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Mixed Carboxylate/Catecholate Bridged Polynuclear Complexes. Tetranuclear Linear Arrays and Pentanuclear Clusters with $[M_4M'O_8]^{3+}$ Cores ($M = Fe^{2+}, Mn^{+2}$; $M' = Fe^{3+}, Mn^{+3}$). Rare Examples of Dodecahedrally Coordinated, First Row, Trivalent Metal Ions

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Dinuclear iron sites that involve oxygen or nitrogen ligands, such as carboxylate and imidazole groups, are important in biological processes essential for the transport, storage, or activation of dioxygen.[1] Equally important in the function of enzymes such as alkaline phosphatase[2] the pseudocatalases[3,4] and the oxygen evolving complex (OEC) of photosystem II (PSII)[5] are dinuclear or multinuclear Mn units also coordinated by similar oxygen or nitrogen ligands. Attempts to obtain synthetic analogues for the biologically important dinuclear or oligonuclear sites[5,6] have led to a wide variety of structurally relevant manganese and iron complexes.

Recently we have directed our attention to the coordination chemistry of mixed carboxylate−catecholate complexes with first-row transition elements.[7] Our interest in this area derives from the known[8] redox characteristics of the catecholate complexes in general and the recognized importance of redox-active phenolate-type ligands in reactions catalyzed by certain enzymes that include galactose oxidase,[9] ribonucleotide reductase,[10] and PSII.[11]

The reaction of $Mn(OAc)_2{\cdot}(H_2O)_4$ with the Bu_4N^+ or Et_4N^+ salts of the catecholate dianion (cat) in pyridine solution in a 2:1 molar ratio affords after unexceptional workup the nearly colorless crystalline $(Bu_4N)_2$ or $(Et_4N)_2[Mn_4(OAc)_6(py)_2(cat)_2]$, **I**. The analogous Et_4N^+/Fe^{2+}, **II**, and the $(Bu_4N)_2[Zn_4(OAc)_6(cat)_2]$ complexes, **III**, also can be obtained in a similar manner.[12] A parallel reaction using $OPiv^-$ (rather than OAc^-) and MX_2 as a source of M (X = Cl or Br), with metal/ligand ratios identical with those used in the synthesis of I and II, afforded in low yield the new $[M_5(OPiv)_2(cat)_4(py)_8]^+$ complexes (M = Fe, **IV**; M = Mn, **V**). These were isolated as Cl^-, Br^-, or PF_6^- salts,[12] and the presence of trivalent manganese and iron ions in these compounds must be due to the presence of adventitious M^{3+} trace impurities in the MX_2 reagents which may be essential as templates for the formation of the pentanuclear clusters.[13] The syntheses of **IV** and **V** were eventually optimized using the appropriate reagent ratios suggested by the observed stoichiometry. Introduction of $FeCl_3$ in the synthesis of **V** and adjusting the Mn^{2+}/Fe^{3+} ratio to 4:1 resulted in the formation of the $[Mn_4Fe(OPiv)_2(cat)_4(py)_8]^+$ complex, **VI**. The presence of Fe^{2+},Fe^{3+} in **IV** and Mn^{2+},Fe^{3+} in **VI** in a 4:1 ratio was anticipated by the observed stoichiometry and verified by Mossbauer spectroscopy which showed two quadrupole doublets in a 4:1 ratio in **IV** and one quadrupole doublet in **VI**.[14]

The structures of Bu_4N-**I,** Et_4N-**II**, Bu_4N-**III**, **IV**-Cl, and **V**-Br have been determined.[15] In the structures of **I**−**III** the dianions show (Figure 1) a centrosymmetric, linear array of Mn^{2+}, Fe^{2+}, and Zn^{2+} ions bridged by two catecholate and four acetate ligands.[16] Each of the two inner (M_i) metal ions in **I** and **III** ($Mn_i{-}Mn_i$ = 3.248(8) Å for **Ia**, 3.348(7) Å for **Ib**;[16] $Fe_i{-}Fe_i$ = 3.264(3) Å; $Zn_i{-}Zn_i$ = 3.188(5) Å) is five-coordinate chelated by one catecholate ligand. The terminal metal atoms (M_t) are six-coordinate in **I** and **II** and four-coordinate in **III** ($Mn_t{-}Mn_i$

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(12) Satisfactory analytical data have been deposited as Supporting Information. Abbreviations used: OAc^- = acetate anion, CH_3COO^-; $OPiv^-$ = the pivalate anion, $(CH_3)_3CCOO^-$; cat = the catecholate dianion; py = pyridine.

