Syntheses and X-ray Structures of Mixed-Ligand Salicylaldehyde Complexes of Mn(III), Fe(III), and Cu(II) Ions: Reactivity of the Mn(III) Complex toward Primary Monoamines and Catalytic Epoxidation of Olefins by the Cu(II) Complex

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The Schiff base (**L**), synthesized from 2-(dimethylamino)ethylamine and salicylaldehyde acts as a tridentate ligand. This ligand, when stirred with 1 equiv of KOH in methanol, undergoes partial hydrolysis of the imine bond. This solution readily takes up Mn(II)/Mn(III) acetate or Fe(III) chloride/perchlorate to form mixed-ligand Mn(III) or Fe(III) complexes, respectively. The neutral dark brown complex, $[\mathrm{Mn(L_{-H})(NCS)}\{o\text{-}(\mathrm{CHO})\mathrm{C_6H_4O^-}\}]$ (**1**), crystallizes in the presence of thiocyanate in the orthorhombic space group *Pbca* with $a = 15.271(8)$, $b = 19.522(7)$, $c = 13.213(7)$ Å; $Z = 8$; $R = 0.060$; and $R_w = 0.062$. The coordination geometry around Mn(III) ion is distorted octahedral with donation from one $\mathbf{L}_{-H}$, one salicylaldehyde and, one thiocyanate ligand. With Fe(III), the dark red complex isolated in the solid state is found to be a neutral μ-oxo Fe(III) dimer with the formula $[\{o\text{-}(\mathrm{CHO})\mathrm{C_6H_4O^-}\}(\mathrm{L_{-H}})\mathrm{Fe}]_2\mathrm{O}$ (**3**). The structure of **3** has been solved and successfully refined in the monoclinic space group *C*2/*c* with $a = 18.558(7)$, $b = 11.231(5)$, $c = 16.943(6)$ Å; $\beta = 95.81(3)°$; $Z = 4$; $R = 0.052$; and $R_w = 0.055$. Each of the Fe(III) ions is hexadentate with donation from one $\mathbf{L}_{-H}$ and one salicylaldehyde besides the bridged O atom. The Fe(III)−O−Fe(III) angle is found to be 166.05(4)°, which is well within the normal range observed for monobridged Fe(III)−O−Fe(III) complexes. Due to structural *trans* effects, the coordination geometry around each metal center is distorted from the ideal octahedral geometry. Cu(II) makes the neutral complex, $[\mathrm{Cu(L_{-H})}\{o\text{-}(\mathrm{CHO})\mathrm{C_6H_4O^-}\}]$ (**2**) when **L**, salicylaldehyde, and a Cu(II) salt are allowed to react in equimolar quantities in the presence of excess of KOH. It crystallizes in the monoclinic space group *C*2/*c* with $a = 18.077(4)$, $b = 11.514(2)$, $c = 16.716(4)$ Å; $\beta = 93.66(2)°$; $Z = 8$; $R = 0.057$; and $R_w = 0.061$. The coordination geometry around Cu(II) is square pyramidal where, out of the four equatorial donors, three are provided by the Schiff base **L** and the fourth one by the phenolate O of the salicylaldehyde group. The Cu(II) ion is 0.170(5) Å above the equatorial plane and is bonded axially to the O atom of the carbonyl group of the salicylaldehyde. The bound salicylaldehyde in the Mn(III) complex **1** readily reacts with the reagents 2-aminophenol, 2-aminothiophenol, or 2-aminoethanol to form mononuclear, neutral Mn(III) complexes **4**−**6**, respectively, with the general formula,$[\mathrm{Mn(L_{-H})(L'_{-2H})}]$. The Schiff base **L′** is formed by condensation of the bound salicylaldehyde in **1** with the amino group of the added reagent. Complex **4** is low-spin ($\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 3.01$; $S = 1$) at 300 K, which is quite rare. It also exhibits a pseudoreversible Mn(IV)/Mn(III) couple with $E_{1/2} = 0.54$ V (vs SCE) in DMF. All the other Mn complexes are high-spin ($\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ range, 4.89−4.94; $S = 2$) at 300 K. The $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ number for **2** is 1.93 and for **3** is 1.84. Complex **2** shows catalytic activity in the oxidation of olefins to epoxides in the presence of 2-methylpropanal and molecular oxygen.

Introduction

Synthesis of transition metal complexes with aldehyde groups has been a subject of considerable importance.[1−5] Due to its bonding with the metal ion, the aldehyde group is activated and can undergo different types of chemical transformation. In these complexes, the aldehyde group is found to bind the metal ion in the η^1 and η^2, and rarely in the η^3-fashion.[1] Hersh and co-workers characterized[6] a cationic η^1-aldehyde complex of W which was shown to be an excellent catalyst for the Diels−Alder reaction between dienes and α,β-unsaturated enones. Faller et al. suggested[7] that involvement of a η^1-aldehyde complex of Mo was crucial in the synthesis of optically active homoallylic alcohols. Burkhardt and co-workers[8] proposed an η^1-aldehyde intermediate in the reaction of a Ni enolate with benzaldehyde. Pedersen and co-workers[9] proposed a η^1-aldehyde intermediate in the V(II)-mediated cross-coupling of aldehydes to produce 1,2-diols. Gladysz and co-workers

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prepared[10] optically active alcohols from optically active η^2-aldehyde complexes of Re. In a later work, this group isolated two more η^2-aldehyde complexes[11] of the same metal. Also, the involvement of metal−aldehyde bonding in the hydroformylation of olefins[12] has been suggested. It should be pointed out here that while a substantial chemistry of metal−aldehyde complexes exists, it has been limited mostly to formaldehyde and its higher homologues. A systematic study[13] of the structures of aldehyde complexes reveals that cationic aldehyde complexes exhibit an η^1-bonding mode while neutral complexes show an η^2-bonding mode. The η^1-bonding mode for neutral complexes is quite rare. In the present paper, we describe the synthesis and characterization of neutral complexes of Mn(III), Fe(III), and Cu(II) where the aldehyde group from salicylaldehyde is bonded to the metal ion in an η^1-fashion. To our knowledge, no X-ray crystallographically characterized salicylaldehyde complexes of Mn(III), Fe(III), and Cu(II) are available. It is important to know the structures of such complexes to rationalize their reactivities toward various reagents. The bound aldehyde group in the Mn(III) complex reacts readily with primary monoamines to form mixed Schiff base complexes which are also described. Research concerning the coordination chemistry of Mn(III) has intensified[14−19] in recent years due to its biological importance. In light of the role that aldehydes may play in the catalytic cycle of some metal-catalyzed oxo-transfer systems, we have probed the effectiveness of the complexes as oxygenation catalysts as well.

