

Template Synthesis, Properties, and Crystal Structure of a Trigonal Bipyramidal Cobalt(II) Octaazamacrocyclic Complex

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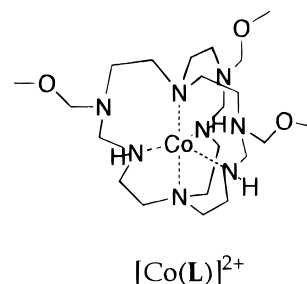
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Introduction

The complexes of encapsulating macrocyclic ligands are often robust over a wide range of pH values,^{1–5} and their spectroscopic and electrochemical properties significantly depend on the contraction or distortion of the ligand.^{6,7} Furthermore, they can be utilized in biological studies^{8–11} since the encapsulated complexes function as sterically protected and kinetically inert redox reagents. Ni(II), Cu(II), and Co(III) complexes of various saturated polyazamacrocyclic ligands have been synthesized by the metal template condensation of aldehydes and amines.^{5,7,12–22} The metal template ions provide simple, selective, and inexpensive routes toward macrocyclic ligands that are not obtainable in the absence of metal ion. However, cobalt(II) ion has been seldom employed as a metal template^{5,7,23–25} probably

because cobalt(II) species are usually air-sensitive and cannot stay as they are during the reaction. In general, cobalt(II) macrocyclic complexes have been prepared by reducing the corresponding cobalt(III) complexes^{2,5,7,22,26} or by inserting the metal ion into the free ligand.²⁷ In this paper, we show that a cobalt(II) macrocyclic complex [Co(L)](BF₄)₂, where L is an encapsulating octaazamacrocyclic ligand, 4,14,19-tris(methoxymethyl)-1,4,6,9,12,14,19,21-octaazabicyclo[7.7.7]tricosane (C₂₁H₄₈N₈O₃), can be prepared by the one-pot template condensation of tris(2-aminoethyl)amine (tren) and formaldehyde in the presence of CoCl₂·6H₂O, carried out in MeOH under a nitrogen atmosphere. The cobalt(II) ion in the macrocyclic complex sits in a trigonal bipyramidal cavity constituted by three secondary nitrogens and two cap tertiary nitrogens of L and exhibits *S* = 3/2 paramagnetic behavior. Although trigonal bipyramidal Co(II) complexes of macrocycles are known,²³ this new species is the first to be crystallographically characterized.



Experimental Section

Reagents. All chemicals and solvents used in the synthesis were of reagent grade and deaerated thoroughly prior to use. For the spectroscopic and physical measurements, solvents were dried, purified according to literature methods,²⁸ and deaerated immediately prior to use.

Measurements. Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. Conductance measurements were performed by using a SUNTEX SC-170 conductivity meter. Elemental analyses were performed by the Korea Basic Science Center, Seoul, Korea. Magnetic susceptibility was measured on a Quantum Design MPMS 5 superconducting quantum interference device (SQUID). Cyclic voltammetry was performed with a BAS 100B/W electrochemical analyzer. The electrochemical data were obtained in MeCN containing 0.1 M (n-Bu)₄NPF₆. The working electrode was a glassy carbon electrode, the auxiliary electrode was a coiled platinum wire, and the reference electrode was a nonaqueous Ag/Ag⁺ (0.01 M MeCN) electrode.

Synthesis of [Co(L)](X)₂ (X = BF₄⁻ and CF₃SO₃⁻). CoCl₂·6H₂O (8.16 g) was dissolved in deaerated MeOH (150 mL). To the solution were added tris(2-aminoethyl)amine (10.0 g) and paraformaldehyde (10.6 g). The mixture was bubbled with nitrogen gas for 10 min and then heated at reflux for 45 h under a nitrogen atmosphere. While the cyclization reaction proceeded, the brownish green color of the mixture gradually turned to red-brown. The solution was filtered while hot with the exclusion of air and a 1.5 times excess amount of an appropriate

