Tuning of Electronic Properties and Reactivity in Four-Coordinate Cobalt(III) Complexes by the Tetraazamacrocyclic Tropocoronand Ligand

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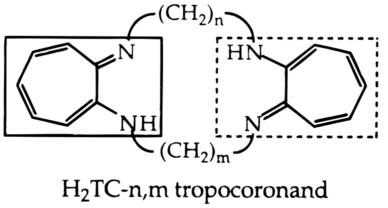
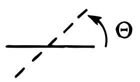
Macrocyclic ligands afford a powerful means by which to manipulate the geometry of metal complexes, ultimately to control their electronic structures and reactivity. In complexes of the tropocoronand macrocyclic ligand system, H_2TC-*n,m* (n, $m = 3-6$), torsional stress imposed at the metal center can be systematically tuned by increasing the length of the linker chains, measured by $n + m$. Concomitantly, the dihedral, or twist, angle Θ between planes defined by the troponiminate rings increases as the rings become non-coplanar. Both the physical properties and chemical reactivity are sensitive to such alterations in the steric requirements of the tropocoronand ligands, as exemplified by the ground state electronic structures of [M(TC-*n,m*)] complexes, M = Co(II) and Ni(II), and the reactivity of pentacoordinate cobalt(III) tropocoronand alkyls.[1] In the present work we have used the tropocoronand ligand system to access four-coordinate cobalt(III) *cations*, a rare species, one of which displays significant distortion toward tetrahedral geometry. Previously reported four-coordinate Co(III) complexes are typically square-planar anions,[2a−j] the exceptions being two neutral complexes[2k,l] and one other tetraaza macrocyclic cation.[2m] Furthermore, we have discovered *electronic* tuning of the reactivity in these Co(III) tropocoronand complexes, both with respect to their reduction potentials and the addition of weak Lewis bases.



H_2TC-n,m tropocoronand



Θ = dihedral angle

Dichloromethane solutions of [Co(TC-*n,m*)], $n = m = 3$ or 4,[1d] are oxidized with Ag^+ or Cp_2Fe^+ in the presence of a noncoordinating anion such as BPh_4^- or $BAr'_4{}^-$ [3] to yield the cationic complexes [Co(TC-3,3)]BPh_4 (**1**-BPh_4), [Co(TC-3,3)]-BAr'_4 (**1**-BAr'_4), and [Co(TC-4,4)]BPh_4 (**2**-BPh_4). ORTEP diagrams of the latter two species are shown in Figure 1. The Co−N_{avg} distances of 1.862(6) Å for **1**-BAr'_4 and 1.87(2) Å for **2**-BPh_4 are very similar to the analogous values of 1.864(9) and 1.88(2) Å in the Co(II) starting materials [Co^{II}(TC-*n,m*)].[1d] This similarity reflects the fact that, in oxidizing cobalt from the +2 to the +3 state, an electron is removed from the d_{yz} orbital which has little σ^* character (vide infra). Although the approximately square-planar geometry exhibited by **1** (twist angle $\Theta = 8°$) is typical of four-coordinate Co(III) complexes, **2** ($\Theta = 41°$) displays the largest distortion toward tetrahedral geometry, the closest analogue being a Co(III) porphyrin with a Θ value of 25°.[2l] The preference for square-planar geometry has an electronic origin, as discussed below, and is supported

