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Cobalt(I), -(II), and -(III) Complexes of a Tetraaza 14-Membered Macrocycle, 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (L). Crystal and Molecular Structures of $[CoL(CO)]ClO_4$, *trans*-$CoLCl_2$, and *cis*-$[CoL(CO_3)]ClO_4$

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The carbon monoxide adduct of the cobalt(I) title macrocycle has been prepared via reaction of CoL^+ with CO_2 and with CO and isolated as a perchlorate salt: IR (Nujol) ν_{CO} 1916 cm^{-1}; UV-vis (CH_3CN, λ_{max} (ϵ)) 310 nm (3900 M^{-1} cm^{-1}), 430 sh (770), 510 sh (360), 1040 (240). In CH_3CN solvent its stability constant is $\sim 3 \times 10^8$ M^{-1} at 25 °C. Structures of the square-pyramidal carbonyl complex and two other complexes of the title macrocycle have been determined from single-crystal X-ray diffraction data collected with use of Mo Kα radiation. Crystallographic data: $[CoL(CO)](ClO_4)$ (**1**), $C2$, $a = 15.362$ (3) Å, $b = 7.580$ (5) Å, $c = 9.611$ (3) Å, $\beta = 108.91$ (2)°, $V = 1059$ (1) Å^3, $Z = 2$ ($R = 0.057$, $R_w = 0.069$); *N-meso,trans*-$CoLCl_2$ (**2**), $Pbca$, $a = 11.570$ (3) Å, $b = 12.695$ (3) Å, $c = 13.309$ (2) Å, $V = 1954$ (1) Å^3, $Z = 4$ ($R = 0.075$, $R_w = 0.070$); *cis*-$[CoL(CO_3)]ClO_4$ (**3**), $C2$, $a = 15.072$ (5) Å, $b = 7.603$ (4) Å, $c = 9.703$ (3) Å, $\beta = 109.74$ (3)°, $V = 1047$ (1) Å^3, $Z = 2$ ($R = 0.033$, $R_w = 0.048$). The three structures contain square-pyramidal, five-coordinate cobalt(I) (**1**), strongly axially distorted "six"-coordinate cobalt(II) (**2**), and six-coordinate cobalt(III) with L occupying cis-coordination positions (**3**). They thus provide a striking illustration of the adaptability of L to a variety of coordination numbers and oxidation states.

Introduction

Since Curtis' template synthesis of the title macrocycle L = $(CH_3)_6[14]$-diene[2] the properties and structures of metal complexes of the macrocycle have proven to be of continuing interest. Four-, five- and six-coordinate complexes of the tetradentate ligand may form, depending upon the nature of the central metal and the conditions.[2-6] In the six-coordinate complexes either trans or cis complexes may be formed. In addition, the two amine nitrogens are chiral. Thus, for planar coordination of the macrocycle (e.g. *trans*-$CoL(X)_2$) there are two diastereomers, N-meso and N-racemic. The factors that determine the relative stabilities of the various isomers and their reactivities remain of considerable interest and are being addressed through molecular mechanics calculations.[7]

Cobalt $(CH_3)_6[14]$-diene complexes have been the focus of mechanistic studies of substitution reactions[8] (cobalt(III)) and both inner- and outer-sphere electron-transfer[9,10] reactions (cobalt(II) and -(III)). In addition they play a versatile role in the binding and activation of small molecules. CoL^{2+} binds O_2,[11] alkylcobalt complexes $CoL(R)H_2O^{2+}$ [12] provide a vitamin B_{12} model, and CoL^+ [13] reduces water[14] to H_2 and CO_2 to CO.[15] In the course of our studies[16] of the last reaction we characterized the reaction of CoL^+ with CO. We also obtained good crystals of the CO adduct *N-rac*-$[CoL(CO)]ClO_4$ (**1**) and *N-meso,-trans*-$CoLCl_2$ (**2**) and *N-rac,cis*-$[CoL(CO_3)]ClO_4$ (**3**). Here we describe the results of our studies of the CoL^+–CO system and the crystal and molecular structures of the three cobalt complexes. The three structures provide a striking illustration of the adaptability of the $(CH_3)_6[14]$-diene ligand and of the natures of the coordination geometries of three oxidation states of cobalt.

Experimental Section

Materials. The crystals of $[CoL(CO)]ClO_4$ and $CoLCl_2$ used in the structure determinations were actually grown from CoL^+–CO_2 reaction mixtures.

