Polymeric and Monomeric Forms of a Schiff Base–Nitridomanganese(V) Complex. Synthesis and Crystal Structure

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(Received, July 31, 2000; CL-000721)

A novel polymeric nitridomanganese(V) complex with a Schiff base ligand [MnN(salpn)] (H_2(salpn): *N*,*N*'-disalicylidene-1,3-propanediamine) (**1**) was prepared by photolysis of the azidomanganese(III) complex, [MnN$_3$(salpn)] in acetonitrile. The monomeric complex (**2**) was obtained by recrystallization of **1** from methanol. X-ray crystal structure analyses of **1** and **2** were carried out. The brown complex **1** has a linear ···Mn≡N···Mn≡N··· chain structure.

Recently, nitridomanganese(V) complexes with tetradentate Schiff base ligands have been extensively studied as nitrogen atom transfer reagents in the fields of coordination chemistry[1,2] and organic chemistry.[3,4] All of these complexes are green and have five-coordinate monomeric structures with square-pyramidal geometry. If a monomeric nitridomanganese complex itself can function as a ligand, polymeric complex with a linear ···Mn≡N···Mn≡N··· chain structure will be formed. Such polymeric nitridometal complexes have been reported for V, Mo, W, and Re.[5–9]

Here we report the preparation and isolation of both the polymeric and monomeric forms of [MnN(salpn)]. X-ray crystal structures, IR and electronic spectra of both of the species are also reported.

In general, two methods are known for the preparation of nitridomanganese(V) complexes with tetradentate Schiff base ligands: (a) oxidation of manganese(III) complexes with NaClO, PhIO, or NBS in the presence of NH$_3$ and (b) photolysis of azidomanganese(III) complexes.[3] [MnN(salpn)] was not prepared by method (a), but was prepared by method (b). The starting material [MnN$_3$(salpn)] was prepared by the literature method.[10] [MnN$_3$(salpn)] (0.57 g, 1.5 mmol) was suspended in acetonitrile (1 dm^3), and the mixture was irradiated with a 400-W high pressure mercury lamp below 20 °C under an argon atmosphere with stirring. After an hour, another 1.5 mmol of the azido complex was added to the reaction mixture, and the irradiation was continued. This procedure was repeated twice.[11] The reaction mixture containing 6 mmol of the complex was irradiated for two days. The color of the mixture gradually turned from light brown to dark brown during the irradiation. Then the mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in dichloromethane, and applied on a silica gel column (ϕ 3.5 cm × 20 cm). The product was eluted with dichloromethane–ethyl acetate (10:1 v/v). The effluent containing a green band was collected, and evaporated to dryness to yield brown needle crystals of [MnN(salpn)] (**1**). Yield: 0.68 g (33%).[12] Green crystals of [MnN(salpn)]·CH$_3$OH (**2**) were obtained by recrystallization of **1** from methanol. These complexes are stable in air at ambient temperature.

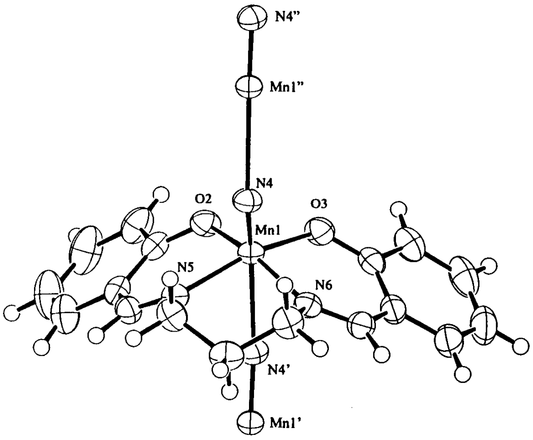

Figure 1. ORTEP drawing of [MnN(salpn)] (**1**) with 50% probability ellipsoids. The Mn≡N moieties of the neighboring complexes are also shown. Selected bond lengths (Å) and angles (°): Mn1–O2, 1.925(2); Mn1–O3, 1.927(2); Mn1–N4, 1.520(3); Mn1–N4', 2.528(3); Mn1–N5, 1.997(2); Mn1–N6, 1.990(2); N4–Mn1–N4', 170.15(6); Mn1–N4'–Mn1', 152.5(1). Primed atoms are generated by 3/2 – x, 1 – y, 1/2 + z.