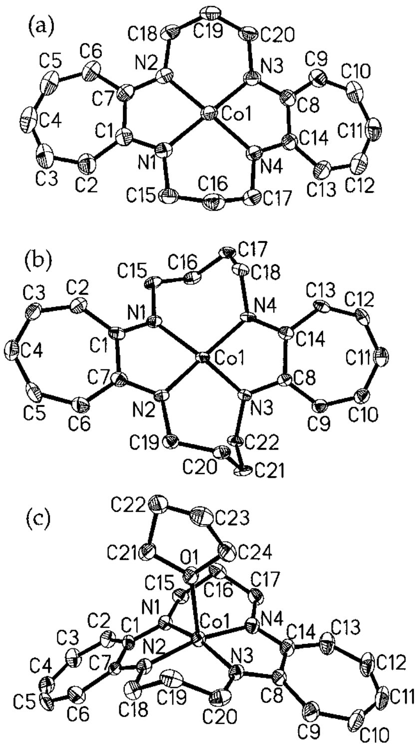


Figure 1. ORTEP diagrams with 40% thermal ellipsoids. Hydrogen atoms and anions have been removed for clarity. Selected bond distances (Å) and angles (deg): (a) **1**-BAr'_4, Co−N_{avg} 1.862(6), N1−Co−N2 82.49(11), N1−Co−N3 176.01(11), N1−Co−N4 97.67(11), N2−Co−N3 96.80(11), N2−Co−N4 173.15(11), N3−Co−N4 82.56(11); (b) **2**-BPh_4, Co−N_{avg} 1.87(2), N1−Co−N2 84.0(2), N1−Co−N3 154.2(2), N1−Co−N4 102.3(2), N2−Co−N3 103.1(2), N2−Co−N4 152.3(2), N3−Co−N4 83.0(2); (c) [Co(THF)(TC-3,3)]$^+$, Co−N_{avg} 1.884(5), Co−O 2.132(4) N1−Co−N2 81.8(2), N1−Co−N3 163.7(2), N1−Co−N4 96.6(2), N2−Co−N3 95.8(2), N2−Co−N4 165.8(2), N3−Co−N4 81.8(2), O−Co−N1 95.7(2), O−Co−N2 98.0(2), O−Co−N3 100.6(2), O−Co−N4 96.2(2).

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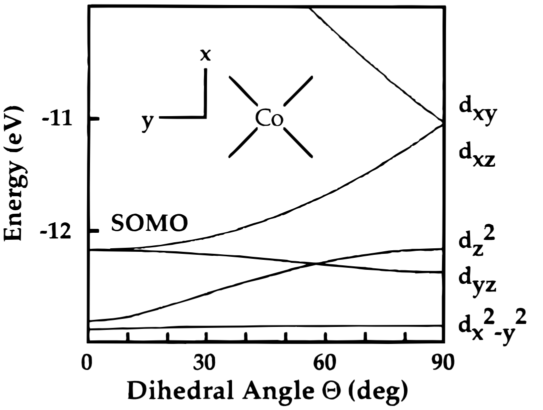

Figure 2. Walsh diagram reflecting orbital energies as a function of twist angle Θ as derived from EHMO calculations for $[\mathrm{Co(NH_2)_4}]^-$. The Co−N distance was fixed at 1.9 Å, and the N−Co−N angle, at 90°.

by the lack of molecular examples of tetrahedral Co(III) complexes. Relief of the torsional stress which would occur in the TC-4,4 ligand linker chains for a planar structure allows the resulting complex to overcome the electronic preference for this stereochemistry.[1d,4] Similar attempts to synthesize the larger macrocyclic cations $[\mathrm{Co(TC\text{-}5,5)}]^+$ and $[\mathrm{Co(TC\text{-}6,6)}]^+$ resulted only in isolation of the Co(II) starting materials.

An understanding of the relative stability of $[\mathrm{Co(TC\text{-}}n,m)]^+$ complexes can be gained from an extended Hückel (EH)/Walsh analysis of the model complex $[\mathrm{Co(NH_2)_4}]^-$ (Figure 2).[5] Both **1** and **2** have $S = 1$ at room temperature with magnetic moments of $\mu_{\mathrm{eff}} = 3.1$ and $3.6\ \mu_{\mathrm{B}}$, respectively. The degenerate set of singly occupied molecular orbitals (SOMO), d_{xz} and d_{yz}, split with increasing Θ as a result of a sharp rise of the d_{xz} energy level. The origin of this effect is an increasingly unfavorable interaction with the filled ligand p_z orbitals which destabilizes tetrahedral geometry at large Θ. A similar Walsh analysis of the $[\mathrm{Co^{II}(NH_2)_4}]^{2-}$ series reveals that the significantly larger Co−N distances of ∼1.97 Å in the complexes [Co(TC-5,5)] and [Co(TC-6,6)] (Θ = 70 and 84°, respectively)[1d] reduce the extent of the destabilizing metal d_{xz}−ligand p_z interaction.

We have also observed tuning of electron transfer both to and from the cobalt center in $[\mathrm{Co^{II}(TC\text{-}}n,m)]$ complexes. The $E_{1/2}$ values obtained from cyclic voltammetric studies of the Co(III/II) and Co(II/I) reduction couples in this series are plotted as a function of $(n + m)$ in Figure 3, where the Θ values range from 9° in [Co(TC-3,3)] to 84° in [Co(TC-6,6)].[1d] The reduction and oxidation of these complexes become more difficult with increasing Θ, as observed by the 230 mV increase in Co(III/II) potentials and the 340 mV decrease in Co(II/I) potentials across the series. Both of these trends can be explained by the rise in energy of the d_{xz} orbital discussed above. Reduction to Co(I) results in double occupation of this orbital, causing greater metal d_{xz}−ligand p_z destabilization. Oxidation of Co(II) to an $S = 1$ Co(III) system depopulates the d_{yz} orbital at $\Theta < 60°$ and the d_{z^2} orbital at larger Θ values. Since the energy levels of these second highest SOMOs remain relatively invariant throughout the series, it is the net destabilization of the d_{xz} level which most affects the $E_{1/2}$ values. The ability of the larger tropocoronand macrocycles [Co(TC-5,5)] and [Co(TC-6,6)] to undergo reversible oxidations is also noteworthy, suggesting that tetrahedral Co(III) species are formed solution.