Experimental Section

Materials. Reagent grade salicylaldehyde, 2-(dimethylamino)-ethylamine, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Mn(CH_3COO)_3{\cdot}2H_2O$, ferric chloride, cupric perchlorate hexahydrate, and potassium thiocyanate (Fluka) were used as received. 2-Aminoethanol, 2-aminophenol, 2-aminothiophenol, *trans*-stilbene, *cis*-stilbene, and chalcone (Aldrich) were also used as received. All solvents were purified prior to use.[20] Elemental analyses and physical and electrochemical studies were carried out as described earlier.[21]

Synthesis of L. The ligand **L** (Figure 1) was prepared by refluxing for 30 min a methanolic solution (10 cm^3) of salicylaldehyde (1 mmol) and 2-(dimethylamino)ethylamine (1 mmol). The solution turned orange. Methanol was removed completely to obtain a highly viscous orange liquid. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.1 (s, 6H), 2.7 (t, 2H), 3.6 (t, 2H), 7.1 (m, 4H), 8.2 (s,1H).

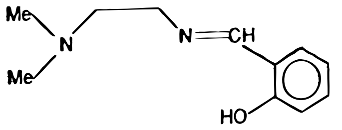

Figure 1. Schiff base ligand **L**.

Synthesis of $[Mn(L_{-H})(NCS)\{o\text{-}(CHO)C_6H_4O^-\}]$ (1). The orange solution containing **L** was stirred with 1 equiv of KOH for 30 min at 293 K. Solid $Mn(CH_3COO)_2{\cdot}4H_2O$ (1 equiv) was added to this solution, which turned dark brown immediately. The reaction mixture was allowed to reflux for 45 min and then treated with 1 equiv of KSCN and filtered. The filtrate evaporated to dryness, and the dark brown solid thus obtained was dissolved in acetonitrile and filtered. Upon slow evaporation of this solution at 293 K, complex **1** deposited as dark brown crystals in the form of rectangular parallelopipeds. The yield was 65% (based on the Mn salt). The same product could be isolated in 59% yield by using $Mn(CH_3COO)_3{\cdot}2H_2O$ instead of the Mn(II) salt. Anal. Calcd for $C_{19}H_{20}N_3O_3SMn$: C, 53.64; H, 4.74; N, 9.88; S, 7.54. Found: C, 54.07; H, 4.89; N, 9.68; S, 7.93.

Synthesis of $[Cu(L_{-H})\{o\text{-}(CHO)C_6H_4O^-\}]$ (2). A slightly different method was adopted for the synthesis of **2**. The ligand **L**, salicylaldehyde, and cupric perchlorate hexahydrate taken in 1:1:1 molar ratio in methanol were heated with 3 equiv of solid KOH at 40 °C for 30 min. The solution turned dark green. The solution was filtered and the filtrate allowed to evaporate slowly at 293 K. Dark green X-ray-quality crystals appeared in 59% yield. Anal. Calcd for $C_{18}H_{20}N_2O_3Cu$: C, 57.52; H, 5.36; N, 7.45. Found: C, 57.23; H, 5.98; N, 7.76.

Synthesis of $[\{o\text{-}(CHO)C_6H_4O^-\}(L_{-H})Fe]_2O$ (3). The Fe(III) complex was isolated following the method adopted for **1** using iron(III) chloride or perchlorate in place of the Mn(II)/Mn(III) salt. The yield was 55%. Single crystals were grown by slow evaporation of a DMF solution of the complex at 295 K. Anal. Calcd for $C_{36}H_{40}N_4O_7Fe_2$: C, 57.46; H, 5.36; N, 7.45. Found: C, 57.83; H, 5.21; N, 7.64.

Synthesis of $[Mn\ (L_{-H})\{o\text{-}(^-OC_6H_4N{=}CHC_6H_4O^-\}]$ (4). Complex **1** (0.1 mmol) and 2-aminophenol (0.1 mmol) were allowed to reflux in MeOH (15 cm^3) in an atmosphere of dinitrogen for 45 min. The resulting dark brown solution was cooled to room temperature and filtered. The filtrate afforded a dark brown solid overnight which was collected by filtration and air-dried. The yield was 65%. Anal. Calcd for $C_{24}H_{24}N_3O_3Mn$: C, 63.01; H, 5.29; N, 9.18. Found: C, 63.13; H, 5.35; N, 8.97.

Synthesis of $[Mn\ (L_{-H})\{o\text{-}(^-SC_6H_4N{=}CHC_6H_4O^-\}]$ (5). This was isolated as above using 2-aminothiophenol in place of 2-aminophenol. The yield was 52%. Anal. Calcd for $C_{24}H_{24}N_3O_2SMn$: C, 60.88; H, 5.11; N, 8.87; S, 6.76. Found: C, 60.31; H, 5.32; N, 8.67; S, 6.87.

