

Crystal Structure of Manganese(III) Complex with 2-Salicylideneamino-4-*t*-butylphenol and Salicylaldehyde

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Manganese can adopt a wide variety of oxidation states and this ability is certainly related to the redox function of the metal ion in biological systems.¹⁻⁶ The metal oxidation state is generally believed to lie in the range 2+ to 4+. It is now firmly established that at least three enzymes use manganese in redox roles at their catalytic center to facilitate the metabolism of the O₂²⁻ unit.^{7,8} All three enzymes probably contain Mn(III) in at least one of their catalytic forms. Therefore, an important area of investigation of the bioinorganic chemistry of manganese is the study of the structure and reactivity of Mn(III) complexes composed of biologically relevant heteroatom donor ligands.

An attractive system for modeling the structure and reactivity of these manganoenzymes is dinuclear Mn(III) complexes containing polydentate Schiff base ligands. Both photochemical water oxidation to generate dioxygen⁹ and acid-promoted hydrogen peroxide production¹⁰ have been reported for such dimers. To understand more fully the chemistry involved in these reactions, we have taken up 2-(salicylideneamino)-4-*t*-butylphenol as a polydentate ligand.

In this note, we report the synthesis and characterization of a new Mn(III) complex, [2-(salicylideneamino)-4-*t*-butylphenolato](salicylaldehydato)(methanoly)manganese(III), as well as its crystal structure determined by X-ray crystallography.

Experimental Section

Materials. Solvents and reagents were obtained from commercial sources and used as received. Mn(CH₃CO₂)₂ · 4H₂O was purchased from Junsei Chemical Co. Salicylaldehyde and 2-amino-4-*t*-butylphenol were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent grade and used without further purification unless otherwise noted. Abbreviations used: H₂sabp = 2-(salicylideneamino)-4-*t*-butylphenol; Hsal = salicylaldehyde; MeOH = methanol.

Measurements. Carbon, Hydrogen, and Nitrogen analyses were carried out using a Carlo Erba Model EA-1106 CHNS/O Analyzer. IR spectrum was recorded as KBr disks using a Mattson Polaris FT-IR spectrophotometer in the 4,000-500 cm⁻¹ region and UV-Vis spectrum was obtained in DMSO using a Milton Roy Spectronic Genesys 2 spectrophotometer. ¹H NMR spectrum of DMSO-*d*₆ solutions was

collected on a Varian Gemini -200 spectrometer. Chemical shifts are in ppm relative to internal Me₄Si. Melting point was carried out with a Laboratory Devices Inc. Mel-Temp II.

[2-(Salicylideneamino)-4-*t*-butylphenolato](salicylaldehydato)(methanoly)manganese(III), [Mn(sabp)(sal)(MeOH)] 1. Two mmol (0.24 g) of salicylaldehyde was added to a distilled methanol solution (20 ml) of 2 mmol (0.34 g) of 2-amino-4-*t*-butylphenol and refluxed for 1.5 h, resulting in a brownish yellow solution. After the solution was cooled to room temperature, 1 mmol of Mn(O₂CCH₃)₂ · 4H₂O (0.25 g) was added with stirring. This reaction mixture was refluxed for 4 h under argon atmosphere, after which the solution was allowed to cool to room temperature and was exposed to dioxygen by bubbling air into the reaction mixture for 12 h. During the period, the mixture was changed to dark brown solution. After it was filtered, the resulting solution was concentrated to approximately half volume. This clear solution was then layered with two times volume of petroleum ether, producing X-ray-quality crystals of **1**. Yield: 0.342 g (72%), mp 182 °C. Anal. Calcd. for C₂₅H₂₈N₂O₅Mn: C, 63.16; H, 5.51; N, 2.95. Found: C, 63.52; H, 5.38; N, 3.02.

Crystal Structure Determination of 1. A dark brown crystal of **1**, approximately 0.32 × 0.12 × 0.08 mm, was crystallized from MeOH/petroleum ether (0 °C) and mounted in glass capillary. Measurement was made on a Enraf-Nonius CAD4 TURBO diffractometer using Mo-K_α radiation (λ = 0.71069 Å) monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample and anode generator. Preliminary experiments for the cell parameters and orientation matrix for crystal was carried out by least-squares refinement, using the setting angles of 25 carefully centered reflections in the range 20° < 2θ < 35°. Diffraction intensity was collected at a constant temperature of 20(1) °C using the ω-2θ scan technique with variable scan speeds. Omega scans of several intense reflections were made prior to the data collection to optimize the proper scan width for crystal.

