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Synthesis and Characterization of a New Class of μ_3-OH-Bridged Trimers That Contain Octahedrally Coordinated Divalent Metal Ions Bridged by Three Acetate Ligands and a Unique Catecholate Ligand. Solid State Molecular Structures of the $[(py)_5M^{II}_3(OAc)_3(\mu_3\text{-}OH)((cat)]$ Complexes (M = Mn(II), Fe(II), Co(II), Ni(II))

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Dinuclear iron sites that are bound exclusively by oxygen or nitrogen ligands are important in the transport of oxygen, the oxygenation of various substrates, and the activation of dioxygen.[1] The central cores of these sites show the two metal ions bridged by one or two carboxylates and oxo, hydroxo, or aqua ligands. Dimeric units with similar structural features also have been found as components of trinuclear sites in certain Zn and Mn enzymes. Included among the trinuclear sites, which have been labeled[2] "trinuclear constellations", are the trizinc centers in alkaline phosphatase,[3] P1-Nuclease,[4] and phospholipase[5] and the trimanganese center in inorganic pyrophosphatase.[6] Carboxylato-bridged Mn_2 units also may exist in the tetramanganese photosynthetic oxidation center.[7]

Coordination chemistry of dinuclear complexes with carboxylate and oxo, hydroxo, or aqua bridging ligands is well developed,[1,8] and a number of these compounds have been found important as synthetic and spectroscopic analogs for the dinuclear sites in biological systems. Another well-known class of carboxylato- and oxo-bridged complexes is the trinuclear $[M_3O(OOCR)_6L_3]^n$ "basic acetate" complexes[9] ($n = 0, +1$) of transition elements with readily accessible trivalent oxidation states (for $n = 1$, M = V^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+} Ru^{3+}, Rh^{3+}, Ir^{3+}). The $[M_3O(OOCR)_6L_3]^+$ complexes (M = Co,[10] Ni[11]) have been reported but have not been structurally characterized.

The unique, oxo-centered $[(py)_5Co_3(\mu_3\text{-}O)(OAc)_3(OH)_2]^{2+}$ complex, **I**, contains Co(III) ions and, in addition to two μ-OH^- ligands, only three μ-acetato bridging ligands.[12] To our knowledge, there exist no examples of trinuclear carboxylato- and oxo-bridged complexes that contain entirely divalent metal ions.

In this communication we report the synthesis and characterization of the $[(py)_5M^{II}_3(OAc)_3(\mu_3\text{-}OH)(cat)]$ complexes (cat = the catecholate dianion, M = Mn, Fe, Co, Ni). These X-ray isomorphous and isostructural complexes contain divalent metal ions and possess a core structure very similar to that in **I**.

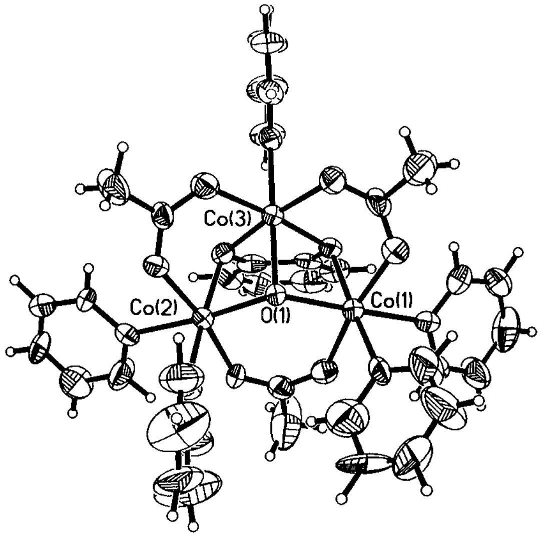

Figure 1. Structure and partial labeling of the $[(py)_5Co_3(\mu_3\text{-}OH)(OAc)_3(cat)]$ complex (**IV**). The corresponding Fe, Mn, and Ni complexes are X-ray isomorphous and isostructural; thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

The reaction of $M^{II}(OAc)_2{\cdot}4H_2O$ (3 mmol) with with an ethanolic solution of 0.2 M Et_4NOH (2 mmol) and 1,2-catechol (1 mmol) in 40 mL of pyridine affords, after addition of diethyl ether and standing at ambient temperature for >12 h, the crystalline $[(py)_5M^{II}_3(OAc)_3(\mu_3\text{-}OH)(cat)]$ neutral complexes[13] (M: Mn, **II**; Fe, **III**; Co, **IV**; Ni, **V**). The μ_3-OH^- ligand in these complexes may be substituted by μ_3-MeO^- when the latter is supplied in the synthetic procedure. Thus, the use of a methanolic Bu_4NOH solution (that contains small amounts of MeO^-) in the synthesis of **II** results in a trimer that, as determined crystallographically, contains equal amounts of MeO^- and OH^- in the bridge. Similarly, NaOMe in MeOH solution in the strictly nonaqueous synthesis of **IV** gives $[(py)_5Co^{II}_3(OAc)_3(\mu_3\text{-}OMe)(cat)]$.[14]

