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Pentacoordinate Cobalt(III) Thiolate and Nitrosyl Tropocoronand Compounds

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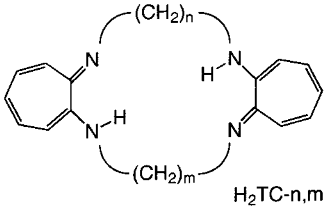
Reaction of [Co(TC-*n*,*m*)]$^+$ with (Me_4N)(SC_6F_5), where (TC-*n*,*m*) is a tropocoronand with *n* and *m* linker chain methylene groups, yielded the thiolate complexes [Co(SC_6F_5)(TC-3,3)] (**1a**), and [Co(SC_6F_5)(TC-4,4)] (**2a**), which were structurally characterized. Use of more electron-releasing thiolates afforded the [Co(TC-*n*,*m*)] reduction product and the corresponding disulfide. The bent nitrosyl complexes [Co(NO)(TC-3,3)] (**1b**) and [Co(NO)(TC-4,4)] (**2b**) were synthesized from [Co(TC-*n*,*m*)] and NO and their structures were also determined. Compounds **1a** and **1b** have square-pyramidal geometry like all other structurally characterized [MX(TC-3,3)] complexes. Compounds **2a** and **2b** have trigonal-bipyramidal stereochemistry, formerly rare for Co(III). Although **1a**, **1b**, and **2a** are paramagnetic, **2b** is diamagnetic due to the strong antibonding π-interaction between the metal and NO π^* orbitals. In the presence of excess NO, [Co(TC-4,4)] exhibited novel reactivity in which a putative Co(N_2) adduct formed.

Introduction

The tropocoronand family of ligands (H_2TC-*n*,*m*) has proved valuable for studying how changes in macrocycle ring size and flexibility can tune the physical and chemical properties of transition metal ions.[1−5] Such changes can also be manifest in unusual reactivity exhibited by these compounds.[6,7] Metal nitrosyl complexes [M(NO)(TC-*n*,*m*)] nicely illustrate these characteristics. The unique properties of [Mn(NO)(TC-5,5)][8] and [Fe(NO)(TC-5,5)][9] that distinguish them from other Mn and Fe nitrosyl species derive from their constrained trigonal-bipyramidal geometries and the strongly donating tetraaza environment provided by the TC-5,5 N_4 donor set. Unlike related complexes of other ligands, these Mn and Fe nitrosyl complexes readily promote the disproportionation of NO.[8,9] Given this precedent, it seemed likely that [Co(TC-*n*,*m*)] complexes would similarly display interesting reactivity with NO. Moreover, by using cobalt it was possible to access compounds with the smallest tropocoronand ring size, TC-3,3, for which we were unable to obtain Mn and Fe analogues.



H_2TC-n,m

Tropocoronand macrocycles afford a series of four-coordinate Co(II) complexes, [Co(TC-*n*,*m*) where ($n + m$) = 6, 7, 8, 9, 10, or 12, having a range of geometries from square planar to tetrahedral.[2] In the present article we report the synthesis, molecular structures, and magnetic and electronic properties of several new 5-coordinate Co(III) tropocoronand complexes, [Co(SC_6F_5)(TC-*n*,*m*)] and [Co(NO)(TC-*n*,*m*)], where $n = m =$ 3 or 4. When $n = 3$, the thiolato and nitrosyl compounds are both square-pyramidal (SP); however, when $n = 4$ the complexes are constrained to be trigonal-bipyramidal (TBP).

The nitrosyl compounds especially demonstrate the physical and chemical tuning achieved with tropocoronands. Whereas [Co(NO)(TC-3,3)] is paramagnetic, [Co(NO)(TC-4,4)] is the first reported diamagnetic TBP Co(III) complex. In the course of studying the NO reactivity of this particular compound, we obtained infrared spectroscopic evidence for a putative cobalt-dinitrogen species produced from reaction with NO.

Experimental Section

General Information. All reactions were carried out in a dinitrogen-filled glovebox or Schlenk line unless otherwise noted. The complexes [Co(TC-3,3)] (**1**) and [Co(TC-4,4)] (**2**) were synthesized as described previously.[2] Pentane, toluene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Methylene chloride and fluorobenzene were distilled from CaH_2. Methanol was distilled from magnesium and stored over 4 Å molecular sieves. All solvents were distilled under dinitrogen. Cp_2FePF_6 was obtained commercially and purified by removing Cp_2Fe by sublimation. NO (Matheson, 99$^+$%) and ^{15}NO (Aldrich, 99%) were purified of higher nitrogen oxides by passage through a column of NaOH pellets and a mercury bubbler and kept over mercury in gas storage bulbs.

UV−vis data were recorded with a Hewlett-Packard 8452A diode array or Cary 1E spectrophotometer. Magnetic moments were determined by the Evans method[10,11] on a 250 MHz Bruker NMR spectrometer by using $(TMS)_2O$ as an internal standard in CD_2Cl_2. ^{1}H NMR data were also collected on this instrument. Standard IR spectra

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were recorded on a Bio Rad FTS-135 instrument; solid samples were prepared as pressed KBr disks and solution samples were prepared in an airtight Graseby-Specac solution cell with CaF_2 windows. In situ IR sample monitoring was performed with a ReactIR 1000 from ASI Applied Systems equipped with a 1-in diameter, 30-reflection silicon ATR (SiComp) probe optimized for maximum sensitivity. Reaction protocols were described previously.[9]

Synthetic Procedures. (Me_4N)(SC_6F_5). A 50-mL round-bottom flask was charged with $Me_4NOH{\cdot}5H_2O$ (4.53 g, 25.0 mmol) in 15 mL of ethanol and purged with N_2 for 5 min. One equivalent of C_6F_5SH (5.0 g, 25.0 mmol) was added via syringe, and the solution was allowed to stir for another 5 min. The solvents were removed in vacuo and triturated with 5 mL of MeOH to remove residual water. The crude product was washed with 10 mL of DME and 5 mL of pentane and dried in vacuo. A white powder was obtained (6.09 g, 89% yield) which showed a single resonance in the ^1H NMR spectrum at 3.22 ppm (DMSO-d_6).

