

Four-Centered Oxotetramanganese(III) Aggregate: A Novel Approach to Redox and Aggregation Chemistry of Manganese

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The redox and oxo chemistry of manganese aggregates is a field of current interest.¹ Our modeling studies led us to investigate the reduction of Mn(II)-Schiff base complexes² to find (i) new modes for storing and releasing electrons and (ii) precursors for manganese aggregates. This preliminary report concerns the reduction and subsequent oxidation of [Mn(salophen)] (1) and [Mn(salen)] (2).³

Reduction of 1⁴ (depicted as two overlapping nonbonded monomeric units) leads to a Mn(II) dimer from a twofold reductive coupling of imino groups⁵ on adjacent [Mn(salophen)] units, as shown in reaction 1.

The structure of 3⁶ is shown in Figure 1. The polynucleating ligand contains a 12-membered planar ring which is nearly coplanar with the C8...C13 aromatic rings. Two centrosymmetric Mn(II) atoms are anchored to the four nitrogen atoms at distances ranging from 2.166(6) to 2.287(7) Å. They lie at 1.332(2) Å from the plane of the N₄ core. The hexacoordination of each Mn

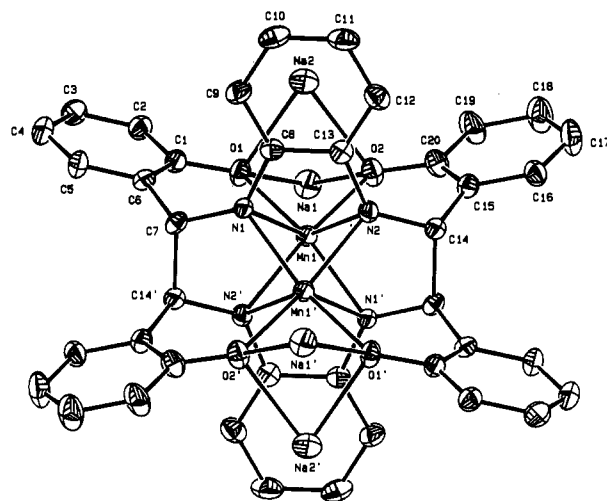
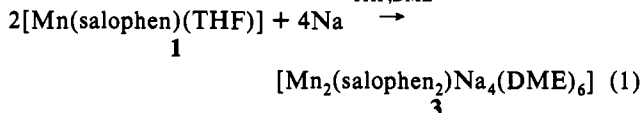
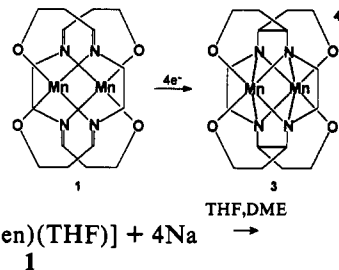


Figure 1. ORTEP drawing of complex 3 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Mn1-O1, 2.167(6); Mn1-O2, 2.116(6); Mn1-N1, 2.258(6); Mn1-N2, 2.287(7); Mn1-N1', 2.184(6); Mn1-N2', 2.166(6); Na1-O1, 2.331(7); Na1-O2, 2.393(7); Na2-O1, 2.455(8); Na2-O2, 2.453(7); Na2-Cb, 2.717(6); C7-C14', 1.630(11); N1-Mn1-N2, 67.0(2); O1-Mn1-O2, 76.6(2); N1'-Mn1-N2', 70.5(2); O1-Mn1-N2', 102.4(3); O2-Mn1-N1', 106.3(2). Prime refers to a transformation of 1 - x, -y, 1 - z. Cb indicates the centroid of the aromatic ring C8-C13. DME molecules bonded to sodium are omitted for clarity.



