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Trigonal Bi- and Monopyramidal Cobalt(II) Complexes of a Novel Guanidine-Based Tripodal Ligand

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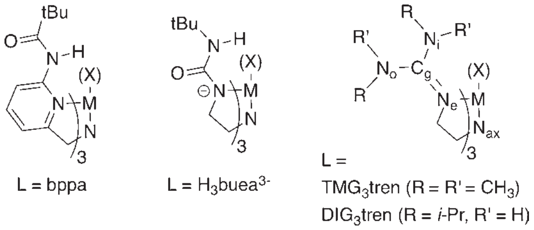
The novel ligand DIG$_3$tren has three *N′*,*N″*-diisopropylguanidinyl (DIG) moieties. We report on the structures of two cobalt complexes that show how an isopropylamino group from each DIG acts as a flap that can either close over the metal or rotate away from the metal to open up a site for auxiliary ligand binding. Two of the −NH(*i*Pr) flaps are open in pink [Co(DIG$_3$tren)(OAc)]OAc (**1**), and each of these flaps provides a hydrogen bond to stabilize acetate binding to trigonal bipyrimidal cobalt. The flaps are closed in blue [Co(DIG$_3$tren)][BPh$_4$]$_2$ (**2**), yielding a rare example of a trigonal (mono)pyramidal [ML]$^{2+}$ ion.

Four-coordinate tripodal ligands (FCTLs) commonly form trigonal bipyramidal metal complexes with an auxiliary monodentate ligand (X) at one of the axial sites; some examples are shown in Chart 1. FCTLs have been designed to form a binding pocket (second coordination sphere) that can favor coordination and/or activation of certain X ligands. For instance, bppa[1] stabilizes a hydroperoxide complex of copper(II),[2] H$_3$buea^{3-} promotes O$_2$ activation reactions in complexes with divalent cobalt,[3] iron,[4] and manganese,[5] and TMG$_3$tren complexes of copper[6,7] and iron[8] have exhibited reversible O$_2$ binding[6] and activated O$_2$.[7,8] Whereas bppa and H$_3$buea^{3-} create an auxiliary ligand binding pocket lined with hydrogen-bond donors, TMG$_3$tren makes a small hydrophobic binding pocket lined with methyl groups.

Chart 1. Structure of ML and MLX Complexes of FCTL, including Positional Nomenclature Used for Selected Atoms in TMG$_3$tren and DIG$_3$tren[a]



[a] ax = axial, e = equatorial, i = inner, o = outer, and g = guanidine.

With this paper, we introduce a guanidine-based FCTL, DIG$_3$tren. Each arm of this tripodal ligand contains two isopropylamino moieties. Although rotation around the guanidine C$_g$−N bonds is facile (on the NMR time scale, for instance[9,10]), their partial double-bond character results in a structural preference for conformations where the isopropyl methine C atoms are nearly coplanar with the guanidine N and C$_g$ atoms; this preference was confirmed by a search of the Cambridge Structural Database.[11,12] At each C$_g$−N bond, these conformations are *Z* or *E* depending on whether

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(1) Abbreviations: bppa, bis(6-pivalamide-2-pyridylmethyl)-(2-pyridylmethyl)amine; H$_6$buea, tris[(*N′*-*tert*-butylureayl)-*N*-ethylene]amine; DMG$_3$tren, tris[(*N′*,*N″*-diisopropylguanidinyl)-*N*-ethylene]amine; TMG$_3$tren, tris[(*N′*,*N′*,*N″*,*N″*-tetramethylguanidinyl)-*N*-ethylene]amine; tren, tris(2-aminoethyl)amine.

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(10) For DIG$_3$tren in organic solvents, we observed broadening of the isopropyl ^{1}H NMR septet below 100 °C. This could be due to slow rotation around the C−N bonds or could indicate a slow tautomeric equilibrium involving the guanidine protons.

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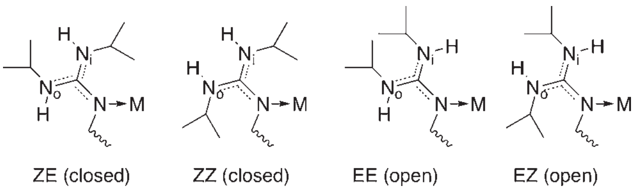
(12) The CSD[11] (update May 2010) contains 67 instances of −NH(*i*Pr) moieties within guanidine or guanidinium groups. The $|\theta|$ [NCNC(*i*Pr)] dihedral angles are 14 ± 11 and $167 \pm 10°$ (mean ± e.s.d), with no $|\theta|$ between 40 and 140°. The deviations from planarity are larger in an additional 12 examples with −NH(*i*Pr) as part of the guanidine groups coordinated to metal ions ($|\theta| = 26 \pm 16$ and $154 \pm 16°$), but still there are no $|\theta|$ between 50 and 130°.

