# Dinuclear Manganese(II) Complex Containing Tetrakis(2-pyridyl)methane as a Spiro-fused Bridge

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A dinuclear manganese(II) complex $[\{Mn(hfac)_2\}_2(py_4C)]$ was synthesized, where hfac and $py_4C$ denote 1,1,1,5,5,5-hexafluoropentane-2,4-dionate and tetrakis(2-pyridyl)methane, respectively. X-Ray crystallographic analysis revealed that the dihedral angle was 87.4(2)° between two chelate rings around the spiro center. Very weak antiferromagnetic interaction is operative between manganese(II) spins.

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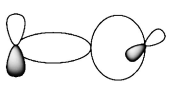
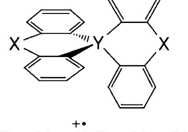
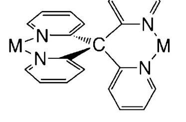
Spiro compounds involving orthogonally fused $\pi$-conjugated moieties are supposed to have potential utility for molecular electronic devices,[1] such as a transistor source-drain channel.[2] The orthogonal arrangement also attracts much attention in magnetochemistry; i.e., in pursuit of ground high-spin systems (**A**, see below).[3–7] Degeneration of singly occupied molecular orbitals has been discussed based on $D_{2d}$ structures like oxygen.[8] Recently, spirobiacridine-derived biradicals (**B**[3] and **C**[7]) have been studied for ground triplet multiplicity. Synthetic efforts can be drastically decreased when genuine organic spin sources are replaced with transition-metal spin sources, but the application of the strategy of organic high-spin molecules to transition-metal complexes is not sufficiently understood with respect to limitation of the $\pi$-conjugation regime.[9] Di- and polynculear complex compounds containing a spiro bridge are rare. Tetrakis(aminomethyl)methanes[10] and spirobi(cyclam)s[11] have been utilized for bridging ligands but they consist of $\sigma$-bond skeletons. The dinuclear spiro complexes involving four Shiff bases has been prepared for 40 years ago, but their physical properties have not yet been studied.[12] We planed to apply the skeleton of **B** and **C** to the coordination compounds (**D**).



**A**



**B** : $X = \overset{+\bullet}{N}\text{-R}$ ; $Y = Si$
**C** : $X = N\text{-}\dot{O}$ ; $Y = C$



**D**

Tetrakis(2-pyridyl)methane ($py_4C$) was synthesized according to the procedure recently reported by Oda and co-workers.[13] A target compound $[\{Mn(hfac)_2\}_2(py_4C)]$ (**1**) was synthesized as follows (hfac denotes 1,1,1,5,5,5-hexafluoropentane-2,4-dionate): Dehydrated $Mn(hfac)_2$ (100 mg from $Mn(hfac)_2{\cdot}2H_2O$; 0.20 mmol) and $py_4C$ (32 mg; 0.10 mmol) in 1/3 $CH_2Cl_2$/heptane (20 mL) was refluxed overnight and then allowed to stand at room temperature for a few days. Light-yellow needle-like crystals of **1** were precipitated together with dark yellow platelet crystals of mononuclear $[Mn(hfac)_2(py_4C)]$ (**2**) as an impurity. The solids were separated on a filter. The crystals of **1** and **2** could be isolated manually under a microscope. The yields of **1** and **2** were 28 and ca. 2%, respectively. The 2/1 and 1/1 metal–ligand ratios of **1** and **2**,[14] respectively, were confirmed by means of elemental analysis (C, H, N) and X-ray crystallographic analysis.

We attempted to synthesize the corresponding dinuclear copper(II) derivatives. We could so far isolate greenish blue $[Cu(hfac)_2(py_4C)]$[14] and green $[Cu(hfac)(py_4C){\cdot}Cu(hfac)_3]$[14] as undesired products. Similarly we tried to prepare oxovanadium(II) derivatives using $VO(hfac)_2$, but no meaningful products were purified.

