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Synthesis and Characterization of Three Novel Ferromagnetic Copper(II) Binuclear Complexes Bridged by Phthalato

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Three novel copper(II) binuclear complexes with phthalate dianion as bridging ligand have been obtained, namely $[Cu_2(phth)(L)_4](ClO_4)_2$, where phth denotes the phthalate dianion and L represents 1,10-phenanthroline (abbreviated as phen), 2,2′-bipyridine (bpy) or 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy). Meanwhile, the IR, electronic spectra, ESR spectra and the temperature-dependent magnetic susceptibility of the three complexes were analyzed. The results of the magnetic analyses show a weak ferromagnetic coupling between the paramagnetic ions in all complexes studied.

Key words: phthalate dianion bridge, copper(II)–copper(II) binuclear complex, ferromagnetic interaction

Studies on molecular ferromagnets are fascinating research fields of current interest. Copper(II) binuclear complexes exhibiting a spin-triplet ground state are very few [1] as compared with those with a spin-singlet ground state. These present copper(II) binuclear complexes, exhibiting a spin-triplet ground state, are surely important for the study of ferromagnetically coupled copper(II) magnetic systems involving magnetic centers far separated from each other *via* multiatom-bridging units. Phthalate dianion, due to both their versatile bonding mode with the copper(II) ions and their peculiar structure-involving carboxylate groups that are non-coplanar with themselves and with the benzene ring, could be good candidates in supporting long-distance ferromagnetic exchange interactions [2]. On the other hand, we hope that these complexes can be good examples for further investigation on the structural variation effects upon spin-coupling.

EXPERIMENTAL

All chemicals were of analytical grade and were purchased from the Peking Chemical Company.

Synthesis of $[Cu_2(phth)(phen)_4](ClO_4)_2{\cdot}H_2O$: Dissolve 66.5 mg (0.4 mmol) phthalate acid and 317.2 mg (1.6 mmol) of 1,10-phenanthroline in the mixed solution of 10 cm^3 methanol and 5 cm^3 DMF, then into which add 4 drops of triethylamine successively. Stir the mixture for several minutes and then

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add 10 cm^3 methanol solution of 296.4 mg (0.8 mmol) $Cu(ClO_4)_2 \cdot 6H_2O$. Blue precipitation formed immediately. After stirring for 2 h, the product was filtered and then washed several times with absolute methanol, acetonitrile, and ether, and dried *in vacuo*. Anal. Calcd. for $C_{56}H_{36}N_8O_{12}Cl_2Cu_2 \cdot H_2O$: C, 54.7; H, 3.1; N, 9.1. Found: C, 54.3; H, 3.4; N, 9.1.

Synthesis of $[Cu_2(phth)(bpy)_4](ClO_4)_2 \cdot 0.5H_2O$: This complex was prepared in the same way as above by replacing phen with bpy (249.9 mg, 1.6 mmol). Light blue microcrystallines are obtained. Anal. Calcd. for $C_{48}H_{36}N_8O_{12}Cl_2Cu_2 \cdot 0.5H_2O$: C, 51.3; H, 3.3; N, 10.0. Found: C, 51.2; H, 3.1; N, 10.0.

Synthesis of $[Cu_2(phth)(Me_2bpy)_4](ClO_4)_2 \cdot H_2O$: Dissolve 132.9 mg (0.8 mmol) phthalate acid and 589.6 mg (3.2 mmol) of Me_2bpy in 40 cm^3 methanol, and successively add 20 drops of triethylamine. Stir the mixture for several minutes and then add 10 cm^3 methanol solution of 592.9 mg (1.6 mmol) $Cu(ClO_4)_2 \cdot 6H_2O$. Dark green solution was obtained first and then blue precipitation formed after 0.5 h. After stirring for 2 h, the product was filtered and then washed several times with absolute methanol, acetonitrile, and ether, and dried *in vacuo*. Anal. Calcd. for $C_{56}H_{52}N_8O_{12}Cl_2Cu_2 \cdot H_2O$: C, 54.1; H, 4.4; N, 9.0. Found: C, 53.7; H, 3.9; N, 8.6.

Physical measurements: Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer elemental analyzer, Model 240. The infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer Model 983G, using KBr pellets. UV-Vis spectra were recorded on a Beckman-DU8B spectrophotometer. X-ray ESR spectra were measured on a Bruker ER 200 D-SRC ESR spectrometer. Variable temperature magnetic susceptibilities (4.99–299 K) were performed at the Institute of Physics, Chinese Academy of Science, using a Superconducting Quantum Interference Device (SQUID) magnetometer and in an applied magnetic field of 10000G. The diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828\,(\chi_M T)^{1/2}$.