- (1) Sargeson, A. M. *Chem. Br.* **1979**, 15, 23.
- (2) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, 104, 6016.
- (3) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, 22, 4022.
- (4) Bernhardt, P. V.; Sargeson, A. M. *Inorg. Chem.* **1987**, 26, 4122.
- (5) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, 106, 5478.
- (6) Bruce, J. I.; Gahan, L. R.; Hambley, T.; Stranger, R. *Inorg. Chem.* **1993**, 32, 5997.
- (7) Geue, R. J.; Hohn, A.; Ralph, S. F.; Sargeson, A. M.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1513.
- (8) Sykes, A. G. *Electron-Transfer Reactions in Metalloproteins. Met. Ions Biol. Syst.* **1991**, 27, 292.
- (9) Toma, H. E.; Murakami, R. A. *Inorg. Chim. Acta* **1984**, 93, L33.
- (10) Scott, R. A.; Conrad, D. W.; Didness, M. K.; Gorren, A. C. F.; Wallin, S. A. *Met. Ions Biol. Syst.* **1991**, 27, 97.
- (11) Pladziewicz, J. R.; Accola, M. A.; Osvath, P.; Sargeson, A. M. *Inorg. Chem.* **1993**, 32, 2525.
- (12) (a) Suh, M. P.; Shin, W.; Kim, D.; Kim, S. *Inorg. Chem.* **1984**, 23, 618. (b) Suh, M. P.; Shin, W.; Kim, H.; Koo, C. H. *Inorg. Chem.* **1987**, 26, 1846.
- (13) Suh, M. P.; Kang, S. *Inorg. Chem.* **1988**, 27, 2544.
- (14) Suh, M. P.; Shin, W.; Kang, S.-G.; Lah, M. S.; Chung, T. M. *Inorg. Chem.* **1989**, 28, 1602.
- (15) Suh, M. P.; Choi, J.; Kang, S.-G.; Shin, W. *Inorg. Chem.* **1989**, 28, 1763.
- (16) Suh, M. P.; Kang, S.; V. Goedken; Park, S. *Inorg. Chem.* **1991**, 30, 365.
- (17) Suh, M. P.; Kim, I. S.; Cho, S.-J.; Shin, W. *J. Chem. Soc., Dalton Trans.* **1994**, 2765.
- (18) Suh, M. P.; Shim, B. Y.; Yoon, T.-S. *Inorg. Chem.* **1994**, 33, 5509.
- (19) Bernhardt, P. V.; Curtis, L. S.; Curtis, N. F.; Lawrance, G. A.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1989**, 42, 797.
- (20) (a) Fabbri, L.; Lanfredi, A. M. M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991**, 3263. (b) Blas, A. D.; Santis, G. D.; Fabbri, L.; Licelli, M.; Lanfredi, A. M. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. Chem.* **1993**, 32, 106. (c) Fabbri, L.; Licelli, M.; Lanfredi, A. M. M.; Vassali, O.; Ugozzoli, F. *Inorg. Chem.* **1996**, 35, 1582.
- (21) Geue, R. J.; Korybut-Daszkiwicz, B.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1454.
- (22) Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Geue, R. J.; Hagen, K. S.; Harrowfield, J. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1994**, 47, 143.

- (23) Long, K. M.; Busch, D. H. *Inorg. Chem.* **1970**, 9, 505.
- (24) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, 92, 3500.
- (25) Lewis, J.; Wainright, K. P. *J. Chem. Soc., Chem. Commun.* **1974**, 169.
- (26) (a) Creaser, I. I.; Harrowfield, M.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, 99, 3181. (b) Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, 106, 8282.
- (27) (a) Tait, A. M.; Busch, D. H. *Inorg. Chem.* **1976**, 15, 197. (b) Osvath, P.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1036.
- (28) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.

