crystals displays peaks at 142.2 and 140.9 ppm, which are close to those of an authentic sample. The remaining carbons of the Triph groups display a complex pattern of peaks between 128.7 and 124.0 ppm. There is no overall change in the ^{13}C NMR resonance pattern at temperatures as low as −80 °C that might indicate association in solution.

In conclusion, it is notable that the Cu···Cu contact in **2** lends support to the idea that interactions between d^{10} centers in organocopper structures may be of considerable significance in determining their structures. Such interactions have already been implicated in the structures of various Cu(I) compounds[13] and the Cu_4R_4 tetramers.[11] The presence of these interactions has been supported by calculations.[14] Finally, it is notable that the isolation of **1** and **2** underline the usefulness of SMe_2 in stabilizing organocopper species.[15]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Tables of data collection parameters, atomic coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for **1** and **2** (17 pages); listing of observed and calculated structure factors for **1** and **2** (69 pages). Ordering information is given on any current masthead page.

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Tuning the Stereochemistry of Pentacoordinate Co(III) Halide Complexes: A Rare Case of Trigonal Bipyramidal Stereochemistry for Cobalt(III)

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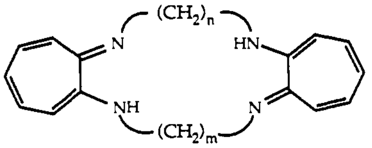
Previously we employed the macrocyclic tropocoronand ligand, $H_2(TC\text{-}n,m)$, to prepare $[M(TC\text{-}n,m)]$ complexes of Cu(II) and Ni(II) with controlled geometries ranging from square planar to tetrahedral.[1] We now report a series of unusual pentacoordinate Co(III) tropocoronand chloride complexes which vary in geometry from square pyramidal to trigonal bipyramidal, depending on the size of the macrocycle. The [CoCl(TC-4,4)] complex, **3**, is a rare example of a structurally characterized trigonal bipyramidal Co(III) complex, and solid-state magnetics measurements indicate that it is paramagnetic at room temperature. In contrast to the variable geometry of the Co(III) chloride complexes, the analogous Co(III) alkyls are diamagnetic and have geometries that are relatively uninfluenced by the ligand constraints.



Tropocoronand, $H_2(TC\text{-}n,m)$

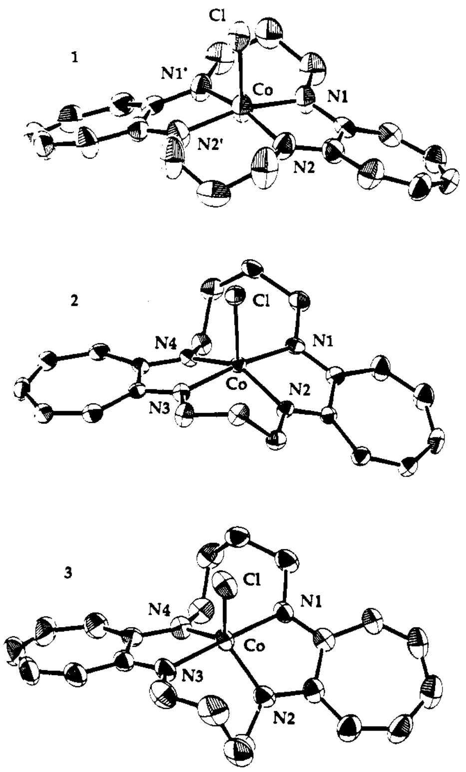


Figure 1. ORTEP drawings of [CoCl(TC-3,3)] (**1**), [CoCl(TC-3,4)] (**2**), and [CoCl(TC-4,4)] (**3**) showing the 50% probability thermal ellipsoids for all non-hydrogen atoms. Selected interatomic distances (Å) and angles (deg) are as follows. **1**: Co–Cl, 2.384 (5); Co–N1, 1.892 (8); Co–N2, 1.889 (8); N1–Co–Cl, 101.9 (3); N2–Co–Cl, 94.8 (3); N1–Co–N1′, 94.6 (5); N1–Co–N2, 82.1 (3); N1–Co–N2′, 163.3 (4); N2–Co–N2′, 96.2 (5). **2**: Co–Cl, 2.343 (1); Co–N1, 1.921 (4); Co–N2, 1.862 (3); Co–N3, 1.919 (4); Co–N4, 1.881 (4); N1–Co–Cl, 98.5 (1); N2–Co–Cl, 108.3 (1); N3–Co–Cl, 90.0 (1); N4–Co–Cl, 109.3 (1); N1–Co–N2, 81.9 (2); N1–Co–N3, 171.5 (2); N1–Co–N4, 96.7 (2); N2–Co–N4, 142.1 (2). **3**: Co–Cl, 2.288 (1); Co–N1, 1.906 (4); Co–N2, 1.870 (4); Co–N3, 1.914 (4); Co–N4, 1.894 (4); N1–Co–Cl, 91.7 (1); N2–Co–Cl, 121.7 (1); N3–Co–Cl, 90.2 (1); N4–Co–Cl, 117.9 (1); N1–Co–N2, 82.0 (2); N1–Co–N3, 178.0 (2); N1–Co–N4, 97.9 (2); N2–Co–N4, 120.4 (2).

