Variable Coordination Geometries in Manganese(II): Eight-, Seven-, and Six-Coordinate Mn(II) Complexes with Pyridyl-Containing Schiff-Base Ligands

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Eight-, seven-, and six-coordinate manganese(II) complexes with *N,N'*-bis(2-pyridinylmethylene)-1,3-diaminopropan-2-ol (HL) and *N,N'*-bis(2-pyridinylmethylene)-1,3-diaminopropane (L'), $[Mn(HL)(NO_3)_2]\cdot C_2H_5OH$, $[Mn(L')(NO_3)_2]$, $[Mn(L')(bipy)(CH_3OH)](ClO_4)_2$, $[Mn(L')(phen)](ClO_4)_2$, and $[Mn_2(L)(CH_3COO)(phen)_2](ClO_4)_2\cdot H_2O$, have been isolated and characterized by X-ray crystallography.

There has been considerable interest in coordination chemistry of manganese complexes because of the significant involvement of manganese in various biological systems.[1] This results in many reports on manganese(II) complexes. Manganese(II) ion has usually a high-spin d^5 electron configuration, which offers no crystal field stabilization energy for any geometry. Thus it might be expected that various coordination geometries would be as common as a typical octahedral configuration. However, the great majority of structurally characterized Mn(II) complexes take invariably a six-coordinate octahedral geometry around the metal atom and complexes with coordination numbers exceeding six are uncommon for Mn(II).[2] We report here a novel series of eight-, seven-, and six-coordinate Mn(II) complexes in our Schiff-base ligand system.

Pyridyl group seems to stabilize Mn(II) state and we obtained Mn(II) species by using some pyridyl-containing ligands.[3] These complexes have also an octahedral geometry around the Mn(II) atom. However, when *N,N'*-bis(2-pyridinylmethylene)-1,3-diaminopropan-2-ol (HL) was reacted with $Mn(NO_3)_2\cdot 6H_2O$ in EtOH, pale yellow plates of $[Mn(HL)(NO_3)_2]\cdot C_2H_5OH$ (**1**) have been isolated. The X-ray crystallography of **1** reveals an eight-coordinate Mn atom which has a distorted square antiprism with four N atoms of HL and four O atoms of two bidentate NO_3 groups (Figure 1).[4] Such an example of square-antiprismatic coordination geometry is very few, although other eight-coordinate geometries have been found for Mn(II).[5-7] The Mn-N and Mn-O distances [Mn-N 2.273(4)—2.354(4), Mn-O2 2.354(5), Mn-O3 2.547(5), Mn-O5 2.292(4), Mn-O6 2.502(5) Å] are comparable to those observed in the eight-coordinate Mn(II) complex $[Mn(dppn)(NO_3)_2]$ (dppn = 3,6-di-2-pyridylpyridazine) [Mn-N 2.29(1)—2.33(1) Å, Mn-O 2.30(2)—2.47(1) Å].[6] The IR spectrum exhibits absorptions indicative of the asymmetric bidentate nature of the NO_3 groups [$\nu(NO_3)$ 1459s, 1443s, 1326s, 1301s cm^{-1}].[6] By using a related Schiff base, *N,N'*-bis(2-pyridinylmethylene)-1,3-diaminopropane (L'), we have also isolated an analogous eight-coordinate complex, $[Mn(L')(NO_3)_2]$ (**2**), which has a square-antiprismatic geometry.[4]

When the ligand L' was treated with $Mn(ClO_4)_2\cdot 6H_2O$ and 2,2'-bipyridyl (bipy) in MeOH/EtOH, we have isolated a seven-coordinate Mn(II) complex, $[Mn(L')(bipy)(CH_3OH)](ClO_4)_2$ (**3**). The X-ray crystal structure of **3** shows that metal coordination site is a novel geometry for seven-coordinate Mn(II) complexes, monocapped trigonal prism, made up by four N atoms of L', two N atoms of bipy, and one methanol O atom (Figure 2).[4] The Mn-N and Mn-O distances are 2.283(4)—2.363(4) and 2.304(3) Å, respectively. Most of reported seven-coordinate Mn(II) complexes have a pentagonal bipyramidal geometry around the metal atom[8] and very few examples are structually verified as a distorted monocapped trigonal prism.[9]