Table 1. Crystallographic Data for [Co(C₂₁H₄₈N₈O₃)](BF₄)₂

chem formula	CoC ₂₁ H ₄₈ N ₈ O ₃ B ₂ F ₈	formula wt	693.22
crys syst	orthorhombic	space group	<i>Pbca</i>
<i>a</i>	14.932(3) Å	<i>T</i>	20 °C
<i>b</i>	15.058(5) Å	<i>λ</i>	0.710 73 Å
<i>c</i>	28.220(10) Å	<i>ρ</i> _{calc}	1.451 g cm ⁻³
<i>V</i>	6345(3) Å ³	<i>μ</i>	0.625 mm ⁻¹
<i>Z</i>	8	<i>F</i> (000)	2904
<i>R</i> ^a (4σ data)	0.0996	<i>R</i> _w (<i>F</i> ²) ^b (4σ data)	0.2560
<i>R</i> ^a (all data)	0.1699	<i>R</i> _w (<i>F</i> ²) ^b (all data)	0.3346

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1309P)^2 + 31.52P]$, $P = (F_o^2 + 2F_c^2)/3$.

anion source such as NaBF₄ or LiSO₃CF₃ was added, dissolved in a minimum amount of degassed MeOH. The solution was allowed to stand at room temperature until reddish brown crystals formed. The crystals were filtered off in the air, washed with MeOH, and dried *in vacuo*. The single crystals for the X-ray diffraction studies were obtained by dissolving the compound in a hot MeCN–MeOH mixture (1:3, v/v) and then allowing the solution to stand at room temperature for 1 day. Yield: ~20%. [Co(L)](BF₄)₂. Anal. Calcd for CoC₂₁H₄₈N₈O₃B₂F₈: C, 36.39; H, 6.98; N, 16.16. Found: C, 36.16; H, 7.30; N, 16.33. [Co(L)](CF₃SO₃)₂. Anal. Calcd for CoC₂₃H₄₈N₈F₆S₂O₇: C, 33.78; H, 5.92; N, 13.70. Found: C, 33.27; H, 5.30; N, 13.74.

X-ray Diffraction Measurements. X-ray examination and data collection procedures were performed at room temperature on an Enraf-Nonius CAD-4 diffractometer. Data were collected with graphite-monochromated Mo Kα radiation through the use of ω–2θ scan technique. Lorentz and polarization corrections were applied to the data. Of the 5577 independent reflections (0 ≤ *h* ≤ 17, 0 ≤ *k* ≤ 17, 0 ≤ *l* ≤ 33) measured within the 2θ range of 2.8–50.0°, 3081 reflections were considered as observed with *F* > 4σ(*F*). The non-hydrogen atoms were determined by direct methods using SHELXS86.²⁹ All calculations were done by using the program SHELXL93.³⁰ The refinement was performed on *F*² for all reflections including those generally believed to be unobserved [*F* < 4σ(*F*)]. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. Full-matrix least-squares refinement was carried out by minimizing the function $\sum w(F_o^2 - F_c^2)^2$. The BF₄⁻ anions and the pendent methoxymethylene groups in the complex clearly suffered from rotational disorder. During the SHELXL93 refinements, several restraints were introduced to keep the ideal geometry based on the known B–F bond length.³¹ We could not build discrete (static) disorder models which satisfied the tetrahedral geometry of BF₄⁻ ions, and the current model accounted for the experimental data most satisfactorily. Calculated positions of all hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values 1.2 times those of the bonded atoms. The crystallographic data are summarized in Table 1.

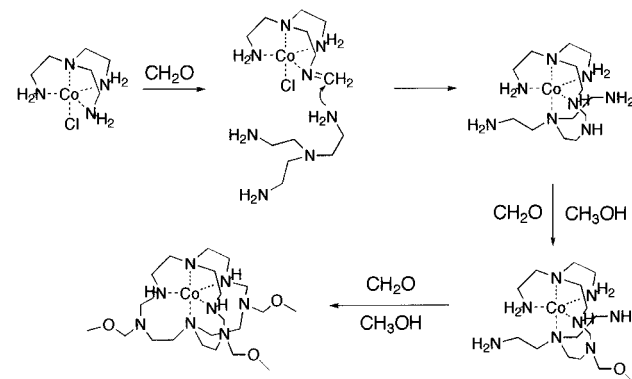
Results and Discussion

Synthesis and Properties. The cobalt(II) complex of macrobicyclic ligand **L**, [Co(L)](BF₄)₂, was prepared from tren and formaldehyde by employing cobalt(II) ion as a metal template (eq 1), in MeOH under the strict exclusion of air. If oxygen



