Intramolecular Magnetic Interaction of Phenylene-Linked Bis-β-diketone Metal Complexes

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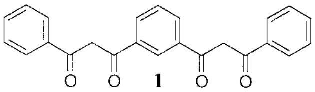
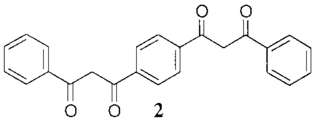
(Received April 24, 2000; CL-000388)

Dinuclear metal complexes of phenylene-linked bis-β-diketone ligands were prepared and the magnetic interactions between the complex units along the π-conjugated linkers were investigated. Both ferro- and antiferromagnetic interactions were observed for the *m*- and *p*-phenylene-linked dimers, respectively.

Recently, a wide variety of supramolecular structures have been constructed by self-assembling technique of molecular building blocks with hydrogen bonding and coordination bonding.[1] These kinds of structures are still more responsible for the design of molecular magnetism, because the dimensionality and the topology of the assembly structures delicately affect their whole electronic structures.[2] *β*-Diketone is one of the best versatile building blocks to construct coordination-based assemblies as multi-nuclear metal complexes with strong interaction through the pseudo-aromatic six-membered ring consisting of the enolate and the coordinated metal ion. When plural *β*-diketones are linked by an appropriate π-conjugated linker, inter-metal, π–π, and metal-π interactions should be considered. Here, the spin exchange interaction between the paramagnetic metal ions was investigated in a series of dinuclear metal complexes consisting of *m*- and *p*-phenylene-linked bis-*β*-diketone ligands **1** and **2** as the smallest models for the extended coordination polymers.[3,4]



1



2

Considerable red-shifts of the UV absorption bands of the bis-*β*-diketone ligands **1** were observed at 356 nm and **2** at 375 nm, compared with 1,3-diphenyl-1,3-propanedione **3** at 343 nm.[5] These spectra suggest an extended π-conjugation due to the phenylene linkers connecting two *β*-diketones. The metal complexes were prepared by mixing the ligands with metal acetate or perchlorate in the 1:1 mixed solution of methanol and dichloromethane. The divalent metal ions, Zn(II), Cu(II) and Ni(II), afforded 1:1 complexes with **1** and **2**, while trivalent metal ions, Mn(III) and Fe(III), afforded 2:3 complexes, based on CHN elemental analysis and ICP measurement.[6] All the FT-IR spectra indicated complete coordination of two enolate anions of the ligands.[7] The ^{1}H-NMR spectra of $\mathbf{1}_2$·Zn_2 suggested the rotation-pinning of the *m*-phenylene linker and the formation of a large cyclic structure, shown as a dotted circle in Figure 1(a). The dinuclear metal complexes of **1** gave consistent parent peaks in the FAB mass spectra. A planar structure with a large ring and a triangular prism structure[8] with three twisted ligands can be concluded as common structures of the divalent and trivalent metal complexes, respectively (Figure 1). The same metal-to-ligand compositions with 1:1 and 2:3 for divalent and trivalent metal ions, respectively, were found in case of the ligand **2**, although the possibility of polymeric structures was not excluded yet.

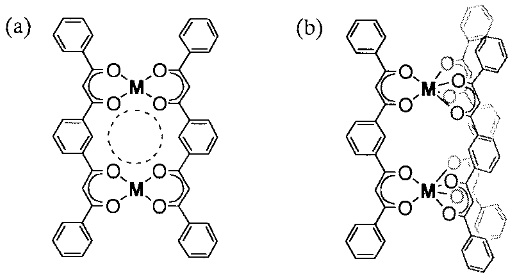


Figure 1. Plausible molecular structures of the dinuclear metal complexes of *m*-phenylene-linked bis-*β*-diketone ligand **1** with (a) divalent and (b) trivalent metal ions.

The magnetic susceptibilities of all the dinuclear complexes in a high temperature range were consistent with the expected spin multiplicities. As lowering temperature, an increasing and a decreasing χT values were observed for *m*- and *p*-phenylene-linked Cu(II) complexes, respectively, whereas the mononuclear **3**·Cu_2 complex showed paramagnetic behavior in a wide temperature range (Figure 2). The temperature-dependent susceptibilities (Figure 3) of several metal complexes of **1** were well fitted by the dinuclear model (eq. (1), solid lines).[9] The evaluated intra- and intermolecular magnetic interactions, *J* and *J'*, are listed in Table 1. All the intramolecular *J* values of the complexes of **1** were positive. Direct through-space interaction should be negligible because of too long intramolecular metal-to-metal distance (approximately 7 Å). The consistent positive values of the spin exchange interaction strongly suggests that the *m*-