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(1) (a) Wiegardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153 and references therein. (b) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 249. (c) Christou, G.; Vincent, J. B. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988, pp 238-255. (d) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 197. (e) Vincent, J. B.; Christou, G. *Adv. Inorg. Chem.* **1989**, *33*, 197. (f) Armstrong, W. H. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH: New York 1992; pp 261-286. (g) Hendrickson, D. N.; Christou, G.; Schmitt, E. A.; Libby, E.; Bashkin, J. S.; Wang, S.; Tsai, H.-L.; Vincent, J. B.; Boyd, P. D. W.; Huffman, J. C.; Folting, K.; Li, Q.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 2455.

(2) Manganese complexes with Schiff base-type ligands have been among the most widely studied systems to date. Some recent and representative papers are the following: (a) Penner-Hahn, J. E.; Fronko, R. M.; Pecoraro, V. L.; Yocum, C. F.; Betts, S. D.; Bowly, N. R. *J. Am. Chem. Soc.* **1990**, *112*, 2549. Larson, E.; Lah, M. S.; Li, X.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 373. Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810. (b) Gohdes, J. W.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 368. (c) Chang, H.-R.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565.

(3) The synthesis of pure, salt-free, anhydrous Mn(II)-Schiff base complexes has been performed by reacting Mn₂Mes₆ with the protic form of the ligand in THF. Yields are very high (~90%) for both [Mn(salophen)(THF)] (1, salophen = *N,N'*-*o*-phenylenebis(salicylideneiminato) dianion) and [Mn(salen)] (2, salen = *N,N'*-*o*-ethylenebis(salicylideneiminato) dianion).

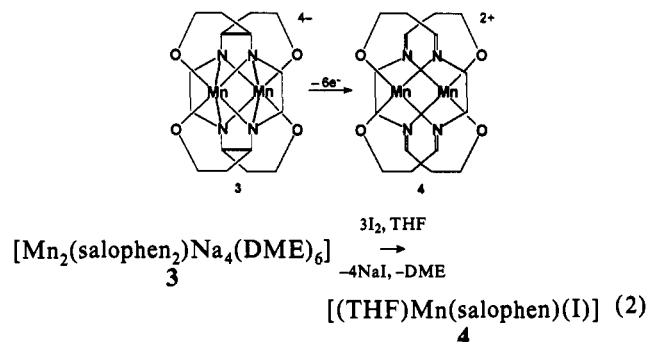
(4) Procedure for 3: complex 1 (2.10 g, 4.73 mmol) was added to a THF (350 mL) suspension of sodium sand (0.81 g, 35.3 mmol). After the mixture was stirred for 24 h, a brown solution formed. The excess sodium was filtered out and the solution evaporated to dryness. Recrystallization of the residue from DME gave yellow crystals of 3 (71%). Anal. Calcd for C₆₄H₈₈Mn₂N₄Na₄O₁₆: C, 56.06; H, 6.47; N, 4.09. Found: C, 55.80; H, 5.89; N, 4.38.

(5) Reductive coupling of imino groups has been reported: Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1116. Gambarotta, S.; Urso, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 3966.

is completed by two *cis* oxygen atoms. The Mn(II)···Mn(II) distance is exceptionally short for such a complex [2.699(2) Å].^{1a} The conformation of the ligand gives rise to cavities which accommodate the four centrosymmetric sodium cations (Na1 and Na2), completing their coordination with DME molecules and with a significant interaction with the C8...C13 aromatic ring (see Figure 1). Magnetic susceptibility for 3 was measured between 1.9 and 300 K. Exchange coupling in these bimetallic Mn(II) complexes may be described by the simple Heisenberg spin Hamiltonian. The best fit of the data yielded $g = 1.97$, $J = -34.6 \text{ cm}^{-1}$, with an agreement factor $R = 1.5 \times 10^{-4}$ [$R = \sum_i (\chi_i^{\text{obs}} T_i - \chi_i^{\text{calc}} T_i)^2 / (\chi_i^{\text{obs}})^2$]. These results show an antiferromagnetic coupling for the μ -amidoMn(II) dimer 3, much stronger than those observed for the μ -hydroxo- or μ -alkoxoMn(II) dimers which have exchange coupling constants of, at most, a few cm^{-1} .^{1a}

