

Synthesis and Characterization of a (μ -Oxo)(μ -carboxylato)dimanganese(III) Polyimidazole Complex

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A novel μ -oxo- and μ -carboxylato-bridged dimanganese(III) complex, $[\text{Mn}_2\text{O}(\text{TMIMA})_2(\text{OAc})](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$ (**1**), where TMIMA is tris(1-methylimidazol-2-yl)methylamine and OAc is the acetate ion, has been synthesized and characterized by X-ray crystallography, visible spectroscopy, variable-temperature magnetism, and electrochemical methods. X-ray crystallographic parameters are as follows for compound **1**: $\text{C}_{36}\text{H}_{51}\text{N}_{16}\text{O}_{15}\text{Cl}_3\text{Mn}_2$, 1164.14 g mol⁻¹, triclinic space group ($P\bar{1}$), $a = 14.909(3)$ Å, $b = 15.544(3)$ Å, $c = 12.530(3)$ Å, $\alpha = 104.74(1)^\circ$, $\beta = 112.98(1)^\circ$, $\gamma = 87.46(2)^\circ$, $V = 2580.5$ Å³, $Z = 2$; 5334 independent reflections with $I > 3\sigma(I)$ to max 2θ of 45° , $R = 0.045$, and $R_w = 0.049$. The structure consists of a discrete μ -oxo- and μ -acetato-bridged dimanganese(III) cation and the three perchlorate counterions as well as two acetonitrile solvate molecules. The two acetonitrile solvate molecules and one perchlorate anion were found to be ordered, while the other perchlorate ions were found to be disordered. The coordination environment around each Mn^{III} ion is best described as a distorted octahedron as expected for Jahn-Teller d⁴ metal ions. Imidazole donors bond trans to the bridging oxo ligand and have short Mn-N bond lengths. The remaining imidazoles and amine ligands are bonded cis to the oxo bridge. The electronic spectral properties of the complex are consistent with other high-spin Mn^{III} complexes. Variable-temperature magnetic susceptibility data indicate that the two Mn^{III} ions are ferromagnetically coupled. Diagonalization of the full Hamiltonian matrix including zero-field interactions (DS_z) and isotropic Zeeman interactions of the Mn^{III} ions gives $g = 2.05$, $D_1 = D_2 = 0.40$ cm⁻¹, and $J = 1.33$ cm⁻¹. Compound **1** displays two one-electron redox processes in acetonitrile at a glassy-carbon electrode corresponding to the Mn^{III}₂ ↔ Mn^{IV}₂ interconversion. The first step is electrochemically irreversible, while the second step is quasireversible ($\Delta E = 70$ mV).

Introduction

Over the past several years there has been considerable interest in a related class of Fe and Mn metalloproteins that are known or thought to have similar binuclear μ -oxo (μ -carboxylato)_{*n*} (*n* = 1, 2) bridged active site structures.^{1,5} The most extensively studied member of this group of metalloproteins is the nonheme iron protein hemerythrin (Hr), which has been shown by X-ray

crystallography to contain a triply bridged (μ -oxo)bis(μ -carboxylato)diiron(III) core structure.^{3,4} The Fe-O-Fe bridge angle and Fe-Fe separation in the azidomet form of hemerythrin (N₃-metHr) are 135° and 3.25 Å, respectively. In addition, Hr contains three histidine imidazoles coordinated to one iron center and two imidazoles coordinated to the other. Ribonucleotide reductase (RR) isolated from *Escherichia coli*,⁵ on the other hand, has a μ -oxo- and μ -carboxylato-bridge core structure and displays magnetic and spectroscopic properties similar to Hr.¹

Interestingly, an emerging class of manganese proteins, such as the ribonucleotide reductase isolated from *Bevibacterius ammoniagenes* and the pseudocatalase from *Lactobacillus plantarum*, appear to have binuclear active sites similar to hemerythrin.^{6,7} Preliminary X-ray crystallographic data on *L. plantarum*⁸⁻¹⁰ suggest that the Mn-Mn separation is 3.6 Å, consistent with a μ -oxo (hydroxo) bridged structure observed for Hr³ and RR.⁵ As with hemerythrin and other non-heme diiron(III) proteins, the ancillary ligands in *L. plantarum* are thought

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- (a) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (b) Que, L., Jr. *ACS Symp. Ser.* **1988**, *No. 372*, 152. (c) Wilkins, R. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195. (d) Kurtz, D. M., Jr. *Chem. Rev.* **1990**, *90*, 585. (e) Vincent, J. B.; Olivier-Lilley, G. L.; Averill, B. A. *Chem. Rev.* **1990**, *1447*. (f) Sanders-Loehr, J. In *Physical Bioinorganic Chemistry*; Loehr, J. M., Ed.; VCH Publishers: New York, 1989; Vol. 5.
- (a) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (b) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *49*, 249. (c) Renger, G. *Angew. Chem., Intl. Ed. Engl.* **1987**, *26*, 643.
- (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618. (b) Holmes, M. A.; LeTrong, I.; Turley, S.; Sicker, L. C.; Stenkamp, R. E. *J. Mol. Biol.* **1991**, *218*, 583.
- (a) Sheriff, S.; Hendrickson, W. A.; Sinita, J. L. *J. Mol. Biol.* **1987**, *197*, 273.
- (a) Reichard, P.; Ehrenberg, A. *Science* **1983**, *221*, 514. (b) Sjöberg, B.-M.; Gråslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87. (c) Lynch, J. B.; Juarez-Garcia, C.; Münck, E.; Que, L., Jr. *J. Biol. Chem.* **1989**, *264*, 8091. (d) Joelson, T.; Uhlin, U.; Eklund, H.; Sjöberg, B.-M.; Hahne, S.; Karlsson, M. *J. Biol. Chem.* **1984**, *259*, 9076. (e) Norlund, P.; Sjöberg, B.-M.; Eklund, H. *Nature* **1990**, *345*, 593.

