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A Novel Carboxylate-Free Ferromagnetic Trinuclear μ_3-Oxo–Manganese(III) Complex with Distorted Pentagonal-Bipyramidal Metal Centers

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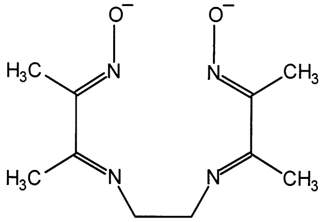
In methanol, the reaction of $Mn(ClO_4)_2\cdot 6H_2O$ and 1,2-bis(biacetylmonoximeimino)ethane (H_2bamen) in the presence of triethylamine affords a trinuclear complex having the formula $[Mn_3(\mu_3\text{-O})(\mu_3\text{-bamen})_3]ClO_4\cdot 2H_2O$. The structure of this complex shows a symmetric planar central $\{Mn^{III}_3(\mu_3\text{-O})\}$ unit coordinated to three hexadentate bridging (via oximate groups) ligands. The N_4O_3 coordination sphere around each metal center is very close to pentagonal-bipyramidal. A cyclic voltammogram of the complex displays two reversible and an irreversible response due to $Mn^{III}_3 \rightarrow Mn^{III}_2Mn^{IV}$, $Mn^{III}_2Mn^{IV} \rightarrow Mn^{III}Mn^{IV}_2$, and $Mn^{III}Mn^{IV}_2 \rightarrow Mn^{IV}_3$ oxidation processes, respectively. Cryomagnetic data reveal that the complex is ferromagnetic.

Trinuclear "basic carboxylates" containing the $\{M_3(\mu_3\text{-O})\}$ core have been known for some time and studied extensively.[1] The triangular ensemble of the metal ions with the central oxo bridge is stabilized by various carboxylates (RCO_2^-) and different neutral monodentate ancillary ligands (L). Interest in such complexes of the general formula $[M_3O(O_2CR)_6L_3]^{0/1+}$ is primarily due to their molecular structures, magnetic properties, and intramolecular electron transfer characteristics of the mixed-valent variety. In these complexes, the coordination sphere around each metal center is very close to octahedral. The central $\{M_3(\mu_3\text{-O})\}$ core is generally planar and has a near 3-fold symmetry. Examples of the $\{M_3(\mu_3\text{-O})\}$ unit in a trinuclear complex without any carboxylate are scarce. A few mixed-ligand complexes of this type are reported.[2] In these complexes, the $\{M_3(\mu_3\text{-O})\}$ unit is asymmetric and pyramidal. Herein we report a carboxylate-free, planar and symmetric $\{M_3(\mu_3\text{-O})\}$ unit in a trimanganese(III) complex cation, $[Mn_3O(bamen)_3]^+$, having distorted pentagonal-bipyramidal metal centers with a hexadentate bridging ligand (bamen^{2-}, **I**).



(**I**)

The complex has been synthesized in ~55% yield from methanolic medium under aerobic conditions at room temperature by stirring a reaction mixture consisting of $Mn(ClO_4)_2\cdot 6H_2O$, H_2bamen (prepared by condensation of 2 mol of biacetylmonoxime and 1 mol of ethylenediamine[3]), and $N(C_2H_5)_3$ in a 1:1:2 molar ratio for 5 h. The complex precipitates directly from the reaction mixture as a green solid. The elemental analysis data[4] are consistent with the formula $[Mn_3O(bamen)_3]ClO_4\cdot 2H_2O$. The complex behaves as a 1:1 electrolyte in acetonitrile solution.[4] Most likely the oxygen in air acts as the oxidant for the oxidation of Mn(II) to Mn(III) in the reaction mixture.