The structures of **II**−**V** have been determined.[15] The complexes are X-ray isomorphous and isostructural and consist of three fused M^{II} octahedral units. A common structural feature in **II**−**V** is the pyramidal $(M^{II})_3(\mu_3\text{-}OH)$ structural unit with three acetate ligands spanning the edges of a $(M^{II})_3$ isosceles triangle (Figure 1). The catecholate ligand in all of the complexes serves as a bidentate chelate for one of the metal ions and also as a bridge between the two podal and the unique axial metal ions. The asymmetry of the pyramidal $(M^{II})_3(\mu_3\text{-}OH)$ unit is apparent

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(1) (a) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344−361. (b) Que, L., Jr.; Scarrow, R. C. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; American Chemical Society: Washington, DC, 1988, p 302. (c) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97. (d) Sanders-Lohr, J. In *Iron Carriers and Iron Proteins*; Lohr, T. M., Ed.; VCH: New York, 1989; pp 375−466.

(2) Fenton, D. E.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1993**, 1350.

(3) Coleman, J. E. *Annu. Rev. Biophys. Biomol. Struct.* **1992**, *21*, 441.

(4) Volbeda, S.; Lahm, A.; Sakijama, F.; Suck, D. *EMBO J.* **1991**, *10*, 1607.

(5) Hough, E.; Hansen, L. K.; Birknes, B.; Junge, K.; Hansen, S.; Hordvik, A.; Little, C.; Dodson, E. J.; Derewenda, Z. *Nature* **1989**, *338*, 357.

(6) (a) Cooperman, B. S.; Baykov, A. A.; Lahti, R. *TIBS* **1922**, *17*, 262. (b) Chirgadze, N. Y.; Kuranova, I. P.; Veirskaya, N. A.; Teplyakov, A. V.; Wilson, K.; Srokopytov, B. V.; Harutynnyan, E. G.; Hohne, W. *Kristallografiya* **1991**, *36*, 128.

(7) (a) Ghanotakis, D.; Yocum, C. F. *Annu. Rev. Plant Physiol. Mol. Biol.* **1990**, *41*, 255. (b) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 244. (c) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328.

(8) (a) Feig, A. L.; Lippard, S. *J. Chem. Rev.* **1994**, *94*, 759−805. (b) Kurtz, D. M. *Chem. Rev.* **1990**, *90*, 585−606.

(9) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195.

(10) Uemura, S.; Spencer, A.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1973**, 2565.

(11) Schall, C.; Thieme-Wiedtmarckter, Ch. *Z. Electrokem. Soc.* **1923**, *45*, 610.

(12) Sumner, C. E., Jr. *Inorg. Chem.* **1988**, *27*, 1320−1327.

(13) Satisfactory analytical data have been obtained for all of these complexes. These data and spectroscopic characterization data have been deposited with the Supporting Information.

(14) Reynolds, R. A., Coucouvanis, D. Work in progress.

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Table 1. Summary of Interatomic Distances (Å)[a] and Angles (deg) in $[(py)_5Co_3(\mu_3\text{-}O)(OAc)_3(OH)_2]^{2+}$ (**I**)[12] and in the $[(py)_5M^{II}_3(OAc)_3(\mu_3\text{-}OH)(cat)]$ Complexes (M = Mn (**II**), Fe (**III**), Co (**IV**), Ni (**V**)

	I	**II**	**III**	**IV**	**V**
			Distances		
$M_{ap}-M_p$	2.780(1)	3.150(3)	3.095(4)	3.054(3)	2.980(6)
	2.791(1)	3.163(3)	3.108(4)	3.038(3)	2.991(5)
M_p-M_p	3.320(1)	3.760(3)	3.684(4)	3.671(3)	3.648(5)
$M_{ap}-\mu OH^b$	1.892(4)	2.207(7)	2.19(1)	2.13(1)	2.06(2)
$M_p-\mu OH^b$	1.872(3)	2.172(6)	2.13(1)	2.09(1)	2.05(1)
	1.862(3)	2.191(6)	2.14(1)	2.09(1)	2.05(1)
$M_{ap}-O_{cat}$	1.880(4)	2.176(6)	2.12(1)	2.083(9)	2.04(1)
	1.894(4)	2.197(6)	2.14(1)	2.082(9)	2.02(1)
M_p-O_{cat}	1.899(4)	2.150(7)	2.15(1)	2.13(1)	2.11(2)
	1.906(4)	2.162(7)	2.11(1)	2.10(1)	2.10(2)
$M-O_{ac}$	1.897(4,6)	2.17(1,6)	2.11(2,6)	2.08(1,6)	2.03(1,6)
M−N(Py)	1.963(5,5)	2.33(1,5)	2.22(2,5)	2.19(2,5)	2.09(4,5)
			Angles		
$M_{ap}-\mu OH-M_p{}^b$	95.2(2)	92.0(2)	92.2(4)	92.2(4)	93.1(6)
	96.1(2)	92.0(2)	91.4(4)	92.6(4)	93.4(7)
$M_p-\mu OH-M_p{}^b$	125.5(2)	119.0(3)	119.9(4)	122.8(4)	125.6(7)

[a] The first number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - x)^2/N(N-1)]^{1/2}$; the second represents the number of chemically equivalent bonds averaged out. [b] ap = apical metal atom (Co(3) in Figure 1), p = podal metal atoms (Co(I), Co(II) in Figure 1). cat = catechol, ac = acetate, Py = pyridine. For **I**, μ-O distances and angles are reported.

in the unequal M−M distances and M−OH−M angles (Table 1). The coordination of pyridine molecules as terminal ligands to each of the metal ions completes the distorted octahedral M^{II} coordination spheres.