(6) Kono, Y.; Fredovich, I. *J. Biol. Chem.* **1983**, *258*, 13646.

(7) Algood, G. S.; Perry, J. *J. Bacteriol.* **1986**, *168*, 563.

(8) Barynin, V. V.; Grebenko, A. I. *Dokl. Akad. Nauk SSSR* **1986**, *286*, 461.

(9) Vainshtein, B. K.; Melik-Adamyanyan, W. R.; Barynin, V. V.; Vagin, A. A.; Grebenko, A. I. *Proc. Int. Symp. Biomol. Struct. Interact., Suppl. J. Biosci.* **1985**, *8*, 471.

(10) Barynin, V. V.; Vagin, A. A.; Melik-Adamyanyan, V. R.; Grebenko, A. I.; Khangulov, S. V.; Popov, A. N.; Andrianova, M. E.; Vainshtein, B. K. *Dokl. Akad. Nauk SSSR* **1986**, *228*, 877.

to be histidine (imidazole) and carboxylate amino acid residues.^{11,12} Recent EXAFS data on the superoxidized (Mn^{III}Mn^{IV}) form of *L. plantarum* indicate that the Mn–Mn separation is 2.7 Å.¹² In its reduced form (Mn^{II}) the metal–metal distance of *L. plantarum* is not well defined. The data also indicate that there are two to four histidine ligands per Mn center and that the Mn ions are likely bridged by a carboxylate ligand from either glutamic or aspartic acid. The oxidized form of the enzyme is thought to have a (μ -oxo)bis(μ -carboxylato)dimanganese(III) core structure similar to hemerythrin.

Even though definitive structural data on the active sites of these manganese proteins are limited, much has been learned about the stability, structures, and electronic properties of oxo-bridged manganese complexes through model studies.^{2,13} For example, compounds containing linear Mn–O–Mn bridged structures display metal–metal separations as large as 3.54 Å.¹⁴ Addition of a second bridging oxo group results in the reduction of the Mn–O–Mn bridging angles to less than 100° concomitant with a reduction in the metal–metal separation to \sim 2.7 Å.¹⁵ Addition of a third bridging ligand, a carboxylate anion, causes only minor structural changes in the bis(μ -oxo) bridge.¹⁶ Triply bridged μ -oxo bis(μ -carboxylato) core units,¹⁷ on the other hand, display more "open" type structures with bonding parameters similar to those reported for hemerythrin³ (Mn–O–Mn = 135° and Mn–Mn = 3.25 Å).

As part of our continuing investigation of the structural and spectroscopic properties of Fe¹⁸ and Mn¹⁹ complexes containing polyimidazole ligands, we report herein the synthesis, X-ray crystal structure, and physical properties of a new polyimidazole complex containing a (μ -oxo)(μ -carboxylato)dimanganese(III) core structure, [Mn₂O(TMIMA)₂(OAc)](ClO₄)₃, where TMIMA represents the polyimidazole ligand tris((1-methylimidazol-2-yl)-methyl)amine.²⁰ Similar strategies using tripodal ligands have been used to stabilize dibrigged core structures of diiron(III) and dimanganese(III). However, the (μ -oxo)(μ -carboxylato)dimanganese(III) core unit observed in this study has only been observed

Table I. Crystallographic Data

Mn ₂ C ₃₆ H ₅₁ H ₁₆ O ₁₅ Cl ₃	space group $P\bar{1}$
MW = 1164.14	Z = 2
a = 14.909(3) Å	d _c = 1.50 g cm ⁻³
b = 15.544(3) Å	d _o = 1.48(1) g cm ⁻³
c = 12.530(3) Å	T = 23(1) °C
α = 104.74(1)°	Mo K α (λ = 0.7107 Å)
β = 112.98(1)°	μ = 7.02 mm ⁻¹
γ = 87.46(2)°	R(F _o) = 0.045
V = 2580.5 Å ³	R _w (F _o) = 0.049

as part of more complex cluster structures and not in discrete binuclear units.^{13,22}

Experimental Section

Materials and Methods. All reagents were used as received unless otherwise noted. Electronic spectra were obtained using a Shimadzu UV-160 spectrophotometer. Electrochemical measurements were made using a conventional three-electrode cell. Cyclic voltammograms were recorded on samples (10⁻³ M) dissolved in dried and degassed CH₃CN solutions containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). A platinum wire and coil was used as the working and counter electrodes, respectively. A Ag/AgCl reference electrode was used in all of the studies.²³ The reversibility of the electrochemical processes were evaluated by standard procedures and referenced against the ferrocene/ferrocenium redox couple.²⁴ Solution magnetic susceptibility measurements were performed on samples dissolved in CD₃CN following the Evans method.²⁵ Variable-temperature magnetic susceptibility data were measured on a polycrystalline sample of compound 1 with a Model VTS-900 SQUID susceptometer (BTi, Inc., San Diego, CA) in the temperature range 5–320 K and with an applied field of 10.0 kG. The temperature was controlled using a BTi digital temperature control unit. The polycrystalline sample was embedded in parafilm to prevent torquing of the crystallites in an external field. A diamagnetic correction, estimated from Pascal's constants, was subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities.