(13) In the absence of M^{3+} ions the same reaction gave noncrystalline, difficult to purify products.

(14) Mössbauer spectra at 125 K. For **IV**: Two quadrupole doublets in a 4:1 ratio; major, $\delta = 1.20$ mm/s (vs Fe), $\Delta_{Eq} = 3.15$ mm/s, minor, $\delta = 0.63$ mm/s (vs Fe), $\Delta_{Eq} = 1.16$ mm/s. For **VI**: One quadrupole doublet, $\delta = 0.63$ mm/s (vs Fe), $\Delta_{Eq} = 1.39$ mm/s.

(15) Crystal data for **I**: space group $P\bar{1}$, $a = 13.718(3)$ Å, $b = 16.283(3)$ Å, $c = 18.667(5)$ Å, $\alpha = 80.81(2)°$, $\beta = 74.73(2)°$, $\gamma = 71.62°$, $z = 2$, $R_w = 0.086$, (3σ data). For **II**: space group $P3_12_1$, $a = 16.931(2)$ Å, $b = 16.931(2)$ Å, $c = 20.594(4)$ Å, $z = 4$, $R_w = 0.097$ (3σ data). For **III**: $P2_1/n$, $a = 11.27(1)$ Å, $b = 21.29(2)$ Å, $c = 14.54(1)$ Å, $\beta = 108.2(1)°$, $\gamma = 92.92(2)°$, $z = 2$, $R_w = 0.073$, (3σ data). For **IV**: space group $C222_1$, $a = 22.266(5)$ Å, $b = 29.118(6)$ Å, $c = 12.620(3)$ Å, $z = 4$, $R_c = 0.070$ (2σ data). For **V**: $P22_12_1$, $a = 12.921(3)$ Å, $b = 21.437(4)$ Å, $c = 28.759(6)$ Å, $z = 4$, $R_c = 0.077$ (2σ data).

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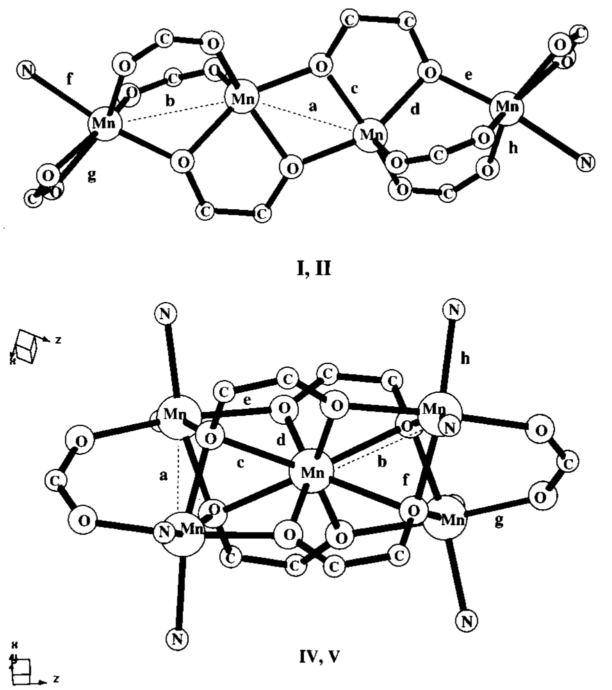

