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Synthesis, Structure and Magnetic Properties of a Linear Trimanganese(III,II,III) Complex Bridged with a (μ-Hydroxo)bis(μ-acetato) Unit

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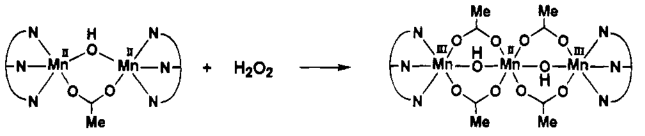
Proteins containing a polymanganese site bridged with carboxylate groups have recently emerged.[1] For most of these proteins, catalytic chemistry is accompanied by redox chemistry with II, III, and IV oxidation states of manganese. In several of these proteins, mixed valence states of $Mn^{II}Mn^{III}$ and $Mn^{III}Mn^{IV}$ have been reported.[2] In order to uncover the unique electronic structures of these metal sites, the magnetic properties of mixed valence manganese complexes with carboxylate bridges have been the subject of numerous studies.[3] As part of our synthetic explorations of manganese complexes with HB-$(3,5\text{-}iPr_2pz)_3$,[4−8] we now report a novel $Mn^{III}Mn^{II}Mn^{III}$ complex bridged with a (μ-hydroxo)bis(μ-acetato) unit.

Scheme 1



Reaction of a dimanganese(II) complex $[Mn(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)_2$ with 1 equiv of acetic acid under argon gave a (μ-hydroxo)(μ-acetato) complex $[Mn(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)(OAc)$ (**1**).[9] When this complex was treated with 20 equiv of H_2O_2 in toluene at room temperature for 1 h, the slightly yellow color of the solution turned deep brown. Removal of the solvent followed by fractional recrystallization from MeCN gave 44% yield (based on acetate) of a novel trinuclear complex formulated $[Mn(HB(3,5\text{-}iPr_2pz)_3)](OH)(OAc)_2Mn(OH)(OAc)_2[Mn(HB(3,5\text{-}iPr_2pz)_3)]\cdot 3,5\text{-}iPr_2pzH\cdot 3(MeCN)$ (**2**·3,5-iPr$_2$pzH·3(MeCN)) as crystals suitable for X-ray diffraction (Scheme 1).[10] The crystalline sample was found to contain 3,5-diisopropylpyrazole as a component of crystallization, which is presumably a product formed during the oxidative degradation of **1** with H_2O_2. A broad IR band observed at ca. 3260 cm^{-1} is assigned to ν(NH) and is diagnostic of pyrazole but not pyrazolate.[6,11] The structure was determined by X-ray crystallography, and a perspective view of **2** is presented in Figure 1.[12] While there is no crystallographically imposed center of symmetry, **2** adopts an approximately centrosymmetric structure. The oxygen atoms O1 and O2 that bridge the two manganese ions are identified as hydroxide on the basis of the Mn−O distances; the distances of Mn2−O1/Mn2−O2 (average 2.01 Å) are almost located in the range known for Mn^{II}_2 (2.05−2.09 Å)[4,13] complexes bridged with hydroxide, but clearly longer than those of μ-oxo−Mn^{III}_2 complexes (1.78−1.81 Å).[3] While, to our knowledge, there are not examples of $Mn^{II}Mn^{III}$ or Mn^{III}_2 complexes bridged with hydroxide, the Mn−O distances for alkoxo-bridged Mn^{III}_2 are ca. 1.9 Å, comparable to those of Mn1−O1 and Mn3−O2 (average 1.85 Å).[14] The sharp IR band observed at 3629 cm^{-1}, attributable to ν(OH), corroborates this assignment. The Mn1−O1/Mn3−O2 distances are considerably shorter than those of Mn2−O1/Mn2−O2, indicating that the oxidation levels of the terminal manganese ions are higher than that of the central one. Since the co-crystallized counterpart found in the crystal of **2**·3,5-iPr$_2$pzH·3(MeCN) is pyrazole, the net charge of the trimeric

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(1) (a) *Manganese Redox Enzymes*, Pecoraro, V. L., Ed., VCH: New York, 1992. (b) Brudvig, G. W.; Beck, W. F.; De Paula, J. C. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 25. (c) Pecoraro, V. L.; Baldwin, M. J.; Gelasco, A. *Chem. Rev.* **1994**, *94*, 807.

