

Synthesis, Crystal Structure, and Characterization of Manganese(IV) Complexes with Tridentate Ligands Comprising Mixed Hard-Soft Donors

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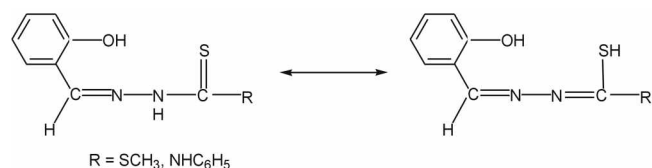
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Manganese complexes play important roles ranging from bioinorganic chemistry to solid-state physics. Low-nuclearity species have been studied extensively as models for the water oxidizing complex in photosystem II,¹ whereas nanometer-size clusters with high-spin ground states are being investigated as single-molecule magnets.² However, the coordination chemistry of manganese is dominated by stable manganese(II)³ and manganese(III) ions,⁴ and the manganese chemistry in the higher oxidation state(IV) is still little known.⁵ To develop the coordination chemistry of manganese in high oxidation states requires the design of new ligands that are resistant to the high oxidizing power of the central metal and are capable of forming strong σ - as well as π -coordination bonds so as to satisfy the high Lewis acidity of the metal.⁶

In this context, we have taken up salicylaldehyde-S-methyldithiocarbazone (sal-mdtcH₂) and salicylaldehyde-4-phenylthiosemicarbazone (sal-phTscH₂) derived from dithiocarbazate or thiosemicarbazone of salicylaldehyde as potential tetrafunctional (O, N, N, S) dianionic ligands comprising both hard and soft donor atoms. The tautomerism of these ligands as well as the well known tendency of oxygen and sulfur donors to act as bridging ligands allow various structural possibilities for the corresponding metal complexes.



The extension of manganese chemistry in high oxidation state by proper use of suitable organic ligands prompted us to work this study. We report here the preparation, X-ray structure, magnetic moment, spectral and electrochemical properties of the manganese complexes having a Mn^{IV}N₂O₂S₂-core.

Experimental Section

Mn(O₂CCH₃)₂·4H₂O was purchased from Junsei Chemical

Co. Salicylaldehyde and 4-phenyl-3-thiosemicarbazide were obtained from Aldrich Chemical Co. Salicylaldehyde-S-methyldithiocarbazone (sal-mdtcH₂) and Salicylaldehyde-4-phenylthiosemicarbazone (sal-phTscH₂) were prepared as described in the literature.⁷ All other chemicals and solvents were obtained from commercial sources and used as received.

Carbon, hydrogen, nitrogen, and sulfur analyses were carried out using a Carlo Erba Model EA-1106 CHNS/O Analyzer. The IR spectra were recorded as KBr disk using a Mattson Polaris FT-IR spectrophotometer in the region 500-4,000 cm⁻¹. UV-Vis spectra were obtained in DMSO, using a Milton Roy Spectronic Genesys 2 spectrophotometer. ¹H NMR spectra of DMSO-d₆ solutions were obtained on a Varian Gemini 200 spectrometer. Chemical shifts are in ppm relative to internal Me₄Si. Melting point determinations were carried out with a Laboratory Devices Inc. Mel-Temp II. Molar conductivities were determined in DMSO at 25 °C with a YSI Model 31 conductivity bridge. Magnetic susceptibilities were obtained at Korea Basic Science Institute and magnetic moments calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the susceptibility uncorrected for diamagnetism of the constituent atoms. Electrochemical measurements were performed using a EG&G Model 263 electrochemical system. A three-electrode cell comprising a platinum electrode, a platinum-wire counter electrode, and a Ag/Ag⁺ was used. The concentrations were 1 × 10⁻³ M with 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte in distilled dimethyl sulfoxide (10 mL).

Bis(salicylaldehyde-S-methyldithiocarbazate)manganese (IV) (1). To a stirred yellow solution of salicylaldehyde-S-methyldithiocarbazone (0.453 g, 2 mmol) in methanol (25 mL) was added Mn(O₂CCH₃)₂·4H₂O (0.735 g, 3 mmol) at room temperature. The mixture was refluxed for 4 h, after which the redish-brown solution was allowed to cool to room temperature and was exposed to dioxygen by bubbling air into the solution for 4 h. The resulting dark brown solid was collected by filtration, washed with a little cold methanol and diethyl ether, and dried in vacuum oven (25 mmHg, 25 °C) for one day. Yield: 0.432 g (29% on Mn), mp: 217-219 °C. μ_{eff} : 3.67 μ_{B} at 27 °C. Λ_{M} (Mho cm² mol⁻¹): 1.8. Anal. Calcd. for C₁₈H₁₆N₄O₂S₄Mn: C, 42.93; H, 3.20; N, 11.13; S, 25.47. Found: C, 42.97; H, 3.29; N, 10.74; S, 26.17. IR (on KBr pellet, cm⁻¹): 1596 ($\nu_{\text{C=N}}$). ¹H NMR (in