Synthesis of $[Mn\ (L_{-H})\{o\text{-}(^-OCH_2CH_2N{=}CHC_6H_4O^-\}]$ (6). Complex **1** (0.1 mmol) and 2-aminoethanol (0.1 mmol) were taken in 15 cm^3 of MeOH containing KOH (0.1 mmol). The resulting solution was refluxed under dinitrogen for 30 min and then filtered after cooling to room temperature. Overnight, the dark brown filtrate afforded **6** in 58% yield. Anal. Calcd for $C_{20}H_{20}N_3O_3Mn$: C, 59.25; H, 4.97; N, 10.36. Found: C, 58.79; H, 5.13; N, 10.12.

***Caution*!** The perchlorate salts must be handled with care as they form potentially explosive mixtures with organic compounds.

X-ray Structural Studies. Single-crystal X-ray data for all three complexes were collected at 298 K either on a Rigaku AFC-5S (for **1**) or on an Enraf-Nonius CAD4-Mach (for **2** and **3**) diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The cell parameters for each were determined by least-squares refinement of diffractometer setting angles for 25 centred reflections that were in the range of $20.0° < 2\theta < 30.0°$. A summary of crystal data, intensity measurements, and structure solution and refinements is given in Table 1. For **1**, systematic absences were consistent with the orthorhombic space group *Pbca*. For **2** and **3**, which belong to the monoclinic crystal system, the systematic absences were consistent with the space group *Cc* and *C*2/*c*. The structure was solved and refined successfully in the space group *C*2/*c* in each case. Three standard reflections were measured at every hour to monitor instrument and crystal stability. The maximum corrections of intensity based on the standard reflections were less than 0.5% for each. Intensity data were corrected for Lorentz and polarization effects; analytical absorption corrections were applied. For **1**, the structure was solved by the heavy atom method and refined on

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Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{19}H_{20}N_3O_3SMn$	$C_{18}H_{20}N_2O_3Cu$	$C_{36}H_{40}N_4O_7Fe_2$
fw	425.39	375.872	752.438
temp, °C	25	25	25
radiation, graphite-monochromated/ λ, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	*C*2/*c*	*C*2/*c*
a, Å	15.271(8)	18.077(4)	18.558(7)
b, Å	19.522(7)	11.514(2)	11.231(5)
c, Å	13.213(7)	16.716(4)	16.943(6)
β, deg		93.66(2)	95.81(3)
V, Å^3	3939(3)	3472(1)	3512(3)
Z	8	8	4
d_{calcd}, g cm^{-3}	1.432	1.438	1.472
abs coeff μ, mm^{-1}		1.28	0.88
crystal size, mm^3	0.2 × 0.2 × 0.2	0.3 × 0.4 × 0.4	0.2 × 0.2 × 0.3
R^a	0.060	0.057	0.052
$R_w{}^b$	0.062	0.061	0.055

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma(F)$; for **1**, $w = 1/\sigma^2(I)$.

F by full-matrix least-squares techniques. TEXAN version 2.0 program package[22] on a micro-VAX computer was used for this purpose. For **2** and **3** , the structures were solved by the direct method and refined on *F* by full-matrix least-squares techniques using the XTAL 3.2 program package[23] and a 486-DX personal computer working under MS-DOS version 5 at 66 MHz. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the usual source.[24] In each case, some of the H atoms could be located in the difference Fourier maps; the rest were calculated by assuming ideal geometries of the atom concerned. H atom positions or thermal parameters were not refined.

Results and Discussion

Syntheses. The Schiff base undergoes partial hydrolysis on stirring for 0.5 h in a moist methanolic KOH medium. Complex **1** or **3** is isolated as the major product when a Mn(II)/Mn(III) or a Fe(III) salt is added to the reaction mixture. We have not been able to isolate any other products with definite compositions. The Mn(III) complex crystallizes, taking up a thiocyanate group to achieve hexacoordination. The Fe(III) ion, on the other hand, achieves hexacoordination by forming the μ-oxo dimer . The Cu(II) ion forms only a pentavalent complex when treated with **L** and salicylaldehyde in the presence of excess KOH. All the complexes are soluble in common organic solvents. They are air-stable in the solid state as well as in solution and so are potentially useful for subsequent reactions. The coordinated aldehyde group in **1** readily reacts with primary amines. Thus, as the Scheme 1 shows, when it is allowed to reflux with 2-aminophenol, 2-aminothiophenol, or 2-aminoethanol, it forms neutral mononuclear complexes with the coordination spheres MnN_3O_3 (**4**), MnN_3O_2S (**5**), and MnN_3O_3 (**6**), respectively. In case of **2** or **3**, however, no such mixed Schiff base complex can be isolated when reacted with the above monoamines. Also, **2** and **3** could not be recovered unchanged from a reaction with the monoamines.

Complexes **1**−**6** are nonelectrolytic in nature in solvents such as methanol, acetonitrile, and DMF. However, in DMF, the conductivity of **1** increases to ∼30 Ω^{-1}cm^2 mol^{-1} in 0.5 h at 295 K, indicating loss of the thiocyanate anion.[25]