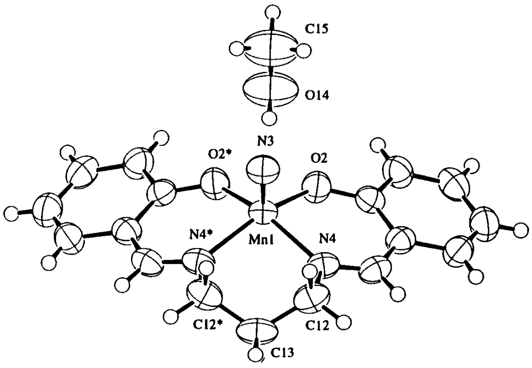

Figure 2. ORTEP drawing of [MnN(salpn)] •CH$_3$OH (**2**) with 50% probability ellipsoids. Selected bond lengths (Å): Mn1–O2, 1.914(2); Mn1–N3, 1.513(3); Mn1–N4, 2.002(2).

X-Ray structure analyses of **1** and **2** were carried out.[13,14] ORTEP drawings of **1** and **2** are shown in Figures 1 and 2. Complex **1** has a polymeric structure with distorted octahedral coordination geometry. The linear ···Mn≡N···Mn≡N··· chains run along the 2_1 screw axes parallel to the *c* axis. The Mn≡N distance is 1.520(3) Å, and the Mn1 atom is displaced by 0.343(1) Å from the N$_2$O$_2$ coordination plane. The Mn···N distance is 2.528(3) Å. Complex **2** has a monomeric structure with square-pyramidal coordination geometry and has crystallographic mirror symmetry. The Mn≡N distance is 1.513(3) Å, and the Mn1 atom is displaced 0.444(1) Å from the N$_2$O$_2$ coordination plane. The O14 atom of methanol is hydrogen bonded to the O2 and O2* atoms of the complex with the O14···O2 distance of 2.964(4) Å. Both of the six-membered N—N chelate rings in **1** and **2** show a chair conformation. The Mn–N bond lengths in the six-membered N—N chelate rings of **1** (1.997(2) and 1.990(2) Å) and **2** (2.002(2) Å) are longer than those in the five-membered N—N chelate ring of monomeric [MnN(salen)] (1.946(3) Å).[3]

The IR spectra of **1** and **2** show the Mn≡N stretching band at 1011 and 1043 cm^{-1}, respectively. The Mn≡N stretching frequency of the polymeric complex is shifted to lower energy than that of the monomeric one. The electronic spectra of **1** and **2** in the solid state,[15] and in acetonitrile are shown in Figure 3.

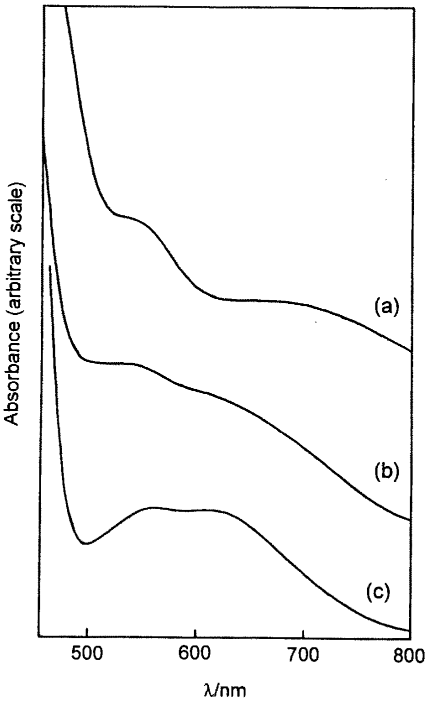

Figure 3. Electronic spectra of (a) **1** and (b) **2** in the solid state, and (c) [MnN(salpn)] (**1** or **2**) in acetonitrile.

