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Synthesis, Tuning of the Stereochemistry, and Physical Properties of Cobalt(II) Tropocoronand Complexes

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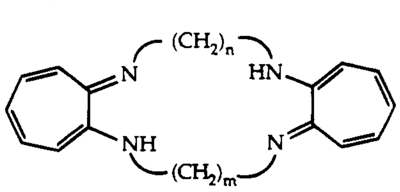
A series of Co(II) complexes of the tropocoronand ligand system $[\text{TC-}n,m]^{2-}$ (n,m = 3,3; 3,4; 4,4; 4,5; 5,5; 6,6; 7,7) have been prepared and fully characterized. X-ray structural analyses have been carried out on [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], [Co(TC-6,6)], and the dinuclear complex $[\text{Co}_2(\mu\text{-OAc})(\mu\text{-OH})(\text{TC-7,7})]$. In the mononuclear series, the coordination geometries vary from square-planar for [Co(TC-3,3)] to tetrahedral for [Co(TC-6,6)]. The twist angle, defined as the dihedral angle between the two five-membered aminotroponiminate chelate rings, increases from 9.0 to 84.5° as a result of increasing torsional strain within the polymethylene linker chains of the tropocoronand macrocycle. The change in geometry from square-planar to tetrahedral, accompanied by a change in spin state from $S = {}^1/_2$ to $S = {}^3/_2$, occurs abruptly between [Co(TC-4,4)] and [Co(TC-4,5)] as determined by X-ray crystallographic and solid state magnetic studies. This dependence of geometry and spin state on ligand size is similar to that observed previously in the Ni(II) system, where the low spin to high spin transformation occurred at the [Ni(TC-4,5)]/[Ni(TC-5,5)] junction. The shift in the position of this transformation with metal ion is an indication of the greater preference of Co(II) for tetrahedral geometry compared with Ni(II). The dinuclear $[\text{Co}_2(\mu\text{-OAc})(\mu\text{-OH})(\text{TC-7,7})]$ compound was prepared from $\text{Co(OAc)}_2\cdot 4\text{H}_2\text{O}$ and $\text{H}_2(\text{TC-7,7})$ in refluxing MeOH. The complex contains two Co(II) atoms sitting in the plane of the macrocycle, bridged by an acetate group on one side of the ligand plane and a hydroxo group on the other. All of the complexes are air sensitive in solution to varying degree but stable in the solid state. Crystallographic data: [Co(TC-3,3)], monoclinic, $P2_1$, $a = 10.187(4)$ Å, $b = 8.466(1)$ Å, $c = 10.227(1)$ Å, $\beta = 97.80(3)°$, $Z = 2$, $R = 0.067$, $R_w = 0.068$; [Co(TC-4,4)], monoclinic, $P2_1/c$, $a = 11.109(3)$ Å, $b = 8.561(1)$ Å, $c = 20.088(6)$ Å, $\beta = 90.53(2)°$, $Z = 4$, $R = 0.039$, $R_w = 0.042$; [Co(TC-4,5)], monoclinic, $P2/c$, $a = 22.041(3)$ Å, $b = 9.351(2)$ Å, $c = 19.859(3)$ Å, $\beta = 106.43(1)°$, $Z = 8$, $R = 0.048$, $R_w = 0.054$; [Co(TC-5,5)], hexagonal, $P6_122$, $a = 10.965(2)$ Å, $c = 30.692(5)$ Å, $Z = 6$, $R = 0.038$, $R_w = 0.048$; [Co(TC-6,6)], orthorhombic, $P2_12_12_1$, $a = 10.644(2)$ Å, $b = 11.426(2)$ Å, $c = 19.083(2)$ Å, $Z = 4$, $R = 0.047$, $R_w = 0.051$; $[\text{Co}_2(\mu\text{-OAc})(\mu\text{-OH})(\text{TC-7,7})]\cdot\text{Et}_2\text{O}$, orthorhombic, *Pbcn*, $a = 12.298(5)$ Å, $b = 16.128(4)$ Å, $c = 17.252(7)$ Å, $Z = 4$, $R = 0.036$, $R_w = 0.042$.

Introduction

We have a long-standing interest in ligands that constrain transition metals in unusual coordination geometries. Metal complexes forced to adopt configurations differing from their idealized ground state stereochemistries often have unusual physical properties and unexpected reactivity. Some remarkable examples of such metal center tuning are found in Nature's metalloenzymes and metalloproteins, which derive their unique and varied reactivity from coordination environments provided by a limited set of amino acids and other biological ligands.

Macrocyclic ligands that are capable of constraining metal coordination geometries form an important part of our research program. Previously we reported structurally characterized mononuclear copper and nickel complexes of the macrocyclic tropocoronand ligand, $\text{H}_2(\text{TC-}n,m)$($n,m$ = 3,3; 4,4; 4,5; 5,5; 6,6).



Tropocoronand, $\text{H}_2(\text{TC-}n,m)$

In these complexes, constraints imposed by the variable-sized ligand enabled the coordination geometry of the metal to be tuned. In the Cu(II) tropocoronand series, the geometry of the complexes varied smoothly from square-planar for [Cu(TC-3,3)] to nearly tetrahedral for [Cu(TC-5,5)], with the [Cu(TC-4,4)] complex having intermediate stereochemistry.[1] A similar stereochemical tuning occurred in the Ni(II) series, with the coordination geometries of the complexes again varying from square-planar to tetrahedral. In the case of the [Ni(TC-n,m)] complexes, however, this stereochemical transformation from square-planar to tetrahedral was accompanied by a change in electronic spin state from $S = 0$ to $S = 1$. As a result, the geometry changed abruptly between distorted square-planar [Ni(TC-4,5)] and distorted tetrahedral [Ni(TC-5,5)].[2] This dramatic difference in physical properties brought about by a slight modification of the ligand led us to inquire whether the phenomenon would occur in other transition metal tropocoronands. In addition, we wanted to explore systems in which the reactivity of the complexes, as well as their stereochemical and physical properties, could be carefully controlled.

Toward this end, we have prepared and studied mononuclear Co(II) tropocoronand complexes which, as in the case of Cu(II) and Ni(II), readily change their geometry as the ligand size is varied. Stereochemical control of Co(II) amine complexes can afford new opportunities for reversible dioxygen binding or

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activation, topics of substantial interest.[3,4] Moreover, Co(II) complexes serve as precursors to Co(III) halides and alkyls, which may also exhibit interesting reactivity. Earlier we reported that oxidation of the Co(II) tropocoronands in the presence of chloride ion leads to Co(III) chloride complexes with unusual pentacoordinate geometries that depended strongly on ligand size.[5] In addition, the stereochemically constrained Co(III) alkyl complexes were more reactive in bond homolysis and CO insertion reactions.[6] Here we describe the synthesis of the Co(II) complexes, [Co(TC-*n,m*)] (*n,m* = 3,3; 3,4; 4,4; 4,5; 5,5; 6,6), the structural characterization of [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)], and the solid state magnetic properties of [Co(TC-4,4)], [Co(TC-4,5)], and [Co(TC-5,5)]. We also report the preparation and structural characterization of a dinuclear complex, $[Co_2(\mu\text{-OAc})(\mu\text{-OH})(TC\text{-}7,7)]$.

Experimental Section

General Information. Diethyl ether, pentane, tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl, and dichloromethane was distilled from CaH_2, all under dinitrogen. MeOH was distilled from $Mg(OMe)_2$ under nitrogen. $CoCl_2{\cdot}6H_2O$ and $Co(OAc)_2{\cdot}4H_2O$ were purchased from a commercial vendor, and the former was dehydrated by heating at 120 °C overnight under vacuum. *n*-Butyllithium (1.6 M in hexane), 1,4-diaminobutane, and MeO_3BF_4 were purchased from Aldrich and used as received. H_2(TC-*n,m*) (*n,m* = 3,3; 5,5; 6,6; 7,7) compounds were synthesized as described previously.[7] The ligands H_2(TC-*n,m*) (*n,m* = 3,4; 4,4; 4,5) were prepared by the modified procedure described below. All experiments, excluding ligand preparations, were carried out either in a nitrogen-filled Vacuum Atmospheres glovebox or with the use of conventional Schlenk line techniques under purified argon unless otherwise noted.

Synthetic Procedures. H_2(TC-3,4). 2,2′-(Trimethylenediamino)-bis(2,4,6-cycloheptatrien-1-one) (4.34 g, 15.4 mmol), prepared as described previously,[7] was combined with Me_3OBF_4 (5.00 g, 33.8 mmol) in 300 mL of dichloromethane under an argon atmosphere, and the mixture was allowed to stir overnight, during which time a milky white precipitate formed. The solvent was removed by evaporation, and the remaining solid was partitioned between 185 mL of water and 140 mL of $CHCl_3$ in air. The organic fraction was separated from the mixture and discarded. The aqueous layer was made basic by the addition of 110 mL of 10% Na_2CO_3(aq) and then was extracted with three 75 mL and four 50 mL portions of $CHCl_3$ until the extracts were only faintly yellow. The extracts were combined, dried over K_2CO_3, and then concentrated under reduced pressure to an orange-brown oil.