Table 2. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for **1**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Mn	0.1225(6)	0.1959(2)	0.1697(6)	0.0417
O(1)	0.2041(8)	0.1015(3)	0.2052(8)	0.0613
O(2)	0.0847(7)	0.1455(2)	0.0568(6)	0.0470
O(3)	0.2222(7)	0.2297(3)	0.1059(6)	0.0517
N(1)	0.1635(8)	0.2337(3)	0.2991(7)	0.0400
N(2)	0.0166(8)	0.1597(3)	0.2582(8)	0.0453
C(1)	0.229(1)	0.0631(4)	0.1380(9)	0.0543
C(2)	0.197(1)	0.0587(4)	0.0376(9)	0.0423
C(3)	0.237(1)	0.0089(4)	−0.023(1)	0.0600
C(4)	0.208(1)	0.0001(4)	−0.1189(9)	0.0653
C(5)	0.143(1)	0.0425(4)	−0.1559(8)	0.0537
C(6)	0.103(1)	0.0907(5)	−0.0974(9)	0.0440
C(7)	0.128(1)	0.0996(4)	0.0021(9)	0.0383
C(8)	0.271(1)	0.2826(4)	0.134(1)	0.0460
C(9)	0.3235(9)	0.3160(4)	0.0616(9)	0.0623
C(10)	0.3757(9)	0.3698(4)	0.087(1)	0.0767
C(11)	0.381(1)	0.3943(3)	0.1840(9)	0.0380
C(12)	0.330(1)	0.3642(4)	0.2550(9)	0.0600
C(13)	0.274(1)	0.3089(4)	0.233(1)	0.0420
C(14)	0.2218(9)	0.2796(3)	0.3103(9)	0.0473
C(15)	0.112(1)	0.2083(3)	0.3848(9)	0.0630
C(16)	0.020(1)	0.2022(4)	0.3519(9)	0.0587
C(17)	−0.069(1)	0.1690(4)	0.208(1)	0.0723
C(18)	0.024(1)	0.0853(4)	0.284(1)	0.0743
S(1a)	0.0292(9)	0.4271(3)	0.0780(8)	0.0827
N(1a)	0.0517(8)	0.2909(3)	0.1387(7)	0.0563
C(1a)	0.043(1)	0.3474(4)	0.1150(9)	0.0423

[a] ESDs in parentheses.

Table 3. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for **2**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Cu	0.55075(6)	0.70028(9)	0.37439(6)	0.0466(4)
O(1)	0.6000(3)	0.6861(5)	0.5020(3)	0.059(2)
O(2)	0.5998(3)	0.8447(5)	0.3640(3)	0.053(2)
O(3)	0.6273(3)	0.6244(5)	0.3200(3)	0.056(2)
N(1)	0.4919(4)	0.5597(6)	0.3786(4)	0.047(3)
N(2)	0.4533(4)	0.7825(7)	0.4015(4)	0.056(3)
C(1)	0.6480(5)	0.7565(8)	0.5273(5)	0.053(4)
C(2)	0.6707(4)	0.8612(7)	0.4912(5)	0.040(3)
C(3)	0.7218(5)	0.9316(8)	0.5376(5)	0.058(4)
C(4)	0.7448(5)	1.0376(9)	0.5121(7)	0.066(4)
C(5)	0.7185(5)	1.0785(8)	0.4376(6)	0.063(4)
C(6)	0.6702(5)	1.0111(8)	0.3902(5)	0.050(3)
C(7)	0.6450(4)	0.9012(7)	0.4135(5)	0.040(3)
C(8)	0.6324(5)	0.5117(8)	0.3047(4)	0.044(3)
C(9)	0.6963(5)	0.4727(9)	0.2664(5)	0.058(4)
C(10)	0.7053(6)	0.358(1)	0.2486(6)	0.069(4)
C(11)	0.6528(6)	0.2796(8)	0.2673(6)	0.072(4)
C(12)	0.5907(5)	0.3106(8)	0.3035(5)	0.062(4)
C(13)	0.5803(5)	0.4275(8)	0.3227(5)	0.050(3)
C(14)	0.5109(5)	0.4585(8)	0.3568(5)	0.050(3)
C(15)	0.4177(5)	0.5781(9)	0.4093(6)	0.067(4)
C(16)	0.4058(8)	0.691(1)	0.416(1)	0.30(2)
C(17)	0.4216(8)	0.850(2)	0.3391(8)	0.19(1)
C(18)	0.4609(6)	0.856(1)	0.4709(6)	0.114(6)

[a] ESDs in parentheses.

Description of the Structures. [Mn(L_{-H})(NCS){*o*-(CHO)-$C_6H_4O^-$}] (1). A perspective view of the molecule with the atom numbering scheme is shown in Figure 2. The molecule is a neutral Mn(III) compound with coordination from one bidentate salicylaldehyde, one tridentate Schiff base (**L**), and one monodentate N-coordinated thiocyanate group thus completing hexacoordination. The atoms O(3), N(1), and N(2) of **L** along with the phenolate oxygen O(2) of salicylaldehyde form the equatorial plane. The Mn−O and Mn−N bond distances (Table 5) for equatorially coordinated heteroatoms are typical for high-spin Mn(III) pseudooctahedral complexes.[16,26] The Mn(III) ion is only 0.088 Å below the mean equatorial plane; the

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[22] TEXAN version 2.0 Software Package for Structure Solution and Refinement. Molecular Structure Corp., The Woodlands, TX, 77381.