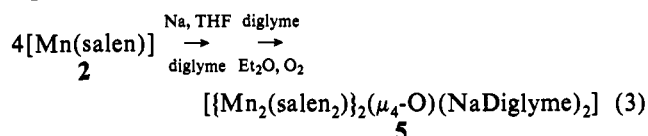
The four reduction electrons are stored in the two C-C bonds C7-C14' and C7'-C14. Oxidation of 3, depending on the oxidizing agent, removes electrons from the C-C bond, the metal, or both but *without* reacting directly with the C-C bond. The latter case is exemplified by reaction 2.⁷

(6) Crystal data for 3: C₆₄H₈₈Mn₂N₄Na₄O₁₆, monoclinic, space group P2₁/n; $a = 12.678(3) \text{ \AA}$, $b = 18.314(3) \text{ \AA}$, $c = 14.807(2) \text{ \AA}$, $\beta = 92.83(2)^\circ$, $V = 3434(1) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.326 \text{ g cm}^{-3}$; Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$), $\mu(\text{Mo K}\alpha) = 4.40 \text{ cm}^{-1}$; crystal dimensions $0.21 \times 0.33 \times 0.42 \text{ mm}$. The structure was solved by the heavy atom method. For 2772 unique observed reflections [$I > 2\sigma(I)$] collected at room temperature ($5 < 2\theta < 50^\circ$) and corrected for absorption, the final R is 0.075 ($R_w = 0.081$). See supplementary material for more details.



Complex 3 undergoes 4e⁻ oxidations by cleaving the two C–C bonds across the dimer to restore the original imino functionalities (complex 4 is shown as two overlapping unbonded monomers). The two additional electrons come from the oxidation of Mn(II) to Mn(III).

Particularly interesting is the reaction of the reduction products with dioxygen. The reduction of [Mn(salen)] (2)³ gives an extremely reactive compound, which was oxidized with traces of O₂ in Et₂O.⁸



The precursor of 5 is the fragment [Mn₂(salen₂)Na₂]⁹ where the two salen ligands are linked by a single C–C bond. Complex 5¹⁰ contains a tetrahedral arrangement of four unbridged Mn(III) atoms around a central oxo group (Figure 2).^{11,12} The molecule has C₂ symmetry. The two [Mn₂(salen₂)] units are bridged by two sodium cations bonded to the O₂, O₃, and O₄ oxygens, while a diglyme molecule acting as a bidentate ligand

(7) Procedure for 4: a THF solution (50 mL) of 3 (0.96 g, 0.72 mmol) was cooled to -60 °C and then reacted with a THF solution of I₂ (50 mL, 0.04 M). The solution was then stirred for 24 h at room temperature and a microcrystalline red solid obtained [(THF)Mn(salophen)(I)] (84%). Anal. Calcd for C₂₄H₂₂IMnN₂O₅: C, 50.72; H, 3.90; N, 4.93. Found: C, 49.05; H, 4.13; N, 4.73.

(8) Procedure for 5: a THF (300 mL) suspension of [Mn(salen)] (1.67 g, 5.20 mmol) was reduced using an excess of sodium (0.38 g, 16.5 mmol). The orange suspension was stirred at room temperature until a brown solution was obtained (12 h). The excess sodium was filtered out. The solution was evaporated to dryness and the solid recrystallized from DME or diglyme by addition of anhydrous, but not degassed, Et₂O. The synthesis was reproduced 10 times with yields going from 70 to 80%. Anal. Calcd for {[Mn₂(salen₂)₂(μ-NaDME)₂(μ-O)]·DME, C₇₆H₈₄Mn₄N₈Na₂O₁₅: C, 56.44; H, 5.36; N, 6.93. Found: C, 56.50; H, 5.44; N, 6.48. Anal. Calcd for {[Mn₂(salen₂)₂(μ-NaDiglyme)₂(μ-O)], C₇₆H₈₄Mn₄N₈Na₂O₁₅: C, 56.47; H, 5.20; N, 6.93. Found: C, 56.40; H, 5.21; N, 6.53.