A six-coordinate Mn(II) complex, $[Mn(L')(phen)](ClO_4)_2$ (**4**), has been isolated from the reaction of the ligand L' with

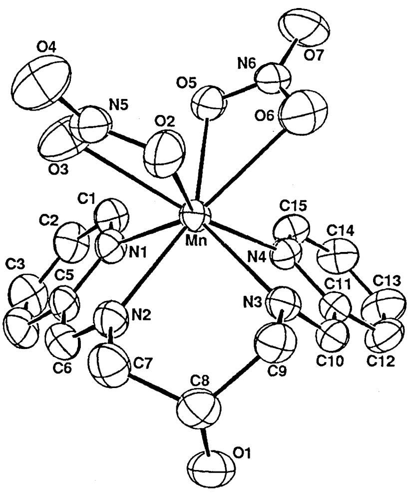

Figure 1. Perspective view of **1**.

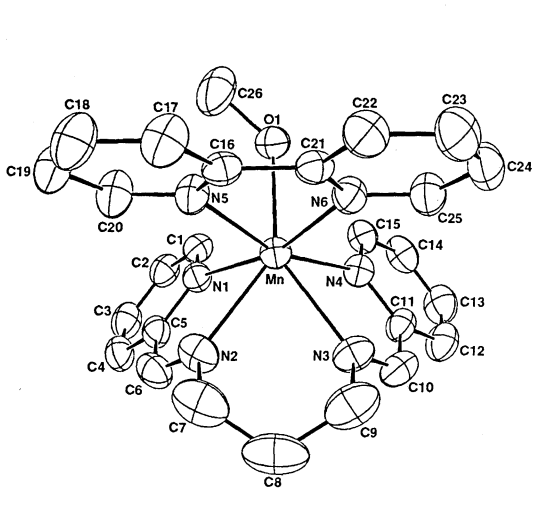

Figure 2. Perspective view of **3**.

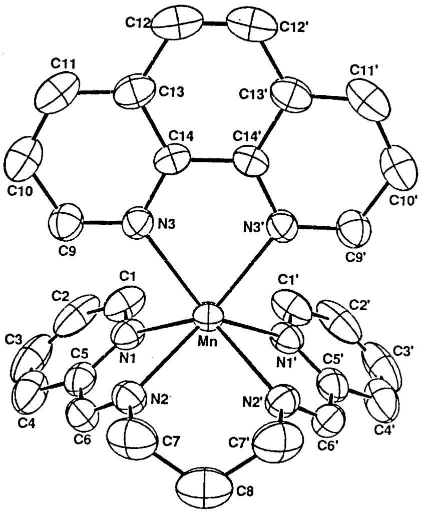

Figure 3. Perspective view of **4**.

$Mn(ClO_4)_2 \cdot 6H_2O$ in the presence of 1,10-phenanthroline (phen). In the crystal structure of **4** (Figure 3),[4] the manganese atom has a trigonal prism with four N atoms of L' and two N atoms of phen. The Mn-N distances are 2.240(5)—2.286(5) Å. Only few examples exist for this geometry.[10,11]

Magnetic moments of these complexes correspond to a high-spin configuration: **1**, 5.73 B.M. (295 K); **2**, 5.98 B.M. (289 K); **3**, 5.89 B.M. (295 K); **4**, 5.88 B.M. (285 K). The X-band ESR spectra for polycrystalline samples of **1**—**4** gave a broad signal around g = 2 which could not be distinguished by the coordination geometries.

In the present series of complexes, the basal four N atoms from the ligand HL or L' are in a nearly planar arrangement, leaving ample space for four, three, or two more donors in the opposite site. A similar range of bond lengths of the basal Mn-N bonds is observed for these complexes and this may be ascribed to the steric constraints forced on the coordination sphere by the Schiff-base ligand. One might expect an octahedral geometry in the absence of the steric requirement of the Schiff-base ligand.