When O_2 was introduced to a stirred mixture of $Li_2(TC\text{-}3,4)$ or $Li_2(TC\text{-}4,4)$ and $CoCl_2$ in THF, the resulting dark green solution[2] turned red-brown. Removal of solvent and extraction into CH_2Cl_2, followed by slow addition of diethyl ether, gave brown crystalline [CoCl(TC-3,4)] or [CoCl(TC-4,4)] in approximately 50% yield. [CoCl(TC-3,3)] could not be prepared by using this procedure, but instead was isolated in low yield by slow diffusion of $CHCl_3$ into a CH_2Cl_2/Et_2O solution of [Co(TC-3,3)].[3]

Single-crystal X-ray structural analysis[4] of the three products revealed substantially different geometries, as summarized in Figure 1. The structure of [CoCl(TC-3,3)] (**1**) is square py-

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(2) The Co(II) compounds will be reported elsewhere.

(3) Analytical and spectroscopic data for compounds **1–3** and the Co(III) alkyl complexes are reported as supplementary material.

(4) Crystal data for **1** at 200 K: size ca. 0.08 × 0.15 × 0.30 mm, orthorhombic $Cmc2_1$, $a = 16.275$ (6) Å, $b = 11.874$ (2) Å, $c = 9.069$ (4) Å, $V = 1752$ (1) Å^3, $Z = 4$, $\rho_{calcd} = 1.56$ g cm^{-3}. For 838 unique, observed reflections with $F^2 > 1\sigma(F^2)$ and 130 variable parameters, the final discrepancy indices were $R = 0.057$ and $R_w = 0.058$. Crystal data for **2** at 200 K: size ca. 0.13 × 0.20 × 0.25 mm, monoclinic, space group $P2_1$, $a = 10.742$ (2) Å, $b = 8.270$ (1) Å, $c = 11.106$ (2) Å, $\beta = 104.30$ (1), $V = 956.0$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 1.48$ g cm^{-3}. For 2233 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 243 variable parameters, the final discrepancy indices were $R = 0.035$ and $R_w = 0.038$. Crystal data for **3** at 296 K: size ca. 0.20 × 0.40 × 0.40 mm, orthorhombic, space group *Pbca*, $a = 9.6713$ (8) Å, $b = 25.948$ (3) Å, $c = 15.901$ (1) Å, $V = 3990$ (1) Å^3, $Z = 8$, $\rho_{calcd} = 1.47$ g cm^{-3}. For 2087 unique, observed reflections with $F^2 > 3\sigma(F^2)$ and 253 variable parameters, the final discrepancy indices were $R = 0.044$ and $R_w = 0.054$.

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ramidal with a Co–Cl axial bond length of 2.384 (5) Å and crystallographically equivalent N–Co–N angles of 163.3 (4)° spanning the base of the pyramid. The geometry of [CoCl(TC-3,4)] (**2**) is best described as intermediate between square pyramidal and trigonal bipyramidal with a Co–Cl bond distance of 2.343 (1) Å and analogous N–Co–N bond angles of 171.5° and 142.1°. Finally, [CoCl(TC-4,4)] (**3**) adopts nearly perfect trigonal bipyramidal stereochemistry with the chloride ion in the equatorial plane and a Co–Cl bond distance of 2.288 (1) Å. As was the case for the [M(TC-*n*,*m*)] complexes, geometric changes occur as $n + m$ varies from 6 to 7 to 8 in order to relieve steric crowding in the polymethylene linker chains. In particular, the α,ω linker chain carbon atoms move farther apart as the structure changes from square pyramidal toward trigonal bipyramidal (see discussion in ref 1). To our knowledge, the only other crystallographically characterized trigonal bipyramidal Co(III) complexes are the paramagnetic species [Co(PMe$_3$)$_2$I$_3$][5] and [Co(PEt$_3$)$_2$Cl$_3$].[6,7] A later report of an improved synthetic route to [Co(PR$_3$)$_2$X$_3$], X = Br, Cl, compounds[8] indicated that they were difficult to purify, decomposing rapidly in anaerobic solution or as solids in the air at room temperature. By contrast, solutions of [CoCl(TC-4,4)] only slowly decompose in air and the solid is indefinitely stable.

