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Synthesis and Properties of Manganese(III) Complex of Salen-Analog Containing Phenolic Pendant Group

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Synopsis. A manganese(III) complex, [Mn(sal-pen)], with *N,N'*-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediaminate trianion (sal-pen^{3-}) has been synthesized and characterized. The complex was shown to have a square-pyramidal structure with a pendant phenolate group at the apex. The electronic spectral and electrochemical properties of the complex are discussed in terms of an axial coordination of the phenolate group.

The salen-analog, composed of a planar N_2O_2-donating system and a pendant phenolic group, *N,N'*-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (H_2(sal-Hpen), Fig. 1), functions as a pentadentate ligand to yield iron(III) and cobalt(III) complexes, [M(sal-pen)], with a deprotonated pendant phenolic oxygen at the apical position.1) In general, iron(III) and cobalt(III) complexes with unidentate phenolic ligands readily undergo dissociations of the phenolate groups. On the other hand, it has been shown that [Co(sal-pen)] is very stable in nondonating solvents2) and [Fe(sal-pen)] is stable even in alcohols.3) The stabilities of these complexes in solutions are probably due to a chelating effect of the pendant phenolate group combined at the ethylene backbone of the salen skelton.

In this study, a manganese(III) complex of H_2(sal-Hpen) was prepared and its chemical properties were examined in view of the axial coordination of the pendant phenolic group.

The synthesis of [Mn(sal-pen)] was as follows: an ethanolic solution (10 cm^3) of manganese(II) acetate tetrahydrate (0.3 g) was added to an ethanolic solution (10 cm^3) of H_2(sal-Hpen)1) (0.5 g) and sodium hydroxide (0.1 g) under a nitrogen atmosphere. The resulting pale-orange solution was then stirred for 3 h in the open air. The color of the solution immediately changed from orange to brown. Then, the solvent was evaporated at room temperature to give brown prisms, which were recrystallized from dichloromethane. The yeild was ca. 0.2 g.

Found: C, 62.35; H, 5.52; N, 5.09%. Calcd for $C_{26}H_{25}N_2O_3Mn\cdot 2H_2O$: C, 61.90; H, 5.79; N, 5.55%.

[Mn(salen)Cl] and [Mn(salen)OAc] were prepared by methods described in the literature.4,5)

The effective magnetic moment of [Mn(sal-pen)] is 4.7 BM at room temperature; this corresponds to the value of high-spin manganese(III) complexes (4.7—5.0 BM).6) A small temperature dependance of the moment in the range 80—300 K suggests a monomeric structure for the complex.

[Mn(sal-pen)] exhibits no IR band which can be attributed to an O-H vibration around 3200—3300 cm^{-1}. However, H_2(sal-Hpen), [Cu(sal-Hpen)], and [Ni(sal-Hpen)] show an O-H vibration in this region.1) This suggests that the phenolic O-H in the pendant group becomes deprotonated and coordinated to the metal. By an analogy of the IR spectrum with those of [Fe(sal-pen)] and [Co(sal-pen)], which possess a pentacoordinate structure with an N_2O_2-donating system at the equatorial plane and a phenolic oxygen at the apical site, [Mn(sal-pen)] is presumed to have a square-pyramidal structure with a phenolic oxygen at the apex.

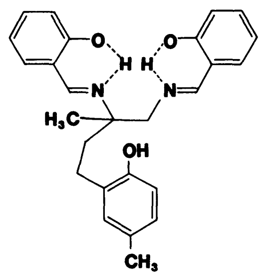

Fig. 1. The chemical structure of H_2(sal-Hpen).