the N_e-C_g-N-C dihedral angle (θ) is closer to 0° or to ±180°. As a result, there are four possible near-planar conformations of each arm of the DIG_3tren (Chart 2). In metal complexes, the conformation of the isopropylamino closest to the metal (which we call the "isopropylamino flap") will exert a strong influence on the auxiliary ligand binding. In the *ZE* and *ZZ* ("closed") conformations, a hydrophobic and bulky isopropyl group is positioned close to the metal and is expected to inhibit binding of auxiliary ligands. In the *EE* and *EZ* ("open") conformations, the isopropyl substituent extends away from the metal, and instead the −NH points toward the metal and can support binding by hydrogen-bond-accepting ligands. Because of its rotatable flaps, DIG_3tren creates an auxiliary ligand binding pocket that is flexible in shape and polarity. We have obtained structures of two DIG_3tren complexes of cobalt(II) that show how rotation of the isopropylamino flaps about the C_g-N_i bonds allows this ligand to support both trigonal bipyramidal and trigonal (mono)pyramidal coordination of the cobalt (i.e., the presence or absence of an auxiliary ligand).

Chart 2. Conformations of Arms of DIG_3tren, Assuming Near-Planarity of Guanidine Units[a]



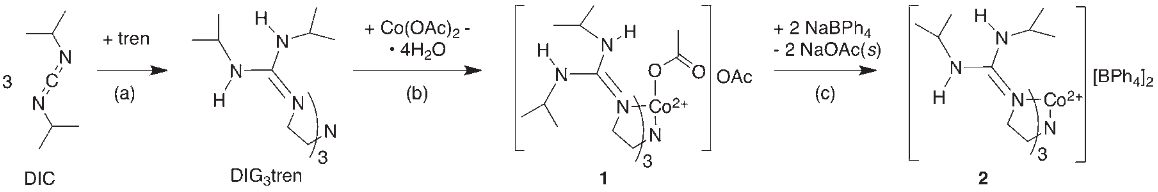
[a] The first letter indicates the conformation around the C_g-N_i bond and the second the conformation around the C_g-N_o bond.

Syntheses are summarized in Scheme 1. DIG_3tren is synthesized from tren and diisopropylcarbodiimide. The product is a viscous yellow oil with some impurities as judged by electrospray ionization mass spectrometry (ESI-MS) and NMR spectroscopy (Figures S1−S4 in the Supporting Information, SI).[13,14] The reaction of 20% excess DIG_3tren with $Co(OAc)_2 \cdot 4H_2O$ in refluxing acetone yields $[Co(DIG_3tren)OAc]OAc$ (**1**) as a pink solid. The ESI-MS spectrum of **1** is clean (Figure S1 in the SI), suggesting that the Co^{2+} ion binds selectively to DIG_3tren rather than to its impurities. Metathesis of **1** with 2 equiv of $NaBPh_4$ in acetone yields a blue-green solution of $[Co(DIG_3tren)][BPh_4]_2$ (**2**), which is purified by crystallization.

Diffraction-quality purple crystals were obtained by vapor diffusion of EtOEt into a dark-pink solution of **1** in 1:1:1 CH_2Cl_2/EtOAc/MeOH. The crystal structure of **1** and selected bond lengths and angles are shown in Figure 1a.[13,15] The cobalt(II) has trigonal bipyramidal geometry. The monodentate acetate ligand accepts hydrogen bonds from N_i on two of the DIG arms. The N_i on arm A and all three N_o are within or close to hydrogen-bonding distance with the O atoms of the counterion acetate.

Teal crystals of **2**·EtOEt were obtained by vapor diffusion of EtOEt into a blue solution of **2** in CH_2Cl_2. The structure is shown in Figures 1b; the SI includes a packing diagram as Figure S5.[13,15] With no symmetry-breaking auxiliary ligand,

Scheme 1. Syntheses of DIG_3tren and Complexes **1** and **2**[a,13]



[a] Conditions: (a) 100°, 2 h, neat; (b) refluxing in acetone, 1 h; (c) refluxing in acetone, 3 h, and then filtering.

