₇, CH₂Cl, CH₂Br, CH₂OCH₃) are stable for months in the solid state. Acidic aqueous solutions are air-stable and show no sign of decomposition within several hours of preparation. The stability on longer time scales has not been checked.

Solutions of $(\text{H}_2\text{O})\text{LCoCH}_2\text{C}_6\text{H}_5^{2+}$ turn cloudy within minutes of preparation and develop a strong odor of bibenzyl, owing to the ready homolysis of the Co–C bond (eq 10).²⁸ Externally added $(\text{H}_2\text{O})\text{LCoCH}_2\text{C}_6\text{H}_5^{2+} \rightleftharpoons (\text{H}_2\text{O})\text{LCo}^{2+} + \cdot\text{CH}_2\text{C}_6\text{H}_5$ (10)

$(\text{H}_2\text{O})\text{LCo}^{2+}$ stabilizes these solutions by displacing the equilibrium of eq 10 to the left.

$(\text{H}_2\text{O})\text{LCoCH}_2\text{OH}^{2+}$ is the first hydroxymethylcobalt(III) complex prepared to date. The highly unsaturated macrocyclic ligands L', used earlier,^{29–31} rendered the hydroxymethyl complexes unstable toward internal electron transfer (eq 11). The fully



saturated ligand [14]aneN₄ used in this work strongly reduces the stability of the Co(I) state^{3a} and rules out reaction 11 as a possible decomposition pathway. Solutions of $(\text{H}_2\text{O})\text{LCoCH}_2\text{OH}^{2+}$ readily react with oxidants such as Fe³⁺ and O₂.

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Registry No. $[(\text{H}_2\text{O})\text{LCoCH}_3](\text{PF}_6)_2$, 111323-54-7; $[(\text{H}_2\text{O})\text{LCoC}_2\text{H}_5](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, 111323-57-0; $[(\text{H}_2\text{O})\text{LCoC}_2\text{H}_5](\text{ClO}_4)_2$, 111323-56-9; $[(\text{H}_2\text{O})\text{LCoC}_3\text{H}_7](\text{ClO}_4)_2$, 111323-59-2; $[(\text{H}_2\text{O})\text{LCoCH}_2\text{Cl}](\text{ClO}_4)_2$, 111323-61-6; $[(\text{H}_2\text{O})\text{LCoCH}_2\text{Br}](\text{ClO}_4)_2$, 111323-63-8; $[(\text{H}_2\text{O})\text{LCoC}_6\text{H}_5\text{OH}](\text{ClO}_4)_2$, 111348-84-6; $[(\text{H}_2\text{O})\text{LCoCH}_2\text{OCH}_3](\text{ClO}_4)_2$, 111323-65-0; $[(\text{H}_2\text{O})\text{LCoCH}_2\text{Ph}](\text{ClO}_4)_2$, 111323-67-2; (py)(dmgH)₂CoCH₃, 23642-14-0; (py)(dmgH)₂CoC₂H₅, 25360-57-0; (py)(dmgH)₂CoC₃H₇, 28182-24-3; (py)(dmgH)₂CoCH₂Cl, 35654-76-3; (py)(dmgH)₂CoCH₂Br, 35654-77-4; (py)(dmgH)₂CoCH₂OCH₃, 35654-83-2; (py)(dmgH)₂CoCH₂Ph, 27860-79-3; $(\text{H}_2\text{O})\text{LCo}^{2+}$, 64784-52-7; $\text{Co}(\text{ClO}_4)_2$, 13455-31-7; [14]aneN₄, 295-37-4.

Supplementary Material Available: Tables SI–SV, listing all angles and distances, thermal parameters, and the derived hydrogen positions (5 pages); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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