X-Ray crystallographic analysis revealed the molecular structure of **1** (Figure 1).[15] Two Mn ions are crystallographically independent and coordinated with two pyridine nitrogen atoms each. Other coordination sites are occupied with hfac oxygen atoms. The dihedral angle between two chelate rings, defined with C1–C2–N1–Mn1–N2–C7 and C1–C12–N3–Mn2–N4–C17, is 87.4(2)°, which is very close to the right angle. Jahn–Teller distortion is very small for both Mn; the Mn–O distances vary from 2.140(5) to 2.180(5) Å and the Mn–N distances from 2.222(6) to 2.234(6) Å. The crystal consists of enanthiomerically pure $\Lambda$–$\Lambda$ (or $\Delta$–$\Delta$) configured molecules in a non-centrosymmetric space group $P2_1$.

Figure 2 shows the temperature dependence of the product $\chi_{mol}T$ for **1** on the basis of a molecule. The data were analyzed by the Curie–Weiss equation $[\chi_{mol} = C/(T - \theta)]$ with $C = 8.01$ $cm^3\,K\,mol^{-1}$ and $\theta = -0.12$ K. The theoretical $C$ value should be 8.75 $cm^3\,K\,mol^{-1}$ from $S_{Mn} = 5/2$ and $g = 2$. The somewhat smaller $C$ value observed seems to be due to impurities such as

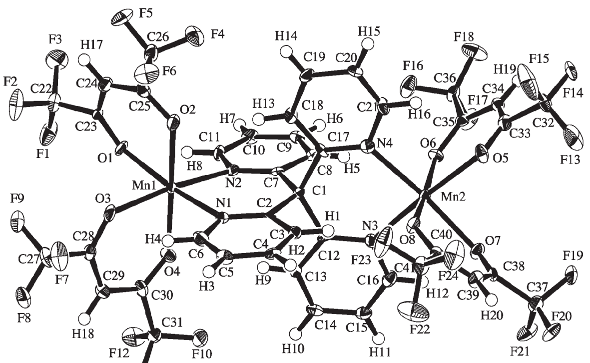


**Figure 1.** Ortep drawing of $[\{Mn(hfac)_2\}_2(py_4C)]$ (**1**) with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Mn1–N1, 2.234(6); Mn1–N2, 2.222(6); Mn1–O1, 2.180(5); Mn1–O2, 2.141(5); Mn1–O3, 2.140(5); Mn1–O4, 2.164(5); Mn2–N3, 2.226(6); Mn2–N4, 2.222(6); Mn2–O5, 2.163(5); Mn2–O6, 2.158(5); Mn2–O7, 2.172(5); Mn2–O8, 2.155(5); N1–Mn1–N2, 86.2(2); N3–Mn2–N4, 87.1(2); C2–C1–C7, 124.0(6); C12–C1–C17, 124.9(6).

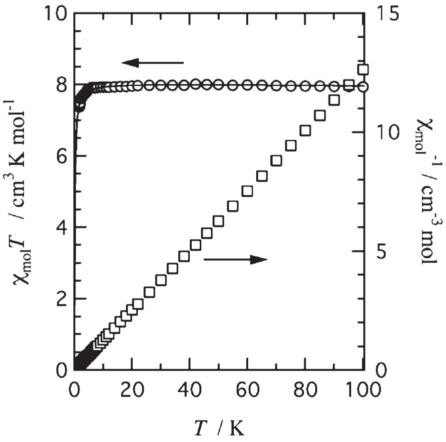


**Figure 2.** Temperature dependence of $\chi_{\rm mol}T$ and $\chi_{\rm mol}^{-1}$ for $[\{\text{Mn-(hfac)}_2\}_2(\text{py}_4\text{C})]$ (**1**). Solid line represents a theoretical fit. For the equation and parameters, see the text.

mononuclear compounds (**2**). Very small antiferromagnetic interaction was indicated by the negative $\theta$. A best fit to the $S = 5/2$ dinuclear model (Eq 1)[16] with $x = J/k_BT$ gave the exchange parameter $J$ of $-0.023$ K, where the spin Hamiltonian is defined as $H = -2JS_i \cdot S_{i+1}$. The purity factor ($f$) was estimated to be 92%. The theoretical curve is superposed in Figure 2.