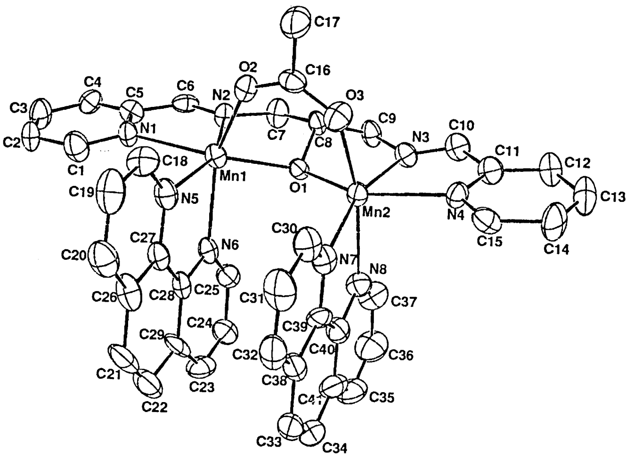

Figure 4. Perspective view of **5**.

Indeed, we have been able to isolate the perchlorate salt of $[Mn_2(L)(CH_3COO)(phen)_2](ClO_4)_2 \cdot H_2O$ (**5**), the dinuclear Mn(II) complex having an octahedral geometry (Figure 4),[4] by the reaction of HL with $Mn(CH_3COO)_2 \cdot 4H_2O$ in the presence of phen, Et_3N, and $NaClO_4$. In **5**, the deprotonated L ligand does not keep the basal N_4 plane, but forms an N_2ON_2 plane bridging the two Mn atoms. The Mn-Mn distance is 3.518(3) Å. Interestingly, the two phen groups are coordinated to the two Mn atoms in a fashion to form some π-π stacking interaction between them.

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References and Notes

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4 Crystallographic data: for **1**; $C_{17}H_{22}MnN_6O_8$, F.W. = 493.3, monoclinic, space group $P2_1/a$, a = 9.618(2), b = 27.984(3), c = 8.255(2) Å, β = 99.85(1)°, V = 2189.8(8) Å^3, Z = 4, D_m = 1.49, D_c = 1.50 gcm^{-3}, μ(Mo Kα) = 6.31 cm^{-1}, 4397 reflections measured ($2\theta_{max}$ = 52°), 2847 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.057, R_w = 0.069. For **2**; $C_{15}H_{16}MnN_6O_6$, F.W. = 431.3, monoclinic, space group $P2_1/a$, a = 19.098(4), b = 7.277(1), c = 13.585(3), β = 106.06(1)°, V = 1814.3(6) Å^3, Z = 4, D_m = 1.60, D_c = 1.58 gcm^{-3}, μ(Mo Kα) = 7.43 cm^{-1}, 3277 reflections mesured ($2\theta_{max}$ = 49°), 1503 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.044, R_w = 0.052. For **3**; $C_{26}H_{28}Cl_2MnN_6O_9$, F.W. = 694.4, monoclinic, space group $P2_1/a$, a = 18.173(2), b = 10.416(1), c = 17.688(2) Å, β = 113.68(1)°, V = 3066.1(6) Å^3, Z = 4, D_m = 1.51, D_c = 1.50 gcm^{-3}, μ(Mo Kα) = 6.47 cm^{-1}, 5112 reflections measured ($2\theta_{max}$ = 48°), 3553 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.052, R_w = 0.060. For **4**; $C_{27}H_{24}Cl_2MnN_6O_8$, F.W. = 686.4, orthorhombic, space group $Pnma$, a = 18.846(4), b = 11.628(1), c = 13.438(2) Å, V = 2944.8(8) Å^3, Z = 4, D_m = 1.53, D_c = 1.55 gcm^{-3}, μ(Mo Kα) = 6.70 cm^{-1}, 2790 reflections measured ($2\theta_{max}$ = 49°), 1276 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.046, R_w = 0.052. For **5**; $C_{41}H_{36}Cl_2Mn_2N_8O_{12}$, F.W. = 1013.6, triclinic, space group $P1$, a = 11.843(8), b = 12.067(12), c = 16.835(17) Å, α = 84.51(6)°, β = 76.01(7)°, γ = 82.58(7)°, V = 2310(4) Å^3, Z = 2, D_m = 1.50, D_c = 1.46 gcm^{-3}, μ(Mo Kα) = 7.06 cm^{-1}, 5654 reflections measured ($2\theta_{max}$ = 44°), 2608 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.069, R_w = 0.085. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.

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