Isolation of 1. $[CoL(H_2O)](ClO_4)_2$[6] (0.2 g) was placed in a Schlenk tube, and 4 g of Na(Hg) (0.5% Na) was placed in a side arm of the tube, separated by a medium-porosity frit. The tube was evacuated to eliminate O_2 and to dehydrate the cobalt(II) salt. After 3 h, 6 mL of CH_3CN was added to the cobalt complex by distillation from a reservoir of ultrapure CH_3CN[16] stored over CaH_2 or molecular sieve 3A. The vessel was tilted to mix the Na(Hg) and Co(II) solution and shaken for 20 min; then the Na(Hg) was decanted from the deep blue Co(I) solution, the side arm containing the Na(Hg) was removed by flame sealing, and research grade (99.998%) CO_2 (1 atm) was introduced. Ultrapure THF (6 mL) was added to the purple solution of $CoL(CO_2)^+$, and the vessel was sealed and then stored at −5 °C. After 5 days the crystalline solid produced was isolated under CO_2 and dried under a stream of CO_2; orange $CoL(CO)ClO_4$ crystals were manually isolated from purple $[CoL]_2(CO_2H)(ClO_4)_3$ crystals.[16] IR (Nujol) for $[CoL(CO)]ClO_4$: ν_{NH} 3255 cm^{-1}; ν_{CO} 1916 cm^{-1} ($\nu_{^{13}CO}$, 1869 cm^{-1}; $\nu_{C^{18}O}$, 1871 cm^{-1}); $\nu_{C=N}$ 1653 cm^{-1}.

Solid $[CoL(CO)]ClO_4$ was also prepared directly from CoL^+ and CO. A CoL^+ solution in CH_3CN was prepared as above. After removal of the Na(Hg), research grade CO was added; the deep blue solution immediately became orange, and orange solid started to form. The solid was collected on a frit and dried under a stream of CO in a CO-filled glovebag. For solution studies of the carbonyl complex, CoL^+ was generated from CoL^{2+} as above and CO was introduced after decanting the Na(Hg). UV-vis-near-IR [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 310 (3900), 430 sh (770), 510 sh (360), 1040 (240).

Isolation of 2. $[CoL(H_2O)_2]Cl_2$ was prepared by anion exchange of the ClO_4^- salt. A 120-mg sample of $[CoL(H_2O)_2]Cl_2$ in 6 mL of CH_3CN was reduced slowly by Na(Hg), precipitating NaCl. The cloudy reddish solution of $CoL(CO_2)^+$ decomposed overnight, and well-shaped tan crystals of $CoLCl_2$ formed at 5 °C.

Isolation of 3. A small amount of pink solid, isolated from a $CoL(CO_2)^+$ solution that had been slowly oxidized by air, was identified by UV-vis spectroscopy as $CoL(CO_3)ClO_4$. The crystals used in the dif-

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Table I. Crystallographic Data for **1**–**3** at 23 °C

	1	**2**	**3**
formula	$[Co(N_4C_{16}H_{32})(CO)](ClO_4)$	$Co(N_4C_{16}H_{32})Cl_2$	$[Co(N_4C_{16}H_{32})(CO_3)](ClO_4)$
a, Å	15.362 (3)	11.570 (3)	15.072 (5)
b, Å	7.580 (5)	12.695 (3)	7.603 (4)
c, Å	9.611 (3)	13.309 (2)	9.703 (3)
β, deg	108.91 (2)		109.74 (3)
V, Å^3	1059 (1)	1954 (1)	1047 (1)
Z	2	4	2
fw	466.85	410.29	499.09
space group	$C2$	$Pbca$	$C2$
λ, Å	0.709 26	0.709 26	0.709 26
ρ_{calcd}, g cm^{-3}	1.464	1.392	1.584
μ, cm^{-1}	10.05	12.3	10.30
transmission coeff: max, min	0.8569, 0.7369	0.8032, 0.7968	0.7576, 0.6882
R, R_w	0.057, 0.069	0.075, 0.070	0.033, 0.048

Table II. Final Positional Parameters for the Non-Hydrogen Atoms in $[Co(N_4C_{16}H_{32})(CO)]ClO_4$[a]

atom	x	y	z
Co	0.0000	0.0000	0.0000
C1	0.0000	0.2370 (14)	0.0000
O1	0.0000	0.3831 (13)	0.0000
N1	0.0465 (3)	−0.0805 (8)	0.2276 (6)
C2	−0.0270 (5)	−0.1936 (11)	0.2487 (7)
C3	−0.1188 (5)	−0.1072 (12)	0.1734 (7)
N4	−0.1261 (4)	−0.0688 (8)	0.0202 (6)
C5	−0.2035 (4)	−0.0690 (9)	−0.0813 (7)
C5′	−0.2948 (5)	−0.0962 (12)	−0.0589 (9)
C6	−0.2054 (4)	−0.0291 (10)	−0.2374 (7)
C7	−0.1426 (4)	−0.1492 (9)	−0.2938 (7)
C7′	−0.1733 (6)	−0.1346 (14)	−0.4623 (8)
C7″	−0.1497 (6)	−0.3385 (10)	−0.2519 (9)
Cl	0.0000	0.3185 (4)	0.5000
O11	0.0000	0.497 (5)	0.5000
O11′	−0.061 (3)	0.456 (4)	0.446 (6)
O12	0.014 (3)	0.285 (3)	0.360 (2)
O13	−0.0833 (19)	0.335 (9)	0.471 (6)
O14	−0.039 (3)	0.183 (5)	0.422 (4)

