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Bis-Tris Propane as a New Polydentate Linker in the Synthesis of Iron(III) and Manganese(II/III) Complexes

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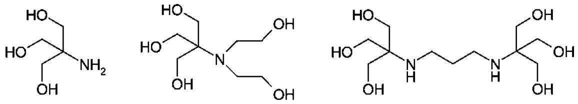
We describe the synthesis, structure, and magnetic properties of two new complexes, one decanuclear iron(III) cluster and one hexanuclear mixed-valence manganese(II/III) cluster, where the previously unexplored polydentate ligand Bis-tris propane $\{(CH_2OH)_3CNH(CH_2)_3NHC(CH_2OH)_3\}$ is used to link small cluster fragments into high-nuclearity complexes.

The synthesis and characterization of polynuclear transition-metal complexes remains a hot topic within the area of inorganic chemistry. Both manganese- and iron-based complexes can show single-molecule magnet (SMM) behavior[1−3] and have been investigated as potential magnetic refrigerants.[4] In addition, iron(III) clusters have been investigated as MRI contrast reagents[5] and as models for corrosion inhibitors bound to iron oxide surfaces.[6] We have embarked upon a program to investigate a series of structurally related ligands containing the Tris unit, producing a heptanuclear cobalt-based SMM using the pro-ligand 2-amino-2-(hydroxymethyl)propane-1,3-diol (Tris) and mixed-valence cobalt complexes or iron(III) complexes by using Bis-tris {2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)propane-1,3-diol}.[7] Herein, we report our first success with the previously unexplored pro-ligand 2,2′-(propane-1,3-diyldiimino)bis[2-(hydroxymethyl)propane-1,3-diol] (Bis-tris propane, H_6L; Chart 1). Bis-tris propane is more commonly used as a biological buffer despite containing multiple binding sites and, hence, excellent potential as a bridging ligand in cluster chemistry. The ligand binds with a N_2O_4 donor set, affording Fe_{10} and Mn_6 complexes.

Chart 1. Tris, Bis-Tris, and Bis-Tris Propane (H_6L)



Na_2H_4L was prepared by the reaction of H_6L with 2 equiv of sodium methoxide in methanol, followed by evaporation of the solvent in vacuo. The iron(III) acetate oxo-centered triangle starting material was prepared according to the literature procedure.[8] Na_2H_4L (0.275 g, 0.80 mmol) was added to $[Fe_3O(OAc)_6(H_2O)_3]Cl$ (0.500 g, 0.80 mmol) in MeCN (30 mL), and the solution was stirred at ambient temperature for 24 h, then filtered, and stored in a sealed vial. Orange blocklike crystals of $[Fe_{10}O_4(H_2L)_2(OAc)_{14}(H_2O)_2]\cdot 9MeCN$ (**1**·9MeCN) formed after 2 months in 15% yield.[9]

Compound **1** is a decanuclear iron(III) complex and crystallizes in the monoclinic space group $P2_1/n$ (Figure 1). The complex contains two distorted Fe_4 butterfly units linked together by two central $\{Fe(H_2L)\}^-$ units to form a chainlike

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(9) Air-dried crystals analyzed as **1**·2MeCN. Anal. Calcd (found): C, 30.54 (30.34); H, 4.56 (4.21); N, 3.96 (3.89). Selected IR data: ν 3274, 2359, 1540, 1410, 1015, 651 cm^{-1}. Crystal data for **1**·$9CH_3CN$: monoclinic, $P2_1/n$, $a = 13.812(9)$ Å, $b = 18.283(8)$ Å, $c = 19.946(8)$ Å, $\beta = 90.18(4)°$, $U = 5037(4)$ Å^3, $M = 2411.25$, $Z = 2$, μ(Mo Kα) = 1.489, $T = 100$ K; refinement used 641 parameters and gave R1 = 0.0379 for 10 867 data with $F_o > 4\sigma(F)$, wR2 = 0.1010 for 14 466 unique data ($2\theta \leq 60°$), and 2 restraints.

