Synthesis and Structure of Tetrakis Carboxylato-Bridged Dinuclear Manganese(II) Quinoline Complexes, with Carboxylates Diphenylacetate and 2,2-Diphenylpropanoate

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Two dinuclear Mn(II) quinoline complexes with diphenylacetate **1** or 2-2-diphenylpropanoate **2** have been prepared. Single crystal X-ray crystallography revealed the molecular structure to be the form of copper(II) acetate's. Bonding distances Mn-Mn, Mn-O, and Mn-N for **1** are 3.131(2), 2.116, and 2.193(5) Å, respectively, and those for **2** are 3.168(4), 2.117, and 2.215(4) Å, respectively. Anomalousness of Mn-Mn magnetic interaction of this type complexes is demonstrated.

In the recent paper of dinuclear Ni(II) complexes,[1] we have pointed out that the measured temperature dependence of magnetic susceptibility, $\chi_A - T$, data is poorly reproduced by the equation of Heisenberg-Dicac-Van Vleck (HDVV). The deviation is apparent in the cases where medium M-M magnetic interaction is expected. For the search of systematic trend in the anomalousness of $\chi_A - T$. data, an equation which is a summation of Bleany-Bowers (BB) equations was introduced.[1] Since the equation consists of only convenient pairs, this treatment can be called exclusive pair interaction (EPI) model. The model is a speculative extraporation from the diamagnetism toward the paramagnetism while HDVV is that of in the opposite direction. Difference between HDVV and EPI equations increases with increasing $-J$ and number of unpaired electrons. Since Mn(II) is d^5, study of this difference on high-spin Mn(II) complexes is definitely important. Dinuclear complexes with four carboxylate bridges, $[Mn(RCOO)_2L]_2$, are expected to meet these demands. However, only a few Mn(II) carboxylate dimers of this form have been prepared.[2,3] Therefore, preparation of this type complexes is important for the further investigation. In this study, we are sucessful in preparing the complexes in the case of R=ph_2CH or ph_2MeC and L=quinoline (quin) and the structures were confirmed by X-ray structure analysis.

The preparation is as follows. Diphenylacetic acid or 2,2-diphenylpropanoic acid (4.2 mmol or 4.4 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (2 mmol) were dissolved with 1-butanol (15 ml) stirring at 60 °C. The solution was condensed by evaporation to about 2 ml under reduced pressure at ca. 75 °C. The evaporation was repeated three times after adding 15 ml of 1-butanol each time to remove released acetic acid. The condensed solution was dissolved with 5 ml of 1-butanol then quin (2 mmol) in p–xylene (3 ml) was added and kept heating at 75 °C. After heating two hours, the solution was kept at room temperature overnight. The crystals of slight yellow color were collected and washed with p–xylene. The yields for the both cases were ca. 35%. Anal. **1**: Found: C, 73.26; H, 4.87; N, 2.29; Mn, 8.88%. Calcd for $C_{37}H_{29}MnNO_4$: C, 73.26; H, 4.83; N, 2.31; Mn, 9.06%. **2**·(p–xylene): Found: C, 75.00; H, 5.62; N, 2.03; Mn, 8.30%. Calcd for $C_{42}H_{36}MnNO_4$: C, 75.09; H, 5.58; N, 2.04; Mn, 7.99%. The crystals of **2** suitable for X-ray analysis were obtained under the non-xylene condition and standing the solution for three days, but the yield was low.

The centrosymmetric dinuclear structure, two square-

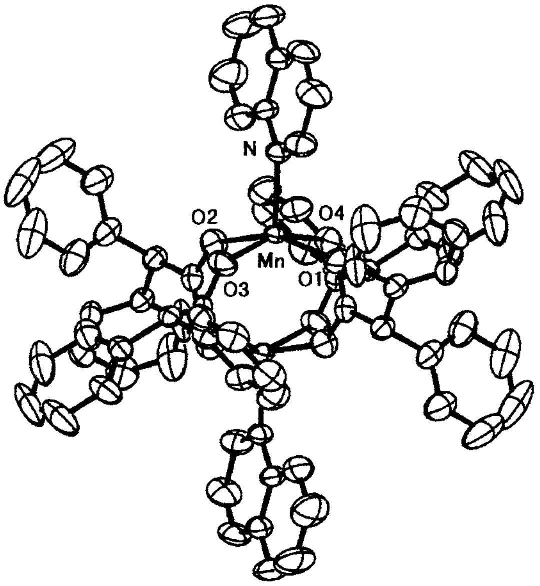

Figure 1. An Ortep drawing of Complex **1**.