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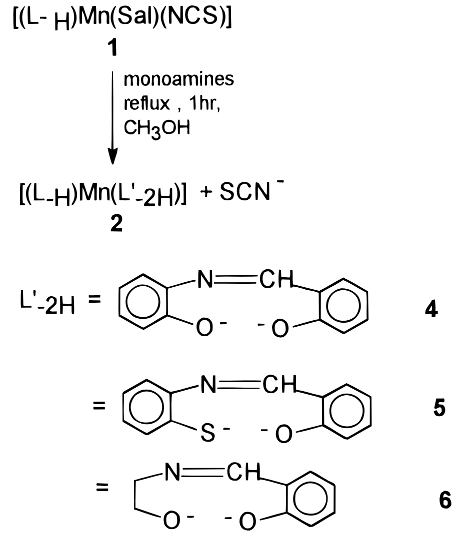
[25] Grey, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table 4. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for **3**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Fe	0.54389(5)	0.28323(9)	0.34773(5)	0.0364(3)
O(1)	0.5921(3)	0.3018(4)	0.4774(3)	0.053(2)
O(2)	0.5898(2)	0.1260(4)	0.3593(2)	0.044(2)
O(3)	0.6306(2)	0.3728(4)	0.3262(3)	0.044(2)
O(4)	$^1/_2$	0.2632(5)	$^1/_4$	0.037(2)
O(1w)	$^1/_2$	−0.0316(7)	$^1/_4$	0.105(4)
N(1)	0.4976(3)	0.4483(5)	0.3733(3)	0.037(2)
N(2)	0.4445(3)	0.2253(6)	0.4036(3)	0.046(2)
C(1)	0.6419(4)	0.2411(7)	0.5088(4)	0.050(3)
C(2)	0.6691(3)	0.1314(6)	0.4809(4)	0.037(3)
C(3)	0.7240(4)	0.0752(7)	0.5298(4)	0.053(3)
C(4)	0.7516(4)	−0.0317(8)	0.5090(5)	0.064(4)
C(5)	0.7227(4)	−0.0831(7)	0.4375(5)	0.063(4)
C(6)	0.6686(4)	−0.300(7)	0.3886(4)	0.049(3)
C(7)	0.6402(4)	0.0792(6)	0.4076(4)	0.035(3)
C(8)	0.6375(4)	0.4824(7)	0.3041(4)	0.042(3)
C(9)	0.6985(4)	0.5158(8)	0.2670(4)	0.055(3)
C(10)	0.7085(4)	0.6297(9)	0.2416(5)	0.065(4)
C(11)	0.6574(6)	0.7156(8)	0.2523(5)	0.070(4)
C(12)	0.5985(5)	0.6883(6)	0.2895(5)	0.060(3)
C(13)	0.5866(4)	0.5725(6)	0.3151(4)	0.041(3)
C(14)	0.5206(4)	0.5502(7)	0.3520(4)	0.047(3)
C(15)	0.4296(4)	0.4419(7)	0.4076(4)	0.056(3)
C(16)	0.4250(5)	0.328(1)	0.4497(6)	0.104(5)
C(17)	0.4566(5)	0.130(1)	0.4602(7)	0.128(6)
C(18)	0.3858(5)	0.191(1)	0.3486(5)	0.125(6)

[a] ESDs in parentheses.

Scheme 1. Reactions of **1** with Monoamines



six-membered and the five-membered rings formed at the Mn are only slightly puckered, thus allowing the N-bonded thiocyanato group to come closer. Hence, unlike other reported structures,[15,16,26,27] the axial Mn(III)−N(1a) distance (2.19(1) Å) is only slightly larger than the equatorial Mn−N(2) distance (2.12(1) Å). The axial Mn(III)−O(1) bond length (2.27(1) Å) compares well with distorted octahedral Mn(III) complexes of Schiff base ligands.[16,26,27] The bond angles around the Mn(III) ion also deviate greatly from the ideal octahedral geometry (Table 5). This distorted geometry around Mn is consistent with a Jahn−Teller distorted Mn(III) (d^4) ion.[27−29] The linear NCS group (N(1a)−C(1a)−S(1a) = 178(1)°) is not coaxial with the axial Mn−N(1a) bond as shown by the angle, Mn−N(1a)−C(1a) being 155.9(4)°. The bond distances and angles of the ligand moieties are within normal statistical errors.

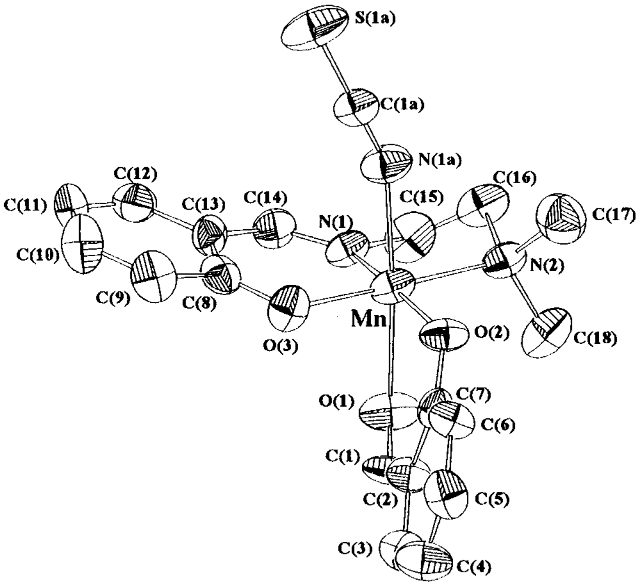


Figure 2. Perspective view of **1** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, and **3**[a]

	1		
Mn-O(1)	2.27(1)	Mn-N(1)	1.96(1)
Mn-O(2)	1.88(1)	Mn-N(2)	2.12(1)
Mn-O(3)	1.86(1)	Mn-N(1a)	2.19(1)
O(1)-Mn-O(2)	84.7(1)	O(2)-Mn-N(1a)	98.3(5)
O(1)-Mn-O(3)	85.1(1)	O(3)-Mn-N(1)	90.0(5)
O(1)-Mn-N(1)	87.2(4)	O(3)-Mn-N(2)	173.4(4)
O(1)-Mn-N(2)	91.9(5)	O(3)-Mn-N(1a)	91.0(5)
O(1)-Mn-N(1a)	175.0(4)	N(1)-Mn-N(2)	83.6(4)
O(2)-Mn-O(3)	94.4(5)	N(1)-Mn-N(1a)	90.1(4)
O(2)-Mn-N(1)	170.4(4)	N(2)-Mn-N(1a)	90.5(4)
O(2)-Mn-N(2)	91.6(4)		
	2		
Cu-O(1)	2.265(7)	Cu-N(1)	1.941(7)
Cu-O(2)	1.898(5)	Cu-N(2)	2.075(7)
Cu-O(3)	1.914(6)		
O(1)-Cu-O(2)	95.6(4)	O(2)-Cu-N(1)	174.0(3)
O(1)-Cu-O(3)	95.1(3)	O(2)-Cu-N(2)	91.6(3)
O(1)-Cu-N(1)	95.2(4)	O(3)-Cu-N(1)	92.9(3)
O(1)-Cu-N(2)	95.6(4)	O(3)-Cu-N(2)	164.0(3)
O(2)-Cu-O(3)	90.0(2)	N(1)-Cu-N(2)	84.1(3)
	3		
Fe-O(1)	2.295(6)	Fe-O(4)	1.784(1)
Fe-O(2)	1.961(4)	Fe-N(1)	2.107(6)
Fe-O(3)	1.962(5)	Fe-N(2)	2.252(5)
O(1)-Fe-O(2)	85.2(3)	O(2)-Fe-N(2)	92.6(3)
O(1)-Fe-O(3)	83.3(3)	O(3)-Fe-O(4)	101.4(2)
O(1)-Fe-O(4)	176.3(2)	O(3)-Fe-N(1)	86.9(2)
O(1)-Fe-N(1)	81.4(3)	O(3)-Fe-N(2)	162.4(3)
O(1)-Fe-N(2)	83.2(2)	O(4)-Fe-N(1)	98.3(2)
O(2)-Fe-O(3)	97.2(2)	O(4)-Fe-N(2)	92.5(3)
O(2)-Fe-O(4)	97.6(2)	N(1)-Fe-N(2)	78.4(3)
O(2)-Fe-N(1)	162.4(2)		

