

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

by S.L. Ma*, L.Z. Zhang, L.L. Lu and M.Y. Tang

*Department of Pharmaceutical Engineering, Tianjin University of Commerce,
Tianjin, 300134, P.R. of China*

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Novel copper(II), cobalt(II) and manganese(II) binuclear complexes have been synthesized, namely $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2$ and $[\text{M}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, where $\text{M} = \text{Co}$ or Mn , phen = 1,10-phenanthroline and 3-NO₂-phth denotes 3-nitro-phthalate dianion. Magnetic susceptibility measurements between 4.2–300 K (or 77–300 K) demonstrate a ferromagnetic interaction between two copper(II) ions in the Cu–Cu complex, and a weak antiferromagnetic interaction between the metal ions in Co–Co and Mn–Mn complexes. Based on spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ ($S_1 = S_2 = 1/2$, $S_1 = S_2 = 3/2$ or $S_1 = S_2 = 5/2$), J is found to be equal to $+5.26 \text{ cm}^{-1}$, -1.72 cm^{-1} and -0.62 cm^{-1} for the Cu–Cu, Co–Co and Mn–Mn complexes, respectively.

Key words: binuclear complex, ferromagnetic coupling, 3-NO₂-phth bridging ligand

Syntheses and magnetic properties of ferromagnetic binuclear metal complexes have been the subject of investigations to understand the factors governing the magnetic properties of transition-metal compounds which are accidental [1–2] and to find appropriate systems applicable as building units for the design of molecular-based ferromagnets [3]. It has been pointed out that two distinct cases, accidental orthogonality and strict orthogonality of magnetic orbitals, can give rise to a ferromagnetic spin coupling between neighbouring paramagnetic metal ions [1]. The former depends on some structure factor in a subtle manner.

Many papers have been published on dicopper(II) complexes containing the μ -terephthalato, μ -phthalato, μ -diphenato or μ -1,8-naphthalato [4–13]. The bridging function and magnetic exchange interaction of these complexes have been revealed by single crystal X-ray and magnetic analysis. Copper(II) binuclear complexes exhibiting a spin-triplet ground state are rare [14], compared with those with a spin-singlet ground state. It should be noticed that there are four ferromagnetically coupled systems [9–12], which have monodentate coordination mode for paramagnetic ions. Since the 3-NO₂-phth ligand has the ability to form dicopper(II) complexes of the same pattern as those mentioned above, we use it as bridging ligand

* Author to whom all correspondence should be directed. E-mail: strulinma@yahoo.com.cn

to prepare the copper(II) binuclear complex, $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2$. The positive J value for the complex $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2$ indicates that the two copper(II) ions undergo a ferromagnetic interaction. For dicobalt(II) and dimanganese(II) complexes, $[\text{Co}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and $[\text{Mn}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, the results of variable-temperature magnetic susceptibility data imply the existence of a weak antiferromagnetic coupling between the metal ions.

EXPERIMENTAL

All starting materials used in the syntheses were of analytical grade and were purchased from the Peking Chemical Company.

Preparation of the 3-nitro-phthalic acid $\text{H}_2(3\text{-NO}_2\text{-phth})$: To phthalic anhydride (37 g), dissolved in 150 ml of sulphuric acid (98%), nitric acid fuming was added slowly, whereafter the mixture was heated to 100–110°C and stirred for 2 h. Microcrystals formed were separated, washed with water and dried *in vacuo*. The color of this product $\text{H}_2(3\text{-NO}_2\text{-phth})$ is pale-yellow.

Preparation of $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1): To $\text{H}_2(3\text{-NO}_2\text{-phth})$ (84.5 mg, 0.4 mmol) and phen (158.6 mg, 0.8 mmol), stirred in absolute MeOH (10 cm³), triethylamine (0.4 mmol) was added dropwisely. Then a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (148.2 mg, 0.4 mmol) in the absolute MeOH (10 cm³) was successively added, and the mixture was stirred for 8 h. Light blue microcrystalline product formed immediately. The solution was filtered off. Microcrystals were washed with CH_3CN and absolute MeOH then with diethyl ether and dried *in vacuo*.

Preparation of $[\text{Co}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (2): This complex was obtained by the same procedure as above, but using $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (146.4 mg, 0.4 mmol) instead of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Orange microcrystals were obtained.

Preparation of $[\text{Mn}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (3): This complex was also prepared as the copper(II) complex, but replacing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (144.8 mg, 0.4 mmol). A yellow microcrystalline solid was collected.

Analytical data of the complexes are collected in Table 1.