[Co(SC_6F_5)(TC-3,3)] (**1a**). A portion of **1** (205.7 mg, 0.545 mmol) was dissolved in 15 mL of CH_2Cl_2, and 1 equiv of Cp_2FePF_6 (180.4 mg, 0.545 mmol) was added with stirring. The dark-green color changed to deep pink-purple. After 4 h, the solvent was removed in vacuo. The dark purple powder was washed three times with 10 mL of pentane until the golden color of Cp_2Fe was no longer observed in the pentane wash. The remaining solid was extracted into 15 mL of CH_2Cl_2 and filtered through Celite. To the filtrate was added 1 equiv of (Me_4N)(SC_6F_5) (149.1 mg, 0.545 mmol) which had been dissolved in 5 mL of THF. The purple solution began to turn orange brown and was stirred for 3 h until the solution was dark orange-brown, after which time the solvents were removed in vacuo. The resultant brown powder was dissolved in CH_2Cl_2, filtered through Celite to remove (Me_4N)(PF_6), and concentrated in vacuo. The product was recrystallized from hot fluorobenzene in 29% yield (92.1 mg). Fine brown needles suitable for an X-ray diffraction study were grown from fluorobenzene solutions layered with pentane. Evans method moment (CD_2Cl_2), $\mu_{eff} = 3.1\ \mu_B$. UV−vis (CH_2Cl_2) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)] 391 (12,900), 477 (15,300), 573 (7700). Anal. Calcd for $CoN_4C_{26}H_{22}SF_5$: C, 54.17; H, 3.85; N, 9.72. Found: C, 54.15; H, 4.18; N, 9.53.

[Co(SC_6F_5)(TC-4,4)] (**2a**). A portion of **2** (101.2 mg, 0.249 mmol) was dissolved in CH_2Cl_2 and oxidized with 1 equiv of Cp_2FePF_6 (82.4 mg, 0.249 mmol) to form the dark maroon cation $[Co(TC\text{-}4,4)]^+$ in situ, which was allowed to react with 1 equiv of (Me_4N)(SC_6F_5) (68.1 mg, 0.249 mmol). Procedures and workup followed those reported for **1a**. A dark orange-brown solution in CH_2Cl_2 was obtained, which was concentrated to dryness, and the product was recrystallized from hot fluorobenzene in 43% yield (64.8 mg). Crystals suitable for an X-ray diffraction study were grown as dark brown plates from a toluene solution layered with pentane. Evans method moment (CD_2Cl_2), $\mu_{eff} = 3.2\ \mu_B$. UV−vis (CH_2Cl_2) [λ_{max}, nm (ϵM, $M^{-1}\ cm^{-1}$)] 371 (21,300), 456 (22,600), 561 (7100), 669 (3000), 742 (3600). Anal. Calcd for $CoN_4C_{28}H_{26}SF_5$: C, 55.63; H, 4.34; N, 9.27. Found: C, 55.85; H, 4.57; N, 9.13.

[Co(NO)(TC-3,3)] (**1b**). A portion of **1** (38.3 mg, 0.101 mmol) was dissolved in 10 mL of THF in a Schlenk flask under N_2. The flask was sealed and purged with NO while stirring. Immediately upon addition of NO the dark green solution turned brown. After 15 min, the solvent was removed in vacuo to give a brown powder which was recrystallized from hot fluorobenzene in 22% yield (9 mg). Long brown-black needles suitable for X-ray diffraction were grown from slow vapor diffusion of pentane into a THF solution of the compound at ambient temperature. Evans method moment (CD_2Cl_2), $\mu_{eff} = 3.1\ \mu_B$. IR (ν_{NO}, KBr) 1656 cm^{-1}. UV−vis (CH_2Cl_2) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)] 342 (14,300), 417 (12,000), 547 (4350), 677 (2300). Due to difficulty in obtaining sufficient quantities of **1b**, elemental analysis was not performed.

[Co(NO)(TC-4,4)] (**2b**). A portion of **2** (161 mg, 0.397 mmol) was dissolved in 15 mL of THF in a 25-mL Schlenk flask. The initially dark green solution turned red-brown upon exposure to NO. After 10 min of purging the solution with NO, the solvent was removed in vacuo to give a brown powder, which was recrystallized from hot fluorobenzene in 65% yield (110 mg). Small, dark brown plate crystals of X-ray quality were grown by cooling a fluorobenzene solution of the compound layered with pentane. ^1H NMR (δ, ppm, CD_2Cl_2) 1.59 (m, 4H, C−CH_2−C), 1.76 (m, 4H, C−CH_2−C), 3.52 (m, 4H, N−CH_2−C), 3.76 (m, 4H, N−CH_2−C), 6.12 (2H, t, $J = 9$ Hz, H_c), 6.62 (4H, d, $J = 11$ Hz, H_a), 6.85 (4H, t, $J = 11$ Hz, H_b). IR (ν_{NO}, KBr) 1584 cm^{-1}. UV−vis (CH_2Cl_2) [λ_{max}, nm (ϵ_M, $M^{-1}\ cm^{-1}$)] 409 (20,300), 486 (9200), 796 (2400). Anal. Calcd for $CoN_5C_{22}H_{26}O$: C, 60.69; H, 6.02; N, 16.08. Found: C, 60.68; H, 6.25; N, 15.55.