[a] O11 and O11′ have occupancy factors of 0.25 and O12, O13, and O14 occupancy factors of 0.5. Numbers in parentheses are errors in the last significant digit(s).

fraction study were grown by gradually cooling an aqueous supersaturated solution of *cis*-$[CoL(CO_3)]ClO_4$, prepared from the reaction of $CoL(ClO_4)_2$ with $K_3Co(CO_3)_3$.[4] ^1H NMR (D_2O, ppm relative to DSS): imine CH_3, 2.179; eq CH_3, 1.411; ax CH_3, 1.010; three multiplets, CH_2 ring skeleton, 3.6, 3.1, and 2.8. UV–vis [H_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 513 (121), 370 (141) [cf. lit.[4] 500 (121), 349 (135)]. IR (Nujol): ν_{NH} 3255 cm^{-1}; ν_{CO} 1660 br, 1635 sharp cm^{-1}.

Instrumentation. IR spectra were determined on a Nicolet MX-1 FTIR spectrometer, NMR spectra were obtained on a Bruker AM-300 spectrometer, and UV–vis–near-infrared spectra were obtained on a Cary 17 or 210 spectrophotometer or an HP 8451 A diode array spectrophotometer.

Collection and Reduction of the X-ray Diffraction Data. 1. The CO adduct $[Co(N_4C_{16}H_{32})CO]ClO_4$ crystallized from CH_3CN–THF as orange prisms. A crystal 0.17 × 0.27 × 0.50 mm, with faces (101), ($\bar{1}0\bar{1}$), ($10\bar{1}$), ($\bar{1}01$), and (010), ($0\bar{1}0$), was coated with petroleum jelly and mounted in a Lindemann glass capillary. The diffraction data indicated monoclinic symmetry and systematic absences hkl, $h + k = 2n + 1$, consistent with the space groups $C2$ (No. 5, C_2^3),[17a] Cm (No. 8, C_s^3),[17b] and $C2/m$ (No. 12, C_{2h}^3).[17c]

2. The cobalt(II) complex $Co(N_4C_{16}H_{32})Cl_2$ crystallized from CH_3CN–THF as tan-yellow prisms. A crystal 0.20 × 0.20 × 0.35 mm with faces ($\bar{1}\bar{1}0$), (110), (001), ($00\bar{1}$), and ($\bar{1}10$), ($1\bar{1}0$) was selected, coated with petroleum jelly, and mounted in a capillary. The diffraction data indicated orthorhombic symmetry and systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, consistent with the space group $Pbca$ (No. 61, D_{2h}^{15}).[17d]

Table III. Final Positional Parameters for the Non-Hydrogen Atoms in $Co(N_4C_{16}H_{32})Cl_2$[a]

atom	x	y	z
Co	0.0000	0.0000	0.0000
Cl1	0.06799 (18)	0.16327 (18)	0.12191 (17)
N1	0.1441 (5)	−0.0270 (4)	−0.0755 (5)
C2	0.1662 (6)	0.0664 (7)	−0.1379 (6)
C3	0.0539 (6)	0.0982 (6)	−0.1852 (6)
N4	−0.0331 (5)	0.1012 (5)	−0.1041 (4)
C5	−0.1159 (6)	0.1682 (7)	−0.1087 (6)
C5′	−0.1339 (7)	0.2446 (8)	−0.1939 (6)
C6	−0.2002 (7)	0.1780 (7)	−0.0228 (6)
C7	−0.2459 (6)	0.0783 (6)	0.0255 (5)
C7′	−0.2989 (7)	0.0068 (8)	−0.0525 (6)
C7″	−0.3379 (7)	0.1078 (8)	0.1024 (7)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table IV. Final Positional Parameters for the Non-Hydrogen Atoms in $[Co(N_4C_{16}H_{32})CO_3]ClO_4$[a]

atom	x	y	z
Co	0.0000	0.0000	0.0000
N1	−0.04400 (13)	0.0086 (5)	−0.21614 (19)
C2	0.0353 (2)	−0.0618 (5)	−0.2575 (3)
C3	0.0798 (2)	−0.2177 (4)	−0.1626 (3)
N4	0.08970 (19)	−0.1758 (3)	−0.0100 (3)
C5	0.14653 (18)	−0.2684 (4)	0.0934 (3)
C5′	0.2066 (2)	−0.4121 (5)	0.0662 (4)
C6	0.1564 (2)	−0.2413 (5)	0.2504 (3)
C7	0.1420 (2)	−0.0566 (5)	0.3002 (3)
C7′	0.1582 (3)	−0.0620 (6)	0.4651 (3)
C7″	0.2109 (2)	0.0724 (6)	0.2732 (4)
O1	0.06946 (17)	0.2081 (3)	−0.0072 (3)
C1	0.0000	0.3084 (6)	0.0000
O2	0.0000	0.4681 (5)	0.0000
Cl	0.0000	−0.5957 (2)	−0.5000
O11	0.0007 (16)	−0.4160 (10)	−0.5212 (10)
O12	0.0651 (8)	−0.6708 (13)	−0.3840 (11)
O13	0.0676 (11)	−0.625 (2)	−0.587 (2)

