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Mixed Carboxylate/Catecholate Polynuclear Complexes. Integral Association of Trivalent Lanthanide Ions with Mn_4 Units in the Pentanuclear Mn_4LaCl and Mn_4Tb Clusters

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Recent interest in the coordination chemistry of manganese[1] with oxygen or nitrogen donor ligands derives to a great extent from the importance of oligonuclear Mn sites in biology and has led to rich, structurally diverse, coordination chemistry.

In this communication we report results of our studies on manganese "mixed" carboxylate catecholate complexes and the synthesis of new $Mn^{II}_4M^{III}$ pentanuclear clusters (M = Mn, La, Tb). Our interest in the catecholate ligands[2] derives from the known redox characteristics of the catecholate complexes[3] and the participation of phenolate-type ligands in redox reactions catalyzed by such enzymes as ribonucleotide reductase[4] and PSII.[1b−g,5] The introduction of lanthanide ions in the synthetic procedures was an attempt to explore the interactions of strong Lewis acids and the Mn-bound carboxylate/catecholate ligands.

The reaction of $MnCl_2$, $OPiv^-$, the Bu_4N^+ or Et_4N^+ salts of the catecholate dianion and ferrocenium, $Fe(cp)_2^+$ (Br^- or PF_6^- salt), in pyridine solution in a 5:2:4:1 molar ratio, after unexceptional workup, afforded in good yield the green $[Mn_5(OPiv)_2(cat)_4(py)_8]^+$ cation, **I**, that is isolated as Br^- or PF_6^- salts and contains a central, eight-coordinate, Mn^{3+} ion.[6] Introduction of $Tb(NO_3)_3{\cdot}5H_2O$ in this synthetic procedure (without $Fe(cp)_2^+$) and adjusting the Mn^{2+}/Tb^{3+} ratio to 4:1 results in the formation of the colorless $[Mn_4Tb(OPiv)_2(cat)_4(py)_8]^+$ complex cation, **II**, that is isolated as a crystalline NO_3^- salt. With $La(NO_3)_3$ and in the presence of 1 equiv of $NaPF_6$, the endecanuclear, $\{[LaMn_4(OPiv)_2(cat)_4(py)_8Cl]_2Mn(py)\}^{2+}$, **III**, cation forms and can be isolated as a crystalline PF_6^- salt from pyridine solution. The same reaction in CH_3CN solution that contains 6% (v/v) pyridine, in the absence of the PF_6^- ion, affords the $[LaMn_4(OPiv)_3(cat)_4(py)_6Cl]Mn(py)_2NO_3$ complex, **IV**, that is isolated in crystalline form in 80% yield upon the slow diffusion of ether to the reaction solution.

The structures of the cations[7] in **I** and **II** are nearly identical (Figure 1), and both contain a pentanuclear core supported entirely by the four bridging catecholate ligands. The catecholate ligands use one oxygen atom in a μ_2-mode and one in a μ_3-mode to support four divalent metal atoms in a distorted tetrahedral