The oil was redissolved in 1.15 L of degassed EtOH, and the mixture was treated with a solution of 1,4-diaminobutane (1.52 mL, 15.1 mmol) in 230 mL of degassed EtOH by dropwise addition over 3 h. The yellow solution was allowed to stir for 18 h, over which time a bright yellow precipitate formed. The reaction mixture was then evaporated to afford a bright yellow paste, which was redissolved in 100 mL of $CHCl_3$. This solution was passed through a 2 cm pad of alumina, which was rinsed with another 100 mL of $CHCl_3$. The solution was evaporated to give a yellow solid, which was redissolved in 100 mL of toluene at 45 °C. This slightly cloudy solution was filtered, 10 mL of EtOH was layered on the clear solution, and the mixture was stored overnight at 5 °C. Two crops of bright yellow crystalline solid were collected, rinsed with EtOH and diethyl ether, and dried under vacuum (1.80 g, 35%; mp 176–179 °C). ^1H NMR ($CDCl_3$): δ 8.31 (s, br, 2 H), 6.77 (m, 4 H), 6.29 (d, 2 H, *J* = 21 Hz), 6.25 (d, 2 H, *J* = 21 Hz), 6.13 (t, 2 H, *J* = 9 Hz), 3.52 (m, 4 H), 3.36 (s, 4 H), 2.19 (m, 2 H), 1.90 (p, 4 H) ppm. MS (FAB): *m/z* 334 (M+), 306 ($M - C_2H_4^+$). Anal. Calcd for $C_{21}H_{26}N_4$: C, 75.41; H, 7.84; N, 16.75. Found: C, 75.20; H, 8.05; N, 16.38.

H_2(TC-4,4). 2,2′-(Tetramethylenediamino)bis(2,4,6-cycloheptatrien-1-one) (1.91 g, 6.45 mmol) was treated with Me_3OBF_4 (2.10 g, 14.2 mmol) followed by 1,4-diaminobutane (0.65 mL, 6.47 mmol) as described above for H_2(TC-3,4). Recrystallization from warm toluene as above gave a bright yellow crystalline solid in three crops (0.89 g, 39%). The ^1H NMR spectrum matched that reported in the literature.[7]

H_2(TC-4,5). 2,2′-(Pentamethylenediamino)bis(2,4,6-cycloheptatrien-1-one) (3.48 g, 11.2 mmol) was treated with Me_3OBF_4 (3.64 g, 24.6 mmol) followed by 1,4-diaminobutane (1.20 mL, 6.47 mmol) as described above for H_2(TC-3,4). Recrystallization from warm toluene as above gave a bright yellow crystalline solid in two crops (0.99 g, 24%). The ^1H NMR spectrum matched that reported in the literature.[7]

[Co(TC-*n,m*)] (*n,m* = 3,3; 3,4; 4,4; 4,5; 5,5; 6,6). General Procedure. In a typical case, *n*-BuLi (193 μL/1.6 M in hexanes, 0.309 mmol) was added to a solution of H_2(TC-3,3) (49.2 mg, 0.154 mmol) in 6 mL of THF at −30 °C. The resulting golden solution was then added to a stirred blue solution of $CoCl_2$ (21 mg, 0.162 mmol) in 6 mL of THF. The dark solution was stirred for 40 min and evaporated to a solid residue. The solid was then extracted with the appropriate solvent as described below.

[Co(TC-3,3)]. The crude green-black solid was prepared as described above and then redissolved in 5 mL of dichloromethane. The solution was filtered, and the filtrate, layered with 1 mL of pentane, was stored at −30 °C. Black microcrystalline solid was collected after 18 h by filtering through a fritted funnel and rinsing with pentane (30 mg, 52%). Crystals suitable for diffraction analysis were grown by slow diffusion of pentane into a dichloromethane solution of [Co(TC-3,3)]. UV−vis (THF) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)]: 372 (18 200), 396 (sh, 17 100), 451 (62 100), 614 (sh, 2490), 659 (3960), 738 (870). FTIR (KBr, cm^{-1}): 1572 (m), 1494 (s), 1443 (m), 1415 (s), 1401 (s), 1383 (m), 1279 (s), 1227 (s), 1146 (m), 1101 (m), 1032 (w), 879 (w), 721 (s), 512 (m). Anal. Calcd for $C_{20}H_{22}N_4Co$: C, 63.66; H, 5.88; N, 14.85. Found: C, 63.71; H, 5.88; N, 14.88.

[Co(TC-3,4)]. H_2(TC-3,4) (90.5 mg, 0.271 mmol) was treated with *n*-BuLi (355 μL/1.6 M, 0.568 mmol), and the mixture was combined with $CoCl_2$ (36.9 mg, 0.284 mmol) as described above. The crude brown-black solid was dissolved in 15 mL of toluene. The solution was filtered, and the filtrate, layered with 2 mL of pentane, was stored at −30 °C. Green-black microcrystalline material was collected after 18 h by filtering through a fritted funnel and rinsing with pentane (77 mg, 73%). UV−vis (THF) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)]: 371 (16 600), 395 (18 900), 454 (51 700), 614 (sh, 2350), 658 (3300), 759 (520). FTIR (KBr, cm^{-1}): 1570 (m), 1499 (s), 1442 (s), 1409 (s), 1277 (s), 1221 (s), 1142 (m), 1103 (m), 1011 (m), 722 (s), 515 (w). Anal. Calcd for $C_{21}H_{24}N_4Co$: C, 64.44; H, 6.18; N, 14.32. Found: C, 64.31; H, 6.14; N, 14.27.

[Co(TC-4,4)]. H_2(TC-4,4) (107.9 mg, 0.310 mmol) was treated with *n*-BuLi (406 μL/1.6 M, 0.650 mmol), and the mixture was combined with $CoCl_2$ (44.2 mg, 0.340 mmol) as above. The crude green-black solid was dissolved in 5 mL of toluene. The solution was filtered, and the filtrate, layered with 2 mL of pentane, was stored at −30 °C. After 18 h, the dark green solution was decanted from the black crystalline solid, which was then rinsed with pentane (95 mg, 76%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a toluene solution of [Co(TC-4,4)]. UV−vis (THF) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)]: 360 (22 700), 408 (sh, 23 600), 455 (40 600), 592 (sh, 4400), 660 (3270), 801 (1270). FTIR (KBr, cm^{-1}): 1569 (s), 1496 (s), 1433 (s), 1411 (s), 1376 (s), 1338 (m), 1266 (m), 1221 (m), 1087 (w), 997 (w), 722 (s), 511 (w). Anal. Calcd for $C_{22}H_{26}N_4Co$: C, 65.18; H, 6.46; N, 13.82. Found: C, 65.15; H, 6.31; N, 13.43.

[Co(TC-4,5)]. H_2(TC-4,5) (105.9 mg, 0.292 mmol) was treated with *n*-BuLi (365 μL/1.6 M, 0.584 mmol), and the mixture was combined with $CoCl_2$ (41.7 mg, 0.321 mmol) as described above. The crude brown solid was dissolved in 6 mL of toluene. The solution was filtered, and the filtrate, layered with 2 mL of pentane, was stored at −30 °C. After 18 h, the dark brown solution was decanted from the black crystalline solid, which was then rinsed with pentane (52 mg,

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Table 1. Experimental Details of the X-ray Diffraction Studies of Cobalt(II) Tropocoronand Complexes

	[Co(TC-3,3)]	[Co(TC-4,4)]	[Co(TC-4,5)]	[Co(TC-5,5)]	[Co(TC-6,6)]	$[Co_2(\mu\text{-}OAc)(\mu\text{-}OH)(TC\text{-}7,7)]\cdot Et_2O$
formula	$CoC_{20}H_{22}N_4$	$CoC_{22}H_{26}N_4$	$CoC_{23}H_{28}N_4$	$CoC_{24}H_{30}N_4$	$CoC_{26}H_{34}N_4$	$Co_2C_{30}H_{42}N_4O_3\cdot Et_2O$
fw	377.36	405.41	419.43	433.36	461.52	698.68
cryst. syst	monoclinic	monoclinic	monoclinic	hexagonal	orthorhombic	orthorhombic
space group	$P2_1$	$P2_1/c$	$P2/c$	$P6_122$	$P2_12_12_1$	*Pbcn*
a, Å	10.187(4)	11.109(3)	22.041(3)	10.965(2)	10.644(2)	12.298(5)
b, Å	8.466(1)	8.561(1)	9.351(2)		11.426(2)	16.128(4)
c, Å	10.227(1)	20.088(6)	19.859(3)	30.692(5)	19.083(2)	17.252(7)
β, deg	97.80(3)	90.53(2)	106.43(1)			
V, Å^3	875(1)	1910.5(8)	3926(1)	3196(1)	2320.9(6)	3422(2)
Z	2	4	8	6	4	4
ρ_{calcd}, g/cm^3	1.422	1.409	1.420	1.351	1.321	1.356
T, K	226	226	183.5	216	225	225
total no. of data	1872	3764	6301	2124	2750	3650
2θ limits, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 46$	$3 \le 2\theta \le 47$	$3 \le 2\theta \le 48$	$3 \le 2\theta \le 49$	$3 \le 2\theta \le 48$
data limits	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,+l$	$+h,+k,+l$
no. of unique data[a]	1523	1979	3471	792	1639	1753
no. of parameters	225	348	505	133	280	299
μ(Mo Kα), cm^{-1}	9.87	9.08	8.91	8.19	7.56	10.17
transmission coeff	0.769−1.510	0.87−0.93	0.83−1.00	0.93−1.00	0.95−1.00	0.79−0.91
R[b]	0.067	0.039	0.048	0.038	0.047	0.036
R_w[c]	0.068	0.042	0.054	0.048	0.051	0.042
largest shift/esd, final	0.005	0.02	0.0002	0.004	0.003	0.05
largest peak, e/Å^3	0.66	0.24	0.60	0.26	0.35	0.38

[a] Observation criterion: $I > 3\sigma(I)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F)$ and $\sigma^2(F)$ is defined in ref 8.

42%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of ether into a warm toluene solution of [Co(TC-4,5)]. UV−vis (THF) [λ_{max}, nm (ϵ_M, M^{-1} cm^{-1})]: 336 (17 700), 394 (31 000), 413 (sh, 29 500), 510 (sh, 4270), 598 (1180). FTIR (KBr, cm^{-1}): 1586 (m), 1506 (s), 1469 (w), 1416 (s), 1379 (m), 1332 (w), 1267 (m), 1228 (m), 1128 (w), 1102 (w), 1070 (m), 1009 (m), 880 (m), 720 (s), 493 (m). Anal. Calcd for $C_{23}H_{28}N_4Co$: C, 65.86; H. 6.73; N, 13.36. Found: C, 65.96; H, 6.74; N, 12.90.