Preparation of [Mn₂O(TMIMA)₂(OAc)](ClO₄)₃·2CH₃CN (1). The ligand tris((1-methylimidazol-2-yl)methyl)amine (TMIMA)²⁰ was prepared as described previously. Mn(CH₃CO₂)₂·2H₂O (0.56 g, 2 mmol) was added to an ethanol solution (20 mL) containing TMIMA (0.60 g, 2 mmol). The resulting brown solution was stirred for 30 min and filtered. To the filtrate was added NaClO₄ (0.37 g, 3 mmol). The red-brown solution was allowed to stir for 2 h and then filtered, and the precipitate was washed with 20 mL of ethanol, giving 0.578 g (66%) of compound 1. Crystals of 1 were obtained by slow evaporation of an acetonitrile solution of the complex. Anal. Calc (found) for C₃₃H₄₅N₁₄O₁₅Cl₃Mn₂: C, 35.52 (35.48); H, 4.19 (4.18); N, 18.12 (18.01). (Analysis was performed on a dried powdered sample.)

Crystallographic Determination for Compound 1. Crystallographic data are included in Table 1. Intensity data were collected using an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator [Mo K α radiation (λ = 0.71073 Å)], with ω - 2θ scans, maximum 2θ = 45°, 5334 independent reflections with $I > 3\sigma(I)$, and data measured on a red-brown block (0.4 × 0.4 × 0.25 mm) at 298 K. Data were corrected for linear decay (−21.3%), and an empirical absorption

- (11) Dikanov, S. A.; Tsvetkov, Y. D.; Khangulov, S. V.; Goldfeld, M. G. *Dokl. Akad. Nauk SSSR* **1988**, *302*, 1255.
- (12) (a) Waldo, G. S.; Yu, S.; Penner-Hahn, E. J. *Am. Chem. Soc.* **1992**, *114*, 5869. (b) Waldo, G. C.; Franko, R. M.; Penner-Hahn, J. E. *Biochemistry* **1992**, *30*, 10486.
- (13) Christou, G.; Vincent, J. B. *ACS Symp. Ser.* **1988**, *No. 372*, 238.
- (14) (a) Vogt, L. H., Jr.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1725. (b) Ziolo, R. F.; Stanford, R. H.; Rossman, G. R.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 7910. (c) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *111*, 9121.
- (15) (a) Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659. (b) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 961. (c) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chem.* **1988**, *141*, 167. (d) Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Ottvos, J. W.; Sreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446. (e) Plaskin, P. M.; Stouffer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121.
- (16) (a) Bashkin, J. S.; Schake, A. R.; Vincent, J. B.; Chang, H.-R.; Li, Q.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1988**, 700. (b) Wiegardt, K.; Bossek, U.; Zsolnai, L.; Huttner, G.; Blondin, G.; Girerd, J.-J.; Babonneau, F. *J. Chem. Soc., Chem. Commun.* **1987**, 651.
- (17) (a) Wiegardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347. (b) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435. (c) Menage, S.; Girerd, J.-J.; Gleizes, A. *J. Chem. Soc., Chem. Commun.* **1988**, 431. (d) Goodson, P. A.; Hodgson, D. J. *Inorg. Chem.* **1989**, *28*, 3606. (e) Wiegardt, K.; Bossek, U.; Bonvoisin, J.; Beauvillain, P.; Girerd, J.-J.; Nuber, B.; Weiss, J.; Henzo, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1031. (f) Wu, F.-J.; Kurtz, D. M., Jr.; Hagen, K. S.; Nyman, P. D.; Debrunner, P. G.; Vankai, V. A. *Inorg. Chem.* **1990**, *29*, 5174.
- (18) (a) Mashuta, M. S.; Webb, R. J.; McCusker, J. K.; Schmitt, E. A.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 3815. (b) Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; O'Brien, R. J.; McCusker, J. K.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1124.
- (19) (a) Buchanan, R. M.; Mashuta, M. S.; Richardson, J. F.; Oberhausen, K. J.; Hendrickson, D. N.; Webb, R. J.; Nanny, M. A. *Inorg. Chem.* **1990**, *29*, 1299. (b) Buchanan, R. M.; Oberhausen, K. J.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 971.
- (20) (a) Oberhausen, K. J.; O'Brien, R. J.; Richardson, J. F.; Buchanan, R. M. *Inorg. Chim. Acta* **1990**, *173*, 145. (b) Ligand abbreviations: TACN, 1,4,7-triazacyclononane; Me₃TACN, *N,N',N''*-1,4,7-trimethyl triaza-cyclononane; TMIP, tris(1-methylimidazol-2-yl)phosphine; BPIA, bis-(2-pyridylmethyl) ((1-methylimidazol-2-yl)methyl)amine; HB(Pz)₃, tris(1-pyrazolyl)borate anion.
- (21) (a) Yan, S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5222. (b) Norman, S. E.; Yan, S.; Que, L., Jr.; Backes, G.; Liang, J.; Sanders-Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 1554. (c) Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659. (d) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967. (e) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167. (f) Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Ottvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446.
- (22) Kessissoglou, D. P.; Kirk, M. L.; Bender, C. A.; Lah, M. S.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1989**, 84.
- (23) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980; Chapter 6.
- (24) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.
- (25) Evans, D. F. *J. Chem. Soc.* **1958**, 2003.