(9) Crystal data for 5: C₇₆H₈₄Mn₄N₈Na₂O₁₅, monoclinic, space group C₂/c; a = 17.701(3) Å, b = 15.504(2) Å, c = 28.713(2) Å, β = 103.49(1)°, V = 7663(2) Å³, Z = 4, ρ_{calcd} = 1.400 g cm⁻³; Cu Kα radiation (λ = 1.541 78 Å), μ(Cu Kα) = 59.47 cm⁻¹; crystal dimensions 0.18 × 0.32 × 0.55 mm. Solution of the structure was as for complex 3. Refinement was anisotropic only for the manganese, sodium, nitrogen, and oxygen atoms of the salen ligand. For 2123 unique observed reflections [I > 2σ(I)] collected at room temperature (5 < 2θ < 140°) and corrected for absorption, the final R was 0.068 (R_w = 0.070). See the supplementary material for more details.

(10) We isolated this fragment in the complex {[Mn₂(salen₂)₂][Mn(salen)]·Na₂(DME)₄·DME, which has been structurally characterized.

(11) Several tetranuclear manganese complexes have recently been reported: 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. Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328. Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907. McKee, V.; Shepard, W. B. *J. Chem. Soc., Chem. Commun.* **1985**, 158. Brooker, G.; McKee, V.; Shepard, W. B.; Pannell, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 2555. Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236. Christmas, C.; Vincent, J. B.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 1303. Bashkin, J. S.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502. Kulawiec, R. J.; Crabtree, R. H.; Brudvig, G. W.; Schulte, G. K. *Inorg. Chem.* **1988**, *27*, 1309. Li, Q.; Vincent, J. B.; Libby, E.; Chang, H.-R.; Huffman, J. C.; Boyd, P. D. W.; Christou, G.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1731. McKee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1334.