[a] The perchlorate anion is disordered; O11 and O13 have site occupancy factors of 0.5. Numbers in parentheses are errors in the last significant digit(s).

Table V. Bond Distances (Å) and Angles (deg) for $[Co(N_4C_{16}H_{32})(CO)]ClO_4$ (**1**)[a]

Cobalt–Ligand			
Co–N1	2.158 (5)	Co–C1	1.797 (10)
Co–N4	2.075 (5)		
N1–Co–N4	81.2 (2)	N1–Co–N11	90.6 (2)
N1–Co–C1	106.4 (2)	N4–Co–C1	104.2 (2)
N1–Co–N8	147.1 (2)	N4–Co–N11	150.9 (2)
Carbon Monoxide			
C1–O1	1.107 (14)	Co–C1–O1	180.0

[a] N8, N11, and C14 are related to N1, N4, and C7 by the symmetry operation $-x$, y, $-z$.

3. The cobalt(III) carbonate complex $[Co(N_4C_{16}H_{32})(CO_3)]ClO_4$ crystallized from water as red prisms. A crystal 0.33 × 0.33 × 0.53 mm with faces (100), ($\bar{1}00$), ($\bar{1}01$), ($10\bar{1}$), and (010), ($0\bar{1}0$) was mounted on a glass fiber and used for data collection. The crystal exhibited systematic absences hkl, $h + k = 2n + 1$, consistent with the space groups $C2$ (No. 5, C_2^3),[17a] Cm (No. 8, C_s^3),[17b] and $C2/m$ (No. 12, C_{2h}^3).[17c]

Crystal data and details of data collection are given in Table I, and, in detail, in Table S15 (supplementary material).

Determination and Refinement of the Structures. All three structures were solved by the standard Patterson, heavy-atom technique. Anisotropic temperature parameters were used for all of the non-hydrogen atoms. The hydrogen atoms were placed at calculated positions (X–H = 0.95 Å) and allowed to "ride" on the C or N atom to which they were bound.[18] A common isotropic temperature factor for all of the hydrogens

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Table VI. Cobalt-Ligand Bond Distances (Å) and Angles (deg) for $Co(N_4C_{16}H_{32})Cl_2$ (**2**)[a]

Co-N1	1.976 (6)	Co-Cl1	2.747 (2)
Co-N4	1.929 (6)		
N1-Co-N4	85.3 (2)	N1-Co-Cl1′	79.1 (1)
N1-Co-N11	94.6 (2)	N4-Co-Cl1	88.8 (2)
N1-Co-Cl1	100.9 (1)	N4-Co-Cl1′	91.2 (1)

[a] N8, N11, C9, and C14 are related to N1, N4, C2, and C7 by the center of inversion at (0, 0, 0).

Table VII. Bond Distances (Å) and Angles (deg) for $[Co(N_4C_{16}H_{32})(CO_3)]ClO_4$ (**3**)[a]

	Cobalt-Ligand		
Co-N1	1.976 (2)	Co-O1	1.912 (2)
Co-N4	1.927 (3)		
N1-Co-N4	87.6 (2)	N4-Co-O1	99.8 (1)
N1-Co-O1	85.7 (1)	N4-Co-N11	92.2 (1)
N1-Co-N8	176.2 (1)	N4-Co-O1′	168.0 (1)
N1-Co-N11	95.0 (1)	O1-Co-O1′	68.3 (1)
N1-Co-O1′	91.2 (1)		
	Carbonate		
O1-C1	1.316 (3)	C1-O2	1.214 (5)
O1-C1-O2	125.4 (2)	Co-O1-C1	91.3 (2)
O1-C1-O1′	109.9 (4)		

[a] N8, C14, and O1′ are related to N1, C7, and O1, respectively, by −*x*, *y*, −*z* and O11′, O12′, and O13′ to O11, O12, and O13 by −*x*, *y*, 1 − *z*.

was included in the refinement (U = 0.063 (6) Å^2 for **1**, 0.065 (3) Å^3 for **2**, and 0.050 (3) Å^2 for **3**). The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinement.[18]

For **1** and **3**, space group $C2$ was assumed, and the successful solution and refinement of the structures indicates that this was the correct choice. At the end of the refinement the absolute configuration of the models were checked for **1** and **3**; the models yielding the lower R_w values[19] are reported here.