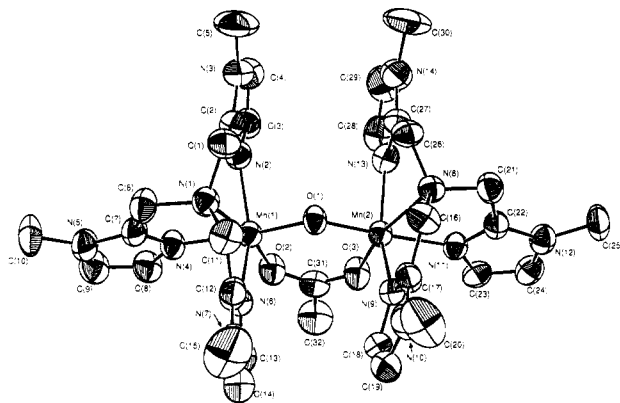


Figure 1. ORTEP diagram of the [Mn₂O(TMIMA)₂(OAc)]²⁺ cation drawn with thermal ellipsoids at the 50% probability level showing atomic labeling scheme.

correction (DIFABS) was applied. The structure was solved by direct methods (SDP package)²⁶ and refined by full-matrix least squares on 689 parameters minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F)^2 + (0.01)F^2 + 1.5]^{-1}$.²⁷ Hydrogen atom positions were calculated and included as fixed contributions ($B_{\text{iso}} = 1.2B_{\text{iso}}$ of bonded atom) in final cycles of least-squares refinement. Two perchlorate ions displayed rotational disordering about a common Cl–O axis. The disorder was modeled using seven oxygen atom positions for each perchlorate group with occupancies of 20 and 80% for one group and 30 and 70% for the other. Atoms with occupancies less than 70% were refined with isotropic thermal parameters. Atomic positional parameters for the cation are given in Table II.

Results and Discussion

Structure of [Mn₂O(TMIMA)₂(OAc)](ClO₄)₃·2CH₃CN (1). An ORTEP view of the dimanganese(III) complex is shown in Figure 1. Selected bond distances and angles are given in Table III. Compound 1 has a μ -oxo- and μ -acetato-bridged structure with a Mn(1)–O(1)–Mn(2) bridging angle of 130.9(2)° and Mn–Mn separation of 3.250(1) Å. The Mn–Mn separation in 1 is larger than the corresponding metal–metal separations reported for triply bridged (μ -oxo)bis(μ -carboxylato)dimanganese(II) complexes, which typically range from 3.15 to 3.18 Å¹⁷ and is more reminiscent of the metal–metal separation reported for ribonucleotide reductase,⁵ known to have a μ -oxo- and μ -carboxylato-bridged structure. The increase in the Mn–Mn separation in going from a triply bridged to a doubly bridged system parallels the structural changes observed for related Fe complexes that model the active sites of Hr and RR and demonstrate that μ -oxo- and μ -carboxylato-bridged complexes have in general less constrained bridged structures compared to μ -oxo bis(μ -carboxylato) analogues. The Mn(1)–O(1) and Mn(2)–O(1) bond distances in compound 1 are 1.784(3) and 1.789(3) Å, respectively, which are consistent with oxo–manganese lengths reported for several (μ -oxo)bis(μ -carboxylato)dimanganese(III) complexes.^{2a} The Mn–acetate bond lengths are 2.029(3) and 2.042(4) Å for Mn(1)–O(2) and Mn(2)–O(3), respectively. In compound 1, each manganese(III) ion is also coordinated to three imidazole pendants and a tertiary amine nitrogen atom associated with the TMIMA ligand. Two of the imidazole pendants from each TMIMA ligand are bonded cis to the oxo group (Mn(1)–N(2) = 2.118(3), Mn(1)–N(6) = 2.124(4), Mn(2)–N(9) = 2.063(3), Mn(2)–N(13) = 2.101(3) Å), while the third imidazole pendant is bonded trans to the oxo bridge (Mn(1)–N(4) = 2.025(4) and Mn(2)–N(11) = 2.022(3) Å). The Mn–N(amine) bond distances in compound 1, Mn(1)–N(1) and Mn(2)–N(8), are significantly longer (2.352(4) and 2.373(4) Å) than the Mn–imidazole lengths.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for Non-H Atoms