[Co(TC-5,5)]. H_2(TC-5,5) (64.4 mg, 0.171 mmol) was treated with *n*-BuLi (224 μL/1.6 M, 0.358 mmol), and the mixture was combined with $CoCl_2$ (23.1 mg, 0.178 mmol) as described above. The crude brown solid was dissolved in 4 mL of toluene. The solution was filtered, and the filtrate, layered with 2 mL of pentane, was stored at −30 °C. After 18 h, the dark brown solution was decanted from the black crystalline solid, which was then rinsed with pentane (44 mg, 59%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a toluene solution of [Co(TC-5,5)]. UV−vs (THF) [λ_{max}, nm (ϵ_M, M^{-1} cm^{-1})]: 332 (19 000), 392 (34 100), 405 (sh, 32 100), 490 (sh, 4480), 596 (sh, 820). FTIR (KBr, cm^{-1}): 1586 (s), 1500 (s), 1448 (m), 1422 (s), 1412 (s), 1388 (s), 1367 (m), 1266 (s), 1226 (s), 1198 (w), 1050 (m), 884 (w), 718 (m), 493 (w). Anal. Calcd for $C_{24}H_{30}N_4Co$: C, 66.50; H, 6.98; N, 12.93. Found: C, 66.74; H, 6.78; N, 12.31.

[Co(TC-6,6)]. H_2(TC-6,6) (54.4 mg, 0.134 mmol) was treated with *n*-BuLi (168 μL/1.6 M, 0.269 mmol), and the mixture was combined with $CoCl_2$ (19.2 mg, 0.145 mmol) as above. The crude red-brown solid was dissolved in 8 mL of diethyl ether. The solution was filtered, and the filtrate, layered with 2 mL of pentane, was stored at −30 °C. After 18 h, the dark brown solution was decanted from the brown-black crystalline solid, which was then rinsed with pentane (28 mg, 45%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a diethyl ether solution of [Co(TC-6,6)]. UV−vis (THF) [λ_{max}, nm (ϵ_M, M^{-1} cm^{-1})]: 336 (18 800), 387 (sh, 33 500), 413 (38 600), 478 (sh, 3890), 565 (sh, 1170), 599 (sh, 950), 670 (sh, 100). FTIR (KBr, cm^{-1}): 1585 (s), 1502 (s), 1473 (m), 1423 (s), 1388 (m), 1338 (m), 1266 (m), 1231 (m), 1095 (w), 983 (w), 882 (w), 720 (m), 566 (w), 465 (w). Anal. Calcd for $C_{26}H_{34}N_4Co$: C, 67.66; H, 7.43; N, 12.14. Found: C, 67.56; H, 7.35; N, 12.21.

$[Co_2(\mu\text{-}OAc)(\mu\text{-}OH)(TC\text{-}7,7)]$. A mixture of H_2(TC-7,7) (25 mg, 0.058 mmol) and $Co(OAc)_2\cdot 4H_2O$ (28.8 mg, 0.116 mmol) was prepared in 5 mL of dry, degassed MeOH. The slurry was refluxed for 1 h, over which time a brick-red solid formed. The mixture was filtered hot through a frit in the air, and the solid was rinsed with 3 mL of MeOH and air-dried (21 mg, 58%). Slow addition of Et_2O to a benzene solution of the product by vapor diffusion in an inert atmosphere yielded ruby red crystals of $[Co_2(\mu\text{-}OAc)(\mu\text{-}OH)(TC\text{-}7,7)]\cdot Et_2O$ suitable for X-ray diffraction analysis. UV−vis (THF) [λ_{max}, nm (ϵ_M, M^{-1} cm^{-1})]: 303 (16 200), 371 (27 800), 423 (20 300), 510 (sh, 1380), 547 (sh, 1070), 574 (sh, 1070). FTIR (KBr, cm^{-1}): 1566 (s), 1505 (s), 1419 (s), 1378 (m), 1268 (m), 1229 (m), 1062 (m), 998 (w), 881 (w), 824 (w), 754 (m), 721 (s), 664 (w), 543 (s), 510 (m). Anal. Calcd for $C_{30}H_{42}N_4O_3Co_2\cdot Et_2O$: C, 58.53; H. 7.37; N, 8.03. Found: C, 58.57; H, 7.16; N, 8.01.

Magnetic Susceptibility Measurements. Magnetic measurements were recorded on 45−55 mg crystalline samples of each complex by using a Quantum Design Corp. SQUID variable-temperature susceptometer. The field dependence was measured and found to be linear from 5 to 25 kG. Sample measurements were made from 5 to 300 K at a magnetic field strength of 15 kG in a Kel-F bucket. Molar susceptibilities for each complex were calculated following corrections for bucket paramagnetism and underlying atomic diamagnetism. Diamagnetic corrections for the ligands were obtained by using the procedure described previously.[1]

Solution and Refinement of Crystal Structures. Table 1 summarizes the details of data collection, reduction, and refinement, which followed typical protocols in our laboratory.[8] All data were collected at low temperature on an Enraf-Nonius CAD-4F diffractometer by using monochromatized Mo Kα (λ = 0.7107 Å) radiation and $\omega/2\theta$ scans. Monitoring of standard reflections showed no crystal decay in any case.

[Co(TC-3,3)]. A black, irregularly shaped crystal of [Co(TC-3,3)] was mounted in silicone grease at low temperature on a quartz fiber. Systematic absences indicated the space group to be $P2_1$ or $P2_1/m$, and the former was confirmed by the structure solution. All non-hydrogen atoms were found with SIR-92.[9] Calculated hydrogen atoms were attached to their appropriate carbon atoms and constrained such that C−H = 0.95 Å. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. A DIFABS absorption correction was applied. The correct enantiomorph choice was made by refinement in the opposite hand, which increased R_w from 0.068 to 0.072. Final coordinates for non-hydrogen atoms are given in Table 2. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and all bond lengths and angles are available as Supporting Information (Tables S1−S4).

[Co(TC-4,4)]. A black rectangular parallelepiped with dimensions 0.08 × 0.15 × 0.33 mm bound by {100}, {010}, and {001} was

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(8) Carnahan, E. M.; Rardin, R. L.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 5193.

(9) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 435.

Table 2. Final Positional Parameters for [Co(TC-3,3)][a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co	0.6761(1)	0.3419	0.6764(1)	2.35(5)
N1	0.6370(7)	0.459(1)	0.8197(7)	2.4(3)
N2	0.5184(7)	0.241(1)	0.7046(7)	1.9(3)
N3	0.7043(7)	0.242(1)	0.5201(8)	2.1(3)
N4	0.8208(7)	0.460(1)	0.6344(8)	2.8(4)
C1	0.514(1)	0.445(1)	0.857(1)	2.8(4)
C2	0.466(1)	0.537(1)	0.950(1)	3.4(5)
C3	0.342(1)	0.537(2)	0.995(1)	3.9(6)
C4	0.230(1)	0.456(2)	0.949(1)	3.5(5)
C5	0.217(1)	0.343(2)	0.852(1)	3.8(5)
C6	0.309(1)	0.277(1)	0.7803(9)	2.6(4)
C7	0.4436(8)	0.312(1)	0.7781(9)	1.8(4)
C8	0.471(1)	0.094(2)	0.637(1)	3.2(5)
C9	0.583(1)	0.008(1)	0.577(1)	3.2(5)
C10	0.636(1)	0.094(1)	0.471(1)	3.0(5)
C11	0.7783(8)	0.316(1)	0.4427(9)	2.2(4)
C12	0.7809(9)	0.281(1)	0.310(1)	3.0(4)
C13	0.8529(9)	0.342(2)	0.219(1)	3.7(5)
C14	0.952(1)	0.459(2)	0.227(1)	4.1(6)
C15	0.993(1)	0.543(2)	0.342(1)	3.3(5)
C16	0.949(1)	0.535(1)	0.466(1)	3.4(5)
C17	0.8532(8)	0.442(1)	0.517(1)	2.2(4)
C18	0.889(1)	0.578(2)	0.727(1)	4.0(6)
C19	0.863(1)	0.554(2)	0.867(1)	3.9(5)
C20	0.723(1)	0.576(2)	0.892(1)	3.9(5)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 1 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

Table 3. Final Positional Parameters for [Co(TC-4,4)][a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co	0.63796(5)	0.22867(6)	0.19814(2)	1.93(3)
N1	0.5900(3)	0.2220(4)	0.1071(1)	2.2(2)
N2	0.4714(3)	0.1923(4)	0.2126(2)	2.0(1)
N3	0.7062(3)	0.1676(4)	0.2792(1)	1.9(1)
N4	0.7831(3)	0.3402(4)	0.1930(1)	1.9(1)
C1	0.4700(4)	0.2059(5)	0.0964(2)	2.5(2)
C2	0.4164(4)	0.2256(6)	0.0331(2)	3.7(3)
C3	0.2975(5)	0.2126(7)	0.0124(3)	4.4(3)
C4	0.1972(5)	0.1676(6)	0.0450(2)	4.0(3)
C5	0.1919(4)	0.1275(6)	0.1122(2)	3.3(2)
C6	0.2804(4)	0.1315(5)	0.1606(2)	2.9(2)
C7	0.4030(4)	0.1766(4)	0.1577(2)	2.2(2)
C8	0.4084(4)	0.1926(6)	0.2772(2)	2.7(2)
C9	0.4792(4)	0.2654(6)	0.3341(2)	2.9(2)
C10	0.5612(5)	0.1518(6)	0.3710(2)	3.1(2)
C11	0.6410(4)	0.0630(5)	0.3240(2)	2.4(2)
C12	0.8119(3)	0.2276(4)	0.2977(2)	1.9(2)
C13	0.8667(4)	0.2018(5)	0.3595(2)	2.3(2)
C14	0.9759(4)	0.2512(5)	0.3855(2)	2.7(2)
C15	0.0660(4)	0.3380(5)	0.3561(2)	3.0(2)
C16	0.0637(4)	0.4018(5)	0.2934(2)	3.1(2)
C17	0.9749(4)	0.3982(5)	0.2452(2)	2.8(2)
C18	0.8616(3)	0.3278(5)	0.2433(2)	2.1(2)
C19	0.8073(4)	0.4426(5)	0.1364(2)	2.4(2)
C20	0.8672(4)	0.3539(6)	0.0802(2)	3.1(2)
C21	0.7994(4)	0.2062(6)	0.0622(2)	3.1(2)
C22	0.6663(4)	0.2292(6)	0.0477(2)	2.9(2)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 1 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