X-ray Crystallography. Single crystal X-ray diffraction data were collected on either an Enraf-Nonius CAD4 four-circle or a Bruker (formerly Siemens) CCD diffractometer. The general procedures for data collection and reduction with each instrument follow those reported previously.[12,13] Structures of **1a**, **2a**, and **2b** were solved with the direct methods package SIR-92, an updated version of SIR88[14] and incorporated into the TEXSAN[15] package of programs, which typically afforded positions for the majority of the non-hydrogen atoms. The structure of **1b** was solved with the program XS by using direct methods, and refinements were carried out with XL, both part of the SHELXTL program package.[16] The structure was refined by full matrix least squares and difference Fourier techniques. Empirical absorption corrections were calculated and applied from the SADABS program.[17] Correct space group assignments were confirmed by successful refinement and checked with the program PLATON.[18] The structure of **1b** was solved in the acentric space group $Cmc2_1$ and refinements were performed with both enantiomorphs to determine the correct absolute configuration. The Flack absolute structure parameter was 0.05(3), compared to expected values of 0.0 for the correct and +1.0 for the inverted structure.[19] Non-hydrogen atoms were refined anisotropically except as noted. Hydrogen atoms were assigned idealized positions and given a thermal parameter 1.2 times that of the carbon atom to which each was attached. One molecule of toluene was found in the lattice of **2a** and refined isotropically with appropriate constraints. Structure solution of **2b** in $P2_1/c$ revealed a disorder of the nitrosyl oxygen atoms O1 and O1* over two positions, which were refined to a 65:35 site occupancy ratio, respectively.

Important crystallographic information for each complex including refinement residuals is given in Table 1. Final positional parameters and all bond distances and angles are provided as Supporting Information.

Reaction of $[Co(TC\text{-}3,3)]^+$ with Pentafluorobenzenethiolate. A 2.56 mL aliquot of a 12.6 μM solution of [Co(TC-3,3)]PF_6 in CH_2Cl_2 was placed in a UV−vis cell with a Teflon septum and cooled to −78 °C. One equivalent of a 5.87 mM solution (5.5 μL) of (Me_4N)(SC_6F_5) in THF was added by syringe. Spectra recorded at approximately 20 s intervals (Figure S1) revealed the rapid formation of [Co(TC-3,3)].

Extended Hückel MO Calculations. Extended Hückel calculations were carried out on a Gateway 2000 Pentium PC computer with the CACAO program.[20] The model complexes $[CoCl(NH_2)_4]^-$, $[Co(SPh)(NH_2)_4]^-$, and $[Co(NO)(NH_2)_4]^-$ were investigated in idealized trigonal-bipyramidal geometries with the fifth ligand in an equatorial position. The following distances and angles were taken from the crystallographically determined parameters in [CoCl(TC-4,4)], **2a**, and **2b**: Co−N_{TC} = 1.92 Å, Co−Cl = 1.80 Å, Co−NO = 1.80 Å, Co−N−O = 130°, Co−S = 2.29 Å, Co−S−C= 107°. In the $[Co(SPh)(NH_2)_4]^-$ and $[Co(NO)(NH_2)_4]^-$ models, the NO and PhS^- groups were bent in the plane containing the principal axis of the trigonal bipyramid, consistent with the structures of **2a** and **2b**.

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Table 1. X-ray Diffraction Studies of Neutral Cobalt(III) Tropocoronand Complexes.

	1a	**2a**·C_7H_8	**1b**	**2b**
formula	$CoSF_5N_4C_{26}H_{22}$	$CoSF_5N_4C_{35}H_{34}$	$CoON_5C_{20}H_{22}$	$CoON_5C_{22}H_{26}$
fw	576.47	696.65	407.36	435.41
cryst system	orthorhombic	triclinic	orthorhombic	monoclinic
space group	*Pbca*	$P\bar{1}$	$Cmc2_1$	$P2_1/c$
a (Å)	12.2478(2)	9.532(5)	16.1983(8)	12.791(1)
b (Å)	9.0636(2)	13.290(5)	12.2557(7)	16.138(2)
c (Å)	41.9264(2)	13.449(5)	8.8952(5)	9.862(1)
α (deg)		71.055(5)		
β (deg)		89.469(5)		104.077(2)
γ (deg)		77.928(5)		
V (Å^3)	4654.2(1)	1572.6(1)	1765.9(2)	1974.5(3)
Z	8	2	4	4
ρ_{calcd}, g/cm^3	1.645	1.471	1.532	1.466
temp (K)	155	193	188	155
μ(Mo Kα), mm^{-1}	8.92	6.74	9.93	8.93
total no. of data	16258	7291	3513	11864
no. of unique data^a	3322	6503	1295	4698
no. of parameters	334	404	130	271
no. of restraints	0	85	1	0
R^b	0.064	0.0714	0.0357	0.086
wR2^c	0.110	0.194	0.0746	0.164
largest peak, e/Å^3	0.361	1.19^d	0.595	0.710
crystal size, mm	0.10, 0.20, 0.30	0.10, 0.18, 0.45	0.1, 0.1, 0.4	0.20, 0.10, 0.05

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$. [d] This peak occurs in the vicinity of a disordered toluene molecule.

