Synthesis, Structure, and Magnetic Properties of Triply Carboxylato-Bridged Dimanganese(II) Complexes

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Two dinuclear manganese(II) complexes, [$Mn_2(Ph_2MeCCOO)_3(bpy)_2](PF_6)$ (**1**) and [$Mn_2(C_6H_5COO)_3(CH_3OH)(bpy)_2](NO_3)$ (**2**), have been prepared. X-Ray structural analyses have revealed that complexes **1** and **2** have a different bridging mode in triple carboxylato-bridges between two manganese(II) ions each other.

A large number of transition metal complexes with carboxylato-bridges have been prepared. In the manganese chemistry, however, manganese(II) complexes containing only carboxylate ions as bridging ligands are still rare.[1,2] We have prepared two dinuclear manganese(II) complexes with different bridging modes consisting of three carboxylato-bridges. In this paper, we report on the preparation, the structural characterization, and the magnetism of the dimanganese(II) complexes, [$Mn_2(Ph_2MeCCOO)_3(bpy)_2](PF_6)$ (**1**) and [$Mn_2(C_6H_5COO)_3(CH_3OH)(bpy)_2](NO_3)$ (**2**), where bpy is 2,2'-bipyridine and $Ph_2MeCCOO$ is 2,2-diphenylpropionato ion.

The compounds were obtained as follows. Complex **1**: The $Mn(Ph_2MeCCOO)_2{\cdot}(CH_3)_2SO$ complex (1.2 mmol), which was prepared by using the technique described in the literature[3], was dissolved in 30 cm^3 of methanol. To this solution a solution of bpy (1.2 mmol) in 18 cm^3 of methanol and a solution of ammonium hexafluorophosphate (0.6 mmol) in 6 cm^3 of water were added under stirring. The reaction mixture was filtered, and the filtrate was allowed to stand for a few days at room temperature. Pale yellow crystals were collected, washed with cold methanol, and dried *in vacuo*. Complex **2**: To a solution of bpy (2 mmol) in 5 cm^3 of methanol manganese(II) nitrate hexahydrate (2 mmol) and a solution of benzoic acid (2 mmol) in 5 cm^3 of methanol were added under stirring, and the resulting solution was adjusted to pH 6.3 with aqueous sodium hydroxide. After stirring for about 30 min., the brownish-yellow solution was filtered and the filtrate was stored for one day at room temperature. Yellow crystals were collected, washed with cold methanol, and dried in air. Efflorescence in crystals of complex **2** took place readily and gave [$Mn_2(C_6H_5COO)_3(bpy)_2](NO_3)$ (**2'**). Anal. Found (**1**) : C, 62.86; H, 4.49; N, 4.47; Mn, 9.01%. Calcd for $C_{65}H_{55}F_6Mn_2N_4O_6P$: C, 62.78; H, 4.47; N, 4.50; Mn, 8.84%. Found (**2'**) : C, 57.91; H, 3.51; N, 8.12; Mn, 12.93%. Calcd for $C_{41}H_{31}Mn_2N_5O_9$: C, 58.04; H, 3.69; N, 8.25; Mn, 12.96%.

The crystal structures of complexes **1** and **2** are shown in Figures 1 and 2, respectively.[4,5] The complex cation of **1** consists of two manganese(II) ions linked by three bidentate bridging carboxylates of diphenylpropionate groups. This is the first example of the triply carboxylato-bridged dimanganese(II) complex with a pentacoordinated Mn(II) geometry. The coordination environment of each manganese(II) ion is a distorted trigonal-bipyramidal geometry. The equatorial plane for Mn1 is composed of O1, O5 and N2, and axial sites are occupied by O3 and N1. While, for Mn2, the equatorial plane is composed of O2, O6 and N3, and axial sites are occupied by O4 and N4. A considerable variation in the Mn-O-C angles is observed, 112.2-162.7°, with the largest Mn-O-C angle(162.7°) encompassing the shortest Mn-O bond(2.009Å). However, there is no corresponding opening of the O-C-O angle; the mean value is 124.3°. The most unusual feature of the structure in **1** is the dihedral angle(δ) observed between the least-squares planes through the bridging carboxylates, [O_a, C, O_b] and [O_a, O_b, Mn].