One of the single crystals obtained by slow evaporation of a methanol−xylene (2:1) solution of the complex was used to determine the molecular structure by X-ray crystallography.[5] The complex cation is depicted in Figure 1. The cation involves three dianionic ligands (bamen^{2-}), one μ_3-oxo group, and three manganese ions. Thus all the manganese ions are in the +3 oxidation state. The metal ions are

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(1) (a) Hendrickson, D. N.; Oh, S. M.; Doug, T.-Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329. (b) Vincent, J. B.; Chang, H.-R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703. (c) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195. (d) Cannon, R. D.; Jayasooriya U. A.; Wu, R.; Arapkoske, S. K.; Stride, J. A.; Nielsen, O. F.; White, R. P.; Kearly, G. J.; Summerfield, D. *J. Am. Chem. Soc.* **1994**, *116*, 11869. (e) Wu, R.; Poyraz, M.; Sowrey, F. E.; Anson, C. E.; Wocadlo, S.; Powell, A. K.; Jayasooriya, U. A.; Cannon, R. D.; Nakamoto, T.; Katada, M.; Sano, H. *Inorg. Chem.* **1998**, *37*, 1913.

(2) (a) Bill, E.; Krebs, C.; Winter, M.; Gerdan, M.; Trautwein, A. X.; Flörke, U.; Haupt, H.-J.; Chaudhuri, P. *Chem. Eur. J.* **1997**, *3*, 193. (b) Chaudhuri, P.; Hess, M.; Weyhermüller, T.; Bill, E.; Haupt, H.-J.; Flörke, U. *Inorg. Chem. Commun.* **1998**, *1*, 39.

(3) Uhlig, V. E.; Friedrich, M. *Z. Anorg. Allg. Chem.* **1966**, *343*, 299.

(4) Anal. Calcd for $C_{30}H_{52}N_{12}O_{13}ClMn_3$: C, 36.43; H, 5.30; N, 16.99. Found: C, 36.23; H, 5.12; N, 16.75. Molar conductivity (Ω^{1-} cm^2 M^{-1}): 180.

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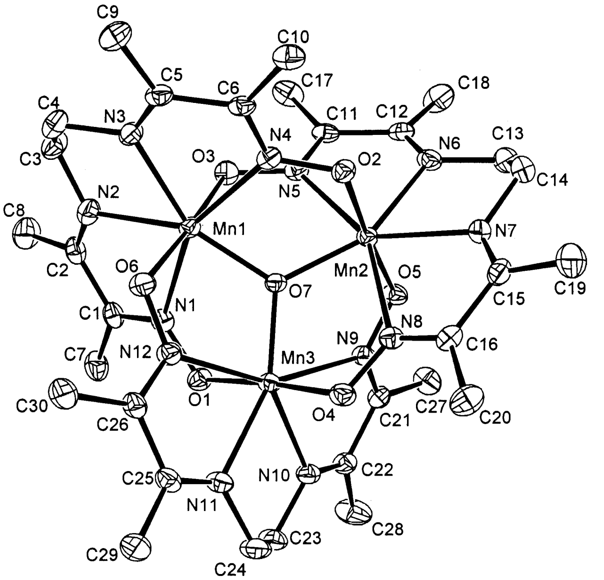

Figure 1. Structure of $[Mn_3(\mu_3\text{-}O)(\mu_3\text{-bamen})_3]^+$. All atoms are represented by their 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn(1)−N(1), 2.343(2); Mn(1)−N(2), 2.253(2); Mn(1)−N(3), 2.246(2); Mn(1)−N(4), 2.370(2); Mn(1)−O(3), 1.9304(18); Mn(1)−O(6), 1.9359(18); Mn(1)−O(7), 1.9081(17); Mn(2)−N(5), 2.331(2); Mn(2)−N(6), 2.238(2); Mn(2)−N(7), 2.246(2); Mn(2)−N(8), 2.362(2); Mn(2)−O(2), 1.9340(18); Mn(2)−O(5), 1.9352(18); Mn(2)−O(7), 1.9088(17); Mn(3)−N(9), 2.371(2); Mn(3)−N(10), 2.267(2); Mn(3)−N(11), 2.232(2); Mn(3)−N(12), 2.338(2); Mn(3)−O(1), 1.9445(19); Mn(3)−O(4), 1.9362(19); Mn(3)−O(7), 1.8978(16); O(7)−Mn(1)−O(3), 91.84(8); O(7)−Mn(1)−O(6), 92.01(7); O(7)−Mn(1)−N(1), 77.57(8); O(7)−Mn(1)−N(4), 76.55(7); O(7)−Mn(2)−O(2), 91.88(7); O(7)−Mn(2)−O(5), 92.01(7); O(7)−Mn(2)−N(5), 77.16(7); O(7)−Mn(2)−N(8), 76.41(7); O(7)−Mn(3)−O(1), 92.55(8); O(7)−Mn(3)−O(4), 91.69(7); O(7)−Mn(3)−N(9), 76.34(7); O(7)−Mn(3)−N(12), 77.51(7); O(3)−Mn(1)−O(6), 175.90(8); O(2)−Mn(2)−O(5), 176.07(8); O(1)−Mn(3)−O(4), 175.68(8); Mn(1)−O(7)−Mn(2), 119.66(8); Mn(1)−O(7)−Mn(3), 119.96(9); Mn(2)−O(7)−Mn(3), 120.36(9).