(2) (a) Waldo, G. S.; Yu, S.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 5869. (b) Khangulov, S. V.; Barynin, V. V.; Antonyuk-Barynina, S. V. *Biochim. Biophys. Acta* **1990**, *1020*, 25. (c) Zheng, M.; Khangulov, S. V.; Dismukes, G. C.; Barynin, V. V. *Inorg. Chem.* **1994**, *33*, 382.

(3) (a) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97. (b) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (c) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328. (d) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344.

(4) Kitajima, N.; Singh, U. P.; Amagai, H.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7757.

(5) Kitajima, N.; Osawa, M.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8952.

(6) Kitajima, N.; Osawa, M.; Tamura, N.; Moro-oka, Y.; Hirano, T.; Hirobe, M.; Nagano, T. *Inorg. Chem.* **1993**, *32*, 1879.

(7) Osawa, M.; Singh, U. P.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Chem. Soc., Chem. Commun.* **1993**, 310.

(8) Abbreviations used: $HB(3,5\text{-}iPr_2pz)_3$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; 3,5-iPr$_2$pzH = 3,5-diisopropylpyrazole; OAc = acetate, OBz = bezoate.

(9) Complex **1** was characterized by elemental analysis, IR, and FD-MS. Although the X-ray analysis has not been succeeded yet, the structure is presumably identical to the analogous iron complex $[Fe(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)(OBz)$: Kitajima, N.; Tamura, N.; Tanaka, M.; Moro-oka, Y. *Inorg. Chem.* **1992**, *31*, 3342. The details will be reported elsewhere: Kitajima, N.; Osawa, M.; Imai, S.; Moro-oka, Y. Manuscript in preparation.

(10) Anal. Calcd for **2**·3,5-iPr$_2$pzH ($C_{71}H_{121}N_{14}B_2O_{10}Mn_3$): C, 8.04; H, 56.21; N, 12.92. Found: C, 8.35; H, 55.91; N, 13.05. IR (KBr, cm^{-1}): ν(OH), 3629; ν(NH), 3260; ν(BH), 2545; ν_a(COO), 1596; ν_s(COO), 1392. UV−vis (in CH_2Cl_2, nm ($\epsilon/cm^{-1}\cdot M^{-1}$)): 485 (485), 514 (sh, 424), 560 (sh, 316), ca. 800 (80).

(11) Hikichi, S.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Chem. Soc., Chem. Commun.* **1992**, 814.

(12) Crystal data: fw 1633.36, monoclinic space group $P2_1/a$ (No. 14); a = 24.834(7) Å, b = 19.573(4) Å, c = 19.267(4) Å, β = 99.81(2)°, V = 9228(3) $Å^3$, Z = 4. For 5723 observed reflections ($2\theta_{max}$ = 42°) with $I > 3\sigma(I)$ collected at −80 °C, the current R (R_w) factor is 6.45% (6.39%).

(13) (a) Bossek, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1989**, *165*, 123. (b) Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J.-J. *J. Am. Chem. Soc.* **1988**, *110*, 7398.

(14) (a) Nishida, Y.; Oshiro, N.; Tokii, T. *Z. Naturforsch* **1988**, *43b*, 472. (b) Torihara, N.; Mikuriya, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1610. (c) Mikuriya, M.; Torihara, N.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1063.