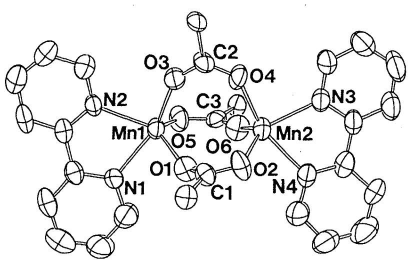


Figure 1. An ORTEP drawing for the complex cation **1**. Phenyl rings and methyl groups were omitted for clarity. Selected bond distances(Å) and angles(°): Mn1...Mn2 3.688(8), Mn1-O1 2.082(8), Mn1-O3 2.094(7), Mn1-O5 2.114(6), Mn1-N1 2.221(8), Mn1-N2 2.250(8), Mn2-O2 2.098(7), Mn2-O4 2.089(7), Mn2-O6 2.009(8), Mn2-N3 2.205(9), Mn2-N4 2.228(8); Mn1-O1-C1 148.1(7), Mn1-O3-C2 144.0(6), Mn1-O5-C3 113.4(7), Mn2-O2-C1 112.2(7), Mn2-O4-C2 133.7(7), Mn2-O6-C3 162.7(7).

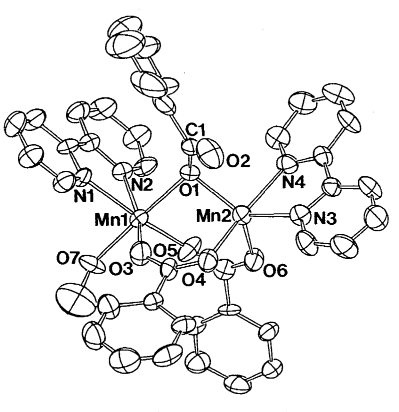
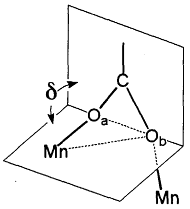


Figure 2. An ORTEP drawing for the complex cation **2**. Selected bond distances(Å) and angles(°): Mn1...Mn2 3.498(4), Mn1-O1 2.229(8), Mn1-O3 2.121(8), Mn1-O5 2.121(8), Mn1-O7 2.22(1), Mn1-N1 2.266(9), Mn1-N2 2.237(9), Mn2...O2 2.54(1), Mn2-O1 2.206(8), Mn2-O4 2.098(9), Mn2-O6 2.127(8), Mn2-N3 2.23(1), Mn2-N4 2.27(1); Mn1-O1-Mn2 104.1(3), Mn1-O1-C1 130.9(8), Mn2-O1-C1 95.8(8), O1-Mn2-N3 142.2(3), O1-Mn2-O6 106.5(3), O6-Mn2-N3 105.9(3).



The values of δ are 134.6° for [the O1, C1, O2 plane /the O1, O2, Mn1 plane] and 158.7° for [the O5, C3, O6 plane /the O5, O6, Mn2 plane], and are very different from 180°. This large distortion from the regular *syn-syn* carboxylato-bridging mode toward the *syn-anti* mode is uncommon in dinuclear manganese(II) complexes. The distortion of the *syn-syn* mode is probably caused by the stereochemical requirement of the trigonal-bipyramidal geometry around each manganese(II) center. The two carboxylato bridges of O1–C1–O2 and O5–C3–O6 through each equatorial site have a large distortion, whereas the strain in the O3–C2–O4 bridge through each axial site is very small (δ=179.5°). The Mn...Mn distance in **1** (3.688Å) is considerably longer than those reported in μ-hydroxo- or μ-phenoxo-bis(μ-carboxylato)dimanganese(II) complexes.[1] The distance is, however, fairly shorter than that reported for the complex, $[Mn_2(CH_3COO)_3L'_2](BPh_4)$, where L' is *N,N',N''*-trimethyl-1,4,7-triazacyclononane, possessing an analogous structure of **1** (4.034Å).[6]