heptacoordinated. Each hexadentate N_4O_2 donor ligand binds all three Mn centers. Four N atoms are coordinated to one metal center forming three five-membered chelate rings, and two oximato O atoms are coordinated to the remaining two metal centers. Consequently each pair of metal centers are bridged by two oximate groups in a reciprocal manner with respect to the N- and the O-atom coordination (Figure 1). The μ_3-oxo atom satisfies the seventh coordination site of each of the three metal atoms. The chelate bite angles for the terminal five-membered rings are in the range 66.70(8)−68.42(8)° and those for the central five-membered rings are within 73.15(9)−73.33(9)°. The C−N and N−O distances of the oximate ($-(CH_3)C{=}N-O^-$) moieties are in the ranges 1.281(4)−1.290(3) and 1.344(3)−1.360(3) Å, respectively. These distances are consistent with the deprotonated form of the oxime functionalities.[6] The $C{=}N_{imine}$ distances (1.270(4)−1.276(4) Å) are significantly shorter than the $C{=}N_{oximate}$ distances. The partial double bond character of the $N-O^-$ bond is likely to cause this difference. The $Mn-N_{imine}$, $Mn-N_{oximate}$, and $Mn-O_{oximate}$ distances for all three metal centers are very similar. However, the $Mn-N_{imine}$ and $Mn-N_{oximate}$ distances are distinctly different. The former is in the range 2.232(2)−2.267(2) Å, and the latter is within 2.331(2)−2.371(2) Å. Most probably the longer $Mn-N_{oximate}$ distances are mainly due to the bridging nature of the oximate ($=N-O^-$) groups. Among the four N atoms of the bamen^{2-} unit that are coordinated to a single metal center, two imine N atoms are in the middle and two oximate N atoms are terminal. Thus the rigidity of the N_4 fragment may also be partially responsible for this difference.[7] The Mn to central oxygen atom distances are comparable with that reported for a trinuclear complex that contains the $\{Mn^{III}_3(\mu_3\text{-}O)\}$ unit.[1e] The central oxygen atom (O7) is marginally displaced by 0.015(2) Å from the Mn_3 plane. The Mn1···Mn2, Mn1···Mn3, and Mn2···Mn3 distances are 3.2999(6), 3.2952(6), and 3.3026(6) Å, respectively.

The N_4O_3 coordination geometry around each metal center can be best described as distorted pentagonal-bipyramidal. The μ_3-oxo atom and the four N atoms of one bamen^{2-} ligand constitute the pentagonal plane, and the two oximate O atoms of the other two ligands occupy the axial sites (Figure 1). Thus the three pentagonal-bipyramidal polyhedra have a common equatorial position, and that is occupied by the μ_3-oxo atom. The mean deviations from the $MnN_4(\mu_3\text{-}O)$ planes are in the range 0.16−0.17 Å. The $O_{oximate}-Mn-O_{oximate}$ angles are within 175.68(8)−176.07(8)°. The dihedral angles between the three pentagonal planes are confined to the range 69.46(5)−70.14(5)°.