Complexes **1** and **2** show almost the same spectrum in acetonitrile, dichloromethane, and DMSO. This result indicates that **1** and **2** have a mononuclear square-pyramidal structure in solution. The spectrum in acetonitrile shows two d–d transition bands at 621 nm (band I) and at 559 nm (band II). The bands I and II can be assigned to the $^1A'[a'(x^2-y^2)]^2 \rightarrow {}^1A'[a'(x^2-y^2)a'(yz)]$ and $^1A'[a'(x^2-y^2)]^2 \rightarrow {}^1A''[a'(x^2-y^2)a''(xz)]$ transitions, respectively.[16] In the spectrum of [MnN(salen)], the corresponding two bands are overlapped and not resolved. The spectrum of green **2** in the solid state shows two shoulders around 640 and 553 nm, and the spectrum is similar to that in acetonitrile. On the other hand, the spectrum of brown **1** in the solid state shows two shoulders around 706 and 553 nm.

In this study, a novel polymeric nitridomanganese(V) complex was prepared by photolysis of the azidomanganese(III) complex. Formation of the polymeric structure for [MnN(salpn)] may be attributed to (a) the weak coordination ability of the salpn ligand compared with salen-type ligands, and (b) crystal packing efficiency.[17]

The authors thank Professor Claus E. Schäffer and Dr. Jesper Bendix of University of Copenhagen for valuable discussions.

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12 [MnN(salpn)]: Anal. Found: C, 58.32; H, 4.64; N, 12.00%. Calcd for $C_{17}H_{16}MnN_3O_2$: C, 58.46; H, 4.62; N, 12.03%. The complex is diamagnetic in the solid state. ^{13}C NMR ($CDCl_3$, TMS): δ 27.8 (C-$\underline{C}$-C), 63.3 (N-$\underline{C}$-C), 115.9, 117.8, 121.9, 133.4, 135.9, 166.0, 168.1 (Ar and N=$\underline{C}$-C). UV–vis spectrum {CH_3CN, λ/nm (log ε/$M^{-1}cm^{-1}$)}: 621 (2.09), 559 (2.13), 444 (sh), 373 (3.79), 268 (4.31), 244 (4.43).

13 Brown needle crystals of [MnN(salpn)] (**1**) were grown from an acetonitrile solution. Crystal data: $C_{17}H_{16}MnN_3O_2$, MW = 349.27, orthorhombic, space group $P2_12_12_1$ (No.19), a = 11.721(1) Å, b = 16.797(2) Å, c = 7.875(2) Å, V = 1550.5(5) $Å^3$, Z = 4, D_c = 1.496 g cm^{-3}, μ(Mo Kα)= 0.864 mm^{-1}, crystal size = 0.40 × 0.10 × 0.10 mm, 2445 reflections measured, 2053 unique reflections. Refinement was based on F^2 with $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.0292P)^2 + 0.3999P$, where $P = (F_o^2 + 2F_c^2)/3$ against all the 2053 reflections. The R value $[\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o)^2]^{1/2}$ was 0.028 for the 1606 reflections with $I > 2\sigma(I)$. The R_w value was 0.071. The absolute structure was determined by the Flack parameter, x = – 0.03(3).

14 Green prismatic crystals of [MnN(salpn)]·CH_3OH (**2**) were grown from a methanol solution. Crystal data: $C_{18}H_{20}MnN_3O_3$, MW = 381.31, orthorhombic, *Pnma* (No.62), a = 8.939(3) Å, b = 15.944(1) Å, c = 12.440(1) Å, V = 1773.0(5) $Å^3$, Z = 4, D_c = 1.428 g cm^{-3}, μ(MoKα)= 0.766 mm^{-1}, crystal size = 0.50 × 0.50 × 0.38 mm, 2491 reflections measured, 2109 unique reflections. The Mn1, N3, C13, O14, and C15 atoms lie on a mirror plane. Refinement was based on F^2 with $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.0372P)^2 + 1.3326P$, where $P = (F_o^2 + 2F_c^2)/3$ against all the 2109 reflections. The R value $[\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o)^2]^{1/2}$ was 0.038 for the 1611 reflections with $I > 2\sigma(I)$. The R_w value was 0.103.

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