Table 1. Physical and chemical data.

| Complex | Color | Found (Calcd.)(%) | | | Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) (in CH_3CN) | IR(cm^{-1}) | | $\Delta(\nu_{\text{as}}-\nu_{\text{s}})$ | $\nu(\text{ClO}_4^-)$ | UV-Vis (10^3cm^{-1}) | |
|---------|------------|-------------------|--------------|--------------|--|---------------------------------|--------------------------------|--|-----------------------|------------------------------------|----------------|
| | | C | H | N | | $\nu_{\text{as}}(\text{COO}^-)$ | $\nu_{\text{s}}(\text{COO}^-)$ | | | $d-d$ | CT |
| 1 | light blue | 52.4 (52.8) | 2.7 (2.9) | 9.8 (9.9) | 292.15 | 1590 | 1350 | 240 | 1095 | 14.66 | 30.30 38.46 |
| 2 | orange | 52.2 (52.4) | 3.0 (3.1) | 9.5 (9.8) | 312.90 | 1585 | 1380 | 205 | 1086 | 11.43 | 33.30 28.57 |
| 3 | yellow | 52.8 (52.8) | 3.2 (3.1) | 9.7 (9.9) | 236.48 | 1590 | 1385 | 205 | 1089 | | 30.30 34.48 |

1. $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
2. $[\text{Co}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$
3. $[\text{Mn}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

Physical measurements: 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 suscepti-

bilities 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 $\mu_{\text{eff}} = 2.828 (\chi_{\text{MT}})^{1/2}$.

RESULTS AND DISCUSSION

Composition and coordination environment: Elemental analyses have indicated that the reaction of 3-NO₂-phth with $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($M = \text{Cu}, \text{Co}$ or Mn) yielded the binuclear complexes. Molar conductance values for these three complexes are shown in Table 1. These values fall in the range for 1:2 electrolytes [15], indicating that the two perchlorate anions are situated outside the metal coordination sphere.

The frequencies of the significant bands in the IR spectra for the complexes are also given in Table 1. In the IR region of the spectra, the complexes exhibited two characteristic strong and broad bands in the 1600–1300 cm^{-1} region, attributed to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ 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 all complexes, indicating non-coordinated modes [16]. This is consistent with the measured conductance data. The electronic absorption spectra of the Cu–Cu complex exhibit two bands. One weak band at 682 nm is assigned to $d-d$ transitions. At higher energy range, two strong CT bands are observed. These data indicate a five-coordinated Cu(II) chromophores with distorted square-pyramidal configuration, supported by well established electronic spectra for copper(II) complexes [17–18]. For the complex (2), a weak absorption in the visible range and two strong bands in the UV range are observed. The former may be attributed to the $d-d$ transition and the latter to the charge-transfer absorption [19]. Meanwhile, for the manganese(II) complex (3), only two CT bands are present in the UV range. According to ligand field theory and assumed O_h symmetry, the ground state of manganese(II) is ${}^6A_{1g}$. Since $d-d$ transitions (${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{G}), {}^4T_{2g}(\text{G}), {}^4A_{1g}(\dots)$) 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-NO₂-phth bridged structures. For the complex (1), the 3-NO₂-phth ligand bridges in a monodentate fashion and metal ions are in distorted square-pyramidal configurations (Fig. 1), but a distorted octahedral environment for the metal ions in the complexes (2) and (3), as shown in Fig. 2.

Spin-exchange interaction of the complexes: For the complex (1), the plot of μ_{eff} versus T is shown in Fig. 3. 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} , increases

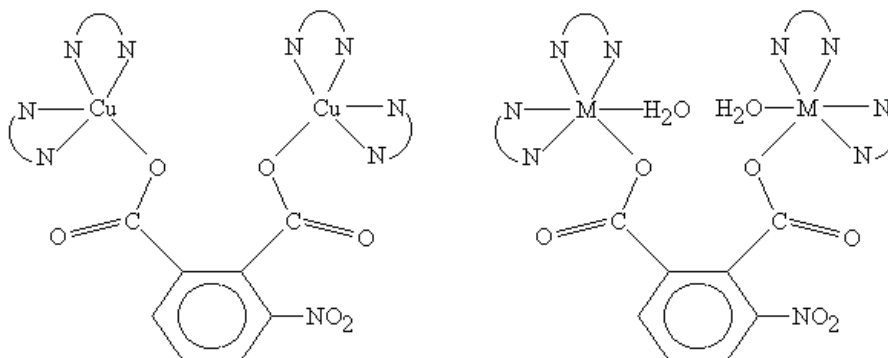


Figure 1. Supposed structure of the complex (1) **Figure 2.** Supposed structure of the complexes (2) and (3) (L = phen; M = Co or Mn).