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Table 1. Crystallographic Data and Intensity Collection for Complex **1**

Empirical formula	C ₁₈ H ₁₆ N ₄ O ₂ S ₄ Mn
F_w	503.53
Crystal system	monoclinic
Space group	$C2c$
Z	4
a (Å)	7.402(1)
b (Å)	23.650(2)
c (Å)	11.876(1)
β (°)	99.839(8)
V (Å ³)	2048.4(4)
D_{calc} (g/cm ³)	1.633
μ (mm ⁻¹ with Mo-K α)	1.076
$F(000)$	1028
Scan type	ω
Scan range (deg)	1.72 to 27.47
No. of reflections measured	4716
No. of reflections observed ($I > 2\sigma(I)$)	4701
No. of variable	263
R^w	0.0473
R_w^b	0.0942
Goodness of fit on F^2	1.138
Largest diff. peak and hole	0.377 and -0.274 eÅ ⁻³

^a $R = \sum(|F_o - F_c|) / \sum F_o$. ^b $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum |F_o|^4]^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (0.0427P)^2 + 1.38.9777P]$, where $P = (F_o^2 + 2F_c^2) / 3$. ^cG.O.F. = $[\sum w(|F_o|^2 - |F_c|^2)^2 / (n-p)]^{1/2}$.

DMSO- d_6 , ppm): 6.8-8.8 (br, ArH). UV/Vis. $\lambda_{\text{max/min}}$ (log ϵ /M⁻¹cm⁻¹): 599 (2.00), 301 (4.63).

Bis(salicylaldehyde-4-phenylthiosemicarbazate)manganese (IV) (2). The complex was prepared according to the method used for **1**, except for using sal-phTsch₂ instead of sal-mdtcH₂. Yield: 0.529 g (30% on Mn), mp: 168 °C (dec.). μ_{eff} : 4.11 μ_B at 27 °C. Λ_M (Mho cm² mol⁻¹): 8.4. Anal. Calcd. for C₂₉H₂₆N₆O₃S₂Mn: C, 55.68; H, 4.19; N, 13.43; S, 10.25. Found: C, 55.10; H, 3.79; N, 13.38; S, 10.48. IR (on KBr pellet, cm⁻¹): 2991 (ν_{NH}), 1597 ($\nu_{\text{C=N}}$). ¹H NMR (in DMSO- d_6 , ppm): 6.8-7.6 (br, ArH). UV/Vis. $\lambda_{\text{max/min}}$ (log ϵ /M⁻¹cm⁻¹): 592 (2.19), 318 (4.53).

Crystal Structure Determination of 1. Dark brown crystals for the single crystal study were grown by slow diffusion of diethyl ether into a dichloromethane solution. A selected crystal had a dimension of 0.07 × 0.19 × 0.38 mm and was mounted in glass capillary. Measurement was made on a STOE STAD14 four-circle-diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using 25 reflections in $1.72^\circ < 2\theta < 27.47^\circ$. Intensities were collected using the ω scan technique and performed up to $2\theta = 25^\circ$. Three standard reflections monitored every 1 h of X-ray exposure: no significant decay was observed. The intensity data were collected for Lorentz and polarization effects. Numerical absorption correction was used. The maximum and minimum transmission factors were 0.9165

and 0.7812. The structure was solved by the direct method (SHELXS-97-2, Sheldrick, 1997) and refined by full-matrix least-squares methods (SHELXL-97-2, Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized ($d(\text{C-H}) = 0.96$ Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of the attached atom. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indices R and R_w .

Results and Discussion

The reaction of manganese(IV) acetate tetrahydrate with each ligand, sal-mdtcH₂ and sal-phTsch₂ in methanol, afforded the corresponding redish-brown solids of monomeric MnL₂. The formulations are well in accordance with the data of elemental analysis and physicochemical measurements. The complexes were soluble in dichloromethane, dimethylformamide, and dimethyl sulfoxide, but were not soluble in nonpolar organic solvents. The molar conductances of the complex **1** and **2** determined at a concentration of ca. 1×10^{-3} M in DMSO show the small values 1.8 and 8.4 Mho cm² mol⁻¹, respectively, indicating that the complexes are non-electrolytes.⁸ The effective magnetic moments (3.67 for **1** and 4.11 μ_B for **2**) are close to the spin-only value (3.87 μ_B) for three unpaired electrons, confirming that manganese oxidation state for both complexes is +4.