atom	x	y	z	B (Å ²) ^a
Mn(1)	0.68909(4)	0.28552(4)	0.40832(5)	3.37(1)
Mn(2)	0.74607(4)	0.10301(4)	0.25921(5)	3.18(1)
O(1)	0.7490(2)	0.2210(2)	0.3189(2)	3.51(6)
O(2)	0.6140(2)	0.1873(2)	0.4251(2)	4.65(7)
O(3)	0.6601(2)	0.0623(2)	0.3326(2)	4.92(7)
N(1)	0.7782(2)	0.4144(2)	0.4290(3)	3.81(8)
N(2)	0.6024(2)	0.3351(2)	0.2598(3)	4.01(9)
N(3)	0.5988(3)	0.3994(3)	0.1217(3)	5.5(1)
N(4)	0.6375(2)	0.3793(2)	0.5116(3)	4.05(8)
N(5)	0.6393(3)	0.5152(3)	0.6186(3)	4.9(1)
N(6)	0.8159(3)	0.2980(2)	0.5686(3)	4.39(9)
N(7)	0.9698(3)	0.3426(3)	0.6751(4)	6.5(1)
N(8)	0.8483(2)	0.1124(2)	0.1567(3)	3.34(8)
N(9)	0.8854(2)	0.1025(2)	0.3855(3)	3.66(8)
N(10)	1.0416(3)	0.1391(3)	0.4619(3)	5.1(1)
N(11)	0.7581(2)	−0.0269(2)	0.1864(3)	3.60(8)
N(12)	0.8114(3)	−0.1347(2)	0.0806(3)	4.24(9)
N(13)	0.6505(2)	0.1158(2)	0.0895(3)	3.94(9)
N(14)	0.6248(3)	0.1594(3)	−0.0727(3)	5.6(1)
N(15)	0.2351(5)	0.4097(4)	0.0204(5)	11.1(2)
N(16)	1.3766(4)	0.1115(6)	0.1637(5)	12.9(3)
C(1)	0.7544(3)	0.4222(3)	0.3063(4)	4.8(1)
C(2)	0.6517(3)	0.3875(3)	0.2307(4)	4.3(1)
C(3)	0.5130(3)	0.3132(3)	0.1648(4)	4.9(1)
C(4)	0.5105(4)	0.3525(4)	0.0797(5)	6.2(2)
C(5)	0.6322(5)	0.4505(4)	0.0578(5)	8.5(2)
C(6)	0.7464(3)	0.4922(3)	0.5017(4)	4.9(1)
C(7)	0.6748(3)	0.4618(3)	0.5426(4)	4.1(1)
C(8)	0.5763(3)	0.3789(3)	0.5714(4)	4.9(1)
C(9)	0.5775(3)	0.4630(4)	0.6368(4)	5.7(1)
C(10)	0.6630(4)	0.6113(4)	0.6701(5)	6.6(2)
C(11)	0.8822(3)	0.3979(3)	0.4900(4)	5.0(1)
C(12)	0.8897(3)	0.3468(3)	0.5777(4)	4.7(1)
C(13)	0.8478(4)	0.2614(3)	0.6657(4)	5.9(1)
C(14)	0.9431(5)	0.2890(4)	0.7310(5)	7.4(2)
C(15)	1.0674(5)	0.3842(5)	0.7108(8)	10.4(3)
C(16)	0.9451(3)	0.1498(3)	0.2488(4)	4.4(1)
C(17)	0.9583(3)	0.1283(3)	0.3639(4)	3.9(1)
C(18)	0.9236(3)	0.0962(3)	0.5028(4)	4.8(1)
C(19)	1.0194(4)	0.1181(4)	0.5508(4)	5.7(1)
C(20)	1.1374(4)	0.1675(5)	0.4722(5)	8.2(2)
C(21)	0.8503(3)	0.0219(3)	0.0818(4)	4.2(1)
C(22)	0.8082(3)	−0.0459(3)	0.1162(3)	3.6(1)
C(23)	0.7293(3)	−0.1068(3)	0.1963(4)	4.1(1)
C(24)	0.7620(3)	−0.1739(3)	0.1304(4)	4.6(1)
C(25)	0.8578(4)	−0.1813(3)	−0.0017(4)	5.7(1)
C(26)	0.7986(3)	0.1726(3)	0.0807(4)	4.1(1)
C(27)	0.6926(3)	0.1487(3)	0.0313(4)	4.0(1)
C(28)	0.5513(3)	0.1056(3)	0.0196(5)	5.2(1)
C(29)	0.5363(4)	0.1321(4)	−0.0795(5)	6.6(2)
C(30)	0.6416(5)	0.1917(5)	−0.1654(5)	9.6(2)
C(31)	0.6189(3)	0.1041(3)	0.3974(4)	4.2(1)
C(32)	0.5717(3)	0.0486(4)	0.4468(4)	6.4(1)
C(33)	0.2079(5)	0.4736(4)	0.0579(5)	8.4(2)
C(34)	0.1737(6)	0.5571(5)	0.1086(6)	10.6(2)
C(35)	1.3553(4)	0.1294(5)	0.2429(5)	8.1(2)
C(36)	1.3280(5)	0.1538(5)	0.3437(6)	9.3(2)

^a For atoms refined anisotropically, B is defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + \dots + ab(\cos \gamma)\beta_{12} + \dots]$.

In general, imidazole ligands are better π donors compared to amine and pyridine ligands and therefore have shorter metal–ligand bond lengths.²⁸

The coordination environment around each manganese ion is highly distorted due to the constraining nature of the TMIMA ligand. The largest distortion is along the *trans*-N–Mn–OAc bonds, presumably due to the Jahn–Teller effect expected for a high-spin d⁴ Mn(III) ion. There is also a noticeable compression of the bond lengths along the Mn–N_{im} bonds *trans* to the bridging oxo group in 1, similar to what has been observed for (μ -oxo)-bis(μ -carboxylato)dimanganese(III) complexes containing tri-

(26) Frenz, B. A. *Computing in Crystallography*; Schenk, H., Olthoff-Hazelkamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(27) Killeen, R. C. G.; Lawrence, J. L. *Acta Crystallogr.* **1969**, *B23*, 1750.

(28) Jones, C. M.; Johnson, C. R.; Asher, S. A.; Shepard, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 3772.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Mn}_2\text{O}(\text{tmima})_2(\text{OAc})]$