Final non-hydrogen atomic positional parameters for the three structures are given in Tables II–IV, and selected interatomic distances and angles are listed in Tables V–VII. The atom-numbering scheme used for the macrocycle is shown in Figure 1. Additional material is provided in Tables S1–S15 (supplementary material).

Results and Discussion

The synthesis of the cobalt(I) carbonyl complex **1** has not been reported previously. We first prepared **1** from CoL^+ and CO_2: a concentrated violet solution of the carbon dioxide adduct[16] $CoL(CO_2)^+$ in THF–CH_3CN was left at −5 °C for 5 days. Crystals of **1** and a CO_2-bridged dimer[16] formed over this time. Under these conditions, the bound CO in **1** is produced from the reduction of CO_2 by CoL^+:

$$3CoL^+ + CO_2 \rightarrow 2CoL^{2+} + CoL(CO)^+ \qquad (1)$$

The fact that **1** can be isolated under these conditions is probably a consequence of the low solubility of this perchlorate salt and the high concentrations in the solution. In contrast, the CO complex is not observed when ≤6 mM $CoL(CO_2)^+$ acetonitrile solutions are monitored by UV–vis spectroscopy during the course of the CO_2-reduction reaction; under such conditions only uncomplexed CO and CoL^{2+} are formed.[16] These observations suggest that formation of $CoL(CO)^+$ under the latter CO_2-reduction conditions is suppressed by the high CO_2 concentration (eq 2 and 3) with $K_3 \approx 10^8$ M^{-1}. To test this hypothesis, we carried

$$CoL^+ + CO_2 \rightleftharpoons CoL(CO_2)^+ \qquad (2)$$

$$CoL^+ + CO \rightleftharpoons CoL(CO)^+ \qquad (3)$$

out two experiments to better evaluate K_3, and we determined the solubility of CO in acetonitrile (0.8 × 10^{-2} M at 25 °C, 1 atm of CO). In the first experiment, 4 mL of a 2 × 10^{-3} M solution of $CoL(CO)^+$ was prepared from CoL^+ and CO in acetonitrile; then CO and solvent were evacuated from the cell. Fresh solvent (4 mL) was distilled into the cell, and the spectrum of the solution was determined. Little CO dissociation occurred (<1%), but the free CoL^+ was readily detected because of its high molar absorptivity at 678 nm. From the CoL^+ and $CoL(CO)^+$ absorbances and with the assumption of CO equilibration with the 24-mL gas space, K_3 = 2.3 × 10^8 M^{-1} is obtained. In the second experiment eq 2 and 3 were used: As above, $CoL(CO)^+$ was prepared, evacuated to dryness, and treated with freshly distilled solvent. Then CO_2 (1 atm) was introduced and the spectrum measured. As expected, a greater extent of CO dissociation occurred (~30%) than in the previous experiment. From the relative intensities of the $CoL(CO_2)^+$ band at 530 nm[16] and the $CoL(CO)^+$ band at 1040 nm, the relative gas solubilities, and the fact that K_2 = 1.2 × 10^4 M^{-1} (CH_3CN, 25 °C),[16] the $CoL(CO)^+$ stability constant K_3 = 4.1 × 10^8 M^{-1} was obtained. Thus, we conclude that $K_3 \approx 3 \times 10^8$ M^{-1} in CH_3CN. In aqueous solutions[20] $K_2 \approx K_3 \approx 10^8$

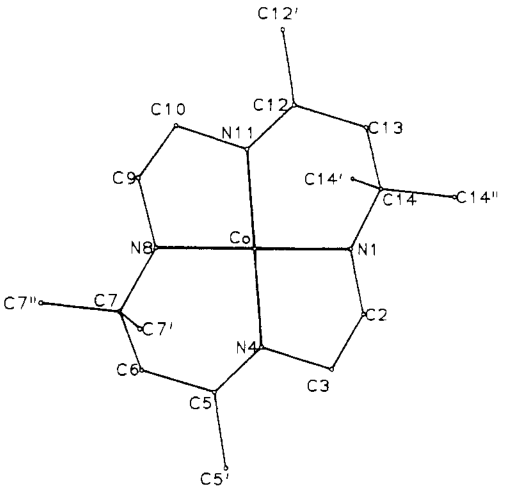

Figure 1. Numbering scheme used for the ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (L). N4 and N11 are imine nitrogens.