The compounds [CoCl(TC-4,4)] and [CoCl(TC-3,4)] display no solution NMR spectra at room temperature, a property indicative of paramagnetism. Measurement of the magnetic susceptibility of a microcrystalline sample of [CoCl(TC-4,4)] by SQUID susceptometry revealed a magnetic moment of 3.0 μ_B from 300 to 50 K, corresponding to the presence of two unpaired electrons. Below 50 K, however, the moment drops sharply and reaches a value of 1.1 μ_B at 5 K, apparently approaching a nonmagnetic ground state. The temperature dependence of the magnetic moment is characteristic of zero field splitting from a spin triplet, and a nonlinear least-squares fitting of the susceptibility data to an expression accounting for this phenomenon gave $D = 55$ cm^{-1}.[9] This value is similar to that reported for [Co(PEt$_3$)$_2$Cl$_3$], 49 cm^{-1}.[7] Observed and calculated χ vs T and μ_{eff} vs T plots are included as supplementary material (Figure S1).

Molecular orbital calculations were carried out with an SCF-multiple scattering-Xα program[10-12] on a simplified model system in which the tropocoronand ligand was replaced by four amido (NH$_2^-$) groups. Both the trigonal bipyramidal and square pyramidal cobalt(III) chloride complexes were found to have paramagnetic, $S = 1$, ground states. In the case of the trigonal bipyramidal complex, the calculations revealed the paramagnetism to arise from a set of nearly degenerate d_{xy}, $d_{x^2-y^2}$, and d_{yz} orbitals, corresponding to a ground-state configuration of $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^1(d_{xy})^1$. An energy level diagram is provided as Figure S2 in the supplementary material. The paramagnetic ground state calculated for the square pyramidal complex is $(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1$. The near degeneracy among the d_{xz}, d_{yz}, and d_{z^2} orbitals arises because the normally low-lying degenerate d_{xz},d_{yz} pair is raised substantially in energy, to within 0.19 eV of the d_{z^2} orbital, as a result of π-antibonding interactions with the nitrogen lone pairs (see Figure S3, supplementary material, for an energy level diagram). This orbital arrangement differs from the electronic configuration proposed for two other paramagnetic square pyramidal [CoX(N)$_4$] complexes, $(d_{xz})^2(d_{yz})^2(d_{xy})^1(d_{z^2})^1$,[13,14] in which π-bonding effects were not considered.

The variable geometries observed in the [CoCl(TC-*n*,*m*)] systems led us to investigate the corresponding Co-alkyl complexes. Reaction of the [Co(TC-3,3)]$^-$ or [Co(TC-3,4)]$^-$ anions, obtained from [Co(TC-*n*,*m*)] by reduction with 40% Na/Hg, with EtBr or *n*-PrBr cleanly yielded the corresponding Co(III) alkyls, whereas [CoMe(TC-4,4)] was prepared by addition of MeLi to a THF solution of [CoCl(TC-4,4)].[3] X-ray structural analyses[15] of [CoR(TC-3,3)] (R = Et, *n*-Pr) and [CoMe(TC-4,4)] revealed that *both* TC-3,3 and TC-4,4 complexes adopt square pyramidal geometries, and their sharp solution NMR spectra indicate that both are diamagnetic in solution. It is intriguing that the solid-state structures of the Co(III) alkyls are relatively insensitive to changes in the ligand steric constraints, whereas the geometry of the Co(III) chlorides has a marked dependence on the size of the macrocycle. The square pyramidal stereochemistry may be favored in both Co(III) alkyls because strong Co–C σ-interactions, preferred by the alkyl ligands, are better accommodated through bonding to the d_{z^2} orbital of the square pyramid than to the d_{xy},$d_{x^2-y^2}$ set in the equatorial plane of a trigonal bipyramid. We are currently investigating differences in reactivity among the various cobalt tropocoronand chloride and alkyl derivatives.

Acknowledgment. This work was supported by grants from the National Science Foundation and the National Institute of General Medical Sciences, for which we are grateful. We also thank K. L. Taft for help with the magnetic measurements.

Supplementary Material Available: Listings of analytical and spectroscopic data for **1**–**3** and the Co(III) alkyl complexes, Tables S1, S2, and S3 reporting atomic positional and equivalent isotropic thermal parameters for **1**, **2**, and **3**, respectively, Figure S1 depicting the observed and calculated χ vs T and μ vs T curves for **3**, and Figures S2 and S3 showing energy level diagrams for trigonal bipyramidal and square pyramidal [CoX(N)$_4$] complexes, respectively (7 pages). Ordering information is given on any current masthead page.

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UO$_2$–Salenes: Neutral Receptors for Anions with a High Selectivity for Dihydrogen Phosphate

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The design and synthesis of neutral macrocyclic receptors that complex cations in apolar solvents with a high degree of selectivity are based on the ability to organize nucleophilic binding sites (Lewis bases) in a complementary array.[1] Although macrocycles with quaternary ammonium salts are known to complex anions,[2] selectivity is not simply introduced. Macrocyclic and acyclic ligands that contain Lewis acidic binding sites such as boron,[3]

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