Mn(1)–O(1)	1.784(3)	Mn(2)–O(1)	1.789(3)
Mn(1)–O(2)	2.029(3)	Mn(2)–O(3)	2.042(4)
Mn(1)–N(1)	2.352(4)	Mn(2)–N(8)	2.373(4)
Mn(1)–N(2)	2.118(3)	Mn(2)–N(9)	2.063(3)
Mn(1)–N(4)	2.025(4)	Mn(2)–N(11)	2.022(3)
Mn(1)–N(6)	2.124(4)	Mn(2)–N(13)	2.101(3)
Mn(1)–Mn(2)	3.2503(8)	Mn(1)–O(1)–Mn(2)	130.9(2)
N(1)–Mn(1)–O(1)	89.5(1)	N(8)–Mn(2)–O(1)	94.8(1)
N(1)–Mn(1)–N(2)	75.2(1)	N(8)–Mn(2)–N(9)	76.0(1)
N(1)–Mn(1)–N(4)	79.2(1)	N(8)–Mn(2)–N(11)	77.7(1)
N(1)–Mn(1)–N(6)	74.6(1)	N(8)–Mn(2)–N(13)	75.0(1)
N(1)–Mn(1)–O(2)	168.1(1)	N(8)–Mn(2)–O(3)	166.0(1)
N(2)–Mn(1)–N(4)	88.2(1)	N(9)–Mn(2)–N(11)	87.2(1)
N(2)–Mn(1)–O(1)	89.0(1)	N(9)–Mn(2)–O(1)	89.3(1)
N(2)–Mn(1)–N(6)	149.9(1)	N(9)–Mn(2)–N(13)	150.9(2)
N(4)–Mn(1)–N(6)	85.0(1)	N(11)–Mn(2)–N(13)	90.0(1)
N(4)–Mn(1)–O(1)	168.6(1)	N(11)–Mn(2)–O(1)	172.2(2)
N(6)–Mn(1)–O(1)	92.0(1)	N(13)–Mn(2)–O(1)	89.9(1)
O(2)–Mn(1)–O(1)	100.5(1)	O(3)–Mn(2)–O(1)	99.2(1)
O(2)–Mn(1)–N(2)	111.1(1)	O(3)–Mn(2)–N(9)	103.1(1)
O(2)–Mn(1)–N(4)	90.8(1)	O(3)–Mn(2)–N(11)	88.3(1)
O(2)–Mn(1)–N(6)	98.4(1)	O(3)–Mn(2)–N(13)	105.8(1)

dentate capping ligands, $[\text{Mn}_2\text{O}(\text{HB}(\text{Pz})_3)_2(\text{OAc})_2]$,^{17b} $[\text{Mn}_2\text{O}(\text{TACN})_2(\text{OAc})_2]^{2+}$,^{17a} and $[\text{Mn}_2\text{O}(\text{Me}_3\text{TACN})_2(\text{OAc})_2]^{2+}$.^{17a} In a related system, $[\text{Mn}_2\text{O}(\text{TMIP})_2(\text{OAc})_2]^{2+}$,^{17f} the largest distortion occurs along one set of the *trans*-N–Mn–OAc bonds. As with the (μ -oxo)bis(μ -carboxylato)dimanganese(III) complexes, the static disorder observed in Mn(III) coordination sphere of **1** should result in the empty d_{z^2} orbitals directed along the Mn–O_{oxo} bonds.^{17b}

Spectroscopic and Magnetic Properties of Compound 1. The UV–visible absorption spectrum of $[\text{Mn}_2\text{O}(\text{TMIMA})_2(\text{OAc})](\text{ClO}_4)_3$ dissolved in CH_3CN resembles the spectra reported for the Mn catalase of *L. plantarum*⁶ and the ribonucleotide reductase isolated from *B. ammoniagenes*²⁹ and is very similar to the spectra reported previously for $[\text{Mn}_2\text{O}(\text{HB}(\text{Pz})_3)_2(\text{OAc})]$,^{17b} $[\text{Mn}_2\text{O}(\text{Me}_3\text{TACN})_2(\text{OAc})](\text{ClO}_4)_2$,^{17a} and $[\text{Mn}_2\text{O}(\text{TMIP})_2(\text{OAc})](\text{ClO}_4)_2$.^{17f} While the Mn-containing proteins exhibit broad absorption bands between 480 and 520 nm, compound **1** exhibits transitions at both 496 nm ($\epsilon_{\text{Mn}} = 405 \text{ M}^{-1} \text{ cm}^{-1}$) and 523 nm ($\epsilon_{\text{Mn}} = 305 \text{ M}^{-1} \text{ cm}^{-1}$) along with several weaker transitions as shoulders at lower energies. In addition, a broad transition is observed at 733 nm ($\epsilon_{\text{Mn}} = 308 \text{ M}^{-1} \text{ cm}^{-1}$), which has also been observed in acetonitrile solutions of $[\text{Mn}_2\text{O}(\text{HB}(\text{Pz})_3)_2(\text{OAc})]$ ^{17b} and $[\text{Mn}_2\text{O}(\text{TMIP})_2(\text{OAc})](\text{ClO}_4)_2$.^{17f}

Solution magnetic susceptibility measurements were recorded at 288 K in CH_3CN . The solution room-temperature effective magnetic moment of compound **1** was found to be $4.99 \mu_{\text{B}}/\text{Mn}$ ($7.04 \mu_{\text{B}}/\text{Mn}_2$), which falls within the range of values (4.9–5.2 μ_{B}/Mn) reported for $[\text{Mn}_2\text{O}(\text{HB}(\text{Pz})_3)_2(\text{OAc})]$ ($4.92 \mu_{\text{B}}/\text{Mn}$),^{17b} $[\text{Mn}_2\text{O}(\text{TMIP})_2(\text{OAc})](\text{ClO}_4)_2$ ($5.01 \mu_{\text{B}}/\text{Mn}$),^{17f} and $[\text{Mn}_2\text{O}(\text{Me}_3\text{TACN})_2(\text{OAc})](\text{ClO}_4)_2$ ($5.12 \mu_{\text{B}}/\text{Mn}$).^{17a} For two uncoupled high-spin Mn(III) ions the effective magnetic moment is expected to be $6.9 \mu_{\text{B}}/\text{Mn}_2$. Curiously, unlike $[\text{Mn}_2\text{O}(\text{HB}(\text{Pz})_3)_2(\text{OAc})]$ ^{17b} and $[\text{Mn}_2\text{O}(\text{TMIP})_2(\text{OAc})](\text{ClO}_4)_2$ ^{17f} (the manganese(III) ions in both complexes are weakly antiferromagnetically coupled), compound **1** does not display a well-resolved ¹H NMR spectrum in deuterated acetonitrile at room temperature and at -20°C . It is important to note that $[\text{Mn}_2\text{O}(\text{TACN})_2(\text{OAc})_2](\text{ClO}_4)_2$ also does not display a ¹H NMR spectrum at room temperature. One possible explanation for the absence of resolvable ¹H signals for **1** is a longer $T_{1\rho}$ for the complex compared to the triply bridged analogues.

