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Dicopper(II) with Ferromagnetic Coupling, Antiferromagnetic Dimanganese(II) Complexes Containing 3-Nitro-phthalato as Bridging Ligand: Synthesis and Magnetism

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The aim of magnetic investigations of ferromagnetic binuclear metal complexes is to understand the fundamental factors governing the magnetic properties of transition-metal compounds [1–2] and to find appropriate systems applicable as building units for the design of molecular-based ferromagnets [3].

Many works have been published on dicoppper(II) complexes containing the μ-terephthalato, μ-phthalato, μ-3-NO_2-phthalato, μ-diphenato or μ-1,8-naphthalato [4–14]. Copper(II) binuclear complexes exhibiting a spin-triplet ground state are rare [15] compared with those with a spin-singlet ground state. It should be noticed that there are five ferromagnetically coupled systems [9–13], which have monodentate coordination mode for paramagnetic ions. Since the 3-NO_2-phth ligand has the ability to form dicopper(II) complexes of the same pattern as mentioned above, we use it as bridging ligand to prepare the copper(II) binuclear complex, $[Cu_2(3\text{-}NO_2\text{-}phth)(bpy)_4](ClO_4)_2\cdot 3H_2O$ (**1**). The positive J value indicates that the two copper(II) ions undergo a ferromagnetic interaction. For dimanganese(II) complex, $[Mn_2(3\text{-}NO_2\text{-}phth)(bpy)_4(H_2O)_2](ClO_4)_2$ (**2**), the result of variable-temperature magnetic susceptibility data imply the existence of a weak antiferrromagnetic coupling between the metal ions.

Complex (**1**) was prepared as follows: To $H_2(3\text{-}NO_2\text{-}phth)$ (84.5 mg, 0.4 mmol) and bpy (125.0 mg, 0.8 mmol) stirred in absolute MeOH (10 cm^3), triethylamine (0.4 mmol) was added dropwisely, then a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (148.2 mg, 0.4 mmol) in absolute MeOH (10 cm^3) was successively added, and the mixture was stirred for 8 h. Light blue microcrystalline product formed immediately. The solution was filtered off. The microcrystals were washed with absolute MeOH and CH_3CN, then with diethyl ether and dried *in vacuo*. Found: C, 47.7; H, 2.9; N, 9.9. Calc. for $C_{48}H_{35}N_9O_{14}Cl_2Cu_2\cdot 3H_2O$: C, 47.5; H, 2.9; N, 10.4%. Complex (**2**) was prepared by similar procedures, but by replacing $Cu(ClO_4)_2\cdot 6H_2O$ with $Mn(ClO_4)_2\cdot 6H_2O$ (144.8

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mg, 0.4 mmol). A yellow microcrystalline solid was collected. Found: C, 48.9; H, 3.0; N, 10.3. Calc. for $C_{48}H_{39}N_9O_{16}Cl_2Mn_2$: C, 48.9; H, 3.3; N, 10.7%.

Analyses for C, H and N were carried out on a Perkin-Elmer analyzer, Model 240. The infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer, Model 983G, using KBr pellets. Electronic spectra were measured on a Hitachi-240 spectrophotometer. The molar conductance was measured on a DDS-11A conductometer, and variable-temperature magnetic susceptibilities were measured on a superconducting quantum interference device (SQUID) magnetometer (sensitivity $\mu = 10^{-6}$ emu). Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828\ (\chi_M T)^{1/2}$.

Elemental analyses have indicated that the reaction of 3-NO_2-phth with $M(ClO_4)_2 \cdot 6H_2O$ (M = Cu or Mn) yielded the binuclear complexes. Molar conductance values for the two complexes are shown in Table 1. These values fall in the range for 1:2 electrolytes [16], indicating that the two perchlorate anions are situated outside the metal coordination sphere.

Table 1. Physical and chemical data.

Complex	Color	Λ_M (Ω^{-1} cm^2 mol^{-1}) in CH_3CN	IR (cm^{-1}) $\nu_{as}(COO^-)$	$\nu_a(COO^-)$	$\Delta(\nu_{as} - \nu_s)$	$\nu(ClO_4^-)$	UV-Vis (10^3 cm^{-1}) *d-d*	UV-Vis (10^3 cm^{-1}) CT
1	light blue	292.15	1600	1350	250	1095	15.22	31.95
2	yellow	300.96	1593	1391	202	1089		30.96, 33.33

1. $[Cu_2(3\text{-}NO_2\text{-phth})(bpy)_4](ClO_4)_2 \cdot 3H_2O$; 2. $[Mn_2(3\text{-}NO_2\text{-phth})(bpy)_4(H_2O)_2](ClO_4)_2$.