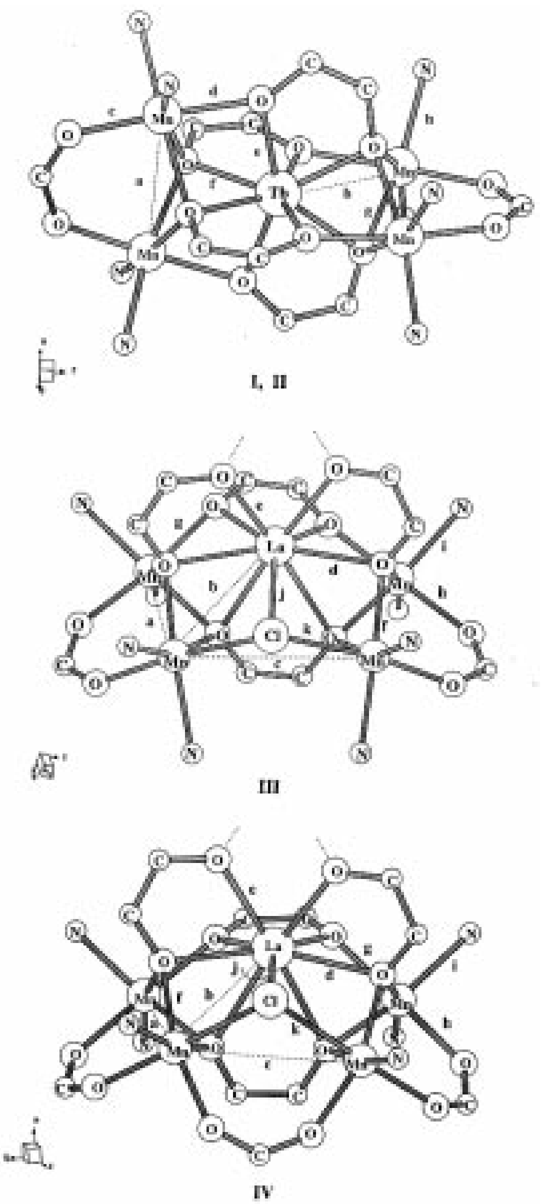

Figure 1. Structure and labeling of the $[Mn_4M'(OPiv)_2(cat)_4(py)_8]^+$ cationic complexes (M′ = Mn (**I**) Tb (**II**), the $[LaMn_4(OPiv)_2(cat)_4(py)_8Cl]$ unit in $\{[LaMn_4(OPiv)_2(cat)_4(py)_8Cl]_2Mn(py)\}^{2+}$, **III**, and the $[LaMn_4(OPiv)_3(cat)_4(py)_6Cl]^-$ unit in $[LaMn_4(OPiv)_3(cat)_4(py)_6Cl]Mn(py)_2NO_3$, **IV.** Only the carbon atoms bridging the oxygen donors in the carboxylate and catecholate ligands are shown. Selected bond lengths (Å): (**I**) **a** = 3.310(2), 3.313(2); **b** = 3.159(2)−3.209(2); **c** = 2.119(6)−2.190(6); **d** = 1.963(5)−1.983(5); **e** = 2.143(5)−2.185(6); **f** = 2.218(5)−2.243(5); **g** = 2.384(5)−2.485(5); **h** = 2.215(7)−2.290(8); (**II**) **a** = 3.208(3), 3.459(3); **b** = 3.206(3)−3.218(4); **c** = 2.08(2)−2.13(2); **d** = 2.28(1)−2.32(1); **e** = 2.17(2)−2.22(1); **f** = 2.34(1)−2.36(1); **g** = 2.21(1)−2.33(1); **h** = 2.21(2)−2.30(1); (**III**) **a** = 3.307(5), 3.310(5); **b** = 3.497(5)−3.618(5); **c** = 4.710(5), 5.881(4); **d** = 2.56(2)−2.73(1); **e** = 2.40(2)−2.47(2); **f** = 2.10(2)−2.29(2); **g** = 2.13(2)−2.15(2); **h** = 2.08(2)−2.17(2); **i** = 2.23(2)−2.34(2); **j** = 2.942(8); **k** = 2.638(8), 2.739(10); (**IV**) **a** = 3.358(1), 3.370(1); **b** = 3.475(1)−3.560(1); **c** = 4.291(1), 5.833(1); **d** = 2.611(3)−2.721(3); **e** = 2.508(3)−2.538(3); **f** = 2.169(3)−2.257(3); **g** = 2.168(3)−2.173(3); **h** = 2.099(4)−2.160(4); **i** = 2.241(4)−2.297(4); **j** = 2.873(1); **k** = 2.681(2), 2.803(2).

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[6] Satisfactory analytical data have been deposited as Supporting Information. Abbreviations used: $OPiv^-$ = the pivalate anion, $(CH_3)_3CCOO^-$, cat = the catecholate dianion, py = pyridine.

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arrangement of D_{2d} symmetry. In the center of the cluster is located the trivalent ion bound by the eight catecholate oxygen atoms in a distorted dodecahedral coordination. The central Mn^{3+} ion in **I** shows two sets of Mn−O bonds with mean Mn−O bond lengths of 1.975(5) and 2.43(3) Å. The corresponding Tb−O distances in **II** are 2.29(1) and 2.35(1) Å. The difference in the M^{3+}−O bond lengths, which shows the shorter bonds associated with the doubly bridging oxygen donors, is in agreement with enhanced O−M π bonding associated with the positions proximal to the $d_{x^2-y^2}$ M orbital in dodecahedral symmetry.[8] Eight coordination for first-row divalent ions is rather rare but has been reported previously for Mn^{2+},[9a,b] Fe^{2+},[10] and Fe^{3+}.[11]