The redox properties of the complex in acetonitrile solution have been investigated by cyclic voltammetry. Three oxidation responses are observed at $E_{1/2} = +0.87$ V ($\Delta E_p = 80$ mV), $E_{1/2} = +1.45$ V ($\Delta E_p = 100$ mV), and $E_{pa} = 1.98$ V (Figure 2a).[8] Under the same experimental conditions, the Fc^+/Fc (Fc = ferrocene) couple is observed at $E_{1/2} = +0.64$ V ($\Delta E_p = 100$ mV). The first two responses displayed by the complex are very close to reversible processes (Figure 2b,c). The current heights of these two responses are similar and comparable with known one-electron processes under identical conditions.[9] The deprotonated ligand (bamen^{2-}) obtained by mixing H_2bamen and tetramethylammonium hydroxide in a 1:2 molar ratio does not display any such response in the potential range 0 to +2.1 V. Thus the first two oxidation responses are assigned to the $Mn^{III}_2Mn^{IV}/Mn^{III}_3$ and $Mn^{III}Mn^{IV}_2/Mn^{III}_2Mn^{IV}$ couples. The highest potential response is irreversible, and the anodic peak current is ~2.5 times larger than that of the first two responses. The potential

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(5) X-ray analysis: The complex $[Mn_3O(bamen)_3]ClO_4{\cdot}2H_2O$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.6591(7)$ Å, $b = 14.8224(9)$ Å, $c = 16.6760(14)$ Å, $\alpha = 84.512(8)°$, $\beta = 81.976(9)°$, $\gamma = 85.358(6)°$, $V = 2104.7(3)$ Å^3, $\rho_{calcd} = 1.561$ g cm^{-3}, and $Z = 2$. With the use of 7397 unique reflections (6104 have $I \geq 2\sigma(I)$) collected at 298 K with Mo Kα radiation ($\lambda = 0.71073$ Å) out to $\theta = 25°$ on a single-crystal X-ray diffractometer, the structure was solved by direct methods (SHELXS97, G. M. Sheldrick) and 532 parameters were refined (SHELXL97, G. M. Sheldrick). The refinement converged to final R1 = 0.0334, wR2 = 0.0879 ($I > 2\sigma(I)$); R1 = 0.0489, wR2 = 0.0947 (all data), and GOF = 1.030 with the largest difference peak and hole as 0.486 and −0.468 e Å^{-3}, respectively.

(6) (a) Birkelbach, F.; Weyhermüller, T.; Lengen, M.; Gerdan, M.; Trautwein, A. X.; Wieghardt, K.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4529. (b) Pal, S.; Mukherjee, R. N.; Tomas, M.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 200.

(7) Pal, S. N.; Pal, S. *J. Chem. Soc., Dalton Trans.* **2002**, 2102.

(8) Meanings of the symbols: E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$.

(9) Pal, S. N.; Pal, S. *Inorg. Chem.* **2001**, *40*, 4807.

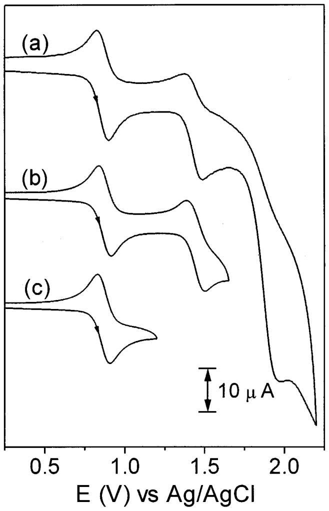

Figure 2. Cyclic voltammograms (scan rate 50 mV s^{-1}) of $[Mn_3(\mu_3\text{-}O)(\mu_3\text{-bamen})_3]ClO_4{\cdot}2H_2O$ in acetonitrile solution (0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$) at a glassy-carbon electrode at 298 K. (a) Successive oxidations of all three Mn(III) centers. (b) Oxidations of two Mn(III) centers. (c) Oxidation of the first Mn(III) center.

(1.98 V) of this oxidation response is very close to the solvent cutoff, and hence solvent may contribute to the observed peak current. Considering that the free ligand does not display any response in this region, we tentatively assign this electrode process to the $Mn^{III}Mn^{IV}_2 \rightarrow Mn^{IV}_3$ oxidation.