10.1021/ic8015386 CCC: $40.75

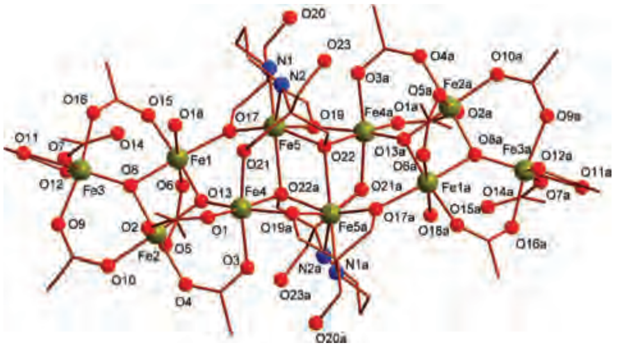

Figure 1. Structure of **1** (ball-and-stick representation with the following: Fe^{III}, gold; O, red; N, blue; C, brown; H omitted for clarity) [atom suffix a signifies the symmetry-equivalent atom: a = $1 - x, 1 - y, 1 - z$. Selected bond lengths in Å: Fe5−O17, 2.006; Fe5−O19, 1.982; Fe5−O21, 2.047; Fe5−O22, 2.080; Fe5−O22a, 2.391; Fe5−N1, 2.225; Fe5−N2, 2.220 (ave esd 0.002 Å).

structure. Oxidation states were confirmed as iron(III) and the oxides assigned by consideration of bond lengths, charge balance, and bond valence sum (BVS) analysis.[10] All of the iron centers within the butterfly units have a distorted octahedral coordination sphere. Fe4 is bound by three oxygen donor atoms from the ligand CH_2O^- arms, two oxygen donor atoms from acetate ligands, and a μ_3-oxide (O13). Fe2 is bound by four oxygen donor atoms from acetate ligands and two μ_3-oxides (O8 and O13). An oxygen donor atom from a ligand CH_2O^- arm, two oxygen donor atoms from the acetate ligands, two μ_3-oxides, and a water molecule complete the coordination sphere of Fe1, while the final butterfly iron center, Fe3, is bound by five oxygen donor atoms from acetate ligands and a μ_3-oxide (O8). Fe5 has a distorted monocapped trigonal-prismatic geometry: the trigonal prism is formed from a $\{N_2O_4\}$ ligand donor set, with the cap from a binding alkoxide oxygen atom (O22a) on the symmetry-equivalent ligand. The most common geometry for seven-coordinate iron(III) ions is pentagonal-bipyramidal, which has been reported previously for iron monomer complexes containing the EDTA ligand and in an Fe_{12} complex containing the EDTE $\{(HOCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2OH)_2\}$ ligand.[11] The monocapped trigonal-prismatic geometry reported for **1** is less common but is found in two iron(III) monomers.[12] The ligand is present in one binding mode (Figure 3, left). The two ligand alkoxide arms that remain protonated are unbound, hydrogen bonding to acetate ligands (O20···O12′ and O23···O7″) on adjacent Fe_{10} molecules.

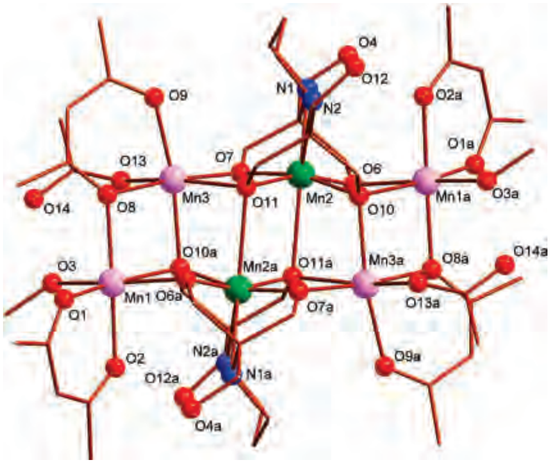

Figure 2. Structure of **2** (ball-and-stick representation with the following: Mn^{III}, green; Mn^{II}, pink; O, red; N, blue; C, brown; H omitted for clarity) [atom suffix a signifies the symmetry-equivalent atom: a = $1 - x, -y, -z$]. Selected bond lengths in Å: Mn2−O6, 1.901; Mn2−O7, 1.913; Mn2−O10, 1.968; Mn2−O11, 1.942; Mn2−O11a, 2.573; Mn2−N1, 2.536; Mn2−N2, 2.390 (ave esd 0.002 Å).