The frequencies of the significant bands in the IR spectra for the complexes are given in Table 1. In the IR region of the spectrum, the complexes exhibited two characteristic strong and broad bands in the 1600–1300 cm^{-1} region, attributed to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching vibrations of the carboxylato groups. In addition, the separation between ν_{as} and ν_s has often been used to diagnose the coordination models of the carboxylato groups. The separate values between ν_{as} and ν_s for the complexes are greater than 200 cm^{-1}, suggesting a monodentate coordination mode for both carboxylato groups [4]. At the same time, the ClO_4^- vibration near 1100 cm^{-1} is present for both complexes, indicating non-coordinated modes [16]. This is consistent with the measured conductance data. The electronic absorption spectrum of the Cu–Cu complex exhibits two bands. One weak band at 657 nm is assigned to *d-d* transition. At a higher energy areas, a CT band is observed, which may be attributed to charge-transfer absorption [17]. These data indicate a five-coordinated Cu(II) chromophores with distorted square-pyramidal configuration, supported by well established electronic spectra for copper(II) complexes [18–19]. Meanwhile, for the manganese(II) complex (**2**), only two strong bands were present in the UV range, which may be attributed to charge-transfer absorption. According to ligand field theory and assumed O_h symmetry, the ground state of manganese(II) is $^6A_{1g}$. Since *d-d* transitions ($^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g}$…) are spin forbidden, in the spectrum of Mn–Mn complex no characteristic band of Mn(II) is found.

Based on the composition of these complexes, IR, electronic spectra and conductivity measurements, all these complexes are proposed to present extended 3-NO_2-phth bridged structures. For both complexes, the 3-NO_2-phth ligand bridges in a monodentate fashion and metal ions are in distorted square-pyramidal configurations for complex (**1**), but a distorted octahedral environment for the metal ions in the complex (**2**).

For the complex (**1**), the plot of μ_{eff} *versus* T is shown in Figure 1. At room temperature, the μ_{eff} value equals 2.46 μB, which is higher than the spin-only value of 2.45 μB for Cu(II)–Cu(II) system, assuming no magnetic interaction. At the same time, the magnetic moment, μ_{eff}, increase slightly on cooling and appears to reach a maximum, which is 2.66 μB and more than the magnetic moment at room temperature. Therefore, the magnetic behavior suggests a ferromagnetic interaction, leading to a triplet ground state. This is consistent with the 3-NO_2-phth bridged analogous binuclear copper(II) complex ($[Cu_2(3\text{-}NO_2\text{-phth})(phen)_4](ClO_4)_2$ [13], $J = +5.26\ cm^{-1}$). In order to understand quantitatively the spin-exchange interaction, the analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, with $S_1 = S_2 = 1/2$. The molar susceptibility of the Cu–Cu system was calculated by the modified Bleaney-Bowers equation [21], $\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1} + N_\alpha$, where χ_M denotes the susceptibility per binuclear complex, N_α is the temperature-independent paramagnetism ($120\times10^{-6}\ cm^3\ mol^{-1}$) and other symbols have their usual meaning. Least-square fitting of the magnetic data is given in Figure 1. It can be noticed, the fitting of theoretical and experimental data is not satisfactory. The disagreement in the lower temperature region (< 40 K) is probably due to zero-field splitting (D) within the triplet state. The zero-field splitting has two origins [22], namely the dipolar interaction (D_{dd}) and the combined effect of spin-orbit coupling anisotropy and antisymmetric exchanges (D_{ex}), $D = D_{dd} + D_{ex}$, a way to explicitly correct this phenomenon is the incorporation of the dipolar interaction (D_{dd}) and the spin-orbit coupling terms in the Hamiltonian equation. However, this is a too complicated problem. Thus, the data below 40 K was deleted in our magnetic analyses, consequently a much better fit was obtained. The magnetic parameters defined are $J = +14.21\ cm^{-1}$, $g = 2.00$ and $F = 2.69\times10^{-6}$, being defined as $F = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma(\chi_M)_{obs}$. This result also indicates that the complex (**1**) undergoes a ferromagnetic spin-exchange interaction between the paramagnetic ions. To describe the mechanism of the exchange interaction, several models have been proposed [22–24]. For the present dicopper(II) complex, the coupling can be attributed to accidental orthogonality between the one single electronic occupied orbital in the two centers.