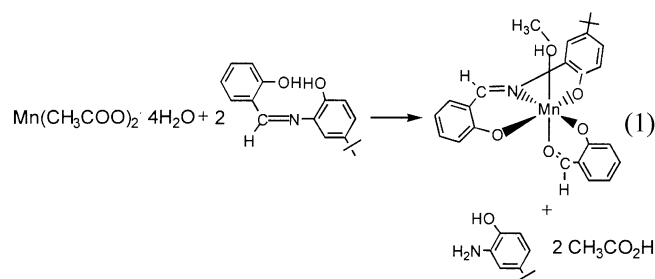
The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability for crystals. Of the reflections collected, those with *I* > 3σ(*I*) were used for structure determination. The structure was solved by direct method (MULTAN)¹¹ and subsequent Fourier difference technique, and refined anisotropically, by full-matrix least-squares, on *F*² (program MOLEN).¹² An absorption correction (Ψ-scan) was applied to all data.

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Hydrogen atoms were located, but not refined, and placed at fixed of 0.95 Å from bonded carbon atoms in the final least-squares refinement.

Results and Discussion

Synthesis and Spectral Properties. In recent report, we described the synthesis and characterization of the $[\text{Mn}^{\text{II}}\text{L}_2]$ complexes with tridentate monoprotic NNS ligands.¹³ The preparation of these complexes require a simple ligand exchange reaction from starting material $\text{Mn}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$. But, the synthesis of $[\text{Mn}(\text{sabp})(\text{sal})(\text{MeOH})]$ is not as straightforward as shown in Eq. 1. Two equivalents of the ligand H_2sabp are required for the reaction while only 1



equivalent of sabp is present in the product. Clearly, hydrolysis of the second ligand must be occurring as shown in Eq. 1. The 2-amino-4-*t*-butylphenol thus generated is probably necessary to neutralize the acid formed upon deprotonation of the phenolate moieties. The complex is air stable in the solid state and have a great solubility in common organic solvents. Elemental analyses and spectral data suggest that the formulation is monomeric $[\text{Mn}(\text{sabp})(\text{sal})(\text{MeOH})]$.

The characteristic spectral data are displayed in Table 1. The infrared spectrum indicates the mode of the ligand coordination. The peak near the 3430 cm^{-1} may be attributed to the stretching frequency of coordinated methanol OH. The intense band at *ca.* 1620 cm^{-1} associated with the azomethine of free ligand is shifted to a lower frequency (*ca.* 1600 cm^{-1}) in the corresponding complex. This fact suggests that the Schiff base is coordinated as an anionic ligand through phenolic oxygen and nitrogen atoms.¹⁴ The significant C–O stretching mode of salicylaldehyde is also observable at near 1633 cm^{-1} . In $^1\text{H NMR}$ spectrum, the aromatic and azomethine proton peaks are absent, suggesting that the complex is paramagnetic presumably due to a high-spin d^4 configura-

Table 1. IR, $^1\text{H NMR}$, and UV/Vis Spectral Data for Complex 1

| Complex | IR ^a | $^1\text{H NMR}^b$ | UV/Vis. ^c |
|---------|------------------------------------|--|---|
| | cm^{-1} | δ , ppm | $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) |
| 1 | 3434 (ν_{OH}) | 1.37 (br. 9H, $(\text{CH}_3)_3\text{C}-$) | 498sh (4.06) |
| | 1633 ($\nu_{\text{C}=\text{O}}$) | 3.17 (d. 3H, CH_3OH) | 462 (4.23) |
| | 1603 ($\nu_{\text{C}=\text{N}}$) | 4.10 (br. 1H, CH_3OH) | 385sh (4.36) |
| | | | 318 (4.52) |
| | | | 258 (4.86) |

^awith KBr pellet. ^bin DMSO-*d*₆. ^cin DMSO.

Table 2. Crystallographic Data and Intensity Collection for Complex 1

| | |
|--|--|
| Empirical formula | $\text{C}_{25}\text{H}_{26}\text{NO}_5\text{Mn}$ |
| F_w | 475.42 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ (#2) |
| Z | 2 |
| Cell parameters | |
| a (Å) | 8.338(2) |
| b (Å) | 11.357(2) |
| c (Å) | 12.423(3) |
| α (°) | 78.07(2) |
| β (°) | 85.64(2) |
| γ (°) | 81.71(2) |
| V (Å ³) | 1137.5(4) |
| D_{calc} (g/cm ³) | 1.075 |
| μ (cm ⁻¹ with Mo-K α) | 5.7 |
| Transmission factor ^d | 86.4329 - 99.9244 |
| Scan type | $\omega - 2\theta$ |
| Scan width (ω) (deg) | $1.05 + 0.66 \tan(\theta)$ |
| $2\theta_{\text{max}}$ (deg) | 52.64 |
| No. of reflections measured | 4836 |
| No. of reflections observed ($I > 3\sigma(I)$) | 1762 |
| $F(000)$ | 496 |
| No. of variable | 367 |
| Discrepancy indices | |
| R^h | 0.045 |
| R_w^i | 0.046 |
| Goodness of fit indicator ^d | 1.17 |
| Maximum shift in final cycles | less than 0.01 |