mounted with silicone grease on a quartz fiber under a cold flowing stream of nitrogen. Open-counter ω scans of low-angle reflections revealed sharp ($\Delta\bar{\omega}_{1/2} = 0.20°$) structureless profiles. The space group was determined to be $P2_1/c$ from the systematic absences. The unit cell parameters were refined by using the setting angles of 25 reflections having $2\theta \geq 20°$. An analytical absorption correction was applied. The structure was solved by standard Patterson and difference Fourier techniques and refined with anisotropic temperature factors for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. Final coordinates for the non-hydrogen atoms are given in Table 3. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and all bond lengths and angles are available as Supporting Information (Tables S5–S8).

[Co(TC-4,5)]. A dark brown spade-shaped plate with approximate dimensions 0.3 × 0.1 × 0.2 mm was placed in silicone grease in the drybox and mounted on a quartz fiber in air. Crystal quality was determined to be acceptable from three open-counter ω scans of low-angle reflections with $\Delta\bar{\omega}_{1/2} = 0.313°$ and structureless profiles. Systematic absences indicated the space group $P2/c$ containing two crystallographically independent molecules in the asymmetric unit. An empirical absorption correction was applied. All non-hydrogen atoms were found using SIR-92[9] and refined with anisotropic temperature factors. Hydrogen atoms were calculated and fixed at 0.95 Å from their bonded carbon atoms. Final coordinates for non-hydrogen atoms are given in Table 4. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and all bond lengths and angles are available as Supporting Information (Tables S9–S12).

[Co(TC-5,5)]. A brown crystal with approximate dimensions 0.30 × 0.32 × 0.35 mm was mounted as described for [Co(TC-4,4)]. Open-counter ω scans of low-angle reflections revealed sharp ($\Delta\bar{\omega}_{1/2} = 0.22°$) structureless profiles. The space group was determined to be $P6_122$ or its enantiomorph $P6_522$ from the systematic absence $000l$, $l \neq 6n$. No absorption correction was applied. The structure was solved and refined in space group $P6_522$ as described for [Co(TC-4,4)], except that hydrogen atoms were placed at fixed C–H distances of 0.95 Å and constrained to ride on the respective carbon atoms. The absolute configuration was determined by inverting the coordinates, changing the space group, and refining again. The space group was reassigned as $P6_122$ because R_w fell from 0.051 to 0.048. Final coordinates for the non-hydrogen atoms are given in Table 5. Anisotropic thermal parameters, hydrogen atom positional parameters, and all bond lengths and angles appear in the Supporting Information (Tables S13–S16).

[Co(TC-6,6)]. A red-brown crystal with approximate dimensions 0.20 × 0.20 × 0.25 mm was mounted as described for [Co(TC-4,4)]. Open-counter ω scans of low-angle reflections revealed sharp ($\Delta\bar{\omega}_{1/2} = 0.18°$) structureless profiles. The space group was determined to be $P2_12_12_1$ from the systematic absences. An empirical absorption correction was applied. The structure was solved and refined as described for [Co(TC-4,4)], except that hydrogen atoms were placed in calculated positions as described for [Co(TC-5,5)]. The correct enantiomer was assigned by inverting the coordinates and comparing the discrepancy factors after refinement. Final coordinates for the non-hydrogen atoms are given in Table 6. Anisotropic thermal parameters, hydrogen atom positional parameters, and all bond lengths and angles appear in the Supporting Information (Tables S17–S20).

[Co$_2$(μ-OAc)(μ-OH)(TC-7,7)]·Et$_2$O. A ruby red crystal with dimensions 0.13 × 0.18 × 0.28 mm bound by {021}, {110}, and {$\bar{1}\bar{1}0$} was mounted as described above. Open-counter ω scans of low-angle reflections revealed somewhat broad ($\Delta\bar{\omega}_{1/2} = 0.37°$), structureless profiles. The space group was determined to be $Pbcn$ from the systematic absences. An analytical absorption correction was applied. The structure was solved and refined as reported for [Co(TC-4,4)]. Final coordinates for the non-hydrogen atoms are given in Table 7. Anisotropic thermal parameters, hydrogen atom positional and thermal parameters, all bond lengths and angles, and observed and calculated structure factors appear in the Supporting Information (Tables S21–S24).

Results and Discussion

Mononuclear Co(II) Tropocoronand Complexes. Synthesis and Solubility. The mononuclear tropocoronand complexes [Co(TC-n,m)] (n,m = 3,3; 3,4; 4,4; 4,5; 5,5; 6,6) were prepared by deprotonation of the ligand with 2 equiv of n-BuLi in THF, followed by addition to a THF solution of anhydrous CoCl$_2$ under an inert atmosphere. This procedure differs from that employed for [Cu(TC-n,m)] and [Ni(TC-n,m)], which were prepared by addition of a dichloromethane solution of the free ligand to an ethanol solution of the hydrated metal acetate in

Table 4. Final Positional Parameters for [Co(TC-4,5)][a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co1	0.74794(4)	0.11945(9)	0.12977(4)	1.44(3)
Co2	0.24296(4)	0.36576(9)	0.36942(4)	1.44(3)
N101	0.8131(2)	0.2427(5)	0.1034(2)	1.6(2)
N102	0.7672(2)	0.2593(5)	0.2002(2)	1.4(2)
N103	0.6532(2)	0.0385(5)	0.0988(2)	1.5(2)
N104	0.7728(2)	−0.0733(5)	0.1062(2)	1.7(2)
N201	0.2672(2)	0.5586(5)	0.4050(2)	1.4(2)
N202	0.1474(2)	0.4432(5)	0.3538(2)	1.6(2)
N203	0.2641(2)	0.2319(5)	0.3081(2)	1.6(2)
N204	0.3101(2)	0.2431(5)	0.4285(2)	1.4(2)
C101	0.8449(3)	0.3445(7)	0.1441(3)	1.6(2)
C102	0.8993(3)	0.4312(7)	0.1332(3)	2.0(3)
C103	0.9371(3)	0.5427(7)	0.1675(4)	2.7(3)
C104	0.9352(3)	0.6024(7)	0.2236(3)	2.2(3)
C105	0.8931(3)	0.5604(7)	0.2598(3)	2.2(3)
C106	0.8434(3)	0.4526(7)	0.2502(3)	2.1(3)
C107	0.8173(3)	0.3547(6)	0.2001(3)	1.6(2)
C108	0.6495(3)	−0.0972(7)	0.0788(3)	1.7(3)
C109	0.5846(3)	−0.1678(7)	0.0522(3)	2.0(3)
C110	0.5684(3)	−0.3065(8)	0.0327(3)	2.6(3)
C111	0.6104(4)	−0.4205(7)	0.0322(4)	3.0(3)
C112	0.6832(4)	−0.4193(7)	0.0502(3)	2.8(3)
C113	0.7292(3)	−0.3095(7)	0.0720(3)	2.3(3)
C114	0.7192(3)	−0.1624(6)	0.0848(3)	1.4(2)
C115	0.8437(3)	0.1905(7)	0.0542(3)	2.4(3)
C116	0.9077(3)	0.0969(7)	0.0826(3)	2.3(3)
C117	0.9002(3)	−0.0100(7)	0.1325(3)	2.4(3)
C118	0.8443(3)	−0.1242(7)	0.1108(3)	2.2(3)
C119	0.7364(3)	0.2596(7)	0.2536(3)	1.8(2)
C120	0.6706(3)	0.1712(7)	0.2407(3)	2.2(3)
C121	0.6050(3)	0.2428(8)	0.1995(3)	2.8(3)
C122	0.5990(3)	0.2562(7)	0.1302(3)	2.4(3)
C123	0.5874(3)	0.1145(7)	0.0946(3)	2.3(3)
C201	0.2135(3)	0.6485(7)	0.3997(3)	1.4(2)
C202	0.2229(4)	0.7922(7)	0.4181(3)	2.3(3)
C203	0.1763(3)	0.9028(7)	0.4166(3)	2.5(3)
C204	0.1040(4)	0.9028(7)	0.3996(3)	2.8(3)
C205	0.0622(3)	0.7848(8)	0.3788(3)	2.7(3)
C206	0.0784(3)	0.6446(7)	0.3671(3)	2.1(3)
C207	0.1433(3)	0.5788(6)	0.3716(3)	1.4(2)
C208	0.3145(3)	0.1380(6)	0.3320(3)	1.6(2)
C209	0.3441(3)	0.0485(7)	0.2943(3)	1.8(3)
C210	0.3946(3)	−0.0570(7)	0.3093(3)	2.1(3)
C211	0.4332(3)	−0.1099(7)	0.3669(3)	2.3(3)
C212	0.4315(3)	−0.0596(7)	0.4253(3)	2.1(3)
C213	0.3929(3)	0.0506(7)	0.4406(3)	1.9(3)
C214	0.3394(3)	0.6119(7)	0.4359(3)	2.1(3)
C215	0.3954(3)	0.4985(7)	0.4406(3)	2.2(3)
C216	0.4061(3)	0.3882(7)	0.4949(3)	2.2(3)
C217	0.3419(3)	0.2956(6)	0.4928(3)	1.6(2)
C218	0.0820(3)	0.3651(7)	0.3236(3)	2.3(3)
C219	0.0943(3)	0.2274(7)	0.2923(3)	2.2(3)
C220	0.1007(3)	0.2479(8)	0.2256(3)	2.7(3)
C221	0.1663(3)	0.3244(7)	0.2194(3)	2.2(3)
C222	0.2334(3)	0.2384(7)	0.2389(3)	1.9(2)
C223	0.3410(3)	0.1412(7)	0.4031(3)	1.5(2)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 1 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

air.[1,7] $CoCl_2$ was chosen as a water-free source of Co(II), and *n*-BuLi was used as a base so that HCl, which will protonate the free ligand, would not be formed in the reaction. Because of the tendency of many Co(II) complexes with nitrogen donors to oxidize readily, all solutions of [Co(TC-*n*,*m*)] were protected from air. The solubility of the complexes in organic solvents increased with the total length of the linker chains, with [Co(TC-3,3)] being only sparingly soluble in toluene and [Co(TC-6,6)] readily dissolving in diethyl ether.