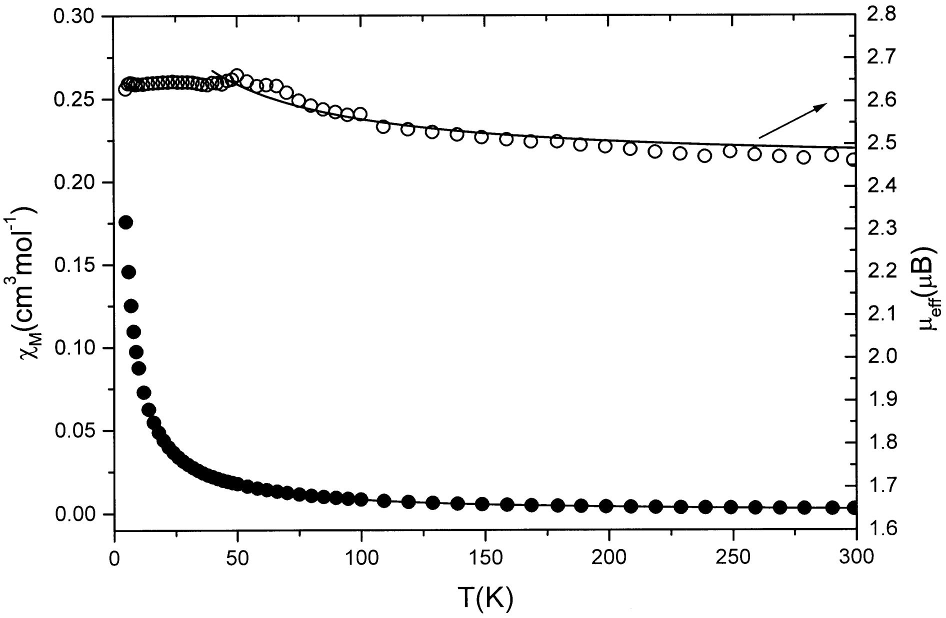

Figure 1. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[Cu_2(3\text{-}NO_2\text{-phth})(bpy)_4](ClO_4)_2{\cdot}3H_2O$.

For the complex (**2**), the variable-temperature susceptibility data were analyzed using an isotropic Heisenberg model with $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ $(S_1 = S_2 = 5/2)$. χ_M may be deduced as $\chi_M = (2N\beta^2 g^2/kT)A/B$ with $A = 55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)$, $B = 11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$, least-squares fitting of the magnetic data leads to $J = -0.38$ cm^{-1}, $g = 2.00$ and $F = 6.80\times10^{-5}$, the J value proves that the overlap between the magnetic orbitals is weak. Therefore, a small antiferromagnetic coupling can be expected.

Kahn [25] has proposed a molecular orbital model to rationalize the mechanism of the exchange interaction. In this model, the experimentally observed exchange parameter J is taken as the sum of a negative antiferromagnetic contribution J_{AF} and a positive ferromagnetic contribution J_F, $J = J_{AF} + J_F$. It is usual to assume that the J_F value is much less than the J_{AF} value. Therefore, only when $J_{AF} = 0$, $J = J_F$, the system exhibits a ferromagnetic interaction, otherwise $J_{AF} \neq 0$, an antiferromagnetic interaction should be observed. J_{AF} depends on the overlap integral between two different magnetic centers, A and B, represented as $J_{AF} = -2\Delta S$, where $S = \langle\psi_A|\,\psi_B\rangle$, Δ is the energy gap between the molecular orbitals built from two magnetic orbitals in the triplet state. ψ_A and ψ_B express one single occupied orbital in the two centers. In this case, no orthogonality could be involved according to the structure of the complex. Thus, it is unreasonable to believe that the value of the overlap integral $\langle\psi_A|\,\psi_B\rangle$ is zero. Actually, $J_{AF} \neq 0$, so an antiferromagnetic exchange interaction should be ex-

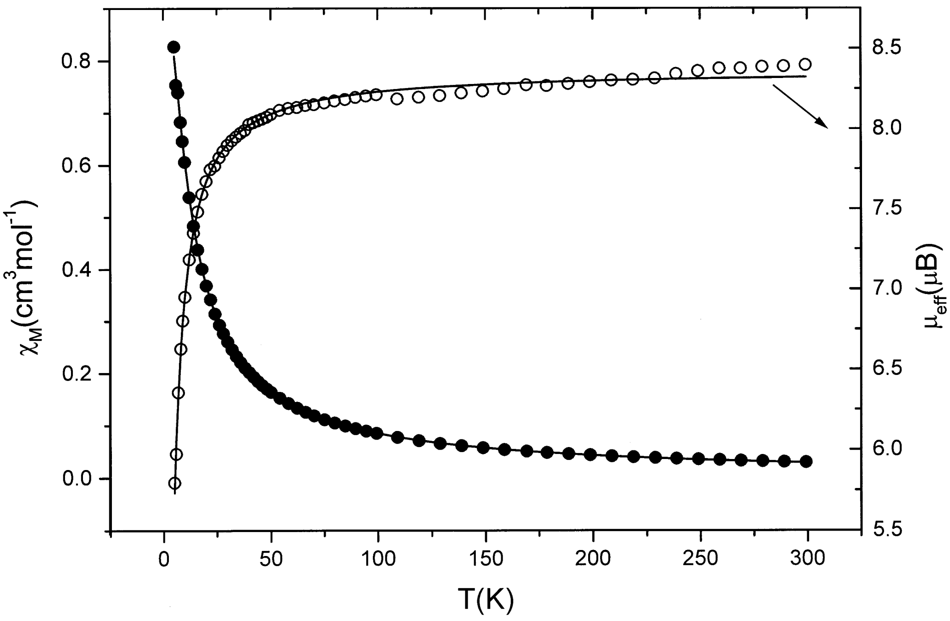

Figure 2. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[Mn_2(3\text{-}NO_2\text{-phth})(bpy)_4(H_2O)_2](ClO_4)_2$.

pected. In addition, owing to the structure of the complex, the two magnetic orbitals are not easily located in the same plane of the 3-NO_2-phth-bridge. Therefore, the interaction will be quite weak.

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