^aA semi-empirical absorption correction was applied. ^b $R = \sum |F_o - F_c| / \sum F_o$. ^c $R_w = [(\sum w(F_o - F_c)^2) / \sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma(F)^2]$. ^dEstimated standard deviation of an observation of unit weight: $[(\sum w(F_o - F_c)^2) / (N_o - N_v)]^{1/2}$, where N_o = Number of observations and N_v = Number of variables.

tion. However, the resonances of *tert*-butyl and methanol protons are observed and distinctly assigned from their position (Table 1) and relative integral ratio ($(\text{CH}_3)_3\text{C} - \text{CH}_3\text{OH} : \text{CH}_3\text{OH} = 13.02 : 4.37 : 1.57$).

A number of absorption bands are observed in the UV-Vis region 250-1000 nm. These all intense bands ($\log \epsilon - 4.06 - 4.86 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) are probably due to charge transfer and intraligand transitions, and d-d band is not found in the region.

X-ray Structural Description of 1. A summary of data collection and crystallographic parameters are given in Table 2. Atomic positional parameters are given in Table 3, while selected bond distances and angles are given in Table 4. The molecular structure and atom-numbering scheme for 1 is shown in Figure 1. The complex is neutral owing to deprotonation of the oxygen atom of the tridentate ligand upon complexation, presumably due to the greater acidity of the phenolate protons compared to that of the methanol. The manganese(III) in the structure has an equatorial plane composed of the two phenolate oxygen atoms and one imine nitrogen atom of the Schiff base ligand in addition to the one

Table 3. Fractional Positional Parameters and Displacement Parameters for Non-Hydrogen Atoms of Complex 1

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> eq/Å ² ^a |
|-------|-----------|------------|------------|---|
| Mn(1) | 0.9768(1) | 0.22796(7) | 0.40847(7) | 3.39(2) |
| O(1) | 0.7943(5) | 0.1047(3) | 0.4738(4) | 5.1(1) |
| O(2) | 0.8317(5) | 0.3270(3) | 0.3093(3) | 4.7(1) |
| O(3) | 1.0613(4) | 0.1274(3) | 0.3088(3) | 4.04(9) |
| O(4) | 1.1740(5) | 0.3424(3) | 0.3447(3) | 4.6(1) |
| O(5) | 1.1151(5) | 0.1366(3) | 0.5194(3) | 3.68(9) |
| N(1) | 0.9063(5) | 0.3279(3) | 0.5219(3) | 2.9(1) |
| C(1) | 0.7426(7) | 0.4326(4) | 0.3143(4) | 3.4(1) |
| C(2) | 0.6516(8) | 0.4908(5) | 0.2250(5) | 4.3(2) |
| C(3) | 0.5579(8) | 0.5985(6) | 0.2263(5) | 5.6(2) |
| C(4) | 0.5515(9) | 0.6526(5) | 0.3142(6) | 5.8(2) |
| C(5) | 0.6360(8) | 0.5983(5) | 0.4037(5) | 5.1(2) |
| C(6) | 0.7326(7) | 0.4866(4) | 0.4069(4) | 3.3(1) |
| C(7) | 0.8139(7) | 0.4320(4) | 0.5053(4) | 3.4(1) |
| C(8) | 0.9758(6) | 0.2734(4) | 0.6240(4) | 2.7(1) |
| C(9) | 0.9399(7) | 0.3127(4) | 0.7225(4) | 3.6(1) |
| C(10) | 1.0118(7) | 0.2512(5) | 0.8186(4) | 3.5(1) |
| C(11) | 1.1247(7) | 0.1480(5) | 0.8093(5) | 4.2(2) |
| C(12) | 1.1605(7) | 0.1102(5) | 0.7115(5) | 4.3(2) |
| C(13) | 1.0862(7) | 0.1710(4) | 0.6166(4) | 3.2(1) |
| C(14) | 0.9721(7) | 0.2862(5) | 0.9304(4) | 3.8(1) |
| C(15) | 0.871(1) | 0.1987(7) | 1.0006(6) | 7.9(2) |
| C(16) | 1.1224(8) | 0.2891(6) | 0.9887(5) | 5.6(2) |
| C(17) | 0.877(1) | 0.4140(6) | 0.9195(5) | 7.2(2) |
| C(18) | 1.2881(7) | 0.3028(5) | 0.2921(5) | 4.5(2) |
| C(19) | 1.3176(7) | 0.1945(5) | 0.2475(4) | 3.5(1) |
| C(20) | 1.4655(7) | 0.1723(5) | 0.1884(5) | 4.9(2) |
| C(21) | 1.5008(8) | 0.0716(6) | 0.1426(6) | 5.8(2) |
| C(22) | 1.3916(8) | -0.0088(5) | 0.1575(5) | 5.2(2) |
| C(23) | 1.2462(7) | 0.0078(5) | 0.2139(5) | 4.2(2) |
| C(24) | 1.2033(7) | 0.1123(4) | 0.2607(4) | 3.3(1) |
| C(27) | 0.6298(9) | 0.1312(6) | 0.4868(7) | 7.2(2) |