Table 1. Selected bond distances(Å) and angles(°)

	1	2	Ref. 2
Mn-Mn	3.131(2)	3.168(4)	3.679
Mn-O1	2.132(4)	2.200(4)	
Mn-O2	2.108(4)	2.162(4)	
Mn-O3	2.107(4)	2.074(4)	2.19[a]
Mn-O4	2.117(4)	2.034(4)	
Mn-N	2.193(5)	2.215(4)	2.28
O_4-Mn[b]	0.4596	0.4862	
O1-Mn-O2	154.8(1)	154.8(1)	
O3-Mn-O4	154.9(1)	151.6(1)	
O1-Mn-O3	86.8(2)	90.7(1)	
O1-Mn-O4	86.7(2)	82.9(2)	
O2-Mn-O3	89.6(2)	86.2(1)	
O2-Mn-O4	86.1(2)	88.1(1)	
O1-Mn-N	96.7(2)	109.0(1)	
O2-Mn-N	108.5(1)	96.0(1)	
O3-Mn-N	99.8(1)	103.5(1)	
O4-Mn-N	105.0(1)	103.4(1)	

[a] Average of four Mn-O bonds. [b] Distance of Mn from Least square plane of four oxygenes.

pyramids bridged by four carboxylates, is revealed by the X-ray structure analysis.[4] Since the molecules of **1** and **2** have the same core structure, only **1** is shown in Figure 1. The bond distances around Mn(II) are shown in Table 1. Metal-metal, average of equatorial four M-O, and axial M-N distances are 3.131(2) , 2.116, and 2.193(5) Å, respectively, in **1**; and those are 3.168(4), 2.117, and 2.215(4) Å, respectively, in **2**. Those bond distances are larger than the copper(II) complexes of the analogous structure, where usual distances M-M, M-O, and M-N are ca. 2.6, 2.0, and 2.1 Å, respectively.[5] This is expected from the larger ionic size and lack of ligand field stabilization in high spin Mn(II). Between the present complexes, the bond distances are larger in **2**. In addition to this, dispersion of O-M-O angles (82.9-90.7°) in **2** is larger than those (86.1-89.6°) in **1**. This difference is against the -I effect of methyl group in **2** which increase coordinating ability of carboxylate to metals. This inversion is ascribable to the steric interaction of the methyl groups with the phenyl groups in the preiferal regeon. In the only one complex ($R{=}C_3F_7$ and L=bipyridine) so far structurally determined, bond distances Mn-Mn, Mn-O, and Mn-N are 3.679, 2.19, and 2.28 Å, respectively.[2] These bonds are considerably larger than **1** and **2**, following the +I effect of fluoro substitution on carboxylate. The long Mn-Mn distance might suggests distortion toward a trigonal-bipyramidal structure from a square-pyramidal one.[6]