[a] ESDs in parentheses.

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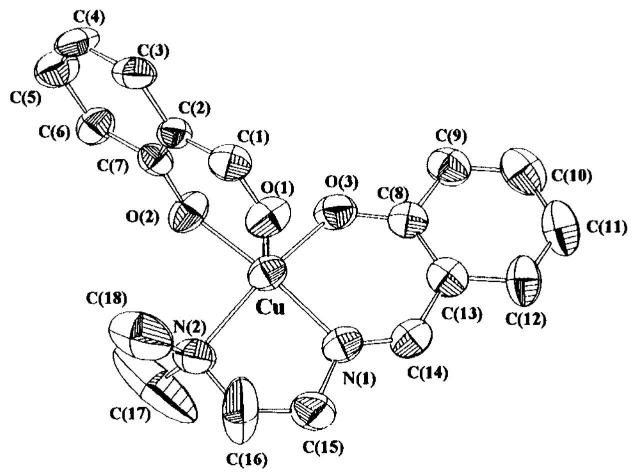

Figure 3. Perspective view of **2** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

$[Cu(L_{-H})\{o\text{-}(CHO)C_6H_4O^{-}\}]$ (2). Complex **2** crystallizes as a neutral monomer with coordination from one tridentate Schiff base **L** and one bidentate salicylaldehyde ligand (Figure 3). The geometry around Cu(II) is square pyramidal where the O atom of the salicylaldehyde group occupies the axial position. The Cu atom in **2** is 0.170(5) Å above the average equatorial plane. When Cu(II) is bonded to a tridentate and one bidentate ligand, the usual geometry is found to be square pyramidal.[30] The equatorial phenolate O(2) of the salicylaldehyde ligand makes a very strong bond with Cu. The bond distance (1.898(5) Å) is one of the shortest Cu(II)−O bond distances known. The other equatorial Cu−O and Cu−N bond lengths are comparable with similar square-pyramidal CuN_2O_3 coordination spheres.[31,32] The axial Cu−O(1) bond length (2.265(7) Å) is longer than normal Cu−O distances, inconsistent with the trend observed in other square-pyramidal Cu(II) complexes.[33] The bond angles around the Cu(II) ion (Table 5) show that the coordination geometry is only slightly distorted from an ideal square-pyramidal one. As in case of **1**, the bond distances and angles in the ligand moieties are within normal statistical errors.

$[\{o\text{-}(CHO)C_6H_4O^{-}\}(L_{-H})Fe]_2O$ (3). Complex **3** crystallizes as a μ-oxo dimer where each Fe(III) is hexadentate with coordination from one tridentate **L** and one salicylaldehyde ligand beside the bridging O atom (Figure 4). The bridging O atom lies on the crystallographic twofold symmetry and therefore only half of the molecule is present in the asymmetric unit. The Fe(III)−O−Fe(III) angle is found to be 166.5(4)°, which is well within the normal range observed[34,35] for μ-oxo monobridged Fe(III) dimers. The Fe−O(4) bond distance (1.784(1) Å) is quite comparable[36] to that obtained with other Fe−O−Fe units with chelating N- and O-donor ligands. The closest nonbonding distance between the terminal ligands (i.e., between C(17) and C(17)′, where C(17)′ is symmetrically related to C(17)) is more than 3.4 (5) Å. The distance between the two Fe(III) ions is 3.54 (6) Å, which is longer than[37] that found in other monobridged Fe−O−Fe complexes where the Fe−O−Fe bond angle is ~165°. The Fe−O(1) bond, which is *trans* to the oxo bridge, has a distance of 2.295(6) Å; whereas, the Fe−O(2) and Fe−O(3) bonds, which are *cis* with respect to the oxo bridge, have distances of 1.961(4) and 1.962(5) Å, respectively. The other two *cis* Fe−N(1) and Fe−N(2) bonds show distances of 2.107(6) and 2.252(5) Å. Thus, the Fe−O(1) bond shows a prominent structural *trans* effect.[38] The longer distance for the Fe−N(2) bond is to avoid greater steric interactions of the two methyl groups with the bound salicylaldehyde moeity. Due to these structural *trans* effects and steric interactions, the coordination geometry around the metal ion is quite distorted from the ideal octahedral geometry.