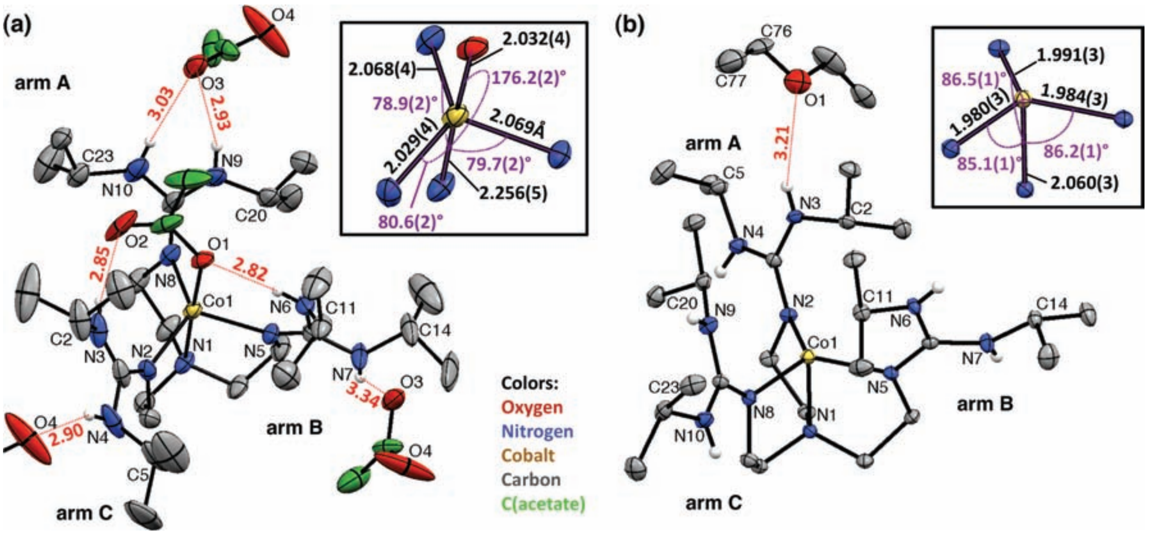
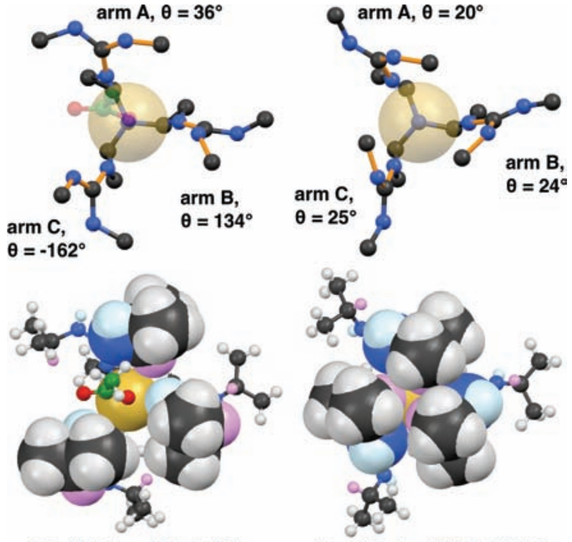


Figure 1. X-ray crystal structures[15] (20% thermal ellipsoid ORTEP) of (a) the cation of **1** and (b) the cation and solvate of **2**·EtOEt. Only H atoms bound to N atoms are shown. The insets show coordination bond lengths (Å) and angles involving N_{ax}. Possible hydrogen bonds are in red and are labeled with the N−O distance (in Å, esd = 0.01 Å). More crystallographic details and measurements are given in Tables S1 and S2 in the SI.[13].



[Co(DIG$_3$tren)OAc]$^+$ (1) **[Co(DIG$_3$tren)]$^{2+}$ (2·EtOEt)**

Figure 2. Views of **1** and **2** cation structures with N_{ax} located directly behind Co. As in Figure 1, the C atoms of acetate are colored green. (Top) Canting of nearly planar guanidine groups as they extend up past the cobalt with a slight helical twist. Methyl groups and H atoms are omitted; cobalt and the acetate ligand are translucent. Dihedral angles ($\theta = \angle N_e-C_g-N_i-C$; orange bonds) for the rotatable $-NH(i\mathrm{Pr})$ flaps are indicated. (Bottom) Hybrid ball and stick/space-filling models of **1** and **2**, illustrating the various conformations of the $-NH(i\mathrm{Pr})$ flaps (shown at van der Waals radii). N-Bound H atoms are colored light blue; in **1**, the two flaps with $|\theta| > 130°$ are oriented so these atoms can donate a hydrogen bond to the acetate ligand. The isopropyl methine (CH) H atoms are colored magenta; in **2**, these three atoms are only 2.45 ± 0.02 Å from the cobalt (Co−C = 3.25 ± 0.01 Å), which prevents auxiliary ligand binding.