X-ray Structural Description of 1. Selected bond distances and angles are given in Table 2. The molecular structure and atom numbering scheme is shown in Figure 1. The structure of **1** consists of two trifunctional schiff base ligands-manganese unit. The basal plane of the Mn octahedral is defined by the two oxygen and two sulfur donors of both sal-mdtc²⁻ ligands, whereas the apical positions are occupied by the azomethine nitrogen atoms. The MnO₂N₂S₂

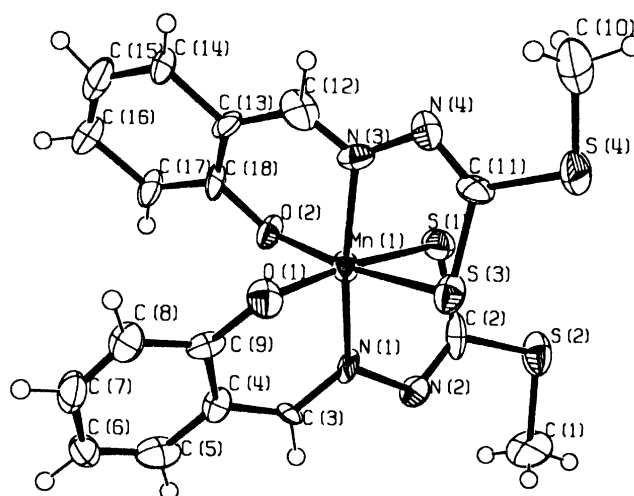


Figure 1. Molecular structure and numbering scheme for complex [Mn(sal-mdtc)₂]. Thermal ellipsoids have been drawn at the 50% probability level.

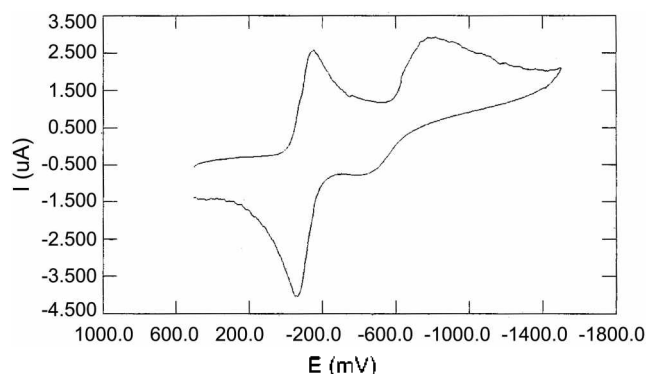
Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 1

Distances			
Mn(1)-O(1)	1.87(1)	Mn(1)-O(2)	1.906(9)
Mn(1)-N(1)	1.94(1)	Mn(1)-N(3)	2.01(1)
Mn(1)-S(3)	2.325(4)	Mn(1)-S(1)	2.329(4)
S(1)-C(2)	1.69(1)	S(2)-C(2)	1.77(1)
S(2)-C(1)	1.83(2)	S(3)-C(11)	1.76(1)
S(4)-C(11)	1.72(1)	S(4)-C(10)	1.75(2)
N(1)-C(3)	1.33(1)	N(1)-N(2)	1.43(1)
N(2)-C(2)	1.28(2)	N(3)-C(12)	1.25(2)
N(3)-N(4)	1.38(1)	N(4)-C(11)	1.32(2)

Angles			
O(1)-Mn(1)-O(2)	89.6(1)	O(1)-Mn(1)-N(1)	91.3(4)
O(2)-Mn(1)-N(1)	92.5(4)	O(1)-Mn(1)-N(3)	94.9(4)
O(2)-Mn(1)-N(3)	90.8(4)	N(1)-Mn(1)-N(3)	173.0(2)
O(1)-Mn(1)-S(3)	93.1(4)	O(2)-Mn(1)-S(3)	172.6(3)
N(1)-Mn(1)-S(3)	94.3(3)	N(3)-Mn(1)-S(3)	82.2(3)
O(1)-Mn(1)-S(1)	172.7(3)	O(2)-Mn(1)-S(1)	91.1(3)
N(1)-Mn(1)-S(1)	81.4(3)	N(3)-Mn(1)-S(1)	92.4(3)
S(3)-Mn(1)-S(1)	87.01(4)		