Results

Cobalt(III) Tropocoronand Thiolate Complexes. Synthesis and Spectroscopy. From [Co(TC-*n,m*)]PF_6 generated in situ, neutral five-coordinate [Co(SC_6F_5)(TC-*n,m*)] complexes were obtained. Reaction of the four-coordinate Co(III) cations in CH_2Cl_2 with (Me_4N)(SC_6F_5) was accelerated by dissolving the thiolate in THF. The previously characterized[7] THF adduct [Co(THF)(TC-3,3)]$^+$ does not form under these conditions, consistent with the greater affinity of $C_6F_5S^-$ versus THF for cobalt(III). The choice of thiolate was critical because the initially formed [Co(SR)(TC-*n,m*)] species decomposed by internal electron transfer to form [Co(TC-*n,m*)] and the corresponding disulfide when more electron-releasing thiolates RSH (R = Me, Et, *i*-Pr, *t*-Bu, or Ph) were used. At room temperature the color of the pink or purple [Co(TC-*n,m*)]$^+$ cation changed during the time of mixing with (Me_4N)(SR) to the dark green color characteristic of [Co(TC-*n,m*)]. At −78 °C, a brown color was observed briefly upon addition of (Me_4N)(SR), which changed to dark-green in less than 3 min. Spectral changes at 452 nm accompanying the reaction of [Co(TC-3,3)]$^+$ with PhS^- at −78 °C are shown in Figure S1. Diphenyl sulfide was detected in the reaction mixture by GC/MS. When R = C_6F_5 the product was quite stable even in boiling fluorobenzene (84 °C). Electronic spectra characteristic of [Co(TC-*n,m*)]$^+$ were observed upon addition of one equivalent of MeOTf or Me_3OBF_4 to **1a** or **2a,** the thiolate presumably being removed as $MeSC_6F_5$.

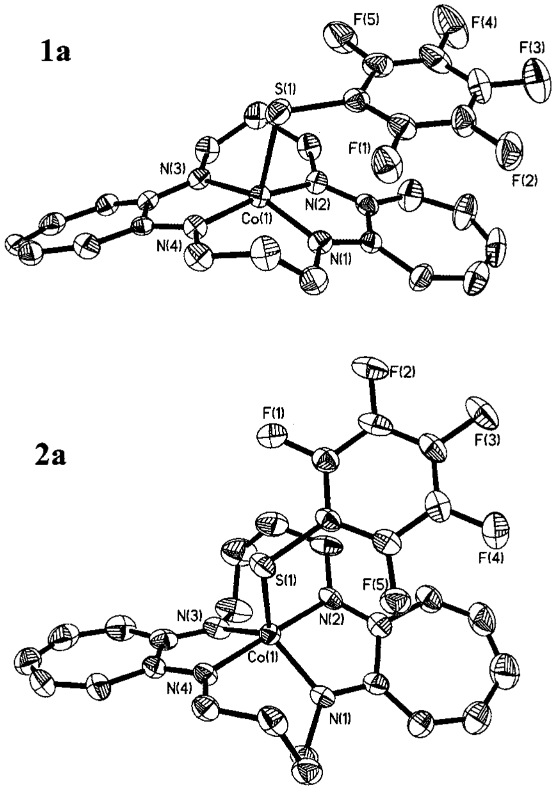

Figure 1. ORTEP drawing for [Co(SC_6F_5)(TC-3,3)], **1a**, and [Co(SC_6F_5)-(TC-4,4)], **2a**, showing 50% probability ellipsoids for all non-hydrogen atoms.

Structures. Figure 1 depicts the structure of **1a**, and selected bond lengths and angles are given in Table 2. The geometry at cobalt is square-pyramidal with the metal displaced from the best N_4 plane by 0.29 Å. The average S−Co−N angle is 98(5)° and the average trans N−Co−N angle is 163(6)°, indicating a slightly distorted square pyramid. The Co−N_{avg} distance of 1.89(1) Å is consistent with previously reported Co−N_{avg} distances in five-coordinate Co(III) complexes. The values for the bend angle at sulfur of 105.6(2)°, the Co−S distance of 2.262(2) Å and the corresponding S−C distance of 1.769(6) Å are unexceptional compared to other crystallographically characterized Co−SC_6F_4X species, X = H, F.[21−23] The pentafluorobenzenethiolate ring is stacked above the C8−C14 aminotroponeiminate ring, with a ring centroid-to-centroid distance of 3.65 Å.

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Table 2. Selected Bond Distances and Angles for Cobalt Thiolate Tropocoronands[a]

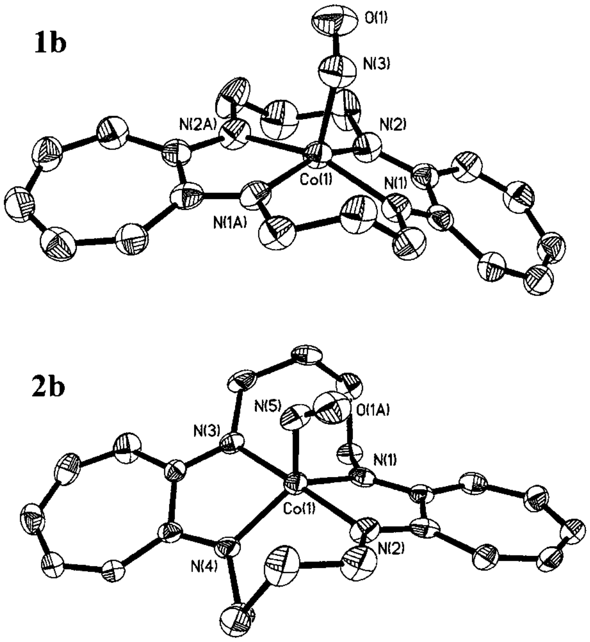
	distances (Å)		angles (deg)	
$[Co(SC_6F_5)(TC\text{-}3,3)]$ **1a**	Co−N1	1.880(4)	N1−Co−N2	81.7(2)
	Co−N2	1.891(4)	N1−Co−N3	158.1(2)
	Co−N3	1.899(4)	N1−Co−N4	96.6(2)
	Co−N4	1.902(4)	N2−Co−N3	95.8(2)
	$Co-N_{avg}$	1.89(1)	N2−Co−N4	167.4(2)
	Co−S	2.262(2)	N3−Co−N4	81.0(2)
	S−C21	1.769(6)	S−Co−N1	95.6(1)
			S−Co−N2	95.3(1)
			S−Co−N3	106.4(1)
			S−Co−N4	97.3(1)
			Co−S−C21	105.6(2)
$[Co(SC_6F_5)(TC\text{-}4,4)]$ **2a**	Co−N1	1.892(4)	N1−Co−N2	81.9(2)
	Co−N2	1.895(4)	N1−Co−N3	120.3(2)
	Co−N3	1.898(4)	N1−Co−N4	97.0(2)
	Co−N4	1.906(4)	N2−Co−N3	97.7(2)
	$Co-N_{avg}$	1.898(6)	N2−Co−N4	178.5(2)
	Co−S	2.293(1)	N3−Co−N4	81.9(2)
	S−C23	1.758(4)	S−Co−N1	122.8(1)
			S−Co−N2	96.0(1)
			S−Co−N3	116.7(1)
			S−Co−N4	85.4(1)
			Co−S−C23	107.3(2)