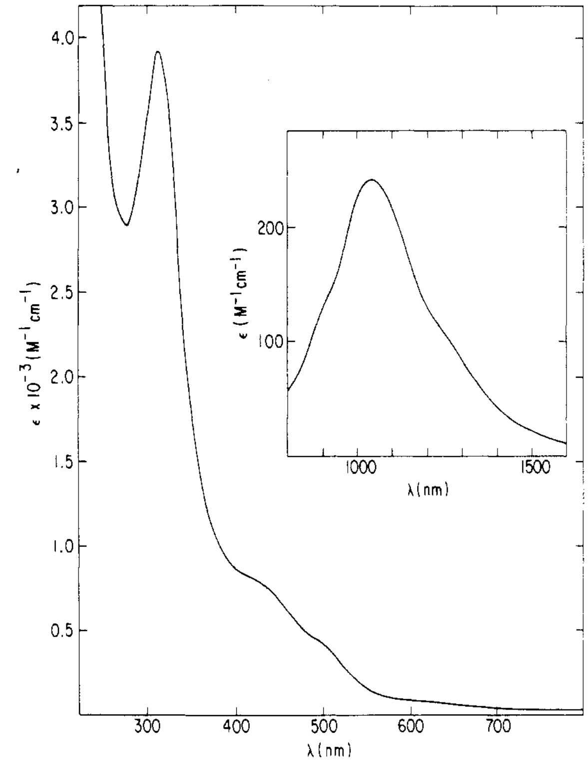

Figure 2. Absorption spectrum of $CoL(CO)^+$ in CH_3CN.

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M^{-1}. For NiL^+, the CO binding constant $4.7 \times 10^4\ M^{-1}$ has been reported for DMF as solvent.[21]

The spectral changes that take place when deep blue CH_3CN or DMF solutions of CoL^+ are exposed to CO (Figure 2) are dominated by the loss of the intense MLCT band[13] of CoL^+. The most intense feature for the CO adduct, the 310-nm band, is evidently a ligand-localized transition.[13] The lowest energy absorption (1040 nm) is ascribed to a metal-centered (ligand field, "d_{z^2}-to-$d_{x^2-y^2}$") transition. Related bands are observed at 1100–2000 nm in the spectra of $Co^{II}L(X)$ complexes (X = CN^- to Br^-).[5]

Description of the Structures. 1. A view of the complex is presented in Figure 3. The cobalt(I) center is five-coordinate with the four nitrogens of the macrocycle forming the base and the carbon of a carbon monoxide being the apex of a square pyramid.[22] The cobalt and carbon monoxide are situated on a crystallographic 2-fold axis that relates the halves of the macrocycle. The cobalt atom lies 0.57 Å out of the plane of the four nitrogens toward the carbon monoxide. The two amine hydrogen atoms on the macrocycle point up toward the carbon monoxide. The macrocycle is folded, and the Co atom is out of the plane of the macrocycle so that the sixth coordination position of the metal center is essentially blocked. The Co–N(amine) bond length is 2.158 (5) Å, and the Co–N(imine) bond length is 2.075 (5) Å.

2. A view of the complex, along with the atom-labeling scheme, is given in Figure 3. The molecule contains a center of inversion, and it takes advantage of this symmetry by crystallizing with the cobalt atom sitting on a crystallographic inversion center (0, 0, 0). The coordination sphere of the cobalt(II) consists of the four nitrogen atoms of the macrocycle, which define an equatorial plane, and two chloride ions in (distant) axial positions. The Co–N(amine) bond length is 1.976 (6) Å, and the Co–N(imine) bond length is 1.926 (6) Å. The Co–Cl distance is 2.747 (2) Å. The cobalt atom is in the plane defined by the four nitrogen atoms as required by the crystallographic inversion center.

3. A view of the complex, along with the atom-labeling scheme used, is presented in Figure 3. The cobalt(III) is six-coordinate, with the coordination sphere consisting of the four nitrogen atoms of the macrocycle and two oxygen atoms of the bidentate carbonate ion. The macrocycle is folded along the Co–N(amine) bonds so that N4 and N11 occupy cis-cordination sites. It has a fold angle, N4–Co–N11, of 92.2 (1)°. The Co–N(amine) bond length is 1.976 (2) Å, and the Co–N(imine) bond length is 1.927 (3) Å. The Co–O(carbonate) bond length is 1.912 (2) Å. There is a crystallographic 2-fold axis passing through the complex, upon which the cobalt and the carbon and uncoordinated oxygen of the carbonate lie. The two hydrogen atoms on the amine nitrogen point in the direction of the carbonate ion as required by symmetry (i.e., this is the N-racemic stereoisomer).