Magnetic susceptibility measurements in the temperature range 20−310 K and at a constant magnetic field of 5 kG were performed with a powdered sample of $[Mn_3O(bamen)_3]ClO_4{\cdot}2H_2O$. A diamagnetic correction (-411×10^{-6} cgsu) calculated from Pascal's constants[10] was applied to obtain the molar paramagnetic susceptibilities. At 310 K the value of the effective magnetic moment (12.04 μ_B) is significantly larger than the spin-only value (8.48 μ_B) for a trinuclear complex containing three Mn(III) ions ($S = 2$). The moment gradually increases to 13.32 μ_B at 95 K. The change of moment below 95 K is much smaller and reaches the value of 13.40 μ_B at 20 K (Figure 3). This behavior clearly indicates the ferromagnetic nature of the complex. The data were fitted using an expression for χ_M vs T for a triangular trimanganese(III) complex in which all the metal ions are equivalent and have the spin state $S = 2$.[1b] The best least-squares fit[11] was obtained with $J = 22.3(1)$ and $g = 2.06(1)$. It may be noted that very few Mn(III) complexes are known where ferromagnetic interaction is operative between the metal ions.[12] Antiferromagnetic interactions are reported for $[Mn_3O(O_2CR)_6(py)_3]^{0/1+}$ complexes.[1b] In this type of species, the metal ions are in a distorted octahedral coordination sphere. The O atoms of the bridging carboxylates form an O_4 square plane. The monodentate ligand and the μ_3-oxo group occupy the remaining two trans sites. In addition to the μ_3-oxo bridge, each pair of manganese(III) centers are bridged by two carboxylates. In these complexes, the magnetic interaction is considered to be propagated mainly via the μ_3-oxo bridge.[1b] In contrast, the metal ions in $[Mn_3O(bamen)_3]^+$ are pentagonal-bipyramidal. Apart from the μ_3-oxo bridge, two oximate groups provide additional bridges between each pair of metal centers. Ferromagnetic interaction through such μ-oximate bridges are known.[6a]

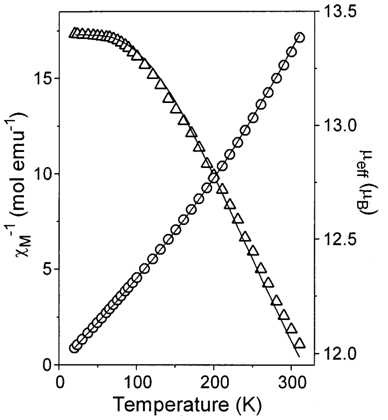

Figure 3. Inverse molar magnetic susceptibility (○) and effective magnetic moment (△) of $[Mn_3(\mu_3\text{-}O)(\mu_3\text{-bamen})_3]ClO_4{\cdot}2H_2O$ as a function of temperature. The solid lines were generated from the best least-squares fit parameters given in the text.

In conclusion, we have been able to isolate the $\{Mn_3(\mu_3\text{-}O)\}$ core in a carboxylate-free environment by using a hexadentate bridging ligand. The metal ions are in a distorted pentagonal-bipyramidal N_4O_3 coordination sphere. The complex is redox active and ferromagnetic. We are currently involved in synthesizing analogous complexes of other transition metal ions with the same ligand to explore their structures and physical properties.

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Supporting Information Available: Experimental details describing the synthesis, characterization data, physical measurements, observed and calculated molar magnetic susceptibilities and effective magnetic moments as a function of temperature and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Hatfield, W. E. In *Theory and Applications of Molecular Paramagnetism*: Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976; p 491.

(11) Chandramouli, G. V. R.; Balagopalakrishna, C.; Rajasekharan, M. V.; Manoharan, P. T. *Comput. Chem.* **1996**, *20*, 353.

(12) (a) 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. (b) Toftlund, H.; Markiewicz, A.; Murray, K. S. *Acta Chem. Scand.* **1990**, *44*, 443. (c) Mikuriya, M.; Yamato, Y.; Tokii, T. *Chem. Lett.* **1992**, 1571.