was introduced during the cyclization reaction, unidentifiable oily material was produced. Once the cobalt(II) macrobicyclic complex is formed under nitrogen, the complex can be manipulated in the air in the solid state and in solution. The reaction scheme leading to the macrobicyclic complex is proposed in Scheme 1. When CoCl₂·6H₂O reacts with tren, it

Scheme 1



forms a five-coordinate species [Co(tren)Cl]⁺.^{32–34} The primary amines of tren react with formaldehyde to form methylenediamine linkages. Since the methylenediamine linkage containing uncoordinated secondary nitrogen is unstable,^{12–16} the secondary nitrogen in the linkage reacts further with formaldehyde and methanol to produce the pendent methoxymethylene groups.

Although lanthanides produce mono-, di-, and tribridged ligand complexes from the template reaction of tren and bis-(dimethylamino)methane,³⁵ the Co(II) ion in the present reaction yields only the completely closed cage ligands. During the reaction, the Co(II) complexes of **L** analogues containing one and two methoxymethylene pendent chains were also isolated.

The cobalt(II) macrocyclic complex [Co(L)](BF₄)₂ is soluble in water, Me₂SO, DMF, MeNO₂, and MeCN. The complex was found to be stable in the solvents even after the solution was bubbled with oxygen as observed by electronic spectroscopy, while the simple Co(II) complex [Co(tren)(H₂O)]²⁺ is air-sensitive.³⁶ The complex is also stable in basic aqueous solution (pH = 12–13) and never produces Co(OH)₂ precipitates. However, the complex (7.4 × 10⁻³ M) decomposes in acidic aqueous solution (0.025 M HCl) with a rate constant of *k* = 7.97 × 10⁻³ s⁻¹. This indicates that the secondary amines of the macrobicyclic ligand **L** are basic enough to be protonated, and cobalt(II) ion is dissociated upon protonation. The amine salt [trenH₂]CoCl₄ was isolated as the protonation product. Upon protonation, the macrocyclic ligand seems to be fragmented into amine and formaldehyde due to the instability of the uncoordinated methylenediamine linkages. The Co(II) cage complex [Co(sepulchrate)]²⁺ has been also reported to be acid-sensitive and decomposed to Co_{aq}²⁺, NH₃(CH₂)₂NH₃²⁺, and NH₄⁴⁺.² The infrared, UV/vis, and conductance data of [Co(L)](BF₄)₂ are summarized in Table 2. The electronic absorption spectrum (Figure 1) for the MeCN solution of the complex shows d–d transitions at 471 nm (ε = 51 M⁻¹ cm⁻¹), 540 nm (ε = 27 M⁻¹ cm⁻¹), and 683 nm (ε = 14 M⁻¹ cm⁻¹), which correspond to the characteristic chromophore of the high-spin d⁷ cobalt(II) complex in a trigonal bipyramidal geometry.^{32,37} The spectra of the complex show little dependence on the solvent used

(29) Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467.

(30) Sheldrick, G. M. *SHELXL93. Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

(31) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, Table 9.5.1.1 (B-F in BF₄⁻), p 691.

(32) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, 5, 41.

(33) Ciampolini, M.; Paoletti, P. *Inorg. Chem.* **1967**, 6, 1261.

(34) Di Vaira, M.; Drioli, P. L. *Inorg. Chem.* **1967**, 6, 955.

(35) (a) Smith, P. H.; Raymond, K. N. *Inorg. Chem.* **1985**, 24, 3469. (b) Smith, P. J.; Reyes, Z. E.; Lee, C.-W.; Raymond, K. N. *Inorg. Chem.* **1988**, 27, 4154.