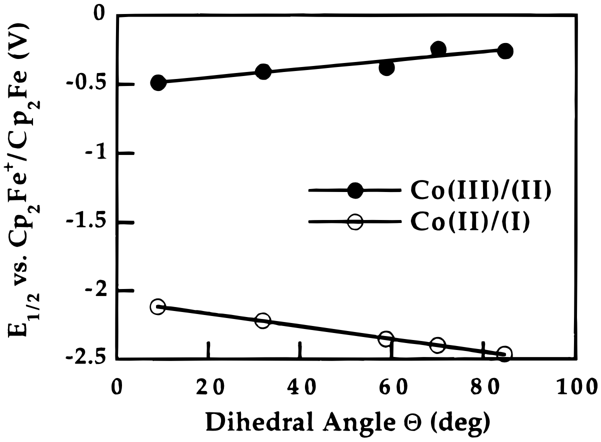

Figure 3. Co(III/II) and Co(II/I) reduction potentials as a function of twist angle Θ for 2 mM $[\mathrm{Co(TC\text{-}}n,m)]$ complexes in THF containing 0.5 M $(n\text{-}\mathrm{Bu_4N})\mathrm{PF_6}$ by using a Pt disk working electrode and a scan speed of 100 mV/s.

The Lewis acid character of Co(III) complexes was previously noted for a series of anionic Co(III) bis(dithiolate) complexes.[2a,b] Substitution of more electron-withdrawing ligands increased the affinity for Lewis bases, affording 5- and 6-coordinate diamagnetic complexes. Both **1** and **2** are coordinatively unsaturated, but only the former readily binds weak Lewis bases such as THF, $\mathrm{CH_3CN}$, or $\mathrm{Et_2O}$. In the presence of excess THF, **1** forms the solvento complex $[\mathrm{Co(THF)(TC\text{-}3,3)}]^+$, as monitored by electronic spectral changes (Figure S1), from which was derived a binding constant of 3.4(3) $\mathrm{M^{-1}}$ at 25 °C. The $[\mathrm{Co(THF)(TC\text{-}3,3)}]^+$ cation has square pyramidal geometry with THF at the apex (Figure 1c). Inspection of the cation **2** revealed no steric hindrance to binding a fifth ligand, but neither THF, $\mathrm{CH_3CN}$, nor $\mathrm{Et_2O}$ reacts with **2** at 25 °C. At 60 °C, however, THF binds as observed by optical spectroscopy (Figure S2), indicating a kinetic barrier to reactivity. The difference in reactivity does not seem to derive from alteration in electron density at cobalt, since the Co(III)/Co(II) reduction potentials for $[\mathrm{Co(TC\text{-}}n,m)]^+$ complexes are significantly more positive than those for other four-coordinate Co(III) compounds which react with Lewis bases.[2a,b,g] Overcoming the energy required to distort the tropocoronand in the transition state needed to convert **2** to $[\mathrm{Co(THF)(TC\text{-}4,4)}]^+$ seems a more likely explanation.

In conclusion, the present investigation of $[\mathrm{Co(TC\text{-}}n,m)]$ complexes has demonstrated electronic tuning of both acid−base and electron-transfer reactions at cobalt by systematic, ligand-induced alterations in twist angle. The electronic effects reflect the frontier d-orbital composition, as revealed by EHMO calculations. The ability of the tropocoronand ligand twist to alter cobalt $E_{1/2}$ values demonstrates fine tuning of the metal reduction potentials. Control of reactivity through geometric tuning has implications for understanding the properties of metal ion sites in metalloproteins and for the design of metal-based catalysts.

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Supporting Information Available: Text containing procedures for the synthesis of all compounds, listings of X-ray data collection and structure solution details, atomic coordinates and B_{eq} values, anisotropic thermal parameters, and intramolecular bond distances and angles (Tables S1−S13), and Figures S1 and S2, displaying optical spectroscopic changes which occur upon addition of THF to **1** and to **2** (39 pages). Ordering information is given on any current masthead page.

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