Comparisons. Both the infrared (ν_{CO} = 1916 cm^{-1}) and structural data (d(Co–C) = 1.797 (10) Å, d(C–O) = 1.107 (14) Å) indicate strong Co → CO back-donation in **1**. The C–O stretching frequency is lower than in NiL^+ (1962 cm^{-1} in pyridine solution).[21] Strong back-donation has also been inferred for the complex[23] $Co^+(C_{10}H_{17}N_8^-)(CO)$: ν_{CO} = 1965 cm^{-1}; d(Co–C) = 1.766 (4) Å, d(C–O) = 1.145 (4) Å. The cobalt coordination sphere in $Co(C_{10}H_{17}N_8)(CO)$ is also square pyramidal, with the Co being 0.4 Å above the plane defined by the equatorial imine nitrogens.[23] In **1** the Co is 0.57 Å above the plane of the N atoms. An analogous, but much smaller, distortion is also found in the binuclear "carbon dioxide" complex[16] $[(CoL)_2(\mu\text{-}CO_2H)](ClO_4)_3$ (see Table VIII), in which the Co atoms are 0.13 and 0.07 Å out of the planes of their four coordinated N atoms toward the C and O atoms, respectively, of the bridging CO_2H unit. The displacement of Co(I) from the macrocycle plane has been attributed[23] to the large size of the low-valent ion. The Co–N distances in **1**, Co–N(amine) = 2.158 (5) Å and Co–N(imine) = 2.075 (5) Å, are 0.15 Å longer than those in **2** and **3** and in other Co(II) and -(III) complexes[10,24] of this macrocycle in support of the size argument. Interestingly the Co–N(amine) bond distances in **1** are quite similar to those[25] in high-spin $Co(bpy)_3^+$.

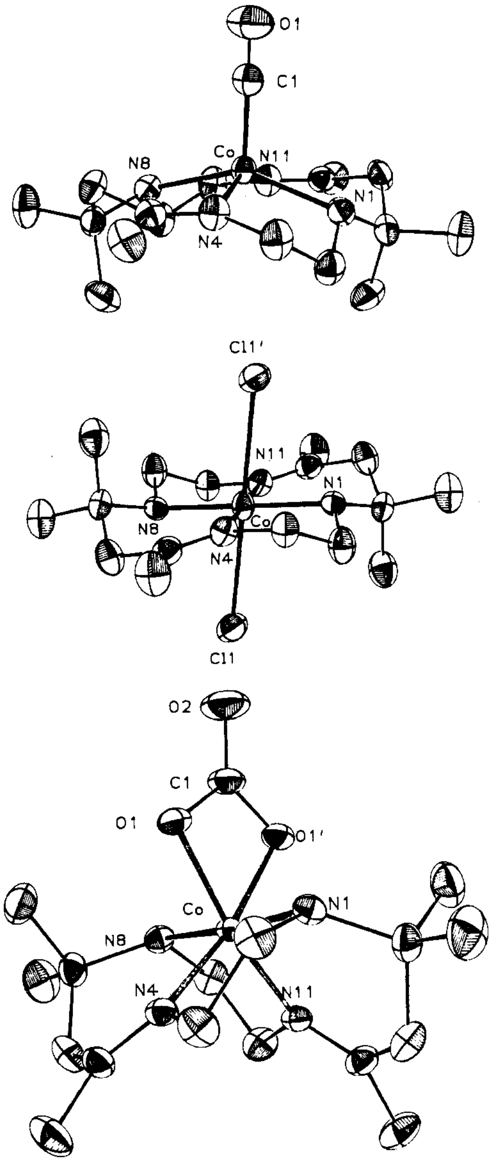

Figure 3. (Top) ORTEP drawing of the $CoL(CO)^+$ cation. The thermal ellipsoids are at the 50% probability level with the hydrogen atoms omitted for clarity. O1, C1, and Co lie on a crystallographic 2-fold axis, which relates N1 to N8, N4 to N11, etc. The hydrogens (not shown) on N1 and N8 are both on the same side of the ligand, facing the carbon monoxide. (Center) ORTEP drawing of *N-meso*-$CoLCl_2$. The thermal ellipsoids are at the 50% probability level with hydrogen atoms omitted for clarity. The cobalt atom sits on a crystallographic inversion center, which relates Cl1 to Cl1', N1 to N8, N4 to N11, etc. (Bottom) ORTEP drawing of the $CoL(CO_3)^+$ cation with thermal ellipsoids at the 50% probability level and hydrogen atoms omitted. C1, O2, and Co lie on a crystallographic 2-fold axis, which relates N1 to N8, N4 to N11, etc. The macrocycle occupies cis coordination sites with the two oxygens of the bidentate carbonate ion completing the coordination sphere.

Both **1** and $[(CoL)_2(\mu\text{-}CO_2H)](ClO_4)_3$ contain the N-racemic stereoisomer of the macrocycle. In both structures, the axial ligand (CO or CO_2H) is bound on the "open" face of the macrocycle

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Table VIII. Comparison of Selected Distances (Å) in **1–3**