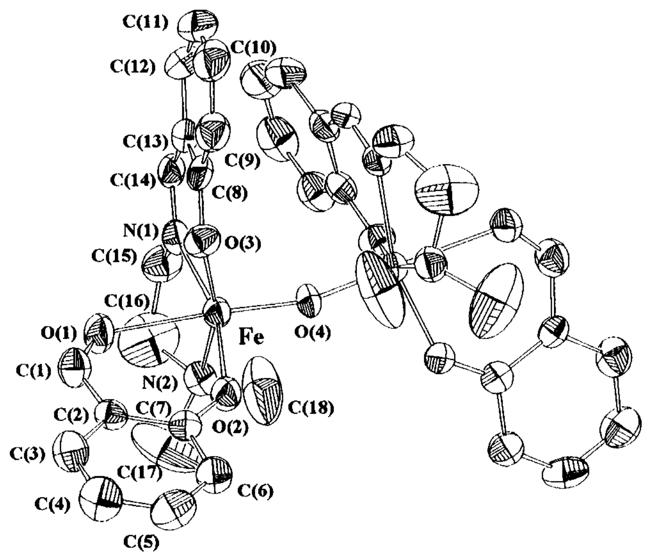

Figure 4. Perspective view of **3** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Infrared Spectroscopy. The metal-bound imine stretching frequency and the η^1-bonded aldehyde group absorb[39,40] at about the same place. A strong broad peak appears in **1**−**3** in the region 1620−1630 cm^{-1} which is attributable to the imine and η^1-bonded aldehyde (C=O) stretching vibrations. Several empirical criteria[41] have been developed to determine the bonding mode of the SCN group. The ν(CN) frequency below 2100 cm^{-1} has been shown to be diagnostic of N-bonded complexes. In **1**, where the thiocyanate group is N-bonded, the ν(CN) stretching frequency appears at 2080 cm^{-1}. For **3**, the additional two strong peaks, which appear at 850 and 405 cm^{-1}, are assignable to ν_{as} (Fe(III)−O−Fe(III)) and ν_s (Fe(III)−O−Fe(III)) vibrations, respectively. The peak positions fit very well in the curve showing the correlation[42] of the Fe−O−Fe symmetric and asymmetric stretching frequencies with the Fe−O−Fe angle. For **4**−**6**, no absorption can be seen around 2100 cm $^{-1}$, indicating absence of the thiocyanate group.

Electronic Spectroscopy. The electronic spectrum of **1** is dominated by an intense peak centering at 25 640 cm^{-1} (ϵ_{max}, 2175 M^{-1} cm^{-1}) attributable[43] to the σ(N) → Mn(III) LMCT transition. One shoulder that appears at ~20 400 cm^{-1} (ϵ_{max},

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530 M^{-1} cm^{-1}) may be attributed to the ligand field transition. The higher intensity of this band is due to intensity borrowing from the nearby charge-transfer band.[44] For the Cu(II) complex (**2**), the ligand field transition occurs as a single broad band centering at 15 870 $cm^{-1}$with an ϵ_{max} of 65 M^{-1} cm^{-1}. In addition, two intense bands appear at higher energies. The peak that appears at 35 715 cm^{-1} (ϵ_{max}, 3830 M^{-1} cm^{-1}) is assignable[45] to the σ(N) → Cu(II) LMCT transition. The strong peak that appears at 27 020 cm^{-1}(ϵ_{max}, 2450 M^{-1} cm^{-1}) is too low for a charge-transfer transition involving a N donor. For tetragonal Cu(II) complexes with phenolate coordination, the Cu(II) → phenolate MLCT absorption occurs[46] near 25 500 cm^{-1}. Therefore, the band at 27 020 cm^{-1} is assignable to the Cu(II) → phenolate MLCT charge-transfer transition. Likewise, the shoulder near 33 330 cm^{-1} (ϵ_{max}, 2700 M^{-1} cm^{-1}) is assigned as the higher energy Cu(II) → π^*-phenolate transition. The lower energy Cu(II) → π^*-phenolate transition which should occur[46] in the near-IR region is not observable in **2**. The electronic spectrum of μ-oxo diferric complexes show[47] a number of bands in the UV, visible and near-IR regions. The complex **3** shows four strong bands at 31 645 (ϵ_{max}, 12 170 M^{-1} cm^{-1}), 35 090 (ϵ_{max}, 21 300 M^{-1} cm^{-1}), 38 460 cm^{-1} (ϵ_{max}, 35 800 M^{-1} cm^{-1}), and 43 480 cm^{-1} (ϵ_{max}, 61 900 M^{-1} cm^{-1}). The band positions as well as intensities compare well with those found[48] for the complex $enH_2[(FeHEDTA)_2O]$, where the angle of the monobridged Fe(III)−O−Fe(III) unit is 165°. Besides, **3** shows a moderately strong band at 20 620 cm^{-1} (ϵ_{max}, 1490 M^{-1} cm^{-1}) assignable[47] as a combination of the LMCT transition involving the exogenous ligand(s) bound to the Fe−O−Fe unit and the ligand field transitions. For **4**−**6**, the electronic spectrum of each complex is dominated by a strong absorption near 25 000 cm^{-1} (ϵ_{max}, ∼1800 M^{-1} cm^{-1}) assignable[43] to σ(N) → Mn(III) LMCT transitions; each of the complexes also exhibits a shoulder near 20 000 cm^{-1} (ϵ_{max}, ∼500 M^{-1} cm^{-1}) which will be due to ligand field transitions. The higher intensity of the ligand field band is attributable to the intensity borrowing[44] from the nearby charge-transfer band.