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

The structure of **2a**, also given in Figure 1, is trigonal bipyramidal with the thiolate ligand in an equatorial position. The atoms N2 and N4 define the principal axis of the trigonal bipyramid. The N−Co−N angle is 178.5(2)° and the angles in the equatorial plane defined by S, N1, and N3 are 122.7(1)°, 116.7(1)°, and 120.3(2)°. The pentafluorobenzenethiolate ring is bent along the principal axis toward N1, with a Co−S−C angle of 107.3(2)°. The Co−S and S−C distances of 2.293(1) and 1.758(4) Å are similar to those in **1a**. Additional structural details are provided in Table 2.

Co(III) Tropocoronand Nitrosyl Complexes. Synthesis and Spectroscopy. Immediately upon exposure to NO, dark green solutions of [Co(TC-*n*,*m*)] turned brown. This color change suggested oxidation of Co(II) to Co(III), since all known five-coordinate Co(III) tropocoronands are brown in solution, with the exception of blue-green $[Co\{C(O)CH_3\}(TC\text{-}4,4)]$.[6] Longer exposure times of **2** to NO resulted in further reactivity and decomposition of the nitrosyl species, as described below. Although similar behavior was not expressly observed for **1**, it was difficult to isolate large enough quantities of **1b** suitable for elemental analysis. Once isolated, however, **1b** could be recrystallized in the presence of air. Solutions of **2b**, on the other hand, rapidly decomposed in air. The formation of **1b** and **2b** was irreversible. Under vacuum, NO was not lost from the solid or solutions, and the compounds were stable in boiling fluorobenzene (84 °C).

In the infrared spectra, $\nu_{N=O}$ bands at 1656 and 1584 cm^{-1} for **1b** and **2b**, respectively, are consistent with data for other bent Co nitrosyls, although these values vary widely and do not correlate with any other property of Co nitrosyls.[24]


1b

2b

Figure 2. ORTEP drawing for [Co(NO)(TC-3,3)], **1b**, and [Co(NO)-(TC-4,4)], **2b**, showing 50% probability ellipsoids for all non-hydrogen atoms. In **2b**, only one of the disordered nitrosyl oxygen atoms is depicted.

Table 3. Selected Bond Distances and Angles for Cobalt Nitrosyl Tropocoronands.[a]

	distances (Å)		angles (deg)	
[Co(NO)(TC-3,3)] **1b**	Co−N1	1.916(4)	N1−Co−N1A	94.4(2)
	Co−N2	1.900(4)	N1−Co−N2	81.2(2)
	$Co-N_{TC(avg)}$	1.90(1)	N1−Co−N2A	159.7(2)
	Co−N3	1.785(6)	N2−Co−N2A	96.0(2)
	O1−N3	1.137(7)	N1−Co−N3	101.8(2)
			N2−Co−N3	98.4(2)
			Co−N3−O1	127.3(6)
[Co(NO)(TC-4,4)] **2b**	Co−N1	1.906(6)	N1−Co−N2	81.0(2)
	Co−N2	1.926(5)	N1−Co−N3	97.0(2)
	Co−N3	1.916(5)	N1−Co−N4	129.3(2)
	Co−N4	1.899(6)	N1−Co−N5	114.1(3)
	$Co-N_{TC(avg)}$	1.91(1)	N2−Co−N3	176.4(2)
	Co−N5	1.779(6)	N2−Co−N4	97.5(2)
	O1A−N5	1.151(9)	N2−Co−N5	90.9(3)
	O1B−N5	1.18(2)	N3−Co−N4	81.4(2)
			N3−Co−N5	92.7(3)
			N4−Co−N5	116.6(3)
			Co−N5−O1A	128.9(6)
			Co−N5−O1B	134.9(9)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figure 2.

Magnetic Properties. Compound **1b** is paramagnetic at room temperature with a μ_{eff} of 3.1 μ_B in solution, whereas **2b** is diamagnetic. The latter is the first example of a diamagnetic trigonal-bipyramidal Co(III) complex. All ligand protons were clearly resolved in the ^1H NMR spectrum and showed the same characteristic shifts and multiplicities observed in the diamagnetic [Zn(TC-*n*,*m*)],[25] [Cd(TC-*n*,*m*)],[25] and [Ni(TC-*n*,*m*)] complexes ($n + m = 6, 8, 9$).[1] Extended Hückel calculations explain this novel feature, as discussed below.