coordination spheres are considerably distorted, which is probably due to the ligand rigidity. The angles at the Mn center show large deviations (Table 2) from the ideal octahedral values of 90° and 180° . The mean deviation of plane O(1)O(2)S(1)S(3) from the least-square plane is 0.13 Å, in contrary to the planes N(1)O(1)N(3)S(1) and N(1)-O(2)N(3)S(3), with mean deviations of 0.02 and 0.03 Å, respectively. The interplanar angles between these planes lie in the interval 87° - 88° . The average bond distances for each of Mn-O, Mn-N, and Mn-S in this coordination geometry are 1.89(1), 1.98(1), and 2.327(4) Å. The values are similar to those of typical Mn(IV) complexes^{5b} and shorter than those of the Mn(II) and Mn(III) complexes.^{9,10} The molecule contains the five- and six-membered chelate rings from the schiff base, respectively. The average C-N distance (C(3)-N(1) and C(12)-N(3)) of the azomethine group in the chelate ring is 1.29(2) Å, which is shorter than a formal single bond (1.52 Å) for Mn^{IV}(amp)₂ (amp²⁻ = *N*-salicylidene-2-amino-phenol).^{5b} The average bond distance, 1.30 Å, for dithiocarbamate C-N bonds (C(2)-N(2) and C(11)-N(4)) is close to the C=N double bond distance of the salicylalimine, indicating the involvement of the 1,3-proton shift. Similarly, the average bond distance, 1.73(1) Å for C(2)-S(1) and C(11)-S(3) is nearly the same as the average value, 1.74(1) Å for the C-S bonds of the S-methyl group. In addition, the average distance of the N-N bond, 1.40(1) Å, (1.43 Å for N(1)-N(2) and 1.38 Å for N(3)-N(4)) is also longer than a double bond (1.26 Å) of the azo group in the complex Mn^{IV}(azp)₂ (azp²⁻ = 2,2'-dihydroxyazobenzene).^{5b} These results indicate that the sal-mdtc²⁻ ligand acts as thiol form.

Spectral and Electrochemical Properties. The infrared spectral bands at 1620 cm^{-1} associated with the azomethine group ($\nu_{\text{C=N}}$) of free ligands are shifted to 1596 and 1597

**Figure 2.** Cyclic voltammogram (scan rate, 100 mVs^{-1}) of $\sim 10^{-3}\text{ M}$ solution (0.1 M TEAP) of $[\text{Mn}(\text{sal-mdtc})_2]$ in DMSO at a platinum electrode (298°K).

cm^{-1} for complex 1 and 2, respectively. The secondary amine vibrations (ν_{NH}) of the free ligands are also observed at 2971 and 2991 cm^{-1} , respectively. However, the NH vibration at 2971 cm^{-1} of sal-mdtcH₂ disappears on complexation. The bands at ca. 3100 cm^{-1} may be attributed to the stretching frequency of phenolic OH for both ligands are also disappeared on complexation. This fact suggests that the Schiff base acts as dibasic tridentate ligands with phenolic oxygen, azomethine nitrogen, and sulfur donor atoms in the thiol form by tautomerism.¹¹ ¹H NMR spectra just show very weak aromatic proton resonances in the range of 6.8-8.8 ppm for both complexes and are not helpful for identification of a functional group due to paramagnetic d^5 configuration.

For octahedral manganese(IV) complexes, the electronic spectra was expected to show three spin-allowed d-d transitions [${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$, ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$, ${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$].^{5a} But, one d-d transition band at ca. 595 nm ($\log \epsilon = \text{ca. } 2.00\text{ M}^{-1}\text{ cm}^{-1}$) and the intense band at ca. 300 nm ($\log \epsilon = \text{ca. } 4.60\text{ M}^{-1}\text{ cm}^{-1}$), probably due to intraligand transitions¹² in the UV region for each complex, are observed.

Cyclic voltammograms for the complexes examined in dimethyl sulfoxide solution displayed two cyclic responses in the potential range 0.00~-2.20 V (Table 3). Current height considerations support the same electron stoichiometry for the responses, which is assigned to the electrode Mn^{IV}L₂-Mn^{III}L₂ and Mn^{III}L₂-Mn^{II}L₂ couples.^{5a} In complex 1 the first couples, as shown in Figure 2, are quasi-reversible with the peak-to-peak separations (ΔE_p) of 71.4 mV regardless of the scan rates, whereas complex 2 is irreversible. The reduction potentials (E°) of complex 1 is more positive compared with

Table 3. Electrochemical Data^a at 25°C

Complexes	Mn(IV)-Mn(III) $E^{o,b}(\Delta E_p^c)$, mV	Mn(III)-Mn(II) $E^{o,b}(\Delta E_p^c)$, mV	scan rate mVs^{-1}
1	-107(71.4)	-617(293)	100
2	-259(118)	-730(240)	100

^aSupporting electrolyte is TEAP (0.1 M); working electrode is platinum; reference electrode is Ag/Ag⁺ (0.01 M). ^b E° is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. ^c $\Delta E_p = E_{pa} - E_{pc}$

complex **2**, indicating that complex **1** is more easily reduced than complex **2** due to the inductive effect of the substituent in dimethyl sulfoxide.

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Supporting Information Materials. Listing of atomic coordinates, complete bond distances and angles, thermal parameters, and least-squares results for **1** are available on request from the corresponding author.

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