I, II

IV, V

Figure 1. Structures of the [Mn$_4$(OAc)$_6$(py)$_2$(cat)$_2$]$^{2-}$ anion in **I** and **II** and the [M$_5$(OPiv)$_2$(cat)$_4$(py)$_8$]$^+$ cations (M = Fe; M = Mn), in **IV** and **V**. In both figures, the Mn complex is shown as a prototype and the structures, drawn by CrystalMaker, show only the carbon atoms bridging the oxygen donors in the carboxylate and catecholate ligands. Selected bond lengths in Å follow. In **Ia** (**Ib**):[16] $a = 3.248(8)$ (3.384(7)); $b = 3.409(5)$ (3.429(6)); $c = 2.04(1), 2.10(2)$; $d = 2.19(2)$; $e = 2.11(2)$; $f = 2.34(3)$; $g = 2.23(2), 2.25(2)$; $h = 2.14(2, 4)$. In **II**: $a = 3.264(3)$; $b = 3.336(3)$; $c = 2.05(1), 2.106(9)$; $d = 2.13(1)$; $e = 2.03(1)$; $f = 2.40(3)$; $g = 2.15(1), 2.31(1)$; $h = 2.08(2, 4)$. In **IV**: $a = 3.303(2), 3.314(2)$; $b = 3.092(2)-3.115(3)$; $c = 2.245(8)-2.301(7)$; $d = 2.056(8)-2.061(7)$; $e = 2.073(8)-2.078(8)$; $f = 2.148(8)-2.178(8)$; $g = 2.030(8)-2.041(8)$; $h = 2.14(1)-2.485(5)$. In **V**: $a = 3.310(2), 3.313(2)$; $b = 3.159(2)-3.209(2)$; $c = 2.384(5)-2.485(5)$; $d = 1.963(5)-1.983(5)$; $e = 2.143(5)-2.185(6)$; $f = 2.218(5)-2.243(5)$; $g = 2.119(6)-2.140(6)$; $h = 2.215(7)-2.290(8)$.

= 3.409(5) Å for **Ia**, 3.429(6) for **Ib**; Fe$_t$−Fe$_i$ = 3.336(3) Å; Zn$_t$−Zn$_i$ = 3.156(4) Å). In the latter, each of the end-Zn^{2+} ions has terminally coordinated monodentate acetate ligands (rather than bidentate as in **I** and **II**) and are not bound by pyridine ligands.[17] The significant difference in the Mn$_i$-Mn$_i$ distances in **Ia** and **Ib**[16] at present is difficult to evaluate and may arise either as a result of remote perturbations within the bridging units or steric requirements of crystal packing.

The structures of the cations in **IV** and **V** are similar (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 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 Fe^{3+} and Mn^{3+} ions in **IV** and **V**, respectively, show two sets of M−O bonds of 1.90 and 2.26 Å in **IV** and 1.80 and 2.30 Å in **V**. The origin of this difference in bonding, which shows the doubly bridging oxygen donors associated with the shorter bonds 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.[18] Eight coordination for first row divalent ions is rather rare but has been reported previously for Mn^{2+},[19a,b] Fe^{2+},[20] and Fe^{3+}.[21] Two pivalate and eight pyridine ligands complete the distorted-octahedral coordination around the four peripheral divalent ions.

Introduction of other trivalent ions into the eight-oxygen cage of **IV** and **V** is possible[22] and depending on the ionic radius the [Mn$_4$M(OPiv)$_2$(cat)$_4$(py)$_8$]$^+$ complexes either assume a structure similar to that of **IV** and **V** (M = Tb^{3+}, $r = 0.92$ Å) or rearrange to a new structure (and new stoichiometry) that places the M^{3+} ion above a rectangular array of four Mn^{2+} ions (M = La^{3+}, $r = 1.03$ Å).

Interest in the reactivity and structural properties of **III**, **IV**, and **V** derives from the spectroscopically supported conclusion that the OEC complex in PSII may be a tetranuclear cluster that contains highly oxidized Mn ions (Mn^{3+}, Mn^{4+}) coordinated by carboxylate and oxo-ligands.[5] The reactivity, redox properties and structural changes that accompany the oxidation of **I**, **IV**, and **V** are currently under investigation.

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Supporting Information Available: Characterization of complexes **I**−**VI**, including the Mössbauer spectra of **IV** and **VI**, ORTEP plots of **I** (two isomers), **II**, **III**, **IV**, and **V**, and tables S1−S6 containing listings of positional parameters, thermal parameters, and selected distances and angles of **I**−**V** (56 pages). Ordering information is given on any current masthead page.

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(16) The asymmetric unit in the structure of **I** contains two independent halves of linear tetramers that are isomers. The isomerism arises from the location of the terminal pyridine ligands on the octahedrally coordinated external Mn ions. In one case (**Ia**) the pyridine ligand is axial to a bridging catecholate oxygen atom, while in the other (**Ib**) the pyridine is axial to a bridging acetate oxygen atom.

(17) A figure of this complex has been deposited in the Supporting Information.

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