Table 5. Final Positional Parameters for [Co(TC-5,5)][a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co	0.58482(7)	0.1696	$^1/_4$	3.55(6)
N1	0.7772(5)	0.3270(5)	0.2599(1)	3.6(2)
N2	0.5714(6)	0.0124(6)	0.2152(1)	3.6(2)
C1	0.8944(6)	0.7888	$^1/_4$	5.5(6)
C2	0.9582(8)	0.7191(8)	0.2679(2)	5.0(3)
C3	0.9162(7)	0.5782(8)	0.2707(2)	4.3(2)
C4	0.7925(6)	0.4551(7)	0.2578(2)	3.4(2)
C5	0.8995(7)	0.3125(8)	0.2698(2)	4.8(3)
C6	0.8821(8)	0.1708(8)	0.2560(2)	5.5(3)
C7	0.9018(8)	0.1566(8)	0.2076(2)	5.9(4)
C8	0.7978(9)	0.1607(7)	0.1766(2)	5.3(3)
C9	0.6534(7)	0.0295(7)	0.1755(2)	4.8(3)
C10	0.4764(6)	0.8861(7)	0.2288(2)	3.6(2)
C11	0.4347(7)	0.7633(8)	0.2038(2)	4.3(3)
C12	0.3463(7)	0.6212(8)	0.2128(2)	5.0(3)
C13	0.2758(5)	0.5515	$^1/_4$	4.9(6)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 1 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

Table 6. Final Positional Parameters for [Co(TC-6,6)][a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co	0.8433(1)	0.9024(1)	0.36997(6)	1.83(5)
N1	0.8683(7)	0.0636(5)	0.4048(3)	1.7(3)
N2	0.9910(6)	0.9468(6)	0.3136(4)	1.6(3)
N3	0.8407(8)	0.7599(5)	0.4277(3)	1.7(3)
N4	0.6790(7)	0.8396(6)	0.3413(3)	1.8(3)
C1	0.9716(8)	0.1187(7)	0.3819(4)	1.8(4)
C2	0.007(1)	0.2301(7)	0.4054(5)	2.2(4)
C3	0.111(1)	0.2992(7)	0.3943(5)	2.4(4)
C4	0.213(1)	0.2788(8)	0.3524(5)	2.8(5)
C5	0.2293(8)	0.1864(8)	0.3072(5)	2.3(4)
C6	0.1551(9)	0.0895(7)	0.2963(4)	2.1(4)
C7	0.0430(8)	0.0480(7)	0.3294(4)	1.7(4)
C8	0.0482(9)	0.8673(8)	0.2615(5)	2.3(5)
C9	0.168(1)	0.8048(8)	0.2859(5)	2.5(4)
C10	0.162(1)	0.7554(8)	0.3594(6)	3.4(5)
C11	0.069(1)	0.6540(7)	0.3652(6)	2.8(4)
C12	0.0278(9)	0.6309(8)	0.4409(5)	3.2(5)
C13	0.946(1)	0.7259(8)	0.4726(5)	2.4(4)
C14	0.7404(8)	0.6910(8)	0.4213(5)	1.8(4)
C15	0.724(1)	0.5874(8)	0.4609(5)	2.9(5)
C16	0.631(1)	0.5049(8)	0.4618(5)	3.2(5)
C17	0.522(1)	0.4948(9)	0.4230(6)	3.5(6)
C18	0.4828(8)	0.5709(7)	0.3730(6)	3.0(5)
C19	0.5344(8)	0.6770(9)	0.3501(5)	2.6(5)
C20	0.647(1)	0.7363(6)	0.3691(5)	2.0(4)
C21	0.5962(8)	0.8990(9)	0.2913(5)	2.7(4)
C22	0.4858(9)	0.9639(8)	0.3250(5)	2.8(5)
C23	0.5261(8)	0.0491(8)	0.3819(5)	2.8(5)
C24	0.6133(9)	0.1466(8)	0.3582(5)	2.8(5)
C25	0.688(1)	0.2042(8)	0.4170(5)	2.8(5)
C26	0.7811(8)	0.1199(8)	0.4522(5)	2.2(4)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 1 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

Stereochemistry of the Complexes. The molecular structures of [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)], all discrete mononuclear four-coordinate complexes, are shown in Figure 1. Geometric information about the metal coordination spheres is available in Table 8. The coordination geometries range from virtually square-planar for [Co(TC-3,3)] to nearly tetrahedral for [Co(TC-6,6)]. The twist angles, Θ, measured between the planes of the two five-membered chelate rings, were 9.0, 31.8, 59.0, 69.9, and 84.5°, respectively, for the five compounds. As discussed previously,[1] increasing the length of the linker chains in the macrocycle causes the complexes to become increasingly twisted toward tetrahedral geometry because of torsional strain that builds up between the methylene units.

Table 7. Final Positional Parameters for $[Co_2(\mu\text{-}OAc)(\mu\text{-}OH)(TC\text{-}7,7)]\cdot Et_2O$[a]

atom	x	y	z	B_{eq}, Å^2 [b]
Co	0.07933(5)	0.41746(3)	0.66888(3)	2.07(3)
O1	0.0504(3)	0.5351(2)	0.6965(2)	3.1(3)
O2	0	0.3610(3)	$^3/_4$	2.2(2)
O3	$^1/_2$	0.3231(3)	$^1/_4$	3.1(2)
N1	0.2336(3)	0.3928(2)	0.6476(2)	2.2(2)
N2	0.0662(3)	0.3913(2)	0.5569(2)	2.2(2)
C1	0.1583(3)	0.3672(2)	0.5234(2)	2.2(2)
C2	0.1612(4)	0.3404(3)	0.4447(3)	3.0(2)
C3	0.2450(5)	0.3136(3)	0.3977(3)	3.3(2)
C4	0.3555(4)	0.3063(3)	0.4119(3)	3.4(2)
C5	0.4063(4)	0.3257(3)	0.4808(3)	3.2(2)
C6	0.3638(4)	0.3526(3)	0.5514(3)	2.8(2)
C7	0.2559(3)	0.3703(2)	0.5749(2)	2.3(2)
C8	0.3212(4)	0.3955(3)	0.7053(3)	2.5(2)
C9	0.2759(4)	0.4169(3)	0.7843(2)	2.7(2)
C10	0.3616(4)	0.4117(3)	0.8485(3)	2.9(2)
C11	−0.0352(3)	0.3931(3)	0.5127(2)	2.3(2)
C12	−0.1277(4)	0.4186(3)	0.5652(3)	2.5(2)
C13	−0.2395(4)	0.4142(3)	0.5276(2)	2.6(2)
C14	−0.3311(4)	0.4533(3)	0.5750(3)	2.8(2)
C15	0	0.5704(4)	$^3/_4$	2.5(3)
C16	0	0.6656(4)	$^3/_4$	3.6(3)
C100	0.6641(6)	0.3171(5)	0.3240(4)	5.0(3)
C101	0.5816(5)	0.3725(3)	0.2863(3)	4.2(3)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. See Figure 4 for atom-labeling scheme. [b] $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

Table 8. Bond Distances (Å) and Angles (deg) for [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)][a]

	distances		angles	
[Co(TC-3,3)]	Co−N1	1.850(9)	N1−Co−N2	81.6(3)
	Co−N2	1.872(7)	N1−Co−N3	173.4(4)
	Co−N3	1.862(8)	N1−Co−N4	98.4(4)
	Co−N4	1.871(8)	N2−Co−N3	98.3(3)
			N2−Co−N4	172.9(4)
			N3−Co−N4	80.9(4)
[Co(TC-4,4)]	Co−N1	1.901(3)	N1−Co−N2	83.0(1)
	Co−N2	1.901(3)	N1−Co−N3	160.0(1)
	Co−N3	1.865(3)	N1−Co−N4	101.3(1)
	Co−N4	1.878(3)	N2−Co−N3	102.1(1)
			N2−Co−N4	158.3(1)
			N3−Co−N4	81.3(1)
[Co(TC-4,5)]	Co1−N101	1.941(5)	N101−Co1−N102	81.1(2)
	Co1−N102	1.982(5)	N101−Co1−N103	141.2(2)
	Co2−N201	1.971(5)	N101−Co1−N104	103.0(2)
	Co2−N202	1.969(5)	N201−Co2−N202	81.3(2)
	Co1−N103	1.962(5)	N201−Co2−N203	141.0(2)
	Co1−N104	1.976(5)	N201−Co2−N204	103.2(2)
	Co2−N203	1.972(5)	N102−Co1−N103	118.7(2)
	Co2−N204	1.953(5)	N102−Co1−N104	143.1(2)
			N103−Co1−N104	81.0(2)
			N202−Co2−N203	119.7(2)
			N202−Co2−N204	140.9(2)
			N203−Co2−N204	81.2(2)
[Co(TC-5,5)]	Co−N1	1.969(5)	N1−Co−N1′	81.3(3)
	Co−N2	1.970(5)	N1−Co−N2	115.4(2)
			N1−Co−N2′	136.2(2)
			N2−Co−N2′	81.4(3)
[Co(TC-6,6)]	Co−N1	1.976(6)	N1−Co−N2	80.6(3)
	Co−N2	1.971(7)	N1−Co−N3	125.8(3)
	Co−N3	1.967(6)	N1−Co−N4	123.6(3)
	Co−N4	1.968(7)	N2−Co−N3	122.0(3)
			N2−Co−N4	130.6(3)
			N3−Co−N4	80.8(3)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 1.