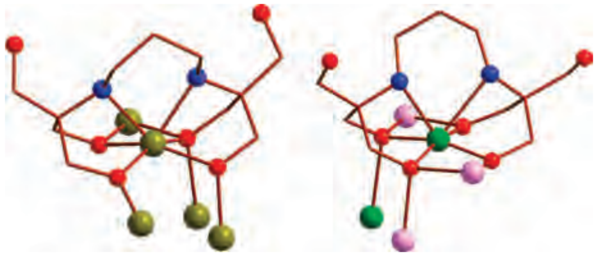

Figure 3. Two binding modes of the H_2L^{4-} ligand in complexes **1** (left) and **2** (right). The color scheme is as for Figures 1 and 2; hydrogen atoms are not shown.

The isolation of compound **1** prompted us to explore the chemistry of Bis-tris propane in the synthesis of mixed-valence manganese complexes. To a solution of $Mn(acac)_2$ (0.253 g, 1 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mmol) in MeOH (15 mL) was added H_6L (0.282 g, 1 mmol) and triethylamine (0.202 g, 0.279 mL, 2 mmol). The solution was stirred at ambient temperature overnight to give a dark-brown solution, which was filtered and stored in a sealed vial. After 2 weeks, large blocklike crystals of $[Mn^{III}_2Mn^{II}_4(H_2L)_2(acac)_4(OAc)_2(MeOH)_2] \cdot 2MeOH$ (**2**·2MeOH) formed from the solution in 30% yield.[13]

Compound **2** is a hexanuclear, mixed-valence manganese complex and crystallizes in the monoclinic space group $P2_1/n$. Oxidation states were assigned on the basis of BVS calculations, by consideration of bond lengths and charge balance.[10] As seen in compound **1**, the Bis-tris propane ligand links smaller subunits together: in **2**, these are manganese(II) dimers. Mn3 is divalent and has a distorted octahedral coordination sphere filled by two oxygen donor atoms from an acac ligand, three oxygen donor atoms from the ligand CH_2O^- arms, and one oxygen donor atom from an acetate ligand. The divalent Mn1 also has a distorted octahedral geometry, which is filled by three oxygen donor atoms from acac (two from the 1,3-bridging acac and one from the 1,1′,3-bridging acac), two oxygen donor atoms from the ligand CH_2O^- arms, and one oxygen donor atom from a MeOH ligand. Like Fe5 in complex **1**, the trivalent Mn2 in complex

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(13) Air-dried crystals analyzed as **2**. Anal. Calcd (found): C, 37.96 (37.90); H, 6.11 (5.95); N, 3.69 (3.79). Selected IR data: ν 3262, 2861, 1594, 1513, 1389, 1256, 1021, 917, 677 cm^{-1}. Crystal data for $2 \cdot 2CH_4O$: monoclinic, $P2_1/n$, $a = 12.3014(5)$ Å, $b = 13.7756(6)$ Å, $c = 19.5216(8)$ Å, $\beta = 98.148(2)°$, $U = 3274.7(2)$ Å^3, $M = 1528.87$, $Z = 2$, μ(Mo Kα) = 1.206, $T = 100$ K; refinement used 415 parameters and gave R1 = 0.0341 for 6449 data with $F_o > 4\sigma(F)$, wR2 = 0.1377 for 9937 unique data ($2\theta \leq 61°$), and 6 restraints.