RESULTS AND DISCUSSION

General characterization: Analytical data of elements indicate that the reactions of phthalate acid with $Cu(ClO_4)_2 \cdot 6H_2O$ and phen, bpy or Me_2bpy yielded binuclear copper(II)–copper(II) complexes. For these complexes, the significant bands in the IR spectra 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 these complexes are larger than 200 cm^{-1}, suggesting a monodentate coordination mode for both carboxylato groups [3]. At the same time, the ClO_4^- vibration at near 1100 cm^{-1} is present for all the complexes, indicating a non-coordinated mode [4], The electronic absorption spectra of the Cu–Cu complexes exhibit two bands. A weak absorption in the visible range is assigned to d-d transition, at higher energy, one strong band is observed for all complexes (see Table 1), which is attributed to an intraligand transition. These data indicate a five-coordinated Cu(II) chromophores with distorted square-pyramidal configuration, supported by well established electronic spectrum for copper(II) complexes [5-6].

Based on the elemental composition, IR and electronic spectra, all the complexes are proposed to present extended phth bridged structure, the phth ligand bridges in a monodentate fashion and metal ions are in distorted square-pyramidal configuration, as shown in Fig. 1.

Table 1. Physical and chemical data.

Complex	Color	IR (cm^{-1})				UV-Vis	(10^3 cm^{-1})	ESR		Decomposition
		ν_{as}(COO$^-$)	ν_s (COO$^-$)	$\Delta(\nu_{as} - \nu_s)$	$\nu(ClO_4^-)$	d-d	CT(ε, L·mol^{-1}·cm^{-1})	$g_{\parallel}$	$g_{\perp}$	Temp. (°C)
1	Blue	1585	1380	205	1090	14.4 (260)	34.1 (3.7×10^4)	2.18	2.03	267
2	Light blue	1570	1369	201	1095	14.7 (223)	33.8 (3.7×10^4)	2.17	2.09	279
3	Blue	1582	1381	201	1099	14.4 (265)	33.9 (3.7×10^4)	2.22	2.04	270

1. $[Cu_2(phth)(phen)_4](ClO_4)_2 \cdot H_2O$; 2. $[Cu_2(phth)(bpy)_4](ClO_4)_2 \cdot 0.5H_2O$; 3. $[Cu_2(phth)(Me_2bpy)_4](ClO_4)_2 \cdot H_2O$.

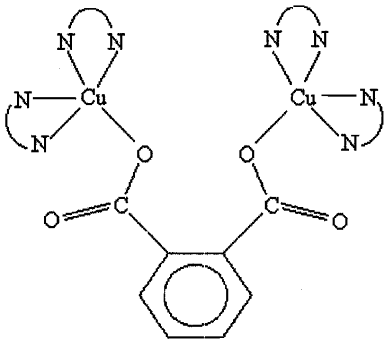

Figure 1. Supposed structure for the cation of the studied complexes. L = phen, bpy, or Me$_2$bpy.

ESR spectra of the complexes: The X-band powder ESR spectra were measured for all the complexes at room temperature. Binuclear copper(II) complexes exhibit a spin-triplet ground state with a total spin value S = 1 and spin-singlet ground state with a total spin state S = 0, which are attributed to the magnetic exchange between paramagnetic centers. At 3600 × 10^{-4} T, these complexes show an asymmetrical shape of upper and lower absorption peaks, which appear on each side of the ground line. The absorption peaks, in correspondence with spin-triplet ground state for its allowed transition at ΔMs = 1, reveal the presence of anisotropic spin-triplet ground state in these three binuclear complexes [7]. The g values of allowed transitions can be evaluated by Mn-reference, the spectrum parameters can be deduced: $g_{||} = 2.18$, $g_{\perp} = 2.03$ (for phen); $g_{||} = 2.17$, $g_{\perp} = 2.09$ (for bpy) and $g_{||} = 2.22$, $g_{\perp} = 2.04$ (for Me$_2$bpy). Meanwhile, a weak absorption ($g \approx 4$) at half field (about 1600 × 10^{-4} T) can be observed for all the complexes, about 10^{-3} times of the normal absorption, appear the half field absorption consistent with the forbidden transition of ΔMs = 2 present further proof for the existence of spin super-exchange interaction between the copper(II) centers [8].