The electronic spectrum of [Mn(sal-pen)] in dichloromethane (1×10^{-3} mol dm^{-3}) exhibits absorption bands at 20.6×10^3 (ε 1450), 25.0×10^3 (3850), 32.3×10^3 (16400), 35.7×10^3 (19200), and 43.5×10^3 (40300) cm^{-1}. The spectrum resembles those of pentacoordinate [Mn(salen)Cl] and [Mn(salen)OAc] with a chloride ion or an acetate ion at the apical site.7) Molar conductivity measurements revealed these Mn complexes to be nonelectrolyte in dichloromethane. Thus, [Mn(sal-pen)] is presumed to have a square-pyramid geometry with a pendant phenolic group at the apex. According to these results, the lowest energy band (20.6×10^3 cm^{-1}) of [Mn(sal-pen)] can be assigned to the d-d band and the absorption at 25.0×10^3 cm^{-1} to the charge-transfer band.7,8) The electronic spectrum of [Mn(sal-pen)] in methanol differs markedly from that in dichloromethane. This suggests a dissociation of the pendant group in polar methanol.4)

The electrochemical properties of [Mn(sal-pen)] were investigated in comparison with those of [Mn(salen)Cl] and [Mn(salen)OAc] by means of polarography and cyclic voltammetry in dichloromethane. A three-electrode cell with a glassy carbon electrode as the working electrode, a platinum coil as the auxiliary electrode, and a saturated calomel electrode as the reference electrode was used for measurements. Tetrabutylammonium perchlorate was used as the supporting electrolyte. All the potentials were normalized using ferrocene as the internal standard (V vs. F_c/F_c^+).9) The electrochemical results are shown in Fig. 2.

[Mn(sal-pen)] exhibits an irreversible wave at +0.32 V and a quasi-reversible wave at −0.76 V. Similar results were obtained for [Mn(salen)Cl] and [Mn(salen)OAc] in this study.10) The redox wave around

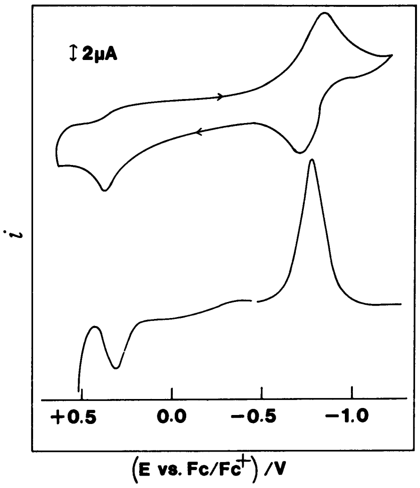

Fig. 2. Cyclic voltammogram (above) and differential pulse polarogram (below) of Mn(sal-pen) in dichloromethane.

−0.7 V was assigned to the Mn(II)/Mn(III) process while the irreversible oxidation at a positive potential was assigned to the Mn(III)/Mn(IV) process.[11–13] There was a slight difference in the Mn(III)/Mn(II) reduction potential among these complexes. The reduction potentials seem to be independant of the axial ligand. This is probably due to the fact that this process is associated with an electron acceptance on the $d_{x^2-y^2}$ orbital and, thus, not substantially influenced by a change in the axial ligand. On the contrary, the Mn(III)/Mn(IV) oxidation potentials are highly dependant upon the axial ligand. This is reasonable since the process involves the release of an electron from the d_{z^2} orbital. This must be much influenced by the charge of the axial ligand. The oxidation of [Mn(sal-pen)] occurred at a considerably lower potential relative to those of [Mn(salen)Cl] and [Mn(salen)OAc]. This suggests that the axial phenolate ligand in [Mn(sal-pen)] donates more strongly than a chloride ion or an acetate ion does.

Manganese(III) complexes with a unidentate phenolate ligand are generally difficult to synthesize because of the high lability of phenolate ligands. The present study reveals that a phenolatomanganese(III) complex can be readily isolated by incorporating a phenolate group into the tetradentate salen moiety.

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10) Redox potentials for [Mn(salen)Cl]: +0.55, −0.69; for [Mn(salen)OAc]: +0.59, −0.72 (V vs. F_c/F_c^+).

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