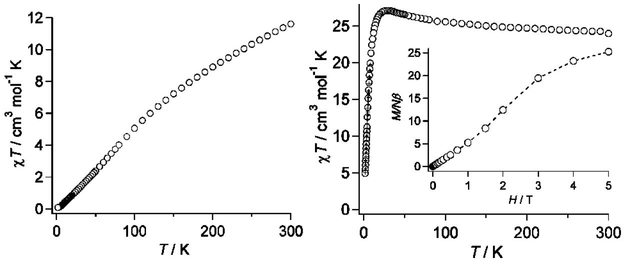

Figure 4. Temperature dependence of χT for **1** (left) and **2** (right) from 300 to 1.8 K measured in a field of 1 kOe. Inset (left): magnetization versus field at 2 K for **2**.

2 also possesses a distorted monocapped trigonal-prismatic geometry due to a binding alkoxide oxygen atom on a symmetry-equivalent ligand. Seven-coordinate manganese (III) ions have been reported previously for an Mn_3 complex and an Mn_{12} complex;[14] however, to the best of our knowledge, this is the first time a monocapped trigonal-prismatic geometry has been reported for a manganese(III) ion. Because the coordination environment of Mn2 is distorted monocapped trigonal prismatic, no Jahn−Teller elongation should be observed.[15] Instead, the long Mn−O and Mn−N bonds result from the enforced ligand binding mode within the structure. The ligand is present in one binding mode (Figure 4, right). Two unbound ligand arms remain protonated, as seen in **1**: O12 forms a hydrogen bond to an acetate group on an adjacent molecule (O14′), while O4 hydrogen bonds to an unbound ligand arm on an adjacent complex (O12″).

The magnetic properties of **1** and **2** were measured as a function of the temperature (Figure 4). The value of χT for **1** at 300 K is 11.6 cm^3 mol^{-1} K, significantly lower than the expected value for 10 uncoupled iron(III) ions of 43.75 cm^3 mol^{-1} K (for $g = 2$), indicating strong antiferromagnetic interactions between the iron(III) centers. The value of χT decreases steadily, reaching a value of 0.1 cm^3 mol^{-1} K at 1.8 K, consistent with an $S = 0$ ground state. This is unsurprising, given that Fe_4 butterfly complexes are reported to display $S = 0$ ground states, resulting from antiferromagnetic interactions between iron(III) centers.[16]

The value of χT for **2** at 300 K is 24.0 cm^3 mol^{-1} K, which is just above the expected value for six uncoupled manganese ions $\{4Mn^{II} + 2Mn^{III}\}$ of 23.5 cm^3 mol^{-1} K for $g = 2$ (Figure 4, right). χT increases gradually, reaching a maximum of 27.1 cm^3 mol^{-1} K at 30 K. Below 30 K, χT decreases rapidly to a value of 4.9 cm^3 mol^{-1} K at 1.8 K. This behavior is indicative of predominant antiferromagnetic interactions within the cluster. The magnetization was measured as a function of the applied field at 2 K (Figure 4 right, inset). The magnetization curve rises almost linearly at low fields and is consistent with the presence of an $S = 0$ ground state for **2**, with low-lying excited states with $S > 12$, which become populated with increasing field. Low-lying excited states are observed in complexes containing multiple manganese(II) centers because these ions promote weak exchange interactions.[17] In-phase alternating current susceptibility measurements in the temperature range 1.8−8 K also support this assignment. Extrapolation of the χT curve to 0 K gives a value of 0.5 cm^3 mol^{-1} K. The rapid decrease in the slope of the χT vs T curve with decreasing temperature also confirms the presence of larger multiplicity excited states lying close to the spin ground state.[18]

In conclusion, we have synthesized the first transition-metal complexes containing the Bis-tris propane ligand, which links small cluster fragments into high-nuclearity complexes. These contain seven-coordinate metal(III) centers, with a monocapped trigonal-prismatic geometry enforced by the ligand binding mode. Future work will target the synthesis of heterometallic complexes using the Bis-tris propane ligand and magnetic studies of **2** under pressure to attempt to stabilize the low-lying large S spin states and hence to increase the spin ground state.

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Supporting Information Available: CIF files for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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