The structure of **III** (Figure 1) consists of two nearly identical $[LaMn_4(OPiv)_2(cat)_4(py)_8Cl]$ units coordinated to a $[Mn(py)]^{2+}$ central ion by the available lone pairs of η^1-coordinated catecholate oxygen donors. In **IV**, a structurally similar $[LaMn_4(OPiv)_3(cat)_4(py)_6Cl]^+$ unit, with a pivalate ligand in place of two pyridine ligands, is bound in the same fashion to a $[Mn(py)_2NO_3]^+$ unit. The pentanuclear cluster "ligand" units in **III** and **IV** although stoichiometrically very similar, are not isostructural to those in **I** or **II** probably because in the latter the O_8 dodecahedral cavity cannot accommodate the large trivalent La^{3+} ion (r_{ion} =1.05 Å for La^{3+} vs 0.92 Å for Tb^{3+} and 0.66 Å for Mn^{3+}).[12] Consequently, the La^{3+} ion lies on top of a rectangle of divalent ions and is coordinated by four bidentate catecholate ligands (in **III**, La−O = 2.40(1)−2.73(1) Å; in **IV**, La−O = 2.508(3)−2.721(3) Å).

At a rather long distance from the La^{3+} ion (2.942(8) Å for **III** and 2.873(1) Å for **IV**) is located a Cl^- ion which also serves as a weak bridging ligand for two of the Mn^{2+} ions (in **III,** Mn−Cl = 2.638(8) and 2.739(10) Å; in **IV**, Mn−Cl = 2.681(2) and 2.803(2) Å). The Mn_4 rectangle in both **III** and **IV** can be described as a dimer of dimers. In **III** two short Mn−Mn distances at 3.307(5) and 3.310(5) Å and two long ones at 4.710(5) and 5.881(5) Å compare with corresponding distances in **IV** of 3.358(1) and 3.370(1) Å and 4.291(1) and 5.833(1) Å.

In the oxygen-evolving complex (OEC) of photosystem II (PSII) a Mn_4 cluster is essential for the catalytic oxidation of H_2O during photosynthesis[1f,5] and is thought to contain Mn^{3+} and Mn^{4+} ions. This cluster is catalytically active only in the presence of Ca^{2+} and Cl^- ions. The roles of the latter, or of the Mn_4 cluster, in catalysis are not well understood. Lanthanide ions have been found effective competitive inhibitors for the Ca^{2+} site, and Cl^- can be replaced by Br^-.[13] The location of the Ca^{2+} or La^{3+} ions and the possible interactions of these and also the Cl^- ions with the tetranuclear manganese cluster of the OEC are not known.

The structures of **III** and **IV** represent the first examples of $Mn_4/Cl^-/La^{3+}$ structural assemblies which show the involvement of a Cl^- ion in tertiary interactions with La^{3+} and a Mn_4 aggregate. At present we are exploring the reactivity of **III** and **IV** in pursuit of oxidized analogues and derivatives where the La^{3+} ion is replaced with Ca^{2+}.

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Supporting Information Available: Characterization of complexes **I**−**IV**, Tables S1−S4 containing listings of positional parameters, thermal parameters and selected distances and angles of **I**−**IV**, and ORTEP plots of **II**−**IV** (79 pages). See any current masthead page for ordering and Internet access instructions.

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[7] Crystal data for **I**·py: space group $P22_12_1$, $a = 12.921(6)$ Å, $b = 21.437(4)$ Å, $c = 28.759(6)$ Å, $z = 4$, $R_c = 0.077$ ($F\sigma^2 > 2\sigma$). **II**·CH_3CN: space group $P22_12_1$, $a = 13.004(3)$ Å, $b = 21.815(4)$ Å, $c = 28.938(6)$ Å, $\underline{z} = 4$, R_c= 0.070 ($F\sigma^2 > 2\sigma$). **III**·$1.5NC_5H_5$·$1.5Et_2O$·MeOH: space group $P\bar{1}$, $a = 20.930(6)$ Å, $b = 21.554(6)$ Å, $c = 25.887(7)$ Å, $\alpha = 62.28(2)°$, $\beta = 81.11(3)°$, $\gamma = 63.30(2)°$, $z = 2$, $R_c = 0.118$, ($F\sigma^2 > 2\sigma$). **IV**·CH_3CN: space group $P2_1/c$, $a = 25.796(1)$ Å, $b = 15.481(1)$ Å, $c = 22.340(1)$ Å, $\beta = 104.49(3)°$, $z = 4$, $R = 0.058$ ($F\sigma^2 > 2\sigma$).

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