Structures. An ORTEP diagram of **1b** is illustrated in Figure 2, and selected bond lengths and angles are reported in Table 3. The cobalt atom sits on a crystallographically required mirror plane that relates the two halves of the molecule. The two central methylene carbon atoms and the nitrosyl group lie on this mirror plane. The linker chains adopt different conformations; one six-membered chelate ring has a chair conformation whereas the other has a boat conformation. As in compound **1a**, the structure of **1b** is square-pyramidal with cobalt displaced out of the best N_4 plane by 0.54 Å and an average $N_{TC}-Co-N_{NO}$ angle of 104(14)°. The average $Co-N_{TC}$ distance of 1.91(1) Å is similar

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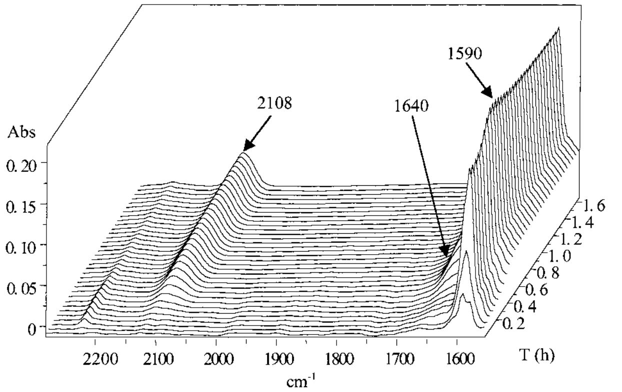

Figure 3. In situ IR spectra of [Co(TC-4,4)] (**2**) in THF at −78 °C as NO is introduced into the headspace above the solution. The increase in intensity at 1590 cm^{-1} depicts the formation of [Co(NO)(TC-4,4)] (**2b**), the NO stretch of which overlaps with a band present in the starting complex. The band at 1640 cm^{-1} may represent the nitrosyl stretch of a {$Co(NO)(NO_2)$} species, whereas the band at 2108 cm^{-1} suggests a $Co(N_2)$ complex.

to Co(III)−N_{avg} distances in [CoEt(TC-3,3)][6] and [CoCl(TC-3,3)][3] cited above. The Co−N−O angle of 127.3(6)° is in the 122−128° range of other axially coordinated nitrosyls of square-pyramidal Co complexes, such as a variety of porphyrins.[26−29] The N−O bond length of 1.137(7) Å in **1a** is slightly shorter than the 1.16−1.18 Å distances found in those same examples.

The structure of **2b** is given in Figure 2 and selected distances and angles in Table 3. Here the geometry is trigonal bipyramidal, with the equatorial plane containing the nitrosyl group and atoms N1 and N4, which form angles at Co of 129.3(2)°, 116.6(3)°, and 114.1(3)°. The N2−Co−N3 angle is 176.4(2)°, and the bent nitrosyl group lies in the plane of the axial ligands. The oxygen atom of the nitrosyl group is disordered over two positions in the N2−Co−N1 plane, which refined to a 65:35 site occupancy ratio for O1A and O1B, respectively. The average Co−N_{TC} distance of 1.91(1) Å is essentially the same as that in **1b**. The average N−O distance is 1.17(2) Å and the Co−N−O angle is 132(4)°. Both nitrosyl complexes have the $\{CoNO\}^8$ configuration.[30]

Reactivity. Figure 3 contains the IR spectra recorded when a THF solution of [Co(TC-4,4)] (**2**) at −78 °C and under an Ar atmosphere was exposed to a stream of NO gas. The initial dark green Co(II) complex rapidly turned red-brown in the presence of NO. The first step in the reaction was formation of **2b**, identified by the characteristic NO stretch at 1590 cm^{-1} in solution, which happens to overlap a band present in the starting Co(II) complex. At about the same time, N_2O appeared at 2223 cm^{-1} and a shoulder developed around 1640 cm^{-1}. Within 20 min, a band developed at 2108 cm^{-1} and the N_2O signal at 2223 cm^{-1} appeared to decay. A blackish precipitate began to form. The reaction continued without noticeable spectral changes for 3 h, after which time the cold bath was removed and the reaction was monitored, without any noticeable changes, for an additional 1 h at room temperature. The bands at 2108 and 1590 and the shoulder around 1640 cm^{-1} did not shift during this time course.

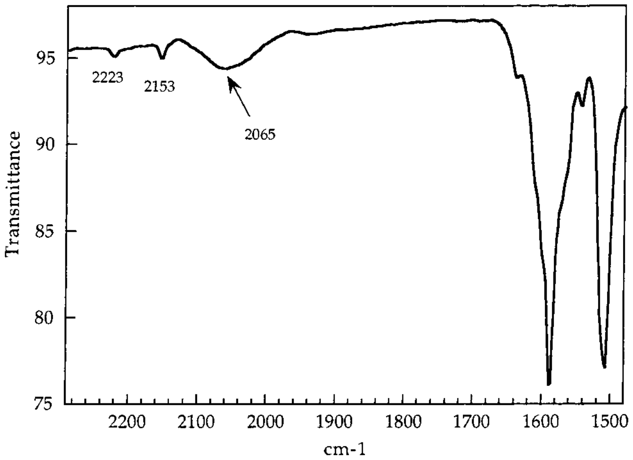

Figure 4. IR spectrum taken in THF solution 2 h after 5 equiv each of ^{15}NO and ^{14}NO were added to a solution of [Co(TC-4,4)] (**2**) under Ar. The bands at 2223 and 2153 cm^{-1} correspond to $^{14}N_2O$ and $^{15}N_2O$, respectively. The broad band centered at 2065 cm^{-1} is attributed to overlapping $\nu(^{14}N^{14}N)$, $\nu(^{14}N^{15}N)$, and $\nu(^{15}N^{15}N)$ stretching modes.