	1	**2**	**3**	$[(CoL)_2(CO_2H)](ClO_4)_3$[a]		NiL^{2+}[b]
axial ligand (axl)	CO	Cl^-, Cl^-	CO_3^{2-}	$-CO_2H$	–OC(OH)	
Co–axl	1.797 (10)	2.747 (2)	1.912 (2)	2.06 (6)	2.28 (3)	
			1.326 (3)			
C–O	1.107 (14)		1.214 (5)			
Co–N(amine)	2.158 (5)	1.976 (6)	1.976 (2)	1.91 (av)		1.902 (9)
Co–N(imine)	2.075 (5)	1.929 (6)	1.927 (3)	1.93 (av)		1.856 (10)
N(amine)–C(H_2)	1.484 (8)	1.471 (9)	1.483 (3)	1.54 (av)		1.51 (2)
N(imine)–C	1.271 (8)	1.282 (9)	1.287 (4)	1.26 (av)		1.28 (2)
δ plane[c]	0.57	0.00		0.10 (av)		0.00
CH_3(ax)–CH_3(ax)	5.50			4.33 (av)		4.32

[a] From ref 16. [b] From ref 5b: square planar, N-racemic isomer. [c] Distance of the Co from the N_4 plane.

(the side toward which the amine N–H groups point). (A related six-coordinate geometry has been reported for *N-rac,trans*-CoL(CH_3)H_2O^{2+} in which the methyl ligand occupies the open face.[12] In the latter, however, the Co(III) lies in the macrocycle plane.) The advantages of the N-racemic configuration for the five-coordinate CO and "CO_2" complexes are readily appreciated since steric interference with the axial methyl groups is minimized in this way. Interestingly, the Co(II) product isolated from the CO_2-reduction solution is the N-meso isomer. It is not, however, clear at what stage the isomerization occurs. This is an interesting issue since the N-meso/N-racemic isomerization is generally base-catalyzed[3] and is therefore not expected to be facile in the poorly basic solvent CH_3CN.[26]

The structures of a number of low-spin cobalt(II) complexes, including $CoLCl_2$ (**2**), pose a descriptive problem. Depending upon the compound and the context, the appropriate description of the coordination sphere may be "square-planar", "square-pyramidal", or "distorted octahedral". While the equatorial Co–N distances in **2** and in $CoL(H_2O)_2(BF_4)_2$[24] are short and virtually identical with those in Co^{III}–L complexes, the axial sites contain Cl^- or H_2O groups at anomalously long distances (2.747 (2) and 2.482 (5) Å, respectively). The Co–Cl distance is significantly greater than in other Co^{II}–Cl^- species (2.425 (5)–2.544 (3) Å, six-coordinate;[27] 2.546 (4) Å, square planar;[28] 2.260 (5)–2.296 (3) Å, tetrahedral and trigonal-bipyramidal geometries[29]). In addition, the Cl–Co–Cl axis of the "octahedron" is greatly distorted from a 90° angle with the equatorial plane; both Cl^- ions are displaced from the ideal values away from the axial CH_3 groups and toward the amine hydrogens (d(N–Cl) = 3.08 Å; N1–Co–Cl1 = 100.9 (1)°). Thus, the Co(II) in **2** might be described as (strongly) Jahn–Teller-distorted octahedral or as square planar with relatively close Cl^-–macrocycle contacts arising through "ion pairing" and (weak) hydrogen bonding involving the N–H groups.

The structure of **3** is unremarkable in the context of Co(III) bond distances[10,12,23] or bidentate carbonate complexes.[30] It is, however, the first structure to be reported for this macrocycle in the cis coordination geometry. The Co–N distances determined for **3** are strikingly similar to those in **2** and to those in *trans*-Co^{III}L species. Within the chelated carbonate ion, the contrast in bound O (d(C–O) = 1.326 (3) Å) and free O (d(C–O) = 1.214 (5) Å) carbon–oxygen distances is consistent with the double-bond character of the C1–O2 bond, also evident in the C–O stretching frequency.

Finally, we note that the structures reported here show the flexibility of the macrocycle L. This ligand can accommodate (4 + 1) square-planar coordination or (4 + 2) tetragonally distorted octahedral coordination or octahedral coordination of the cobalt center. In the octahedral coordination the ligand is able to adopt either cis or trans coordination geometry. The Co–N bond lengths in these complexes range from 1.929 (3) to 2.158 (5) Å. The ligand is also able to adjust its fold, represented by the dihedral angle between the N1, N4, N8 plane and the N1, N8, N11 plane, depending on the coordination and oxidation state of the cobalt center. In the three complexes reported here this fold angle is 0.0, 5.2, and 92.1° for complexes **2**, **1**, and **3**, respectively. Rather remarkably, the intraligand bond distances vary little (Table VIII) from conformer to conformer.

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Supplementary Material Available: Final thermal parameters for the non-hydrogen atoms (Tables S4–S6), calculated hydrogen atom positions (Tables S7–S9), best planes (Table S10), possible hydrogen bonds (Table S11), all bond lengths and angles (Tables S12–S14), and complete crystal data and details of the data collection (Table S15) (18 pages); observed and calculated structure factors (Tables S1–S3) (17 pages). Ordering information is given on any current masthead page.

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