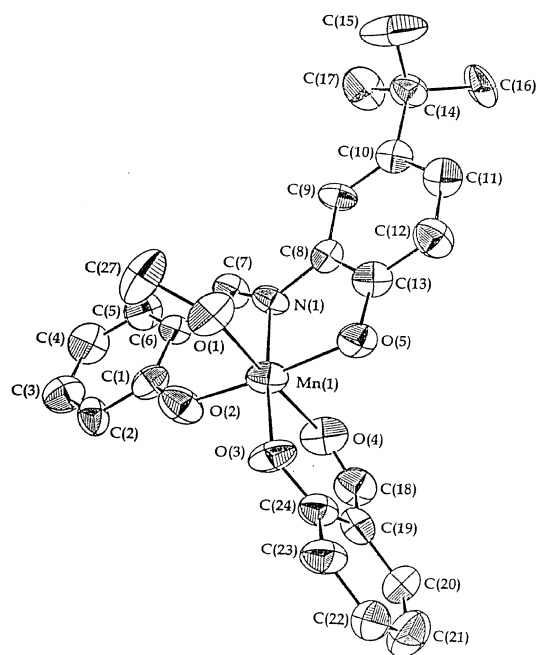
^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)(2,3)]$.

phenolate oxygen (O(3)) of the salicylaldehyde. The axial positions of the manganese(III) coordination sphere are filled by another oxygen (O(4)) of the salicylaldehyde and a methanol (O(1)) molecule. The molecule contains the five- and six-membered N, O chelate rings from Schiff base, and only six-membered O, O chelate ring from salicylaldehyde, respectively, formed on complexation. These rings constitute a very mediocre plane. The five- and six-membered rings as well as a phenyl and *tert*-butylphenol planes in sabp ligand are very excellent individual planes (mean deviations, ~ 0 Å), but there is 6.5° fold at their intersection. The interplanar angle of the phenyl and MnOCCCO fragments in salicylaldehyde is also 4.3° . Above results account for the good overall planarity of coordinated ligands. The crystal structure exhibits distortions from idealized octahedral geometry at the metal, due to the rigidity of the Schiff base ligand and to the bite angle of the chelate rings: the *trans* O-Mn-O