(36) Shinohara, N.; Shibukawa, H.; Shinozaki, K.; Yoshikai, M. *Bull. Chem. Soc. Jpn.* **1995**, 68, 178.

(37) (a) Lever, A. B. P., Ed. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Science Publishers B. v.: Amsterdam, The Netherlands, 1984; pp 491–493. (b) Morassi, M.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, 11, 343. (c) Paoletti, P.; Ciampolini, M.; Sacconi, L. *J. Chem. Soc.* **1963**, 3589. (d) Bertini, I.; Ciampolini, M.; Gatteschi, D. *Inorg. Chem.* **1973**, 12, 693.

Table 2. Properties of $[\text{Co}(\text{L})](\text{BF}_4)_2$

IR: ^a ν_{NH} , cm^{-1}	UV/vis: λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	Λ_{M} , ^b Ω^{-1} $\text{cm}^{-1} \text{M}^{-1}$	$E_{1/2}$: ^e Co(II) \rightarrow Co(III)
3340	471 (51), 540 (27), 683 (14) ^b 470 (55), 539 (28), 677 (14) ^c 470 (50), 541 (24), 672 (13) ^d	280	+1.07 (i)

^a Measured with Nujol mull. ^b Measured in MeCN. ^c Measured in MeNO₂. ^d Measured in H₂O (pH = 12). ^e Measured in MeCN with 0.1 M (*n*-Bu)₄NPF₆, volts vs Ag/Ag⁺ (0.01 M in MeCN); i = irreversible.

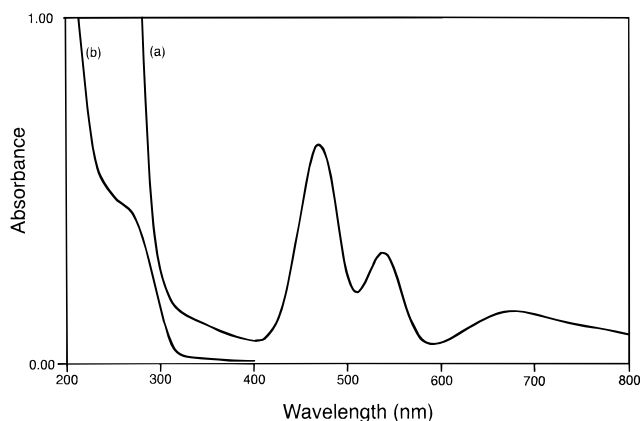


Figure 1. Electronic absorption spectra of $[\text{Co}(\text{L})](\text{BF}_4)_2$ in MeCN: (a) 1.08×10^{-2} M; (b) 2.16×10^{-4} M.