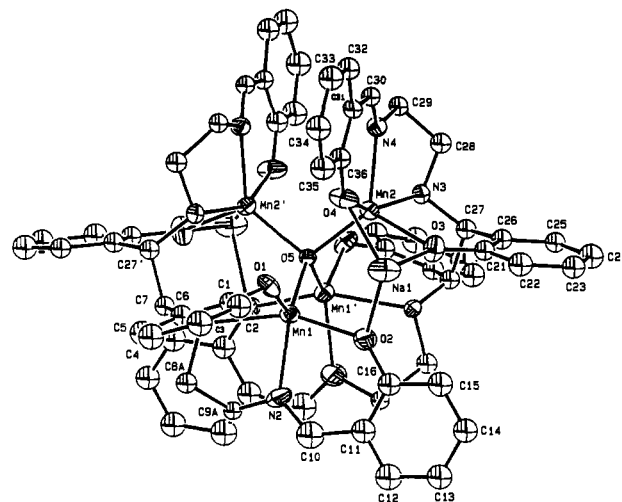


Figure 2. ORTEP drawing of complex 5 (30% probability ellipsoids). Selected bond distances (Å) and angles (deg): Mn1–O1, 2.043(8); Mn1–O2, 2.090(10); Mn1–N1, 2.320(10); Mn1–N2, 2.205(11); Mn1–O5, 2.073(6); Mn2–O3, 2.053(9); Mn2–O4, 2.213(9); Mn2–O5, 2.059(6); C7–C27', 1.542(17); Na1–O2, 2.312(10); Na1–O3, 2.471(9); Na1–O4, 2.275(10); O1–Mn1–O5, 112.9(3); O1–Mn1–N2, 96.9(3); O5–Mn1–N2, 130.0(4); O2–Mn1–N1, 155.2(3); O3–Mn2–O5, 114.5(3); O3–Mn2–N4, 113.7(3); O5–Mn2–N4, 131.4(3); O4–Mn2–N3, 154.1(3); Mn1–O5–Mn2, 115.2(1), Mn1–O5–Mn1', 107.5(1); Mn1–O5–Mn2', 108.8(1), Mn2–O5–Mn2', 101.6(1). Prime refers to a transformation of -x, y, 0.5 - z. Diglyme molecules bonded to sodium and disorder of C8–C9 ethylenic bridge are omitted for clarity.

completes the coordination sphere. The magnetic susceptibility of 5 has been measured from 300 K down to 1.9 K. The μ_{eff} per Mn at 300 K is 4.6 μ_{B} , which is slightly lower than expected for four uncoupled Mn(III), S = 2, spin centers, and decreases to 2.8 μ_{B} at 1.9 K. The best fit of the data was obtained as function of three exchange parameters J_{12} , J_{34} , and J' , with $J_{12} = -12.6$ cm⁻¹, $J_{34} = +22.0$ cm⁻¹, and $J' = -5.6$ cm⁻¹, $g = 2.03$, the agreement factor being $R = 5.7 \times 10^{-4}$. The energy splitting pattern shows that the ground state is a quintet with a septet at only 6.0 cm⁻¹, a triplet at 19.2 cm⁻¹, and many other closely spaced states above 34 cm⁻¹.¹³

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Supplementary Material Available: Tables of experimental details associated with data collection, fractional atomic coordinates, fractional atomic coordinates for hydrogen atoms, thermal parameters, bond distances, and bond angles, Schakal drawings for complexes 3 and 5 (17 pages); listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(12) For a μ_4 -oxo group, see: Tremel, W. *J. Chem. Soc., Chem. Commun.* **1992**, 709. Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 2619. Cotton, F. A.; Feng, X.; Kibala, P. A.; Sandor, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2148. Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1991**, *30*, 3120. Ingham, S. L.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1993**, 166. Lee, C. F.; Chin, K.-F.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 467. Beagley, B.; McAuliffe, C. A.; Mac Rory, P. P.; Ndifon, P. T.; Pritchard, R. G. *J. Chem. Soc., Chem. Commun.* **1990**, 309. Stucky, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 4821. Bragg, W. H.; Morgan, G. T. *Proc. R. Soc. London, Ser. A* **1923**, *104*, 437. Baikie, A. R.; Howes, A. J.; Hursthouse, M. B.; Quick, A. B.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1986**, 1587. Dickinson, R. C.; Helm, F. T.; Baker, W. A., Jr.; Black, T. D.; Watson, W. H., Jr. *Inorg. Chem.* **1977**, *16*, 1530. Gill, N. S.; Sterns, M. *Inorg. Chem.* **1970**, *9*, 1619. Churchill, M. R.; DeBoer, B. G.; Mendak, S. *J. Inorg. Chem.* **1975**, *14*, 2496. Swank, D. D.; Nielson, D. O.; Willett, R. D. *Inorg. Chim. Acta* **1973**, *7*, 91. Bertrand, J. A. *Inorg. Chem.* **1967**, *6*, 495. Köhler, K.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Freire-Erdbrügger, C.; Scheldrick, G. M. *Chem. Ber.* **1993**, *126*, 921.

(13) The following coupling scheme has been used: $J_{12} = J_{\text{Mn1},\text{Mn2}}$; $J_{34} = J_{\text{Mn1},\text{Mn2}'}$; $J' = J_{\text{Mn1},\text{Mn2}'} = J_{\text{Mn1},\text{Mn2}} = J_{\text{Mn1},\text{Mn1}} = J_{\text{Mn2},\text{Mn2}'}$. Details of the magnetic data will be published elsewhere.