$$\chi_{\rm mol} = f\,\frac{2Ng^2\mu_{\rm B}{}^2}{k_{\rm B}T} \times \frac{{\rm e}^{-2x} + 5{\rm e}^{-6x} + 14{\rm e}^{-12x} + 30{\rm e}^{-20x} + 55{\rm e}^{-30x}}{1 + 3{\rm e}^{-2x} + 5{\rm e}^{-6x} + 7{\rm e}^{-12x} + 9{\rm e}^{-20x} + 11{\rm e}^{-30x}} \qquad (1)$$

The intramolecular Mn–Mn coupling dominantly contributes to the observed antiferromagnetic interaction because the Mn1–Mn2 distance (7.328(1) Å) is shorter than any intermolecular Mn–Mn distances (8.686(1) Å or longer). A possible exchange mechanism is proposed as follows. The electron configuration $(\text{e}_\text{g})^2(\text{t}_{2\text{g}})^3$ of manganese(II) ions has both $\sigma$- and $\pi$-type spins. As for $\sigma$ spins, any combination of magnetic orbitals from two manganese ions gives orthogonal arrangement owing to the spiro structure. Similarly, any $\pi$ spins are orthogonal between the two Mn ions. On the other hand, some combinations of $\sigma$ spins and $\pi$ spins have substantial through-space orbital contacts. As Figure 3 shows, the $d_{xz}$ orbital on Mn1 and the $d_{x^2-y^2}$ orbital on Mn2 are arranged parallel, for example.

The total magnetic exchange interaction is defined with the sum of ferromagnetic and antiferromagnetic terms.[17] The experimental result indicates that the latter slightly surpasses the former, giving rise to very small antiferromagnetic coupling in the present case.

In summary, the present spiro-fused structure was easily introduced by means of self-assembly of ligands and metal ions. Although the magnetic coupling in **1** has been clarified to be antiferromagnetic, this strategy may be applied to di- and polynuclear complexes containing other metal centers and counter ions.

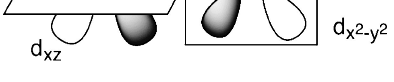


**Figure 3.** A schematic drawing for an orbital overlap between manganese(II) magnetic orbitals leading to antiferromagnetic contribution to the total Mn–Mn exchange interaction.

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14 The molecular structures of $[\text{Mn(hfac)}_2(\text{py}_4\text{C})]$ (**2**), $[\text{Cu(hfac)}_2\text{-}(\text{py}_4\text{C})]$, and $[\text{Cu(hfac)(py}_4\text{C)}\cdot\text{Cu(hfac)}_3]$ were determined by means of X-ray crystallographic analysis. A. Okazawa, T. Ishida, and T. Nogami, unpublished results.
15 Selected crystallographic parameters for **1**: $\text{C}_{41}\text{H}_{20}\text{F}_{24}\text{N}_4\text{Mn}_2\text{O}_8$ monoclinic, $P2_1$, $a = 9.1363(3)$, $b = 15.0475(6)$, $c = 17.1982(8)$ Å, $\beta = 93.427(2)°$, $V = 2360.2(2)$ Å$^3$, $D_{\rm calcd} = 1.776$ g cm$^{-3}$, $\mu(\text{Mo K}\alpha) = 0.686$ mm$^{-1}$, $R$ $(I > 2\sigma(I)) = 0.062$, $R_{\rm w}$ (all data) $= 0.107$, $T = 90$ K for 9856 reflections. CCDC reference number 244742. Elemental analysis. Found: C, 38.84; N, 4.93; H, 1.40%. Calcd.: C, 39.01; N, 4.44; H, 1.60% for $\text{C}_{41}\text{H}_{20}\text{F}_{24}\text{N}_4\text{Mn}_2\text{O}_8$.
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