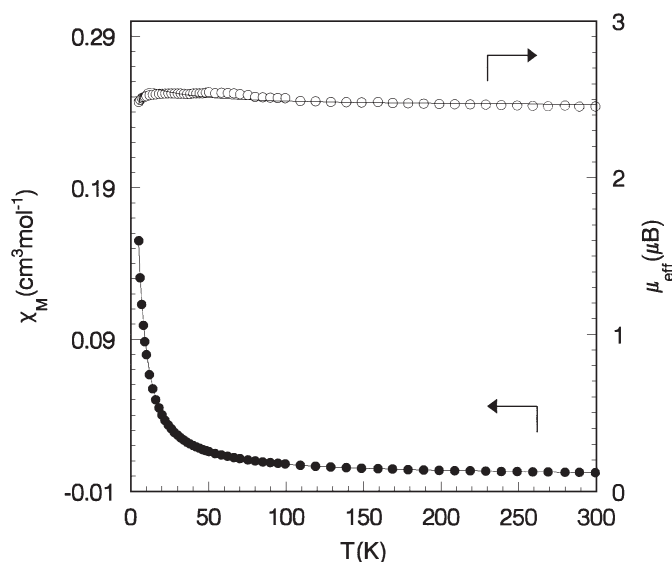


Figure 3. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[\text{Cu}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4](\text{ClO}_4)_2$.

slightly on cooling and appears to reach a maximum, which is $2.54 \mu\text{B}$ and more than the magnetic moment near room temperature. Therefore, the magnetic behavior suggests a ferromagnetic interaction, leading to a triplet ground state. This is consistent with the analogous NAPH bridged binuclear copper(II) complex $[\text{Cu}_2(\text{NAPH})(\text{phen})_4](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ [12], $J = +0.28 \text{ cm}^{-1}$). 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 $S_1 = S_2 = 1/2$ and adding a term to correct the intermolecular interaction ($Z'J'$). The molar

susceptibility of the Cu–Cu system was calculated by the modified Bleaney-Bowers equation (1) [20],

$$\begin{aligned}\chi_M' &= \chi_M/[1 - (2Z'J'/N\beta^2g^2)\cdot\chi_M] \\ \chi_M &= (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1} + N_\alpha,\end{aligned}\quad (1)$$

where χ_M denotes the susceptibility per binuclear complex, N_α is the temperature-independent paramagnetism ($120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) and other symbols have their usual meaning. As shown in Fig. 3, a good least-square fits to the experimental data was attained with eq. (1). The magnetic parameters thus determined are $J = +5.26 \text{ cm}^{-1}$, $g = 2.01$, $Z'J' = -1.58 \text{ cm}^{-1}$ and the agreement factor F equals to 3.18×10^{-5} , being defined as $F = \Sigma[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \Sigma(\chi_M)_{\text{obs}}$. These results indicate that the complex (1) undergoes a ferromagnetic spin-exchange interaction between the paramagnetic ions and a weak intermolecular antiferromagnetic coupling was found.

For the dicobalt(II) complex (2), variable-temperature magnetic susceptibility data (4.2–300 K) were collected from powder samples. The cobalt(II) ion under O_h -symmetry possesses the $^4T_{1g}$ ground state, where the magnetic moment is temperature dependent. Therefore, the magnetic susceptibility for a binuclear cobalt(II)–cobalt(II) ($S_1 = S_2 = 3/2$) complex with cobalt(II) under O_h -symmetry is difficult to explain. However, the configuration around the cobalt(II) ion for the present case is somewhat distorted from O_h -symmetry. Therefore, according to Sinn [21], the magnetic susceptibilities for the present cobalt(II)–cobalt(II) complex can be interpreted by the Heisenberg model. Based on this model, the molar magnetic susceptibility for a cobalt(II)–cobalt(II) ($S_1 = S_2 = 3/2$) complex is given by equation (2) taken from [22]

$$\begin{aligned}\chi_M &= (2N\beta^2g^2/kT)A/B \\ A &= 14 + 5\exp(-6J/kT) + \exp(-10J/kT) \\ B &= 7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT).\end{aligned}\quad (2)$$

The least-square fitted magnetic data are given in Figure 4. It can be noticed, that fitting of theoretical and experimental data is not satisfactory. The disagreement in the lower temperature region ($< 24 \text{ K}$) is probably due to spin-orbit coupling. A way to explicitly correct this phenomenon is the incorporation of the spin-orbit coupling term in the Hamiltonian equation. However, this is a too complicated problem. Thus, the data below 16 K was deleted in magnetic analyses, consequently a much better fit was obtained. The magnetic parameters defined are $J = -1.72 \text{ cm}^{-1}$, $g = 2.41$ and $F = 5.08 \times 10^{-4}$. These results imply a weak antiferromagnetic coupling in the cobalt(II)–cobalt(II) complex. For the complex (3), the variable-temperature susceptibility data were analyzed (77–300 K) 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 described by equation (3),

$$\begin{aligned}\chi_M &= (2N\beta^2g^2/kT)A/B \\ A &= 55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT) \\ B &= 11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT).\end{aligned}\quad (3)$$