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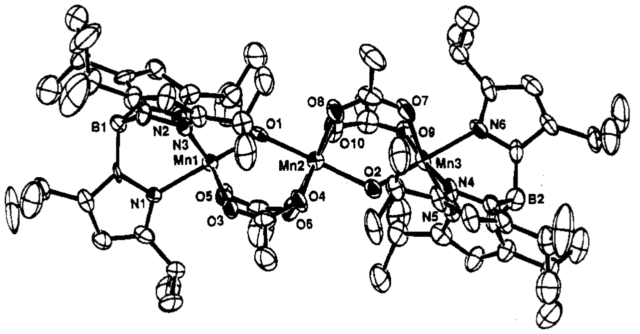

Figure 1. Crystal structure of $2{\cdot}3,5\text{-iPr}_2\text{pzH}{\cdot}3(\text{MeCN})$. All hydrogen atoms and the 3,5-diisopropylpyrazole and MeCN molecules are omitted for clarity. Selected bond distances (Å) and bond angles (deg) are as follows: Mn1−O1, 1.840(6); Mn1−O3, 2.071(7); Mn1−O5, 2.034(7); Mn1−N1, 2.079(8); Mn1−N2, 2.170(8); Mn1−N3, 2.183(8); Mn2−O1, 1.980(6); Mn2−O2, 2.042(6); Mn2−O4, 2.199(7); Mn2−O6, 2.076(7); Mn2−O8, 2.116(7); Mn2−O10, 2.109(8); Mn3−O2, 1.850(6); Mn3−O7, 2.106(7); Mn3−O9, 1.995(7); Mn3−N4, 2.097(9); Mn3−N5, 2.258(9); Mn3−N6, 2.058(8); Mn1··Mn2, 3.394(2); Mn··Mn3, 3.439(2); Mn1··Mn3, 6.831(2); Mn1−O1−Mn2, 125.3(3); Mn2−O2−Mn3, 124.1(3); O1−Mn2−O2, 179.0(3).

cluster **2** is neutral, leading to the most reasonable valence assignment as $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$. The distances between the manganese ions and the bridging carboxylate oxygen atoms are also consistent with this formulation. Whereas the average $\text{Mn2−O}_{\text{carb}}$ is 2.13 Å, the averages of $\text{Mn1−O}_{\text{carb}}$ and $\text{Mn3−O}_{\text{carb}}$ are distinctly shorter, 2.05 Å. Since the $\text{Mn−O}_{\text{carb}}$ known for carboxylate-bridged Mn^{II}_2 and Mn^{III}_2 complexes are 2.12−2.19 and 2.00−2.17 Å respectively,[3] it follows that Mn2 is in the II and Mn1 and Mn3 are in the III oxidation state. Moreover, there is a discernible tetragonal distortion of the coordination environment around Mn1 and Mn3 consistent with Jahn−Teller activity of the Mn(III) oxidation state. The lengthening of Mn3−O7 and Mn3−N5 relative to the comparable pair Mn3−O9 and Mn3−N9 reflects an axial elongation of the pseudooctahedral coordination. A similar but smaller distortion is evident around Mn1.

Figure 2 indicates the temperature dependence of the effective magnetic moment of $2{\cdot}3,5\text{-iPr}_2\text{pzH}$ per the trinuclear cluster. An analysis of the data has been performed using the spin Hamiltonian given in eq 1,where the terminal atoms have S_1 =

$$H = -2[J_{12}{\cdot}S_1{\cdot}S_2 + J_{23}{\cdot}S_2{\cdot}S_3 + J_{13}{\cdot}S_1{\cdot}S_3] + \mu_B[g_1S_1 + g_2S_2 + g_3S_3]{\cdot}H \quad (1)$$