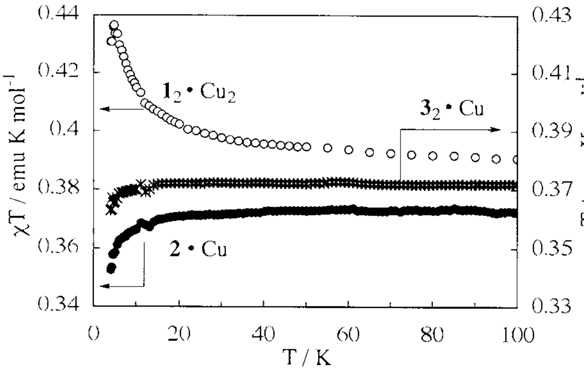


Figure 2. Temperature dependence of the magnetic susceptibility for the Cu(II) complexes of **1**, **2**, and **3**.

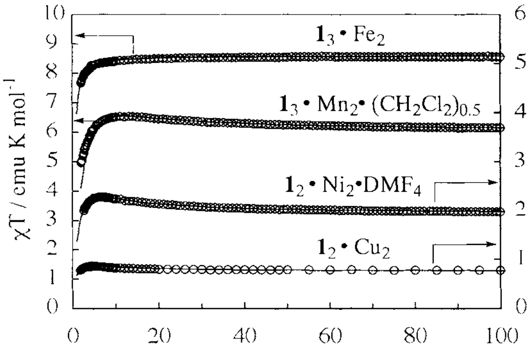


Figure 3. Temperature dependence of the magnetic susceptibility for the metal complexes of **1**. The solid lines represent the theoretical fit by the dinuclear model with antiferromagnetic intermolecular interaction.

$$\chi = \frac{N g^2 \beta^2 \mathrm{F}(J,T)}{k_B T - zJ' \mathrm{F}(J,T)} \qquad (1)$$

$$\left(\begin{array}{ll} \mathrm{F}(J,T) = \dfrac{\sum\limits_{S} S(S+1)(2S+1)\exp[-\mathrm{E}(S)/kT]}{3\sum\limits_{S} (2S+1)\exp[-\mathrm{E}(S)/kT]} & \\ \mathrm{E}(S) = -\dfrac{J}{2}\, S(S+1) & z\text{: the number of the nearest neighbor} \end{array} \right)$$

Table 1 Intramolecular (J) and intermolecular (J') spin-exchange interaction of dinuclear metalcomplexes of **1**.

compound	J/hc / cm^{-1}	zJ'/hc / cm^{-1}
$\mathbf{1}_3$•Fe_2	+0.090	-0.065
$\mathbf{1}_3$•Mn_2•$(CH_2Cl_2)_{0.5}$[a]	+1.32	-0.30
$\mathbf{1}_2$•Ni_2•DMF_4[a]	+3.47	-0.39
$\mathbf{1}_2$•Cu_2	+6.26	-0.52

[a] The solvent molecules in crystallization were included.

phenylene linker carries ferromagnetic through-bond interaction between two metal ions, whereas the *p*-phenylene does antiferromagnetic interaction. These results can be explained by the spin polarization mechanism, well-established for the phenylene-linked diradicals (Figure 4).[10] The metal-dependence of the observed J values is similar to a series of dinuclear metal complexes consisting of 2,2'-bipyrimidine ligands,[12] implying that the d–π interaction[13] at the coordination bonds also plays an important role in the interaction path.[14]

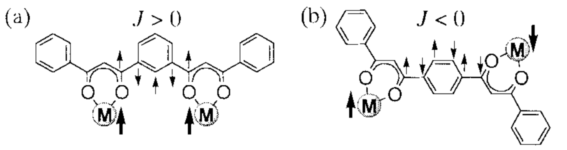


Figure 4. Spin-exchange interactions in the metal complexes of (a) *m*-phenylene-linked **1** and (b) *p*-phenylene-linked **2**. The arrows are added on the basis of well established spin polarization mechanism of the phenylene linkers.[10,11]

In conclusion, the present dinuclear metal complexes based on the phenylene-linked bis-β-diketone ligands should become the potential prototype for the coordination-based molecular architecture with the manipulation of the path-specific electronic interactions such as the spin polarization.

This work was partially supported by Grant-in-Aid for Scientific Research (A) (No. 11305061), and Scientific Research on Priority Area (B) of "Development of Molecular Conductors and Magnets by Spin-Control" (No.730/11224207) from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

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3 The *β*-diketone dimers, **1** and **2**, were prepared from dimethylphthalate isomers and acetophenone by Claisen condensation: D. F. Martin, M. Shamma, and W. C. Fernelius, *J. Am. Chem. Soc.*, **80**, 4891 (1958).