As the complexes distort, the distance between the α and ω carbon atoms of the linker chains increases and the torsional strain is reduced. For the approximately square-planar Co(II) tropocoronands, the average α to ω distance increased from 2.52 Å in [Co(TC-3,3)] to 2.98 Å in [Co(TC-4,4)]. The [Co(TC-4,5)] α to ω distances showed a predictable asymmetry, the value being 3.20 Å for the linker chain with four methylene units and 4.12 Å for the one with five methylene linkers. The shorter of these two distances is 0.22 Å greater than the corresponding distance in [Co(TC-4,4)]. The [Co(TC-5,5)] average α to ω distance is 4.12 Å, identical to the longer distance in [Co(TC-4,5)]. Clearly, the shorter linker chain in [Co(TC-4,5)] is being stretched by the longer chain on the opposite side of the macrocycle. The [Co(TC-6,6)] distance of 4.45 Å displays the greatest twist, as expected for the longest linker chains.

The torsion angles (ω) for the bonds in the linker chains of the structurally characterized [Co(TC-*n*,*m*)] complexes are listed in Table 9. Strain energies of metal-chelating diamine ligands depend almost exclusively on the torsion angles between the C−C bonds rather than the conformation of the ring.[10] According to this analysis, the size of the deviations of the torsion angles in the tropocoronand linker chains from their ideal values should approximate the degree of strain within the complex. Ideal values for $C(sp^3){-}C(sp^3)$ torsion angles are 60 or 180°, and those for $C(sp^3){-}N(sp^2)$ are 30, 90, or 150°.[11] Deviations from these values are listed in the Table 9 (Δ_{ideal}). The [Co(TC-3,3)] complex shows minimal strain in the linker chains with Δ_{ideal} values of 6° or less. In contrast, two of the C−C torsion angles in the linker chains of [Co(TC-4,4)] deviate from their ideal values by greater than 27°, indicating substantial strain within the seven-membered chelate rings. Significant strain is also present in [Co(TC-4,5)], which has two torsion angles with $\Delta_{ideal} > 24°$. Notably, these angles are in the five methylene unit linker chains, whereas the deviations in the four methylene linker chains are smaller than in [Co(TC-4,4)]. By comparison, the largest deviation in [Co(TC-5,5)] or [Co(TC-6,6)] is 20.3°, revealing that the strain associated with addition of methylene units in the chains is partially alleviated by distortion of the complex toward tetrahedral geometry.

Other aspects of the ligand geometry in the [Co(TC-*n*,*m*)] complexes are similar to those observed in the Cu(II) and Ni(II) tropocoronands.[1,2] The seven-membered tropone rings adopt nearly planar geometry, and the C−C bond lengths and angles fall in expected ranges. The Co−N distances increase as the coordination geometry changes from planar to tetrahedral, with average values of 1.864(9) Å for [Co(TC-3,3)], 1.88(2) Å for [Co(TC-4,4)], 1.96(1) Å for [Co(TC-4,5)], 1.970(5) Å for [Co(TC-5,5)], and 1.971(4) Å for [Co(TC-6,6)]. Similar increases in the average M−N bond lengths were observed in both the Cu(II) and Ni(II) complexes as the number of methylene units in the linker chains increased. Some asymmetry exists between the sets of bond lengths Co−N1/Co−N2 (average 1.901(3) Å) and Co−N3/Co−N4 (average 1.872(7) Å) in the structure of [Co(TC-4,4)].

A comparison of the twist angles of the structurally characterized Co(II) complexes with those of the Ni(II) complexes of the same ligands[1] plotted as a function of the total length of the linker chains ($n + m$) reveals that the coordination geometries are nearly identical for both metals (Figure 2). As noted previously, the Ni(II) system exhibits a change in spin state from $S = 0$ to $S = 1$ as the coordination geometry is altered from square-planar to tetrahedral. As a consequence, the change

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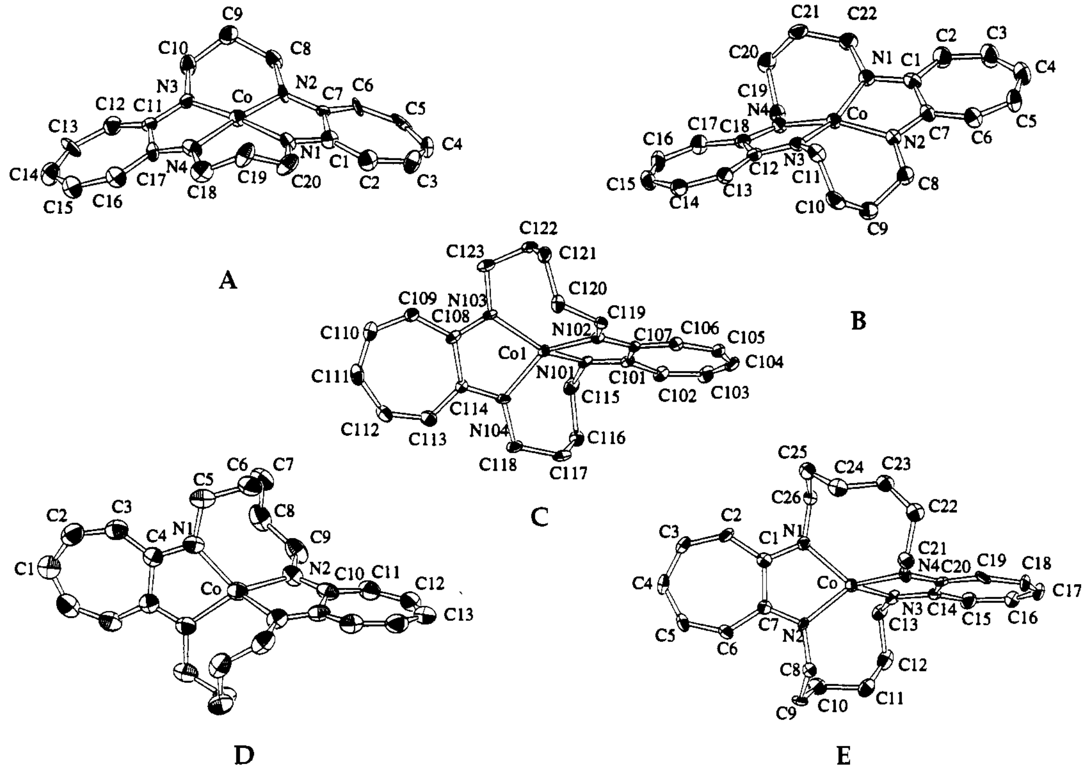

Figure 1. ORTEP drawings of [Co(TC-3,3)] (A), [Co(TC-4,4)] (B), [Co(TC-4,5)] (C), [Co(TC-5,5)] (D), and [Co(TC-6,6)] (E) showing 40% probability thermal ellipsoids for all non-hydrogen atoms. Only one molecule of the asymmetric unit of [Co(TC-4,5)] is shown. The halves of [Co(TC-5,5)] are related by a crystallographically imposed 2-fold axis through atoms C1, Co, and C13.

in geometry is discontinuous through the series. Specifically, the geometry of [Ni(TC-4,5)] is distorted square-planar while that of [Ni(TC-5,5)] is distorted tetrahedral. A d^7 Co(II) ion is also expected to have a spin state change upon distorting from square-planar to tetrahedral geometry, in this case $S = {}^1/_2$ to $S = {}^3/_2$, and the similarity in coordination geometries for the two series of complexes suggested that a similar discontinuity, both electronic and stereochemical, should exist. The X-ray crystallographic studies of the [Co(TC-*n,m*)] series confirmed our expectation. The [Co(TC-4,4)] and [Co(TC-5,5)] complexes have dihedral angles very similar to those of their Ni analogs, as shown in Figure 2. In contrast, the dihedral angle of [Co-(TC-4,5)] is 59.0°, closer to tetrahedral than square-planar, and unlike the [Ni(TC-4,5)] dihedral angle of 27.1°. This difference is a result of the greater preference of Co(II) versus Ni(II) for tetrahedral geometry as discussed below.

Magnetic Measurements. Magnetic susceptibility studies were carried out on [Co(TC-4,4)], [Co(TC-4,5)], and [Co(TC-5,5)] in anticipation that the $S = {}^1/_2$ to $S = {}^3/_2$ electronic spin state transition would be located at the boundary between the [Co(TC-4,4)] and [Co(TC-4,5)] complexes, as dictated by the single-crystal diffraction results. Measurement of the effective magnetic moments at temperatures ranging from 5 to 300 K gave values of 2.12, 4.93, and 4.71 μ_B, respectively, for the three complexes at 300 K, and all of the moments diminished slightly at values less than 50 K, as shown in Figure 3. A value of 2.12 μ_B is typical of square-planar Co(II) complexes having $S = {}^1/_2$, most of which fall in the range 2.2–2.7 μ_B.[12-15] In contrast, values of 4.93 and 4.71 μ_B are in the range for known tetrahedral Co(II) complexes with $S = {}^3/_2$, where the magnetic moment is higher than the expected spin-only value of 3.89 μ_B because of significant spin–orbit coupling.[15,16] Solution state magnetic studies of the related bis(aminotroponiminato) complexes of Co(II), believed to have distorted tetrahedral geometry, revealed magnetic moments in the range 4.2–4.3 μ_B.[17]

The magnetic moments of the complexes confirm that the spin state transition occurs between [Co(TC-4,4)] and [Co(TC-4,5)] unlike the Ni(II) complexes, where the corresponding switch occurs between [Ni(TC-4,5)] and [Ni(TC-5,5)]. Apparently, the four-coordinate [M(TC-4,5)] complexes are situated very near the energetic barrier between the low-spin square-planar and high-spin tetrahedral states. As a result, the actual configuration is determined less by the ligand than by the electronic properties of the metal atom. Co(II), with a relatively stable half-filled t_2 shell in an $e^4t_2{}^3$ electronic configuration, adopts tetrahedral geometry, whereas the Ni(II) complex adopts square-planar geometry in which it has a diamagnetic ground state.