$S_3 = 2$ and the central atom has $S_2 = 5/2$. Two satisfactory fits corresponding to well-defined minima in the parameter space were found: $J_{12} = J_{23} = -4.0\ \text{cm}^{-1}$, $J_{13} \approx 0\ \text{cm}^{-1}$; $J_{12} = J_{23} = -3.3\ \text{cm}^{-1}$, $J_{13} = -6.4\ \text{cm}^{-1}$. Variation of the g value between 1.92 and 1.97 led to variations in the J values of no more than 10 %, usually much less. With both models, the electronic structure of the cluster is interpreted in terms of a weakly antiferromagnetically coupled mixed valence state of $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$, consistent with the bond length data described above. The first model is chemically reasonable based on expectations from dimeric systems and the common assumption of near-zero terminal coupling in weakly coupled linear trimers.[15] On the other hand, the latter fit is clearly statistically superior. In linear trimeric systems, the terminal coupling constant is expected to be of smaller magnitude than that of the adjacent atoms.[16] The second fit, having $|J_{\text{term}}| > |J_{\text{adjac}}|$, is therefore notable, despite appearing chemically less reasonable.[17]

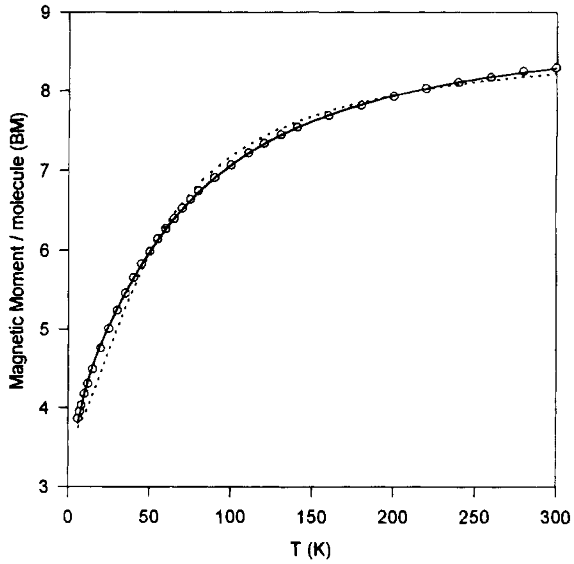

Figure 2. Plot of effective magnetic moment per trinuclear cluster of **2** versus temperature (data taken at 10 kG). Dashed line: $g = 1.92$, $J_{12} = J_{23} = -4.0\ \text{cm}^{-1}$, $J_{13} = 0.5\ \text{cm}^{-1}$. Solid line: $g = 1.99$, $J_{12} = J_{23} = -3.3\ \text{cm}^{-1}$, $J_{13} = -6.4\ \text{cm}^{-1}$.

The present structure is a rare example of a linear trinuclear manganese complex.[15,20] It shows that a (μ-hydroxo)bis(μ-carboxylato) bridging unit can mediate a weak antiferromagnetic interaction between manganese(II) and manganese(III) ions. More systematic explorations will be required to determine how the sign and magnitude of the coupling constants vary with structure. Although the trinuclear structural motif found in **2** is currently unknown in biological systems, it may be possible to evaluate the existence of such a bridging group in proteins based on magnetic studies on the $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ states.[1,2]

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Supplementary Material Available: Text giving the experimental details and tables giving crystal data and details of the structure determination, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations, and a figure showing the numbering of **2** (20 pages). Ordering information is given on any current masthead page.

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(15) Kessissoglou, D. P.; Kirk, M. L.; Lah, M. S.; Li, X.; Raptopoulou, C.; Hartfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 5424.

(16) Kahn, O. *Struct. Bonding (Berlin)* **1987**, *68*, 89.

(17) Possible influences of double exchange,[18] electron transfer, and vibronic coupling[19] on these effective J values could be considered. However, in localized mixed valence systems, the contribution of such effects is ferromagnetic.[18] The present alternate fit for J_{term} shows an increased *anti*ferromagnetic interaction.

(18) Blondin, G.; Borshch, S.; Girerd, J.-J. *Comments Inorg. Chem.* **1992**, *12*, 315.

(19) Bersuker, I. B.; Borshch, S. A. *Adv. Chem. Phys.* **1992**, *81*, 703.

(20) Rardin, R. L.; Poganiuch, P.; Bino, A.; Goldberg, D. P.; Tolman, W. B.; Liu, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 5240.