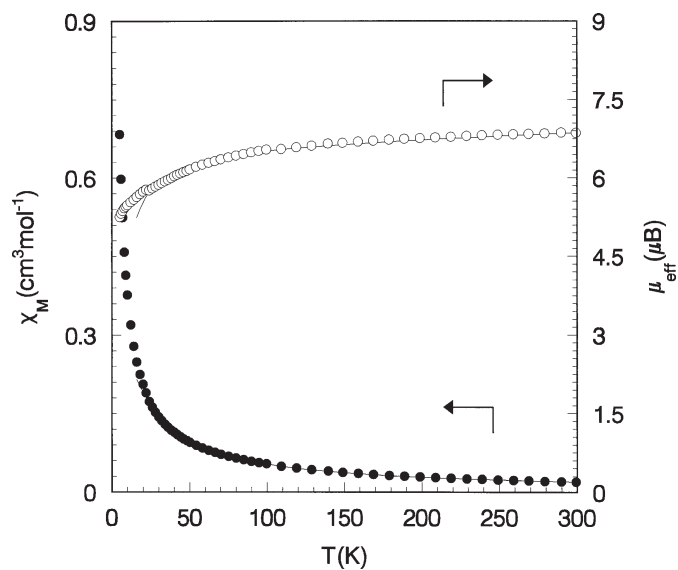


Figure 4. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[\text{Co}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

As shown in Fig. 5, a good fit to the experimental data was attained using this equation. The best-fit parameters are $J = -0.62 \text{ cm}^{-1}$, $g = 2.03$ and $F = 4.49 \times 10^{-6}$. These results indicate that there occurs a very weak antiferromagnetic superexchange interaction between the manganese(II) ions of the complex (3).

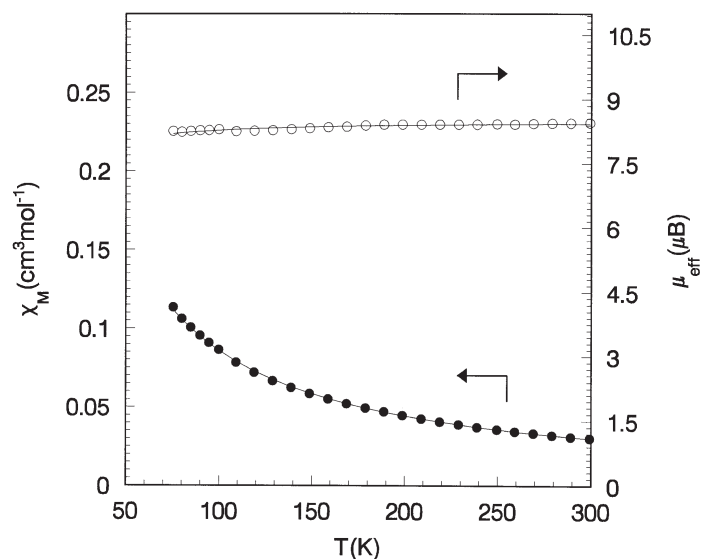


Figure 5. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[\text{Mn}_2(3\text{-NO}_2\text{-phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

We compared the present J value with those previously reported for the dicopper(II), dicobalt(II) and dimanganese(II) complexes with similar bridging ligands (see Table 2), and found that the present coupling constants are similar to all the others and that the couplings between the copper(II) ions is ferromagnetic, dicobalt(II) and dimanganese(II) are antiferromagnetic.

Table 2. Magnetic data of the complexes.

| Complexes | J (cm ⁻¹) | Ref. |
|---|-------------------------|-----------|
| [Mn ₂ (NAPH)(phen) ₄](ClO ₄) ₂ | -0.49 | 13 |
| [Mn ₂ (3-NO ₂ -phth)(phen) ₄ (H ₂ O) ₂](ClO ₄) ₂ | -0.62 | This work |
| [Co ₂ (NAPH)(phen) ₄](ClO ₄) ₂ | -0.54 | 12 |
| [Co ₂ (3-NO ₂ -phth)(phen) ₄ (H ₂ O) ₂](ClO ₄) ₂ | -1.72 | This work |
| [Cu ₂ (NAPH)(phen) ₄](ClO ₄) ₂ | +0.28 | 12 |
| [Cu ₂ (3-NO ₂ -phth)(phen) ₄](ClO ₄) ₂ ·H ₂ O | +5.26 | This work |

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