Magnetic Studies. All the magnetic data were collected in the solid state. Complex **1** gives a μ_{eff} value of 4.90 μ_B at 298 K that corresponds[15,16,19] to a high-spin ($S = 2$) Mn(III) complex with partial quenching of the orbital angular momentum. The magnetic moment number for **2** is 1.91, which is typical[49] of a discrete mononuclear Cu(II) complex. For **3**, the μ_{eff} value is found to be 1.86 μ_B, which compares[34,35] well with the values obtained on monobridged Fe(III)−O−Fe(III) complexes. The effective magnetic moment number (3.01) for **6** indicates[19] that it is low-spin ($S = 1$), the rest are high spin ($S = 2$), and the numbers lie in the range 4.91−4.94. Mn(III) is known[19,50,51] to form low-spin octahedral complexes only with strong donors like cyanide, oxime, or porphyrins. Complexes **6** provides a rare example of a low-spin Mn(III) complex with N and O donors from Schiff base ligands. All our efforts to have this complex in single-crystal form for X-ray crystallographic studies remain unsuccessful. Therefore, whether **6** is a dimer or a monomer cannot be ascertained. However, the cyclic voltammetric results as discussed below indicate that **6** is probably a monomeric species. Complexes **2** in the solid state at 298 K gives a broad EPR signal with $g_{av} = 2.08$, which sharpens somewhat on lowering the temperature to 77 K. In MeCN solution at 298 K, it exhibits a typical four-line signal; in MeCN glass, the signal changes to the one obtained in the solid state. Thus, the EPR spectra of **2** are not indicative of its stereochemistry.

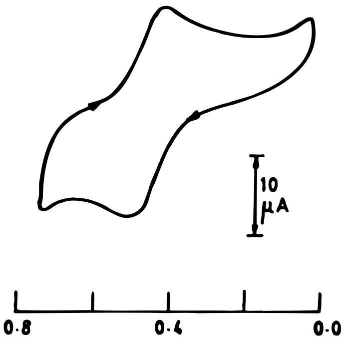

Figure 5. Cyclic voltammogram of **6** in DMF using a glassy carbon working electrode at the scan rate of 50 mV s^{-1}; Bu_4NClO_4 as supporting electrolyte. The potential values shown are vs SCE.

Electrochemistry. Electron-transfer properties of **1**−**6** were probed by room-temperature cyclic voltammetry in DMF. Complex **1** exhibits a quasi-reversible cyclic voltammogram assignable[43] as a Mn(IV)/Mn(III) couple with the following characteristics: $E_{1/2} = 0.14$ (vs SCE), $\Delta E_p = 140$ mV at the scan rate of 50 mV s^{-1} using a glassy carbon working electrode; the ratio $i_{pa}/i_{pc} = 1.0$ within experimental error for the scan rate employed (50, 100, 150, 200, 250 mV s^{-1}); increase in ΔE_p value by 15% on increasing the scan rate from 50 to 250 mV s^{-1}. The Mn(III)/Mn(II) couple does not exhibit down to −1.2 V, showing high stability of the Mn(III) state in the present ligand environment. Complex **6** exhibits a quasi-reversible Mn(IV)/Mn(III) couple (Figure 5) with the following charateristics: $E_{1/2} = 0.54$ (vs SCE), $\Delta E_p = 80$ mV at the scan rate of 50 mV s^{-1} using a glassy carbon working electrode; the $i_{pa}/i_{pc} = 1.0$ within the experimental error for the scan rate employed (50, 100, 150, 200, 250 mV s^{-1}); the ΔE_p value increases by 10% on increasing the scan rate from 50 to 250 mV s^{-1}. The Mn(III)/Mn(II) couple does not show down to −1.2 V. Other complexes do not show any well-defined response in the range studied (−1.2 to +1.0V).

Catalytic Activites of the Complexes. Only complex **2** was found to be able to act as a catalyst in the epoxidation of alkenes by molecular oxygen and 2-methylpropanal[52] (Table 6). The epoxides were the only oxygenation products in these reactions. A direct oxidation without using **2** did not lead to any substantial reaction. In a typical experiment, a substrate (10 mmol) and 2-methylpropanal (20 mmol) were added to actonitrile (15 cm^3)

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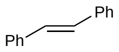
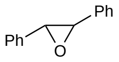
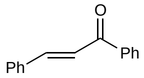
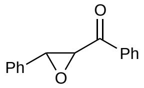
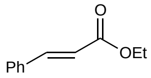
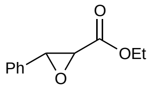
Table 6. Summary of Catalyzed Oxidation of Olefinic Substrates

entry	substrate	product[a]	% yield (isolated)
1			40
2			35
3			22

[a] Characterized by IR and ^{1}H-NMR spectroscopy.

containg **2** (5 mol%) under an atmosphere of molecular oxygen at ambient pressure and temperature. Progress of the reaction was followed by TLC. Aqueous workup followed by column chromatography afforded the corresponding epoxides. In absence of 2-methylpropanal, none of the complexes was able to cause epoxidation even if used stoichiometrically.

In summary, the present work not only shows that aldehyde complexes can be easily synthesized in high yields but also provides the first structurally characterized salicylaldehyde complexes of Mn(III), Fe(III), and Cu(II) ions. These structural studies assume importance in light of the role that aldehydes may play in some metal-catalyzed oxo-transfer systems. The complexes are soluble in common organic solvents where they retain their identities, making them suitable for use in organic transformation reactions of the aldehyde group. The bound aldehyde group in **1** reacts with monoamines forming new Schiff base ligands. Thus, in principle, it is possible to have polynuclear Mn complexes when **1** is allowed to react with polyamino compounds. This will afford the design and synthesize polynuclear Mn complexes of bioinorganic significance. The accessibility of Mn(IV) state (in **6**) with the Schiff base ligands can be profitabely used to have oxo-transfer catalysts. Cu(II) complex **2** shows marginal catalytic activities in the epoxidation of olefins by molecular oxygen in the presence of 2-methylpropanal. In the absence of 2-methylpropanal, however, no catalytic activities could be observed. We have not been able to observe addition or insertion of oxygen into the salicylaldehyde moiety with any of these complexes. Perhaps with lower valent metal complexes such an insertion reaction can be observed. Some of these aspects are presently under investigation in our laboratory.

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Supporting Information Available: Tables of crystallographic data, hydrogen positional parameters, anisotropic thermal factors, and all the bond distances and angles for **1**−**3** (9 pages). Ordering information is given on any current masthead page.

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