The solid-state variable-temperature magnetic properties of compound **1** have been investigated. The data support the presence of a weak ferromagnetic exchange interaction between

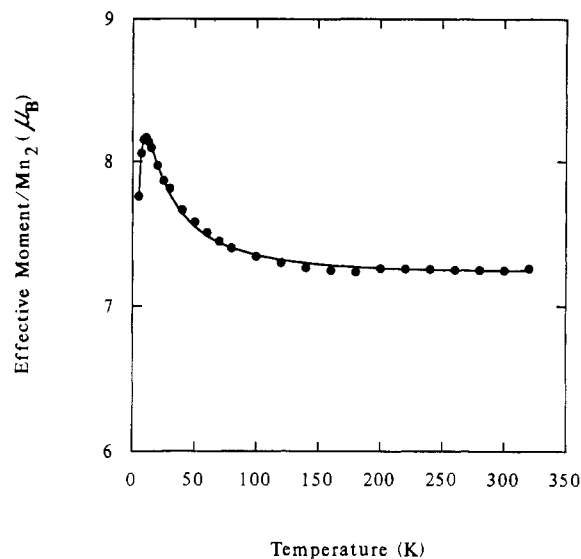


Figure 2. Plot of effective magnetic moment per dinuclear complex ($\mu_{\text{eff}}/\text{Mn}_2$) versus temperature for a polycrystalline sample of $[\text{Mn}_2\text{O}(\text{TMIMA})_2(\text{OAc})](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$ (**1**) restrained in parafilm. The solid line represents a full-matrix diagonalization fit of the data including single-ion zero-field and Zeeman interactions. See text for the parameters.

the manganese(III) ions. A plot of the magnetic moment per Mn_2 versus temperature is given in Figure 2. The data were fit using a full matrix diagonalization method as described elsewhere.³⁰ Since J is small for complex **1**, the isotropic spin Hamiltonian for the binuclear $S_1 = 2, S_2 = 2$ complex included zero-field interactions (DS_z^2) associated with the Mn^{III} ion and isotropic Zeeman interactions. Diagonalization of the full Hamiltonian matrix gives $g = 2.05$, $D_1 = D_2 = 0.40 \text{ cm}^{-1}$, and $J = 1.33 \text{ cm}^{-1}$. Two points need to be mentioned. First, we have found that it is important to prevent polycrystalline samples of Mn^{III} complexes from partially torquing in the external magnetic field. This is necessary to determine accurately the magnetic moment at low temperature. To this end the polycrystalline sample of compound **1** was restrained by embedding it in a parafilm film. Finally, axial zero-field fitting parameters cannot be accurately determined by fitting bulk magnetic susceptibility data. The data for compound **1**, however, could not be fit with a negative value of D .

As noted by others,^{17f,31} the weak magnetic coupling observed for (μ -oxo)bis(μ -carboxylato)dimanganese(III) complexes ($-3.4 \leq J \leq 9 \text{ cm}^{-1}$) compared to their diiron(III) congeners ($-100 \leq J \leq 134 \text{ cm}^{-1}$) is due to the empty d_{z^2} orbitals directed along the Mn–O_{oxo} bonds, reinforcing the notion that the d_{z^2} orbitals are the magnetic orbitals involved in the major pathway for spin exchange coupling. Wiegardt *et al.* have elegantly shown that the d_{z^2} – d_{xz} “crossed” pathway influences the strength of the ferromagnetic exchange contribution of the total spin exchange parameter (J).³¹ For the (μ -oxo)bis(μ -carboxylato)dimanganese(III) complexes it appears that the antiferromagnetic exchange contribution originating from the d_{yz} – d_{yz} pathway is offset by the d_{z^2} – d_{xz} “crossed” pathway in cases where $J \sim 0 \text{ cm}^{-1}$. At the present time, no structural correlation associated with the sign of J has been developed. As noted by others,^{17f} the sign of J is most likely a subtle balance between structural and electronic factors. We have prepared and are currently evaluating the structures and electronic and magnetic properties of several (μ -oxo)(μ -carboxylato)dimanganese(III) complexes containing mixed

(30) Schmitt, E. A.; Hendrickson, D. N. Unpublished results.

(31) Hotzelmann, R.; Wiegardt, K.; Flörke, V.; Haupt, H.-J.; Weatherburn, D. C.; Bonvoisin, J.; Blondin, G.; Girerd, J.-J. *J. Am. Chem. Soc.* **1992**, *114*, 1681.

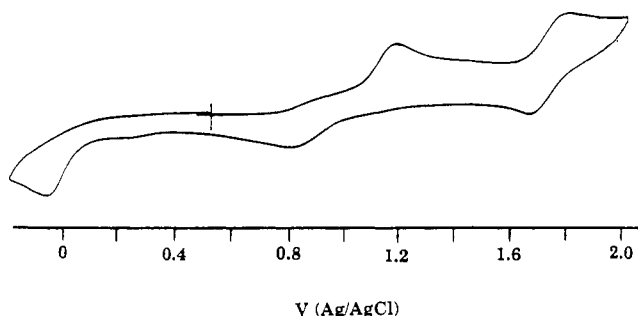


Figure 3. Cyclic voltammogram of [Mn₂O(TMIMA)₂(OAc)](ClO₄)₂ in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte. The voltammogram was generated using a glassy-carbon working electrode and platinum wire counter electrode and is referenced against a Ag/AgCl electrode.