The complex cation of **2** consists of a dimanganese(II) core with three benzoate bridges, two bidentate ligands of bpy, and one methanol molecule. The Mn1 ion has pseudo-octahedral geometry with three oxygen atoms(O1, O3, O5) of three bridging benzoates, two nitrogen atoms(N1, N2) of bpy, and one oxygen atom(O7) of a methanol molecule. Whereas, the coordination around Mn2 is a distorted trigonal-bipyramidal geometry with O1, O6 and N3 in the equatorial plane and O4 and N4 at apices. In **2**, two of the benzoates are in the familiar bidentate *syn-syn* bridging mode, and the other has the rare μ_2,η^1 bridging mode.[2,7] This type of the triply bridging mode is the first example for dinuclear manganese(II) complexes. This unusual bridging mode makes a significant difference in the length of the two carboxylato CO bonds. The C1–O1 distance is 1.32Å, whereas the C1–O2 distance is 1.20Å. The Mn2...O2 distance is 2.54Å and the dangling benzoate ligand is tilted toward Mn2, as obviously in the Mn1–O1–C1 angle(130.9°) being significantly larger than the Mn2–O1–C1 angle(95.8°). Consequently, in the equatorial plane, the O1–Mn2–N3 angle increases to 142.2° and the O1–Mn2–O6 and O6–Mn2–N3 angles correspondingly decrease to 106.5° and 105.9°, respectively. The weak bonding interaction between Mn2 and the dangling benzoate oxygen O2 may cause this distortion from the regular trigonal-bipyramidal configuration. It seems that the formation of these two complexes with the different carboxylato-bridging modes is attributable to the difference in the extent of steric hindrance on the carboxylato groups.

Magnetic susceptibility measurements for complexes **1** and **2'** were carried out in the temperature range of 80–300K. Temperature dependence of magnetic susceptibilities(χ_A) and effective magnetic moments(μ_{eff}) per Mn(II) ion for **1** and **2'** are shown in Figure 3. The μ_{eff} values of **1** and **2'** at the room temperature are 5.92 B.M. and 5.84 B.M., respectively, and slightly decrease with decreasing temperature down to 5.83 B.M. and 5.54 B.M. at 80.9 K and 81.3 K, respectively. A least-squares fitting procedure of the magnetic data to the theoretical expression derived from Heisenberg model spin-exchange Hamiltonian ($H = -2J\, S_1 \cdot S_2$; $S_1 = S_2 = {}^5/_2$) gave the following spin exchange coupling parameters : (**1**), $-J = 0.2$ cm^{-1}; (**2'**), $-J = 1.1$ cm^{-1}. These results suggest that a weak antiferromagnetic interaction is operative in **1** and **2'**.

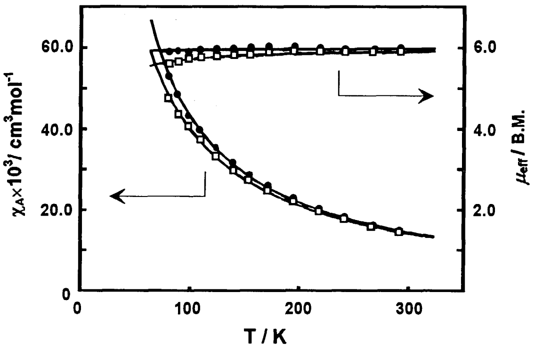


Figure 3. Magnetic susceptibilities χ_A and effective magnetic moments μ_{eff} for **1**(●) and **2'**(□). The solid curves were obtained as described in the text.

References and Notes

1 L. Que, Jr. and A. E. True, *Prog. Inorg. Chem.*, **38**, 97(1990), and references cited therein.

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3 S. Husebye, M. Kato, K. Maartmann-Moe, Y. Muto, M. Nakashima, and T, Tokii, *Acta Chem. Scand.*, **48**, 628(1994).

4 Crystal data for **1**: $C_{65}H_{55}F_6Mn_2N_4O_6P$, Mw = 1243.02, monoclinic, $P2_1/n$, a = 10.63(2), b = 21.808(2), c = 25.345(4) Å, β = 92.64(5)°, V = 5870(12) Å^3, Z = 4, D_{calcd} = 1.407 g cm^{-3}, R = 0.057 and R_w = 0.061 for 7948 unique reflections.

5 Crystal data for **2**: $C_{42}H_{35}Mn_2N_5O_{10}$, Mw = 879.65, triclinic, $P\bar{1}$, a = 12.15(2), b = 17.158(8), c = 10.524(3) Å, α = 92.72(4), β = 91.0(1), γ = 106.95(7)°, V = 2096(3) Å^3, Z = 2, D_{calcd} = 1.394 g cm^{-3}, R = 0.063 and R_w = 0.072 for 5489 unique reflections.

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