We wondered whether the feature at 2108 cm^{-1} might be signaling formation of a cobalt-dinitrogen species.[31] Isotope-labeling experiments should be diagnostic of such a unit. Assuming a classic diatomic oscillator model, $\nu(^{15}N^{15}N)$ should shift by 70 cm^{-1} compared with the corresponding $\nu(^{14}N^{14}N)$ stretch, whereas the difference between $\nu(^{15}NO)$ and $\nu(^{14}NO)$ should be 30 cm^{-1}. Indeed, when the reaction was performed with ^{15}NO, bands appeared at 2031 cm^{-1} and 1612 cm^{-1}, suggesting the ^{15}N-shifted versions of the 2108 ($\nu^{14}N^{14}N$) and 1640 $cm^{-1}(\nu^{14}NO)$ bands that are seen in Figure 3. In addition, a band at 2153 cm^{-1} signaled the formation of $^{15}N_2O$. When a mixture of ^{14}NO and ^{15}NO was introduced to a THF solution of **2** under Ar, one broad band spanning from 2130 to 1966 cm^{-1} appeared, centered at 2065 cm^{-1}. The IR spectrum is shown in Figure 4. We attribute this band to overlapping contributions from $\nu(^{14}N^{14}N)$, $\nu(^{14}N^{15}N)$, and $\nu(^{15}N^{15}N)$ in a 1:2:1 ratio. For an observed $\nu(^{14}N^{14}N)$ band at 2108 cm^{-1}, the calculated, isotopically shifted frequencies are 2072 cm^{-1} for $\nu(^{14}N^{15}N)$ and 2036 cm^{-1} for $\nu(^{15}N^{15}N)$. The 165 cm^{-1} width (measured from baseline to baseline) of the 2065 cm^{-1} peak is considerably broader than the 110 cm^{-1} peak width of the 2108 cm^{-1} band in Figure 3.

Because reduced metal centers react with N_2O, we tested for the formation of "$Co(N_2)$" by exposing the known Co(I) compound[6] $[Co(TC\text{-}4,4)]^-$ both to N_2 and N_2O, but saw no evidence for a dinitrogen adduct. Likewise, we saw no evidence for reaction of **2** with N_2O.

Discussion

Structural Properties of Cobalt(III) Tropocoronand Thiolate and Nitrosyl Complexes. Cobalt thiolate complexes in which the mercaptide donor is monodentate and not a part of a chelate ring are rare. The proclivity for RS^- to reduce metal atoms or to bridge them is well-known. Most structurally characterized examples[32] have either strongly electron-withdrawing R groups, $R = C_6F_4H$[21,22,33] or C_6F_5,[23] or low oxidation states, Co(II)[23,34−37] or Co(I),[36,38,39] the latter being unlikely to undergo further reduction. The requirement of a strongly

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electron-withdrawing thiolate in [Co(SR)(TC-*n*,*m*)] complexes in order to avoid electron transfer from sulfur to Co(III) is therefore not surprising.

The geometries of the 5-coordinate Co(III) complexes presented here reflect the tendencies of the particular TC-*n*,*m* ligand used in each case. The limited flexibility of the TC-3,3 ligand imposes a square-pyramidal configuration on **1a** and **1b**; no other stereochemistry has been observed for any [MX(TC-3,3)] complex.

Trigonal-bipyramidal geometry is much less common for Co(III), but has been observed previously in the tropocoronand complex [CoCl(TC-4,4)];[3] a few $[CoX_3(PR_3)_2]$[40−43] complexes also share this stereochemistry. Compounds **2a** and **2b** offer two new examples of this formerly rare geometry for Co(III), which is now routinely accessible because of the tuning properties of the TC-4,4 ligand. From the torsional angles in the linker chains of [CoCl(TC-4,4)][3] it was apparent that the trigonal bipyramid was less strained than square pyramid for 5-coordinate TC-4,4 complexes, although one example, [Co(Me)(TC-4,4)], does exhibit the latter configuration.[6] Because the methyl group is a σ-donor with no ability to serve as a π-donor or acceptor, it does not coordinate in the equatorial plane of a trigonal bipyramid where it would have to share to the $d_{x^2-y^2}$ orbital with two other ligands. Rather, it coordinates in the axial position of a square pyramid, binding to the d_{z^2} orbital, which is not similarly shared. The nitrosyl is both a σ-donor and a π-acceptor and can bind in the equatorial position of the trigonal bipyramid, like chloride ion, which is both a σ- and π-donor.

The nitrosyl complexes **1b** and **2b** exemplify the two types of geometries known for pentacoordinate $\{CoNO\}^8$ systems, square-pyramidal and trigonal-bipyramidal, and further delineate the control of stereochemistry by ligand twist. Many other square-pyramidal $\{CoNO\}^8$ complexes with bent nitrosyl groups have been structurally characterized, including $[Co(dmgH)_2(NO)]$,[44] a substituted tmtaa complex $[Co(NO)(Me_2(COOEt)_2\text{-}taa)]$,[45] salicylideneiminate derivatives,[46] a variety of porphyrins[26−28,30,47,48] and others.[49,50] The bond distances and angles in **1b** are unexceptional compared to the ones in these other cobalt nitrosyls.

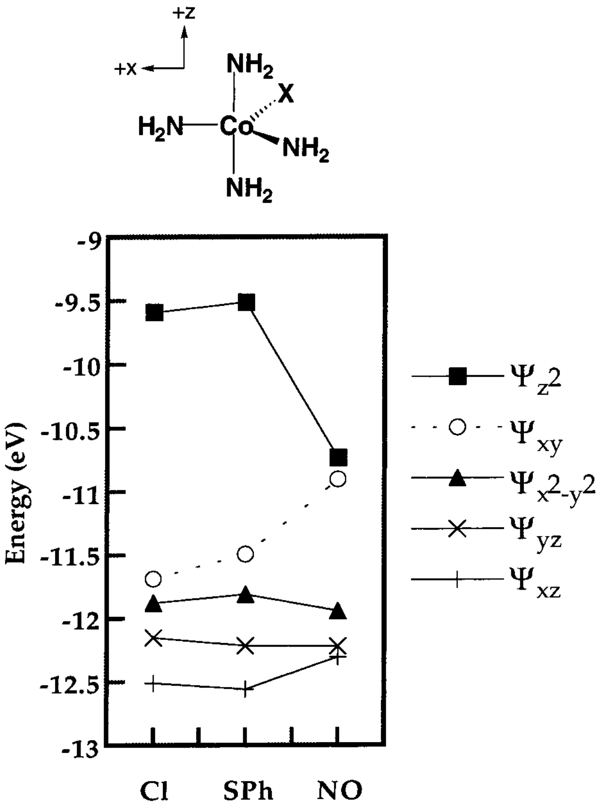

Figure 5. Energies of frontier molecular orbitals for $[CoCl(NH_2)_4]^-$, $[Co(SPh)(NH_2)_4]^-$, and $[Co(NO)(NH_2)_4]^-$ from EHMO calculations.