The preference of Co(II) and Ni(II) complexes of similar ligands for tetrahedral vs square-planar geometry has been previously examined. Co(II) and Ni(II) bis(β-keto amininato) complexes were prepared in which substitution of the N–H group adjacent to the metal with N–R resulted in changes in the coordination geometry and spin state.[18,19] By studying solution state high-spin/low-spin equilibria for Co(II) and Ni(II) complexes of a series of related complexes using NMR and magnetic susceptibility techniques, the authors concluded that the enthalpy difference between tetrahedral and square-planar Ni(II) is 2–4 kcal/mol greater than that between tetrahedral and square-planar Co(II). As a consequence, a Co(II) complex of

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Table 9. Torsion Angles, ω (deg), within the Linker Chains of [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)][a]

			ω	$\lvert\Delta_{\mathrm{ideal}}\rvert$[b]
[Co(TC-3,3)]	C−N	C1−N1−C20−C19	166(1)	16
		C7−N2−C8−C9	−168.3(9)	18.3
		C9−C10−N3−C11	167.1(9)	17.1
		C17−N4−C18−C19	−166(1)	16
	C−C	C8−C9	−66(1)	6
		C9−C10	−66(1)	6
		C18−C19	−65(1)	5
		C19−C20	−64(2)	4
[Co(TC-4,4)]	C−N	C1−N1−C22−C21	−165.4(4)	15.4
		C7−N2−C8−C9	−159.6(4)	9.6
		C10−C11−N3−C12	87.5(5)	2.5
		C18−N4−C19−C20	93.5(4)	3.5
	C−C	C8−C9	−87.8(5)	27.8
		C9−C10	51.5(5)	8.5
		C11−C10	52.0(5)	8.0
		C19−C20	50.8(5)	9.2
		C20−C21	52.5(5)	7.5
		C21−C22	−87.2(5)	27.2
[Co(TC-4,5)]	C−N	C101−N101−C115−C116	73.1(7)	17.0
		C107−N102−C119−C120	167.0(5)	17.0
		C108−N103−C123−C122	168.9(6)	18.9
		C114−N104−C118−C117	176.9(6)	26.8
		C201−N201−C215−C216	178.4(5)	28.4
		C207−N202−C219−C220	166.5(5)	16.5
		C208−N203−C223−C222	166.7(5)	16.7
		C214−N204−C218−C217	72.5(7)	17.5
	C−C	C115−C116	43.0(8)	17.0
		C116−C117	62.7(7)	2.7
		C117−C118	79.3(7)	19.3
		C119−C120	−79.0(7)	19.0
		C120−C121	73.3(8)	13.3
		C121−C122	70.0(7)	10.0
		C122−C123	85.0(6)	25.0
		C215−C216	−80.0(7)	20.0
		C216−C217	61.4(7)	1.4
		C217−C218	−45.2(7)	14.8
		C219−C220	−84.2(7)	24.2
		C220−C221	69.5(7)	9.5
		C221−C222	73.3(7)	13.3
		C222−C223	78.4(7)	18.4
[Co(TC-5,5)]	C−N	C4−N1−C5−C6	−160.0(5)	10.0
		C8−C9−N2−C10	−151.2(7)	1.2
	C−C	C5−C6	77.8(7)	17.8
		C6−C7	−64.8(8)	4.8
		C7−C8	−74.1(9)	14.1
		C8−C9	71(1)	11.1
Co[TC-6,6)]	C−N	C1−N1−C26−C25	81(1)	9
		C7−N2−C8−C9	73(1)	17
		C12−C13−N3−C14	75(1)	15
		C20−N4−C21−C22	79(1)	11
	C−C	C8−C9	44(1)	16
		C9−C10	68(1)	8
		C10−C11	−160.4(8)	19.6
		C11−C12	69(1)	9
		C12−C13	50(1)	10
		C21−C22	53(1)	7
		C22−C23	61(1)	1
		C23−C24	−159.7(8)	20.3
		C24−C25	65(1)	5
		C25−C26	55(1)	5

[a] The sign of ω is positive if, when the species is viewed from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4. Atoms 1 and 4 are omitted for C−C angles. [b] $\Delta_{\mathrm{ideal}} = [\lvert\omega\rvert - \text{ideal angle}]$ where ideal angles are 30, 90, or 150° for C−N and 60 or 180° for C−C.

a ligand that can adopt either planar or tetrahedral geometry is more likely to be tetrahedral than the Ni(II) complex of the same ligand. The $[\mathrm{TC}\text{-}4{,}5]^{2-}$ complexes studied here reveal that these conclusions are valid in the solid state as well as in solution.

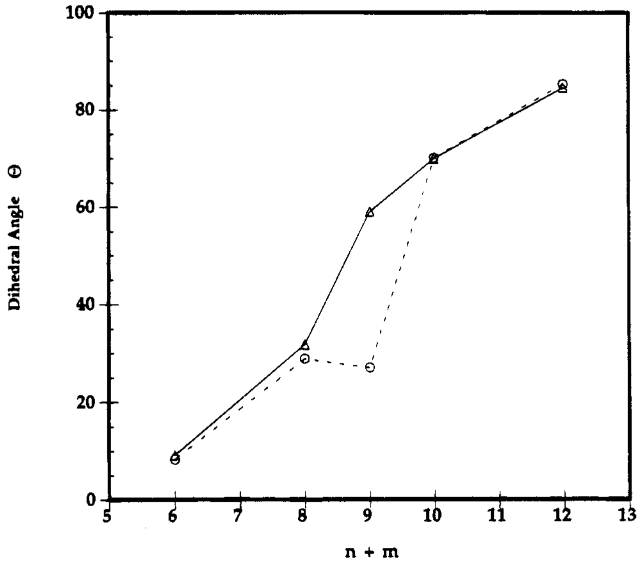

Figure 2. Plot of the dihedral twist angle, Θ, vs total length of the linker chains for mononuclear Ni(II) tropocoronands (circles) and Co(II) tropocoronands (triangles).

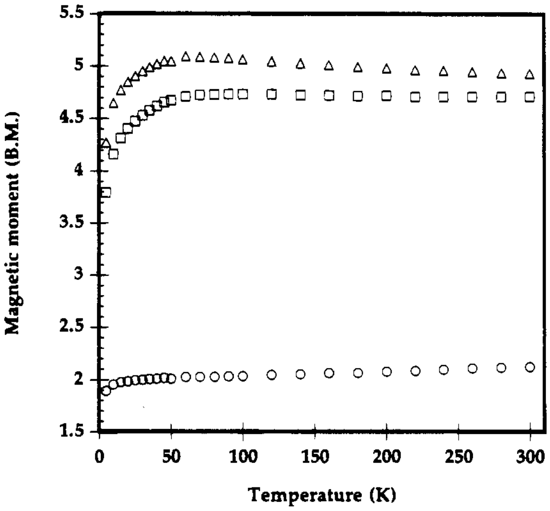

Figure 3. Plot of the magnetic moment vs temperature for [Co(TC-4,4)] (circles), [Co(TC-4,5)] (triangles), and [Co(TC-5,5)] (squares) from 5 to 300 K.

Although we have not carried out solution state magnetic measurements, the electronic spectra discussed below indicate that the solid state geometries and attendant spin values of the complexes are maintained in solution. The macrocyclic tropocoronand complexes are expected to have considerably less conformational flexibility than the bis(β-keto aminato) complexes, which consist of two independent chelating ligands.

Another case in which alterations of ligand steric properties, rather than ligand crowding at the metal center, affected the electronic properties is the series of high- and low-spin bis-chelate Co(II) triazene 1-oxide compounds.[20] Preference for square-planar versus tetrahedral coordination in these N_2O_2 complexes was effected by phenyl group ligand substituents. Ortho substituents caused steric clashes with the azene nitrogen atoms, twisting the phenyl rings out of plane and disrupting conjugation to the triazene chelate ring. As a consequence, the ligand field strength at cobalt increased substantially, forcing square-planar conformation. In the absence of ortho substitu-

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Table 10. Electronic Spectral Properties of the Co(II) Tropocoronands[a]

[Co(TC-3,3)]	[Co(TC-3,4)]	[Co(TC-4,4)]	[Co(TC-4,5)]	[Co(TC-5,5)]	[Co(TC-6,6)]	assign[b]
372 (18 200)	371 (16 600)	360 (22 700)	336 (17 700)	332 (19 000)	336 (18 800)	
396 (17 100)	395 (18 900)	408 (sh, 23 600)	394 (31 000)	392 (34 100)	387 (sh, 33 500)	CT
451 (62 100)	454 (51 700)	455 (40 600)	413 (sh, 29 500)	405 (sh, 32 100)	413 (38 600)	CT
			510 (sh, 4270)	490 (sh, 4480)	478 (sh, 3890)	CT
614 (sh, 2490)	614 (sh, 2350)	592 (sh, 4400)	598 (sh, 1180)	596 (sh, 820)	565 (sh, 1170)	d−d
					599 (sh, 950)	d−d
					670 (sh, 100)	d−d
659 (3960)	658 (3300)	660 (3270)				CT
738 (870)	759 (520)	801 (1270)				d−d

[a] Absorption maxima are given in nm with molar extinction coefficients (M^{-1} cm^{-1}) in parentheses. [b] Legend: CT, charge transfer; d−d, metal d-orbital internal transitions.

ents, both conformations were observed, and the energy required to switch from the low-spin to the high-spin state was estimated to be 0.25−4 kcal/mol.