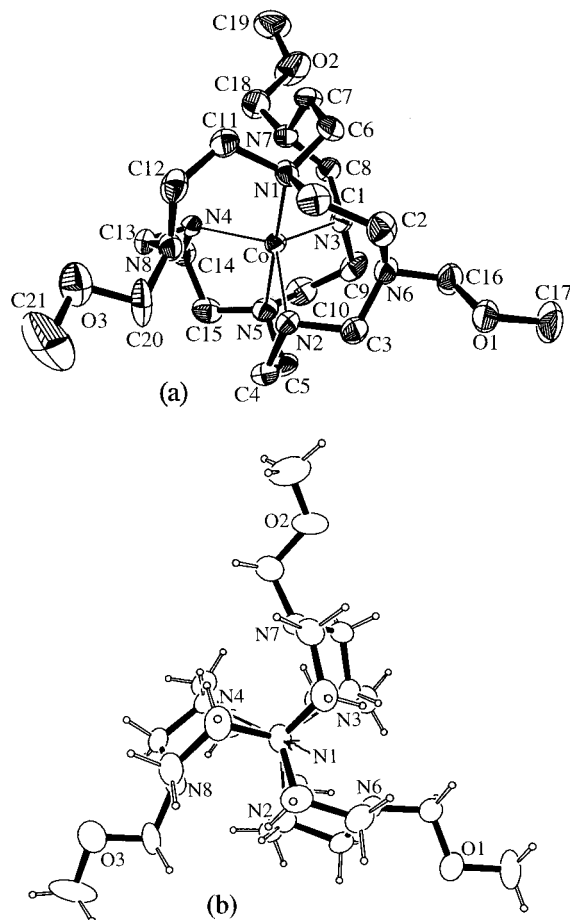


Figure 2. ORTEP views of the cation in $[\text{Co}(\text{C}_{21}\text{H}_{48}\text{N}_8\text{O}_3)](\text{BF}_4)_2$ showing the atomic numbering scheme: (a) side view; (b) top view. Thermal ellipsoids are drawn at the 20% probability level.

(Table 2). For example, the spectrum of the freshly made aqueous solution is the same as that of the acetonitrile solution. However, when the aqueous solution was allowed to stand in

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Co}(\text{C}_{21}\text{H}_{48}\text{N}_8\text{O}_3)](\text{BF}_4)_2$

Co–N1	2.129(7)	C14–N4	1.480(12)
Co–N2	2.109(8)	C5–N5	1.465(14)
Co–N3	2.105(8)	C10–N5	1.500(15)
Co–N4	2.090(7)	C15–N5	1.463(14)
Co–N5	2.243(8)	C2–N6	1.448(15)
C1–N1	1.492(13)	C3–N6	1.467(13)
C6–N1	1.469(13)	C16–N6	1.439(14)
C11–N1	1.496(12)	C7–N7	1.468(14)
C3–N2	1.476(12)	C8–N7	1.455(13)
C4–N2	1.458(13)	C18–N7	1.46(2)
C8–N3	1.474(12)	C12–N8	1.469(15)
C9–N3	1.493(14)	C20–N8	1.51(2)
C13–N4	1.489(12)	C13–N8	1.431(12)
N1–Co–N5	179.7(3)	C14–N4–Co	112.1(6)
N2–Co–N1	101.0(3)	C14–N4–C13	113.9(8)
N3–Co–N1	98.9(3)	C5–N5–Co	107.6(7)
N4–Co–N1	100.6(3)	C10–N5–Co	105.9(6)
N2–Co–N5	78.8(3)	C15–N5–Co	108.5(6)
N3–Co–N5	81.1(3)	C5–N5–C10	111.8(10)
N4–Co–N5	79.7(3)	C15–N5–C5	111.5(9)
N3–Co–N2	117.7(3)	C15–N5–C10	111.3(10)
N4–Co–N2	116.4(3)	C3–N6–C2	115.8(10)
N4–Co–N3	116.7(3)	C2–N6–C16	110.5(11)
C1–N1–Co	109.4(6)	C16–N6–C3	110.1(9)
C6–N1–Co	110.4(6)	C8–N7–C7	113.9(9)
C11–N1–Co	110.1(6)	C18–N7–C7	110.6(10)
C6–N1–C1	108.3(8)	C18–N7–C8	110.5(10)
C1–N1–C11	108.6(9)	C13–N8–C12	114.5(9)
C6–N1–C11	110.1(9)	C12–N8–C20	115.4(10)
C4–N2–Co	112.3(6)	C20–N8–C13	112.2(9)
C4–N2–C3	112.1(8)	N1–C1–C2	115.5(9)
C3–N2–Co	110.2(6)	N6–C2–C1	114.7(9)
C9–N3–Co	110.0(7)	N1–C6–C7	115.1(9)
C9–N3–C8	112.3(9)	N7–C7–C6	116.4(9)
C8–N3–Co	112.6(6)	N1–C11–C12	113.9(10)
C13–N4–Co	109.4(6)	N8–C12–C11	114.1(9)