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 1

| (a) Distances | | | |
|-----------------|----------|-------------------|----------|
| Mn(1)–O(1) | 2.212(4) | C(1)–O(2) | 1.327(6) |
| Mn(1)–O(2) | 1.873(4) | C(13)–O(5) | 1.338(7) |
| Mn(1)–O(3) | 1.885(4) | C(8)–N(1) | 1.419(6) |
| Mn(1)–O(4) | 2.239(4) | C(27)–O(1) | 1.365(8) |
| Mn(1)–O(5) | 1.900(3) | C(18)–O(4) | 1.199(7) |
| Mn(1)–N(1) | 1.990(4) | C(19)–C(18) | 1.433(8) |
| C(7)–N(1) | 1.302(6) | C(24)–O(3) | 1.290(7) |
| (b) Angles | | | |
| O(1)–Mn(1)–O(2) | 91.7(2) | Mn(1)–O(1)–C(27) | 129.2(3) |
| O(1)–Mn(1)–O(3) | 90.2(2) | Mn(1)–O(2)–C(1) | 130.5(4) |
| O(1)–Mn(1)–O(4) | 176.3(1) | Mn(1)–O(3)–C(24) | 131.1(4) |
| O(1)–Mn(1)–O(5) | 88.0(2) | Mn(1)–O(4)–C(18) | 119.6(4) |
| O(1)–Mn(1)–N(1) | 91.3(2) | Mn(1)–O(5)–C(13) | 113.5(3) |
| O(2)–Mn(1)–O(3) | 94.0(2) | Mn(1)–N(1)–C(7) | 125.4(4) |
| O(2)–Mn(1)–O(4) | 91.5(2) | Mn(1)–N(1)–C(8) | 111.1(3) |
| O(2)–Mn(1)–O(5) | 174.4(2) | O(2)–C(1)–C(6) | 123.0(5) |
| O(2)–Mn(1)–N(1) | 91.2(2) | O(5)–C(13)–C(8) | 119.2(4) |
| O(3)–Mn(1)–O(4) | 87.7(2) | C(7)–C(6)–C(1) | 123.3(4) |
| O(3)–Mn(1)–O(5) | 91.6(2) | N(1)–C(8)–C(13) | 112.3(5) |
| O(3)–Mn(1)–N(1) | 174.5(2) | C(6)–C(7)–N(1) | 125.6(5) |
| O(4)–Mn(1)–O(5) | 89.1(1) | O(3)–C(24)–C(19) | 124.8(5) |
| O(4)–Mn(1)–N(1) | 90.6(2) | O(4)–C(18)–C(19) | 131.2(6) |
| O(5)–Mn(1)–N(1) | 83.2(2) | C(18)–C(19)–C(24) | 122.0(5) |

($174.4(2)$ – $176.3(1)^\circ$) and *trans* O-Mn-N ($174.5(2)^\circ$) axes are less than 180° in the complex. The Mn–O and Mn–N bond distances (Table 4) for equatorially coordinated heteroatoms are typical for Mn(III) complexes.¹⁵ Elongation along the

**Figure 1.** Molecular structure and numbering scheme for complex [Mn(SABP)(SAL)(MeOH)]. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

O(1)-Mn(1)-O(4) axis vs. the average Mn-O (equatorial) length is very pronounced, which reflects the Jahn-Teller distortion of this high-spin d^4 ion. Especially, the longer distance of Mn(1)-O(1) is indicative of definite coordination as a neutral form of methanol molecule, suggesting that the oxidation number of manganese ion is +3. For example, a comparison of the axial (Mn(1)-O(1) = 2.212 Å, Mn(1)-O(4) = 2.239 Å) and equatorial bonds (Mn(1)-O(2) = 1.873 Å, Mn(1)-O(3) = 1.885 Å, Mn(1)-O(5) = 1.900 Å) demonstrates a lengthening of the axial metal-oxygen distances by > 0.3 Å.

Supplementary material available. Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths and angles (34 pages) and calculated and observed structure factors (19 pages) for complex **1**. Ordering information is given upon your request to the correspondence author.

References

1. Kirby, J. A.; Robertson, A. S.; Smith, J. P.; Thompson, A. C.; Cooper, S. R.; Klein, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5529.
2. Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328.
3. Brudvig, G. W.; Crabtree, R. H. *Prog. Inorg. Chem.* **1989**, *37*, 99.
4. Vincent, J. B.; Christou, G. *Adv. Inorg. Chem.* **1989**, *33*, 197.
5. Weighardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153.
6. Que, L. Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97.
7. (a) Ludwig, M. L.; Patridge, K. A.; Stallings, W. C. *Manganese in Metabolism and Enzyme Function*, Academic Press: New York, 1986; Chapter 21, p 405. (b) Beyer, W. F. Jr.; Fridovich, I. *Manganese in Metabolism and Enzyme Function*, Academic Press: New York, 1986; Chapter 12, p193.
8. (a) Pecoraro, V. L. *Photochem. Photobiol.* **1986**, *48*, 249. (b) Asmecz, J. *Biochim. Biophys. Acta* **1983**, *726*, 1.
9. Ashmawy, F. M.; McAuliffe, C. A.; Parish, R. V.; James, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1391.
10. Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1975**, *14*, 1289.
11. Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN 80*; University of York: 1980.
12. *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, Netherlands, 1990.
13. Mo, S. J.; Lim, W. T.; Koo, B. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 1175.
14. (a) Hill, W. E.; Atabay, N.; McAuliffe, C. A.; McCullough, F. P.; Razzolci, S. M. *Inorg. Chim. Acta* **1979**, *35*, 35. (b) Chandra, S.; Sharma, K. K. *Transition Met. Chem.* **1984**, *9*, 1.
15. Bonadies, J. A.; Kirk, M. L.; Lah, M. S.; Kessissoglou, D. P.; Hatfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 2037.