Electronic Spectra. The electronic spectral properties of the mononuclear Co(II) tropocoronands in the region 300−900 nm are summarized in Table 10. The table suggests tentative assignments of the transitions as d−d or CT in origin, on the basis of their intensities and assignments made for similar complexes. For [Co(TC-3,3)], [Co(TC-3,4)], and [Co(TC-4,4)], the d−d transition between 700 and 800 nm shifts to increasingly lower energy, reflecting the greater distortion from planar geometry and subsequent weakening of the ligand field. A similar planar tetradentate complex, *N,N'*-ethylenebis(*o*-aminobenzylideneaminato)cobalt(II), was reported to have a single d−d transition in approximately this energy range.[13,15] Because of the complexity of d^7 Co(II) spectra, however, and the dominant overlapping charge transfer band at approximately 660 nm, no attempt was made to assign the specific d−d transitions in these planar tropocoronand complexes. For the approximately tetrahedral complexes [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)], a single d−d transition, $^4A_2 \rightarrow {}^4T_1(P)$, is expected to occur at approximately 600 nm.[21,22] The spectra of [Co(TC-4,5)] and [Co(TC-5,5)] reveal slight shoulders at 598 and 596 nm, respectively, which probably correspond to this transition. Three shoulders are apparent in the same region in the spectrum of [Co(TC-6,6)] (Table 10).

Reactivity of the Complexes with O_2. The reactivity of the Co(II) tropocoronands with dioxygen depends strongly on the coordination geometry of the metal and thus on the size of the macrocycle. Whereas all of the mononuclear complexes are air-stable as crystalline solids, solutions of the compounds show varying sensitivity to O_2. Black-green THF solutions of [Co(TC-3,3)], with or without halide present, react with air over several hours to yield an uncharacterized black gummy solid. THF solutions of [Co(TC-3,4)] and [Co(TC-4,4)] react with O_2 in the presence of chloride ion over 18 and 1 h, respectively, to give the stereochemically novel five-coordinate [CoCl(TC-3,4)] and [CoCl(TC-4,4)] complexes reported previously.[5] Red-brown solutions of [Co(TC-5,5)] and [Co(TC-6,6)], by contrast, do not react with air over several hours as monitored by UV−visible spectroscopy. The inertness of these compounds may result from their tetrahedral coordination geometry, which leaves no sterically unhindered approach for dioxygen. Cyclic voltammetric studies have shown the Co(III) redox state for all these [Co(TC-*n*,*m*)] complexes to be easily accessible in CH_2Cl_2 and THF.[23]

A Dinuclear Co(II) Tropocoronand Complex. Synthesis of [Co_2(*μ*-OAc)(*μ*-OH)(TC-7,7)]. Reaction of $Co(OAc)_2{\cdot}4H_2O$ with H_2(TC-7,7) in dry refluxing MeOH under argon resulted in a brick-red solid after 2 h. Recrystallization from benzene/diethyl ether gave ruby-red crystals which were suitable for X-ray structural determination. The compound, shown in Figure 4, proved to be the dinuclear species [Co_2(*μ*-OAc)(*μ*-OH)(TC-7,7)]·Et_2O, containing two tetrahedral Co(II) atoms sitting in the slightly saddle-shaped surface defined by the ligand and separated by a distance of 3.40 Å. Bond lengths and angles within the metal coordination sphere are listed in Table 11. Each Co(II) atom is bound to one set of chelating nitrogen atoms and bridged by acetato and hydroxo groups. The average Co−N bond length of 1.978(6) Å is similar to that found in tetrahedral [Co(TC-6,6)]. A crystallographically imposed 2-fold axis relates the halves of the molecule and passes through the hydroxo oxygen and hydrogen atoms and both acetato carbon atoms. The absorption spectrum of the complex consists of three intense charge transfer bands at 303, 371, and 423 nm as well as three weak shoulders, presumably arising from d−d transitions, at 510, 547, and 574 nm. The three d−d transitions are similar in energy and intensity to the three d−d absorbances observed for the tetrahedral [Co(TC-6,6)].

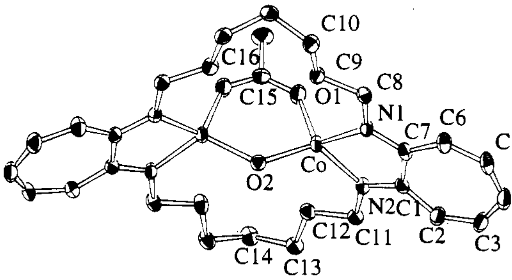

Figure 4. ORTEP drawing of [Co_2(*μ*-OAc)(*μ*-OH)(TC-7,7)] showing 40% probability thermal ellipsoids for all non-hydrogen atoms and a side view. The halves of the molecule are related by a crystallographically imposed 2-fold axis through atoms C16, C15, and O2.

Table 11. Bond Distances (Å) and Angles (deg) for the Coordination Sphere of [Co_2(*μ*-OAc)(*μ*-OH)(TC-7,7)][a]

	Bond Distances		
Co−O1	1.989(3)	Co−N1	1.972(4)
Co−O2	1.934(2)	Co−N2	1.983(3)
	Bond Angles		
O1−Co−O2	100.7(1)	O2−Co−N2	124.3(1)
O1−Co−N1	114.1(1)	N1−Co−N2	81.6(1)
O1−Co−N2	114.9(1)	Co−O1−C15	134.4(3)
O2−Co−N1	121.7(1)	Co−O2−Co'	123.8(2)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 4.

Previously, it was reported that the larger tropocoronand ligands H_2(TC-*n*,*m*) (*n*,*m* = 5,5; 6,6; 7,7) could form dinuclear metal complexes with Cu(I), Cu(II), and Rh(I) under appropriate conditions.[24] The dinuclear Cu(II) complex [Cu_2(*μ*-OAc)(*μ*-OMe)(TC-6,6)] was prepared from $Cu(OAc)_2{\cdot}H_2O$ and H_2(TC-

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6,6) in methanol at room temperature. This complex is structurally similar to [$Co_2(\mu$-OAc)(μ-OH)(TC-7,7)], but its macrocycle is more distorted toward a saddle-shaped conformation, and the bridging acetate and methoxy groups are *both* situated above the ligand. The Cu−Cu distance is 3.10 Å, compared to the Co−Co distance of 3.40 Å. In this dinuclear conformation, the Cu(II) atoms maintain a distorted square-planar configuration, as found in the smaller mononuclear Cu(II) complexes, yet the linker chains are allowed to extend, further relieving the torsional strain among the methylene units. In the case of the dinuclear Co(II) complex, the extension of the linker chains reduces the torsional strain in a similar fashion. The propensity of Co(II) to adopt tetrahedral geometry, however, allows the metal atoms to be situated within the saddle surface of the macrocycle, with the bridging acetate and hydroxy groups occupying opposite sides of the complex.

THF or toluene solutions of [$Co_2(\mu$-OAc)(μ-OH)(TC-7,7)] react irreversibly within minutes with air or dioxygen to give a brown solution with brown precipitate. Martell has reported several dinuclear Co(II) macrocyclic complexes that react irreversibly with dioxygen by initially forming (μ-peroxo)-dicobalt(III) adducts.[4,25] Initial formation of a peroxide is likely to occur in the [$Co_2(\mu$-OAc)(μ-OH)(TC-7,7)] reaction as well.

Conclusions

A series of mononuclear Co(II) tropocoronand complexes have been prepared and structurally characterized. The coordination geometry of the complexes is strongly dependent on the size of the macrocycle, with the smaller complexes, [Co(TC-3,3)] and [Co(TC-4,4)], adopting distorted square-planar geometry and the larger complexes, [Co(TC-4,5)], [Co(TC-5,5)], and [Co(TC-6,6)], adopting distorted tetrahedral geometry. Magnetic susceptibility studies revealed that [Co(TC-4,4)] has a spin of $S = {}^1/_2$, whereas [Co(TC-4,5)] and [Co(TC-5,5)] have spins of $S = {}^3/_2$. The abrupt geometric and electronic spin state change is similar to that found in the Ni(II) tropocoronand system but occurs earlier in the Co(II) series, between [Co(TC-4,4)] and [Co(TC-4,5)] instead of between [Ni(TC-4,5)] and [Ni(TC-5,5)]. The shift in position of the electronic transformation reflects the relative preference of Co(II) for tetrahedral geometry compared to Ni(II) and indicates that the geometric constraints of the $[TC\text{-}4,5]^{2-}$ ligand positions the metal complexes on an energetic transfer point between square-planar and tetrahedral geometry.

In addition to the mononuclear complexes, we have also prepared and structurally characterized dinuclear [$Co_2(\mu$-OAc)(μ-OH)(TC-7,7)]·Et_2O. Research continues in this laboratory to determine whether the reactivity of both the mononuclear and dinuclear Co(II) tropocoronands can be controlled by utilizing the stereochemical constraints of the ligand system in order to develop useful dioxygen-carrying or dioxygen-activation systems.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Supporting Information Available: Tables S1−S24, giving anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, and all bond lengths and angles for [Co(TC-3,3)], [Co(TC-4,4)], [Co(TC-4,5)], [Co(TC-5,5)], [Co(TC-6,6)], and [$Co_2(\mu$-OAc)(μ-OH)(TC-7,7)] (30 pages). Ordering information is given on any current masthead page.

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