Magnetism of the copper(II)–copper(II) complexes: The magnetism of the complexes in solid state was studied at 1.0 T, over the temperature range 4.99–299 K. Figs. 2–4 were plotted according to the observed data for the molecular susceptibility and the effective magnetic moment. All of the three effective moments increase with the temperature decrease, which indicates a ferromagnetic coupling between the copper(II) centers. In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic analysis was carried out with the modified Bleaney-Bowers equation based on the exchange Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ with $S_1 = S_2 = 1/2$ and adding a term to correct the intermolecular interaction (zJ′). The molar susceptibility of copper(II)–copper(II) system is given by

$$\chi'_M = \chi_M/[1 - (2zJ'/N\beta^2g^2)\cdot\chi_M]; \qquad \chi_M = (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1} + N_\alpha \quad (1)$$

where χ_M denotes the susceptibility per binuclear complex, N_α the temperature independent paramagnetism (120×10^6 $cm^3 \cdot mol^{-1}$) and the other symbols have their usual meanings. As shown in Figs. 2–4, good least-squares fits to experimental data are attained with (1). The magnetic parameters determined for $[Cu_2(phth)(phen)_4](ClO_4)_2 \cdot H_2O$

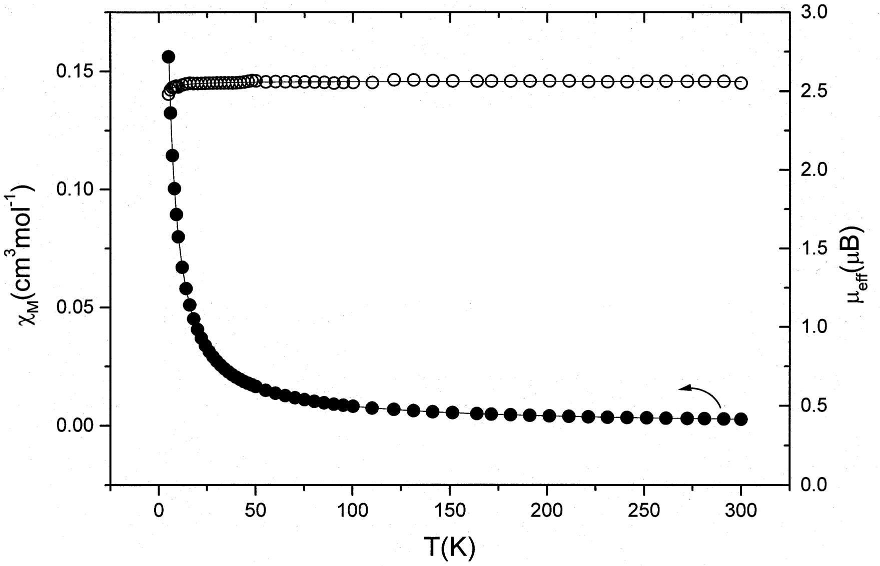

Figure 2. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[Cu_2(phth)(phen)_4](ClO_4)_2 \cdot H_2O$.

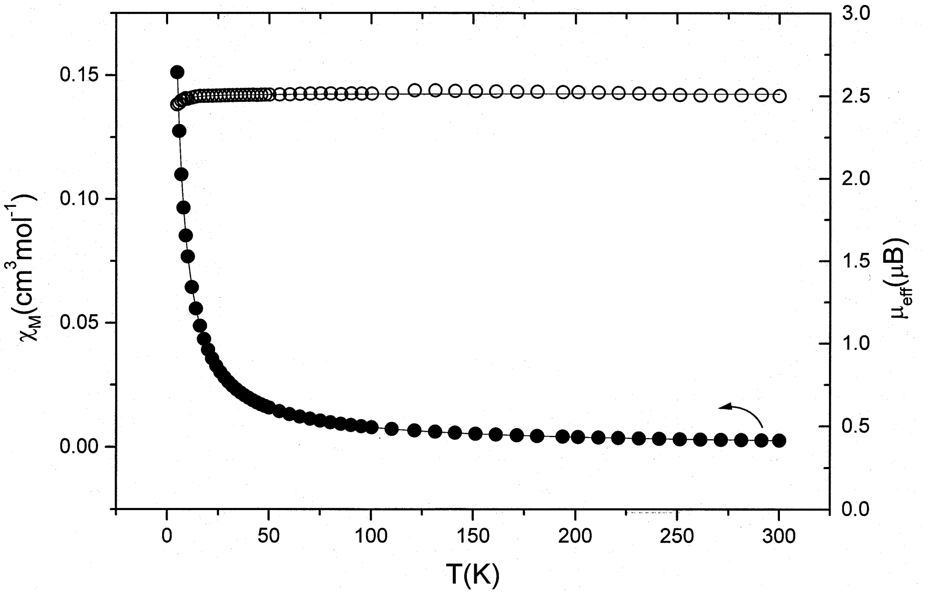

Figure 3. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[Cu_2(phth)(bpy)_4](ClO_4)_2 \cdot 0.5H_2O$.