Magnetic susceptibility in the temperature range 80 – 300 K is shown in Figure 2 with the best fit curves of HDVV equation at $g{=}2.0$. Poor fitting is apparent, though, the curves are antiferromagnetic. The values of the interaction parameter, $-J$, were obtained as 14.7 and 15.4 cm^{-1} for **1** and **2**·(p−xylene), respectively. Deviations were partly reduced with $-J{=}19.5$ cm^{-1} at $g{=}2.28$ and $-J{=}20.4$ cm^{-1} at $g{=}2.27$ for **1** and **2**·(p−xylene), respectively. Improvement of the fitting at large g-values is the same trend with the case of Ni(II) complexes.[1] Though, orbital contribution obscurs anomalousness by increasing g-values in Ni(II) complexes. For high-spin Mn(II) complexes, g-values of near 2.3 is apparently not normal where no orbital contibution is expected. In the complex of $R{=}C_3F_7$ reported value is $-J{=}2.6$ cm^{-1}, and it is antiferromagnetic.[2] The magnetic parameters of $R{=}Me_3C$, where L= quin, 2-Mepy, Pph_3, $AsOph_3$, are $-J = 15 \pm 2$ cm^{-1}. The comparison of $R{=}C_3F_7$ and $R{=}Me_3C$ suggests that the basisity of the bridging carboxylate is determinative for the magnetic interaction. However, $-J$ values of **1** and **2**·(p−xylene) is within the range of $-J$ for the latter cases suggesting influence of some other factors. Lack of the X-ray structure data and small $-J$ change by changing L among $R{=}Me_3C$ complexes in the HDVV equation prevent from further discussion. In the present cases, EPI equation consists of five BB equations. Even setting a common g-value to each BB equation, the EPI equation has five J-parameters. At the procedures of least-square fitting, number of J-parameters was reduced by setting $J_{123}{=}J_1{=}J_2 {=}J_3$ and $J_{45}{=}J_4{=}J_5$ to avoid divergence at computing. The curves of the EPI equation fit with the measured points at $g{=}2.00$ and with average deviation of less than 0.5%. Interaction parameters were $-J_{123}{=}161.0$ and $-J_{45}{=}51.9$ cm^{-1} for **1**, and $-J_{123}{=}175.3$ and $-J_{45}{=}54.1$ cm^{-1} for **2**·(p−xylene). Though the EPI equation has no concrete quantum theoretical background, it has given the normal g-value. Study of dimeric Mn(II) complexes with $R{=}ph_2MeC$ and ph_2CH are in progress for the further investigation of the magneto-structural correlation.

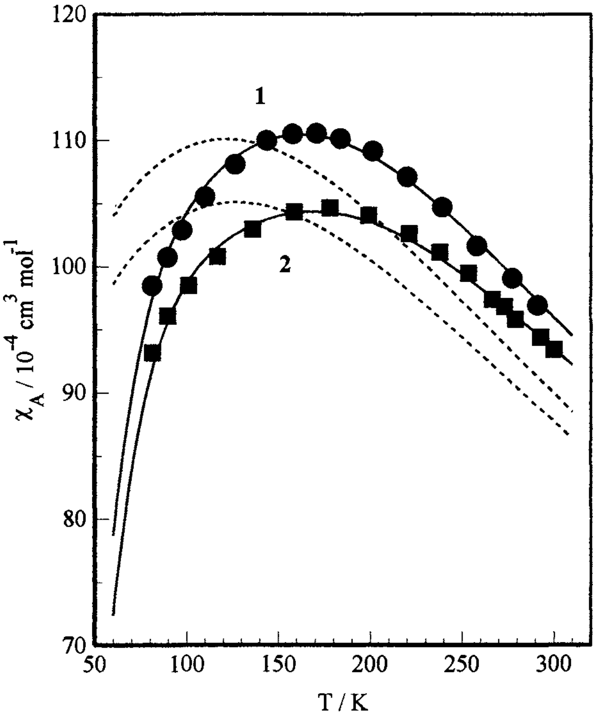

Figure 2. Temperature dependence of magnetic susceptibility. Best fit curves by the EPI equation are solid lines and those by the HDVV equation are dashed lines.

References and Notes

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4 The crystal data for **1**: $C_{74}H_{58}Mn_2N_2O_8$, Mw= 1213.16, triclinic, $P\bar{1}$, $a{=}11.85(2)$, $b{=}12.006(8)$, $c{=}11.484(4)$ Å, $\alpha{=}102.45(4)$, $\beta{=}98.4(1)$, $\gamma{=}70.6(1)°$, $V{=}1500(3)$, $Z{=}1$, $\mu(MoK_\alpha){=}4.61$ cm^{-1}, $Dc{=}1.342$, $R{=}0.048$, $Rw{=}0.049$ (388 variables on 3297 > 3σ); for **2**: $C_{78}H_{66}Mn_2N_2O_8$, Mw=1269.26, triclinic $P\bar{1}$, $a{=}11.63(1)$, $b{=}13.55(2)$, $c{=}11.62(1)$ Å, $\alpha{=}105.9(1)°$, $\beta{=}112.69(7)°$, $\gamma{=}71.56(9)°$, $V{=}1579(7)$ $Å^3$, Z=1, $\mu(MoK_\alpha){=}4.41$ cm^{-1}, $Dc{=}1.334$, $R{=}0.048$, $Rw{=}0.049$ (406 variables on 4128 > 3σ).

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