Among the structurally characterized five-coordinate $\{CoNO\}^8$ complexes, bent nitrosyl groups occur almost exclusively in the axial positions of square-pyramidal structures, like **1b**, whereas linear nitrosyls occupy an equatorial position of a trigonal biypramid.[51] Compound **2b** is only the second structurally characterized example of a $\{CoNO\}^8$ system with a bent nitrosyl in the equatorial position of a trigonal bipyramid. The other example is $[Co(NO)Cl_2(PMe_3)_2]$,[52] in which the nitrosyl is clearly bent, but disorder of the NO moiety and a chlorine atom over two sites prevented accurate determination of the nitrosyl bond distances and angles. The disorder in **2b** has been successfully modeled.

The compounds $[Co(NO)I_2(PMe_3)_2]$[52] and $[Co(NO)Cl_2(PMePh_2)_2]$[53] also have trigonal-bipyramidal geometry, but their symmetry is C_{2v} and the nitrosyl groups are linear. The bending of NO in $[Co(NO)Cl_2(PMe_3)_2]$ has been attributed to mixing of the $d_z{}^2$ and NO π^* orbitals.[52] Consistent with this argument is the bent nitrosyl group in $[Co(NO)Cl_2(PMe_3)_2]$, which has stronger phosphine donors than $[Co(NO)Cl_2(PMePh_2)_2]$ bearing a linear nitrosyl. Finally, the MO calculations described elsewhere revealed that the tropocoronand ligand is a strong π-donor,[2,54] consistent with the bent NO groups in **1b** and **2b**.

Compound **2b** is distinct from all other trigonal-bipyramidal cobalt nitrosyls and all other trigonal-bipyramidal Co(III) tropocoronand complexes because it is diamagnetic. This

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property can be explained by the results of extended Hückel MO calculations presented in Figure 5, which plot the relative d-orbital energies of three trigonal-bipyramidal models, $[CoCl(NH_2)_4]^-$, $[Co(SPh)(NH_2)_4]^-$, and $[Co(NO)(NH_2)_4]^-$, based on the compounds [CoCl(TC-4,4)], **2a** and **2b**. The energy of the d_{xy} orbital greatly increases when NO is the fifth ligand, compared to the thiolate and chloride cases, owing to interaction with the NO π* orbitals. Neither chloride nor sulfur has π* acceptor orbitals to interact with the d_{xy} orbital. This difference in orbital energies readily explains the observed diamagnetism of **2b** compared to [CoCl(TC-4,4)] and **2a**, which are both paramagnetic. The d_{xy} orbital in **2b** is sufficiently raised in energy that the gap between the d_{xy} orbital and the $d_{x^2-y^2}$ orbital is greater than the pairing energy, resulting in an $S = 0$ complex.

Reactivity. Difficulties in obtaining sufficient quantities of **1b** limited detailed studies of the reactivity of [Co(TC-3,3)] with NO. Some important differences between **1b** and **2b** are apparent, however. No N_2O was observed in the reactions between **1** and excess NO, either by IR spectroscopy or gas chromatography. Nor did we observe a stretch around 2100 cm^{-1} in the IR spectrum after **1** had been exposed to NO for several hours. We were able, however, to recrystallize **1b** in air, indicating that this nitrosyl compound is not air sensitive.

The lack of reactivity of **1b**, both in the presence of excess NO and in air, contrasts sharply with the reactivity previously reported for [Mn(NO)(TC-5,5)][8] and [Fe(NO)(TC-5,5)],[9] as well as the new results presented here for [Co(NO)(TC-4,4)]. In these cases, the nitrosyl adducts rapidly decayed in the presence of air. In the presence of excess NO, the Mn and Fe compounds reacted further to disproportionate NO, affording N_2O and NO_2. The latter was either metal-bound, as in $[Mn(NO_2)(TC\text{-}5,5)]$,[8] or it nitrated the aromatic rings of the ligand to give $[Fe(NO)(TC\text{-}5,5\text{-}NO_2)]$.[9] When supported by the TC-4,4 ligand however, cobalt further reduced NO to give some fraction of what we propose to be a dinitrogen adduct. Although the reaction was not clean and an insoluble precipitate formed, the infrared data strongly suggest the presence of a "$Co(N_2)$" species. When ^{15}NO or a mixture of $^{14}NO/^{15}NO$ was used, the IR stretch of this postulated functionality shifted by the expected amount for Co-$^{15}N^{15}N$ or Co-$^{15}N^{14}N$, respectively. The $^{14}N_2$ and labeled $^{15}N_2$ bands at 2108 and 2031 cm^{-1} correspond closely to the reported values of a well characterized cobalt dinitrogen complex, $[CoH(N_2)(PPh_3)_3]$, for which $\nu(^{14}N^{14}N) = 2092\ cm^{-1}$ and $\nu(^{15}N^{15}N) = 2026\ cm^{-1}$.[55] We have not yet, however, been able to isolate and characterize the molecular structure of this alleged dinitrogen-containing species. No other metal-bound dinitrogen adduct has to our knowledge arisen from the reaction of a metal complex with NO, although free N_2 has been produced via such reactions.[56,57]

Acknowledgment. This work was supported by a grant from the National Science Foundation. Dr. B. Spingler thanks the Swiss Scientific National Foundation for postdoctoral fellowship support.

Supporting Information Available: Figure S1, showing the absorbance changes of $[Co(TC\text{-}3,3)]^+$ upon reaction with PhS^- at −78 °C and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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