N_e-Co-N_e bond angles in **2** are closer to the 3-fold ideal; they range from 118 to 122°, as opposed to 111−128° in **1**. The coordination geometry of **2** is "external" trigonal pyramidal (eTP) because the metal ion is outside (by 0.14 Å) the pyramid defined by the four ligating atoms, leaving more than an entire hemisphere of the metal without coordination bonds. A search of the Cambridge Structural Database[11] found only 63 eTP structures in mononuclear complexes (Table S3 in the SI). Over half involve Cu^I or Ag^I, for which low coordination numbers are common, but there are 18 eTP complexes with di- or trivalent metal ions, including Fe^{II},[16,17] Co^{II},[3,16,18] Ni^{II},[16,19] and Zn^{II}.[16,20,21] In these 18 cases, the metal ions are coordinated by anionic tripodal ligands to form complexes with net charges between 1− and 1+. The cation of **2** differs from previously reported eTP structures in that it has a neutral ligand with a multiply charged metal; therefore, although strong σ donation of negatively charged ligands may be favorable for trigonal pyramidal coordination of divalent cations,[16] it is not necessary.

Figure 2 shows views of the cations of **1** and **2** looking down the $Co-N_e$ bond. The partial space-filling views show that, in **1**, a patch of the cobalt surface is available for binding by acetate, while in **2**, the cobalt is closely covered by the isopropyl substituents from the three isopropylamino flaps. The DIG groups in **2** adopt *ZE* (closed) conformations that are sterically incompatible with auxiliary ligand binding. The $N_e-C_g-N_i-C$ dihedral angles (θ) are about 20° rather than the planar ideal of 0°; this small deviation mitigates steric clashes between the isopropyl groups from adjacent arms. The degree to which DIG$_3$tren blocks access the cobalt was quantified using the program *Solid-G*.[22,23] In **2**, DIG$_3$tren obscures 91.9% of the cobalt surface. In **1**, DIG$_3$tren is more open, covering 79.5% of the cobalt. Creation of an auxiliary ligand binding pocket (in **1**) is accomplished by a large rotation of the flaps from arms B and C. This gives *EZ* (open) conformations and allows hydrogen bonding to the O atoms of the acetate ligand, similar to the hydrogen bonding found in complexes of bppa, H_3buea^{3-}, and similar ligands.[2−5] The remaining flap from arm A rotates by a lesser amount (ca. 15° relative to structure **2**) to provide sufficient space for the acetate to ligate; this arm adopts the *ZZ* conformation and forms a pair of hydrogen bonds to the counterion (Figure 1).

We have begun exploring the affinity of other ligands for the auxiliary binding site of [Co(DIG$_3$tren)]$^{2+}$. UV/vis spectra of **2** in CH_2Cl_2 and potentially coordinating solvents pyridine, CH_3OH, and CH_3CN (Figure S6 in the SI) show closely spaced peaks near 600 nm, characteristic of trigonal pyramidal cobalt(II);[16] however, the CH_3CN solution is purple, and its spectrum suggests the partial formation of five-coordinate [Co(DIG$_3$tren)CH$_3$CN]$^{2+}$. The persistence of relatively rare trigonal pyramidal geometry in potentially coordinating solvents shows that the isopropylamino flaps of the DIG$_3$tren ligand can inhibit auxiliary ligand binding. Selective control of auxiliary ligand binding by the DIG$_3$tren ligand may be useful in promoting catalytic cycles in which the coordination number of the metal is variable.

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Supporting Information Available: Experimental details of syntheses and crystallography, CIF file for **1** and **2**·EtOEt, Tables S1−S3, and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Details of syntheses and crystallography are given in the Supporting Information; see the note at end of paper.

(14) The desired 1+ ion mass peak at 525 amu accounts for about 70% of the total ions; the major impurity at 399 amu presumably results from the reaction of only two of the primary amines of tren with DIC. Using an excess of DIC results in the formation of higher mass species (651 and 777 amu), presumed to include biguanidine groups.

(15) **1**: monoclinic, $P2_1/c$, a = 16.458(5) Å, b = 13.570(4) Å, c = 18.185(5) Å, β = 97.521(5)°, V = 4027(2) Å^3, Z = 4. A total of 7076 unique reflections (100% with θ = 1.88−25.00°) were fit to 447 parameters and 385 restraints to give R ($I > 2\sigma_I$) = 0.0932. CCDC 786125. **2**·EtOEt: triclinic, $P\bar{1}$, a = 13.736(6) Å, b = 15.958(7) Å, c = 17.452(8)Å, α = 84.654(7)°, β = 81.050(8)°, γ = 88.922(8)°, V = 3762(3) Å^3, Z = 2. A total of 18 591 unique reflections (100.0% with θ = 1.50−28.34°) were fit to 875 parameters and 40 restraints to give R ($I > 2\sigma_I$) = 0.0708. CCDC 786126. The atomic coordinates for these structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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