A comparison of the structure of **IV** with the previously reported[12] structure of **I** shows (Table 1) differences in corresponding interatomic distances as expected for the ionic radius differences between the Co(III) ions in **I** and the Co(II) ions in **IV**. The larger M−OH−M angles in **I** and the slightly "flattened" $(M^{III})_3(\mu_3\text{-}O)$ pyramidal unit, by comparison to the $(M^{II})_3(\mu_3\text{-}OH)$ unit in **IV**, undoubtedly reflect the effects of the more pronounced Co(III)−Co(III) electrostatic repulsive interactions in **I**.

The high-spin octahedral ions in the complexes **II**−**V** are weakly exchange coupled. Temperature-dependent magnetic susceptibilitty studies reveal antiferromagnetic intratrimer interactions. A least-squares fit of the data for **II**−**V** using the usual Heisenberg−Dirac−Van Vleck exchange Hamiltonian,[16] gave the following values of J and J_{13}, respectively: -2.36 cm^{-1}, -1.92 cm^{-1} ($g = 2.00$) for **II**; -0.63 cm^{-1}, -0.32 cm^{-1} ($g = 2.00$) for **III**; -1.88 cm^{-1}, -1.32 cm^{-1} ($g = 2.56$) for **IV**; and -2.09 cm^{-1}, -0.07 cm^{-1} ($g = 2.16$) for **V**.

The Mossbauer spectrum of **III** at 125 K consists of a quadrupole doublet with $\delta = 1.22$ mm/s, $\Delta E_q = 1.91$ mm/s, and $\Gamma = 0.38$ mm/s. The spectrum obtained from a frozen pyridine solution of **III** at 125 K was fit with three doublets having the following δ, ΔE_q values (mm/s^{-1}): of 1.18, 2.91; 1.20, 2.62; 1.21, 1.89. The values both in the solid state and in solution are typical of divalent iron in an octahedral environment although the exact structure is difficult to ascertain in pyridine solution.

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Supporting Information Available: Text giving analytical, structural, and spectroscopic data for **II**−**V**, an ORTEP plot of the general structure, a stereo pair of one of the isomorpous trinuclear clusters, listings of positional parameters, thermal parameters, and selected distances and angles for **II**−**V**, a discussion of the magnetic properties and fits of magnetic moment vs temperature curves, EPR spectra of the low-field regions of for **II**−**V**, and Mossbauer spectra of **III** in the solid state and in pyridine solution at 125 K (53 pages). Ordering information is given on any current masthead page.

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(15) **II**−**V** are X-ray isomorphous and isostructural and crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$. Cell dimensions (Å, deg) for **II**, $a = 11.944(5)$, $b = 19.457(6)$, $c = 20.84(1)$, $\beta = 97.67(4)$; for **III**, $a = 11.805(4)$, $b = 19.123(4)$, $c = 20.655(8)$, $\beta = 99.21(3)$; for **IV**, $a = 11.641(3)$, $b = 18.954(4)$, $c = 20.481(6)$, $\beta = 99.65(2)$; for **V**, $a = 11.649(4)$, $b = 18.786(4)$, $c = 21.082(6)$, $\beta = 95.76(3)$. Single-crystal X-ray diffraction data for all crystals were collected on a Nicolet R3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniuques, direct methods, and Fourier methods. Full-matrix refinement of 532 parameters on 4260 data ($2\theta = 45°$, $I > 3\sigma_I$) for **II**, 384 parameters on 2519 data ($2\theta = 45°$, $I > 3\sigma_I$) for **III**, 487 parameters on 3094 data ($2\theta = 45°$, $I > 3\sigma_I$) for **IV**, and 252 parameters on 1501 data ($2\theta = 35°$, $I > 2\sigma_I$) for **V** gave final R values of 0.063, 0.081, 0.073, and 0.103, respectively. Over time, **V** decomposed under irradiation.

(16) For an isolated trimer, the spin Hamiltonian is $H_{ex} = -2[J_{12}S_1{\cdot}S_2 + J_{23}S_2{\cdot}S_3 + J_{31}S_3{\cdot}S_1]$ which reduces to $H_{ex} = -2J[S_1{\cdot}S_2 + S_2{\cdot}S_3\ ] - 2J_{31}S_3{\cdot}S_1$ assuming $J_{12} = J_{23} = J$ due to the C_{2v} symmetry of the triangular array. In the exchange scheme, J represents coupling between Co(1)−Co(2) and Co(1)−Co(3) and J_{13} coupling between Co(2) and Co(3) (Figure 1).