4 A few crystallographic studies on a series of dinuclear metal complexes based on the identical bis-β-diketone ligands have been reported, but no information on the electronic interaction was given: V. A. Grillo, E. J. Seddon, C. M. Grant, G. Aromí, J. C. Bollinger, K. Folting, and G. Christou, *J. Chem. Soc., Chem. Commun.*, **1997**, 1561.

5 Only enol-type tautomer exists in benzene solution.

6 $\mathbf{1}_2$·Zn_2·H_2O: white solid, Found: C, 64.76; H, 3.60; Zn, 14.47%. Calcd for $C_{48}H_{34}O_9Zn$: C, 65.10; H, 3.87; Zn, 14.77%. ν_{COO}: 1591 cm^{-1}, ν_{O-Zn}: 236 cm^{-1}. $\mathbf{1}_2$·Cu_2: green solid, Found: C, 66.24, H, 3.67%. Calcd for $C_{48}H_{32}Cu_2O_8$: C, 66.74; H, 3.73%. ν_{O-Cu}: 283 cm^{-1}. $\mathbf{1}_2$·Ni_2·DMF_4: yellowish green crystal, Found: C, 60.50, H, 4.45%. Calcd for $C_{52}H_{44}N_4Ni_2O_{12}$ C, 60.38; H, 4.29%. $\nu_{C=O}$: 1597 cm^{-1}, ν_{O-Ni}: 261 cm^{-1}. MS(FAB): *m/z* 853 $(M+1)^+$. $\mathbf{1}_3$·Mn_2·$(CH_2Cl_2)_{0.5}$: dark green crystals, Found: C, 69.36, H, 3.83%. Calcd for $C_{145}H_{98}Cl_2Mn_4O_{12}$: C, 69.25; H, 3.93%. $\nu_{C=O}$: 1593 cm^{-1}, ν_{O-Mn}: 320 cm^{-1}. $\mathbf{1}_3$·Fe_2: red crystal, Found: C, 70.96, H, 3.96%. Calcd for $C_{72}H_{48}Fe_2O_{12}$: C, 71.07; H, 3.98%. $\nu_{C=O}$: 1591 cm^{-1}, ν_{O-Fe}: 293 cm^{-1}. **2**·Cu: green solid, Found: C, 66.97, H, 3.63%. Calcd for $C_{24}H_{16}CuO_4$: C, 66.74; H, 3.73%. ν_{O-Cu}: 273 cm^{-1}. **2**·Ni·DMF_2: yellowish green crystal, Found: C, 60.35, H, 4.50%. Calcd for $C_{52}H_{44}N_4Ni_2O_{12}$ C, 60.38; H, 4.29%. $\nu_{C=O}$: 1591 cm^{-1}, ν_{O-Ni}: 285 cm^{-1}. $\mathbf{2}_3$·Mn_2·CH_2Cl_2: brown solid, Found: C, 66.58, H, 4.15%. Calcd for $C_{73}H_{50}Cl_2Mn_2O_{12}$: C, 67.45; H, 3.88%. $\nu_{C=O}$: 1593 cm^{-1}, ν_{O-Mn}: 321 cm^{-1}.

7 The complete coordination of the complexes were confirmed by FT-IR measurements: (1) The disappearance of the C–H bending of the keto-type tautomer at 758 cm^{-1}. (2) The red-shift of the C=O stretching band (3) The appearance of the Metal–O stretching band in a far-infrared region.

8 Crystal data for $\mathbf{1}_3$·Fe_2: $C_{72}H_{48}Fe_2O_{12}$, molecular weight = 1216.18, *monoclinic*, space group *C2/c* (No. 15), a=23.0620(8), b=17.9239(12), c=18.2615(3) Å, β=127.244(5)°, V=6267.2(4) $Å^3$, Z=4, D_{calcd} = 1.3013 g/cm^3, R (Rw) =0.048 (0.043) for 2406 unique reflections with $I > 3\sigma$ and 386 parameters. The ORTEP drawing of the molecular structure is shown in the graphical abstract. Another structure on the $\mathbf{1}_3$·Fe_2, was reported as one of polymorphism. The Mn(III), Ti(III), and V(III) complexes were also reported: see Ref. 4.

9 The dinuclear model with isotropic antiferromagnetic intermolecular interaction: O. Kahn, "Molecular Magnetism," VCH Publishers, Inc., New York (1993).

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11 The drawing in Figure 4 stands on the spin polarization mechanism, well-established in the phenylene linkers. Although the spin alternation on the aromatic system might be influenced through intervening heteroatoms, it dose not influence the whole metal–metal interaction in these dinuclear complexes, because the structural symmetry found in the dinuclear complexes gives the consistent result on the whole metal-to-metal interaction.

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