pyridine/imidazole tripod ligands.³² The results of these studies will be published elsewhere.³³

Electrochemical Properties of [Mn₂O(TMIMA)₂(OAc)](ClO₄)₃ (1). The cyclic voltammogram of compound **1** recorded in acetonitrile under anaerobic conditions is shown in Figure 3. An irreversible reduction peak is observed for the complex at 0.0 V vs Ag/AgCl. Two one-electron redox processes were observed between +0.5 and +2.0 V. The first oxidation step is clearly irreversible ($E_{1/2} = 1.12$ V vs Ag/AgCl and $\Delta E = 340$ mV) and is associated with the III,III/III,IV couple. The second redox process is quasireversible with $E_{1/2} = 1.70$ V vs Ag/AgCl and $\Delta E = 70$ mV and corresponds to the III,IV/IV,IV redox couple. Curiously, the isostructural [Mn₂O(bpia)₂(OAc)](ClO₄)₃ complex displays two quasireversible one-electron redox processes at potentials similar to **1**, so it would seem that the irreversible first oxidation step observed for **1** does not involve its decomposition. On the contrary, the electrochemical response of the first redox couple of **1** is reminiscent of the EC redox behavior observed for [Mn₂O(OH)(bispicen)]³⁺ in aqueous solutions.³⁴ In this case, a proton-coupled redox step is observed in shuttling between the III,III (protonated) and III,IV (unprotonated) oxidation levels. The III,IV to IV,IV oxidation step does not involve a proton-coupled electron-transfer step, as observed for compound **1**, and as a result is quasireversible. Therefore one explanation for the irreversible, III,III to III,IV redox step observed for **1** is the presence of trace levels of water from the solvent and/or the TBAP supporting electrolyte that most likely hydrogen bonds to

the bridging oxo group. There is precedence for such a proposal. We have observed for a series of [Fe₂O(bmima)₂(OX)₂]³⁺ complexes (X = Ac, Bz) that the bridging oxo group forms strong hydrogen bonds with water molecules occluded in the crystal lattice.^{18b} The resulting hydrogen bonding interactions are of sufficient strength to attenuate the magnetic exchange coupling in both complexes (room temperature $\mu_{\text{eff}} = 2.2 \mu_{\text{B}}$ /[Fe₂O-(bmima)₂(OAc)₂](ClO₄)₂·2CH₃CN and $\mu_{\text{eff}} = 5.2 \mu_{\text{B}}$ /[Fe₂O-(bmima)(OAc)₂](ClO₄)₂·2CH₃CN·1.5H₂O). Electrochemical measurements in very dry acetonitrile show some improvement in ΔE for the first oxidation process, but overall this electrochemical step remains irreversible possibly due to the presence of trace levels of water in the solvent. Addition of a small amount of water to the acetonitrile solution significantly broadens the first oxidation step but has no effect on the second redox step.

An alternative explanation for the irreversibility of the III,III/III,IV redox couple in compound **1** is that there are substantial structural changes in the manganese coordination environment during the first electron-transfer step. The Mn^{III}-N(amine) bond lengths in compound **1** are quite long (Mn(1)-N(1) = 2.352(4) Å and Mn(2)-N(8) = 2.373(4) Å) for Mn^{III} complexes and may be considered to be only weakly coordinated to the metal ions. In the related [Mn₂O(bpia)₂(OAc)]³⁺ complex, the Mn^{III}-N(amine) bond lengths are more than 0.1 Å shorter than those observed for compound **1**. Additional electrochemical studies on this and related compounds are in progress and will be the subject of another study.

In conclusion, a new binuclear dimanganese(III) complex (**1**) of the tripodal ligand TMIMA has been prepared and found to have a μ -oxo- and μ -carboxylato-bridged structure. The spectral, magnetic, and electrochemical properties of **1** are consistent with a species having a (μ -oxo)(μ -acetato)dimanganese(II) structure, and the compound is the first example of a doubly bridged dimanganese(III) complex as a discrete dimeric unit. More importantly, the structure of **1** is reminiscent of those reported for other diiron(III) complexes of N₄-tripodal ligands and the non-heme diiron protein ribonucleotide reductase, thus supporting the proposals of others^{2,6,7,12} that manganese proteins such as *B. ammoniagenes* and *L. plantarum* have binuclear active site structures similar to those of, non-heme oxo-iron proteins.

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Supplementary Material Available: Tables of crystallographic data, bond lengths and angles for the cation, anisotropic displacement parameters, positional and isotropic thermal parameters, bond distances and angles for the anions, and hydrogen atom parameters and a figure showing electronic spectra of the cation and Mn proteins (14 pages). Ordering information is given on any current masthead page.

- (32) The crystal structure of [Mn₂O(BPIA)₂(OAc)](ClO₄)₃ has been determined. Crystal data: monoclinic space group, *P*2₁/*n*, *a* = 10.887(2) Å, *b* = 22.674(4) Å, *c* = 20.273(4) Å, $\beta = 101.09(2)^\circ$, *V* = 4910.9 Å³, *R* = 7.2%, *d_c* = 1.51 g cm⁻³, Mn-Mn = 3.249(1) Å, Mn-O-Mn = 131.6(2)°, Mn(1)-N(1) = 2.276(5) Å, and Mn(2)-N(6) = 2.229(5) Å.
- (33) Buchanan, R. M.; O'Brien, R. J.; Latour, J.-M.; Costa, R.; Hendrickson, D. N. Unpublished results.
- (34) (a) Manchanda, R.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 494. (b) Carroll, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 8744. For additional information on these and related complexes see: Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pederson, E. *Inorg. Chem.* **1990**, *29*, 503. Also see ref 21c,e.