the air for 4 weeks, the d–d transition bands of the complex disappeared and an intense band appeared at 352 nm ($\epsilon = 918 \text{ M}^{-1} \text{cm}^{-1}$), which is identical to the absorption of $[(\text{tren})\text{Co}(\text{OH}^-, \text{O}_2^{2-})\text{Co}(\text{tren})]^{3+}$.³⁶ It is suggested that the present Co(II) cage complex is very slowly decomposed in the air to $[\text{Co}(\text{tren})(\text{H}_2\text{O})]^{2+}$ in aqueous solution due to the slow dissolution of CO₂ and the consequent decrease of pH. Since $[\text{Co}(\text{tren})(\text{H}_2\text{O})]^{2+}$ is sensitive to oxygen, it results in $[(\text{tren})\text{Co}(\text{OH}^-, \text{O}_2^{2-})\text{Co}(\text{tren})]^{3+}$.³⁶ The cyclic voltammogram for the MeCN solution of $[\text{Co}(\text{L})]^{2+}$ exhibits irreversible one-electron oxidation corresponding to Co^{II}/Co^{III} at +1.07 V vs Ag/Ag⁺ (0.01 M in MeCN). The values of magnetic susceptibilities of the complex are proportional to $1/T$, exhibiting the normal paramagnetic behavior. The magnetic moment of the complex (μ_{eff}) at 290 K is $4.18 \mu_{\text{B}}$, which suggests that the cobalt(II) ion of the complex is in the high-spin d^7 electronic state with $S = 3/2$.

Crystal Structure of $[\text{Co}(\text{L})](\text{BF}_4)_2$. ORTEP³⁸ views of the complex are shown in Figure 2. Table 3 shows the bond distances and angles. The octaazamacrobicyclic **L** acts as a pentadentate ligand, and the cobalt(II) ion is encapsulated by the ligand in a trigonal bipyramidal geometry, coordinated with two cap tertiary nitrogens (N1 and N5) and three secondary nitrogens (N2, N3, and N4). The angles N(sec)–Co–N(sec) in a trigonal plane average 117° , and the N1–Co–N5 angle is $179.7(3)^\circ$. The cobalt(II) ion locates $0.370(5) \text{ \AA}$ out of the trigonal plane toward the N1 cap nitrogen. The distances from the trigonal plane to the cap nitrogens N1 and N5 are significantly asymmetric, $2.498(8)$ and $1.872(9) \text{ \AA}$, respectively,

(38) Johnson, C. K. *ORTEP II*. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

although the Co–N1 and Co–N5 bonds are 2.129(7) and 2.243(8) Å, respectively. It seems that the Co(II) ion adopts the best position to form the least distorted trigonal bipyramidal structure. The bond distances [average 2.178(5) Å] of Co–N(axial) are longer than those [average 2.100(4) Å] of Co–N(equatorial). A Co(II) macrocyclic complex with a trigonal bipyramidal geometry is not very common. It was reported previously that [Co(CR)Br]X {CR = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaene} had a trigonal bipyramidal structure,²³ proposed by the electronic spectrum. The difference between [Co(CR)Br]X and the present [Co(L)](BF₄)₂ is that the former is in a low-spin while the latter is in a high-spin d⁷ electronic state. Although the bridgehead tertiary nitrogen atoms involving methylenediamine linkages often display sp² hybridization with shortening of N–C bonds and flattening of the bond angles^{12–18} and thus show poor binding ability, the cap nitrogens in the present complex are sp³-hybridized and their lone pairs bind the metal ion. The N–C

bonds and the C–N–C angles involving the cap nitrogens average 1.48 Å and 110°, respectively. The bond angles involving C1, C2, C6, C7, C11, and C12 (114–116°) are significantly larger than the normal, indicating the existence of significant strain in the seven-membered chelate ring around cap nitrogen N1. The whole cation has a noncrystallographic 3-fold rotational symmetry along the N1–Co–N5 axis, and it looks like a three-blade propeller as shown in Figure 2b.

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex [Co(L)](BF₄)₂ is available on the Internet only. Access information is given on any current masthead page.

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