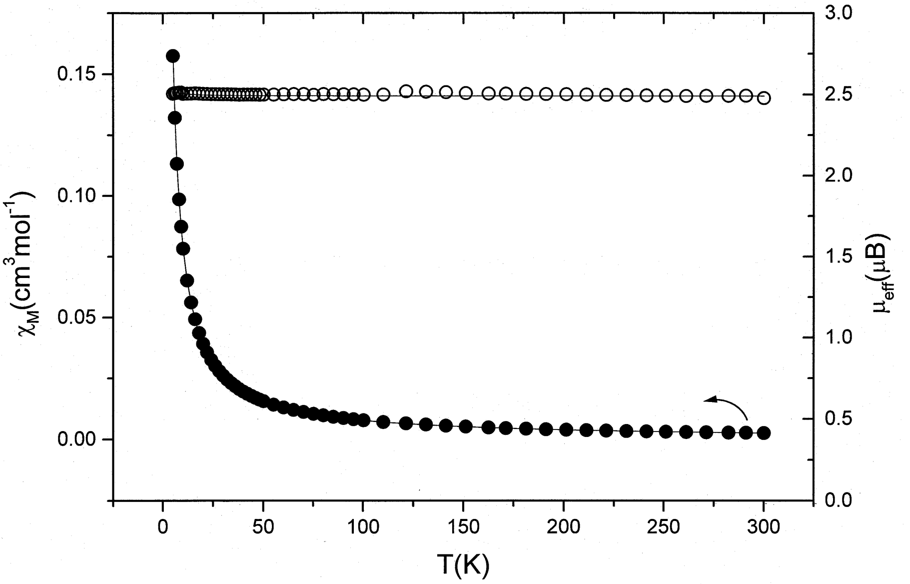

Figure 4. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $[Cu_2(phth)(Me_2bpy)_4](ClO_4)_2{\cdot}H_2O$.

are: J = 0.14 cm^{-1}, g = 2.09, zJ′ = –0.47 cm^{-1} and F = 5.45×10^{-6} [F = $\Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$], for $[Cu_2(phth)(bpy)_4](ClO_4)_2{\cdot}5H_2O$, J = 0.18 cm^{-1}, g = 2.05, zJ′ = –0.47 cm^{-1} and F = 2.84×10^{-6} and for $[Cu_2(phth)(Me_2bpy)_4](ClO_4)_2{\cdot}H_2O$, J = 0.18 cm^{-1}, g = 2.03, zJ′ = –0.02 cm^{-1}, and F = 2.69×10^{-6}. These data also provide support that the studied complexes undergo a ferromagnetic spin-exchange interaction, and a weak intermolecular antiferromagnetic coupling was found.

To describe the mechanism of the exchange interaction, several models have been proposed [9–11]. For the present dicopper(II) complexes, the coupling can be attributed to accidental orthogonality between the one single electronic occupied orbital in the two centers. We compared the present J value with those previously reported for the dicopper(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 coupling between the copper(II) ions is ferromagnetic.

Table 2. Magnetic data of the complexes.

Complexes	J (cm^{-1})	Ref.
$[Cu_2(NAPH)(phen)_4](ClO_4)_2{\cdot}1.5H_2O$	+0.28	12
$[Cu_2(3\text{-}NO_2\text{-}phth)(phen)_4](ClO_4)_2{\cdot}H_2O$	+5.26	13
$[Cu_2(phth)(phen)_4](ClO_4)_2{\cdot}H_2O$	+0.14	This work

NAPH: Naphthalato.

REFERENCES

1. Kahn O., *Comm. Inorg. Chem*., **3**, 105 (1984).
2. Shakhatreh S.K., Bakalbassis E.G., Brudgam I., Hartl H., Mrozinski J. and Tsipis C.A., *Inorg. Chem*., **30**, 2801 (1991).
3. Verdaguer M., Gouteron J., Jeannin S., Jeannin Y. and Kahn O., *Inorg. Chem*., **23**, 4291 (1984).
4. Rosenthal M.R., *J. Chem. Educ*., **50**, 331(1973).
5. Foley J., Tyagi S. and Hathaway B.J., *J. Chem. Soc. Dalton Trans*., **1** (1984).
6. Hathaway B.J. and Billing D.E., *Coord. Chem. Rev*., **5**, 143 (1970).
7. Julve M., Verdaguer M. and Charlot M.F., *Inorg. Chim. Acta,* **82**, 5 (1984).
8. Folgado J.V., *Inorg. Chem*., **27**, 19 (1988).
9. Lambert S., Spiro S.L.,Gagne R.R. and Hendrickson D.N., *Inorg. Chem.*, **21**, 68 (1982).
10. Dance I.G., *Inorg. Chim. Acta*, **9**, 77 (1974).
11. Hayp J., Thibeault J.C. and Hoffmann R., *J. Am. Chem. Soc*., **97**, 4884 (1975).
12. Gao J., Ma S.L. and Liao D.Z., *Polish J. Chem*., **71**, 695 (1997).
13. Ma S.L., Zhang L.Z., Lu L.L. and Tang M.Y., *Polish J. Chem*., **76**, 511 (2002).