

Synthesis and Magnetic Studies of Binuclear Iron(II) Complexes Bridged by Tetracarboxylato Groups

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Four novel binuclear iron(II) complexes, namely $[\text{Fe}_2(\text{PMTA})\text{L}_4]$, where L denotes 4,4'-dimethyl-2,2'-bipyridine ($\text{Me}_2\text{-bpy}$); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), respectively, and PMTA stands for the tetraanion of pyromellitic acid, have been synthesized and characterized. Based on elemental analyses, magnetic moments at room-temperature and molar conductivity measurements, and spectroscopic (electronic and IR spectra) studies, extended PMTA-bridged structures consisting of two iron(II) ions, each in a distorted octahedral environment, are proposed for these complexes. The variable temperature magnetic susceptibilities (4–300 K) of the complexes $[\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]$ (**1**) and $[\text{Fe}_2(\text{PMTA})(\text{phen})_4]$ (**2**) were measured and the magnetic analysis was carried out by least-square method to the observed data with the susceptibility equation derived from the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, giving the exchange integrals $J = -1.09 \text{ cm}^{-1}$ for (**1**) and $J = -1.18 \text{ cm}^{-1}$ for (**2**). The results indicate that there is a very weak antiferromagnetic spin-exchange interaction between the Fe(II) ions within each molecule.

Key words: μ -tetracarboxylato-bridge, binuclear iron(II) complexes, synthesis, magnetism

The study of long-range magnetic interactions of binuclear transition-metal complexes propagated by multiatom bridges has been an active field of research. Interest in this field stems from attempts to gain some insight into the pathways of electron transfer, to mimic the structural and functional properties in biological systems [1], and to obtain some useful information concerning the design and synthesis of novel molecule-based magnets [2–4]. So far, much effort has been devoted to the development of multiatom bridging ligands that can afford long-distance magnetic interactions [5–12]. The tetraanion of pyromellitic acid (abbreviated as PMTA), due to its peculiar structure, could be a good candidate in supporting long-distance magnetic exchange interactions. Chaudhuri *et al.* [6] first utilized PMTA as a multiatom bridge to synthesize the binuclear copper(II) complex $[\text{LCu}(\mu\text{-tetracarboxylato})\text{CuL}] \cdot 4\text{H}_2\text{O}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). It has been revealed by the single crystal X-ray and magnetic analyses [6] that the long-range antiferromagnetic coupling could occur between the copper(II) ions bridged by the PMTA ligand although the $\text{Cu} \cdots \text{Cu}$ separation is 7.8 Å. In order to provide more examples of PMTA-bridged

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binuclear complexes and to understand better the factors affecting the superexchange interaction propagated by PMTA, it is necessary to synthesize a series of binuclear complexes of essentially the same structure except for the metal ion. In this paper we describe the synthesis, characterization and magnetism of four new iron(II) binuclear complexes using PMTA as a bridging ligand: $[\text{Fe}_2(\text{PMTA})\text{L}_4]$, where L represents 4,4'-dimethyl-2,2'-bipyridine ($\text{Me}_2\text{-bpy}$); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen), respectively, and PMTA denotes the tetraanion of pyromellitic acid.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Pyromellitic acid (H_4PMTA), $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ and the terminal ligands 4,4'-dimethyl-2,2'-bipyridine ($\text{Me}_2\text{-bpy}$); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen), 5-bromo-1,10-phenanthroline (Br-phen) (analytical grade) were used as commercially obtained.

Synthesis of $[\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]$ (1): To a solution of 254.3 mg (1 mmol) of pyromellitic acid in methanol (20 mL) was added dropwise a methanol solution (20 mL) of 167.8 mg (4 mmol) of $\text{LiOH}\cdot\text{H}_2\text{O}$ under stirring at room temperature. The stirring was continued until the mixture became clear. The resulting solution was then filtered. To the filtrate was added a methanol solution (15 mL) of 762 mg (2.1 mmol) of $\text{Fe}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ and 737 mg (4 mmol) of $\text{Me}_2\text{-bpy}$ in 20 mL methanol solution under N_2 . The color of the solution changed immediately from green to red-brown and a small amount of precipitate formed. The mixture was subsequently refluxed for 6 h. After cooling to room temperature, red-brown microcrystals thus formed were filtered, washed with methanol, water and diethyl ether several times and dried with P_2O_5 under reduced pressure. Recrystallization was carried out from acetonitrile/ethanol (1:1) mixture. Yield, 890 mg (81%); m.p., 201.2°C.

Synthesis of $[\text{Fe}_2(\text{PMTA})(\text{phen})_4]$ (2): This complex was obtained as brown microcrystals by the same procedure and the same amounts of reagents as above, but by using phen instead of $\text{Me}_2\text{-bpy}$. Recrystallization was carried out from DMF/ethanol (1:2) mixture. Yield, 757.9 mg (70%); m.p., 239.8°C.

Synthesis of $[\text{Fe}_2(\text{PMTA})(\text{Cl-phen})_4]$ (3): This complex was obtained as brown microcrystals by the same procedure and the same amounts of reagents as above, but by using Cl-phen instead of $\text{Me}_2\text{-bpy}$. Yield, 1037.4 mg (85%); m.p., 189.4°C.

Synthesis of $[\text{Fe}_2(\text{PMTA})(\text{Br-phen})_4]$ (4): This pale-red compound was prepared as described for complex (1), except that Br-phen instead of $\text{Me}_2\text{-bpy}$. Yield, 1230.4 mg (88%); m.p., 199.8°C.

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Model 240 Perkin-Elmer elemental analyzer. The iron content was determined by EDTA titration. All the analytical data are commensurate with the theoretical values. The infrared spectra were measured on a Model 810 Shimadzu infrared spectrometer in KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. The melting points of the complexes were determined on a Model XT 7-1 micro-melting point apparatus. Molar conductances were measured (DMF solution) with a Shanghai DDS-11A conductometer. Variable temperature magnetic susceptibilities (4–300 K) were measured using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [13] for all the constituent atoms and the effective magnetic moments were calculated by $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the magnetic susceptibility per molecule corrected for diamagnetism of the constituting atoms.

RESULTS AND DISCUSSION

Composition and coordination environment of the complexes: The PMTA-bridged binuclear complexes were obtained by the reaction of H_2PMTA with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the terminal ligand L (L = $\text{Me}_2\text{-bpy}$, phen, Cl-phen, Br-phen) in methanol in the presence of a base. The use of $\text{LiOH} \cdot \text{H}_2\text{O}$ as the base gave good results because this compound and its salt (LiClO_4) formed in the reaction are all fairly soluble in methanol and the products are little contaminated with these inorganic materials. Indeed, elemental analytic data for the newly prepared complexes indicate that the reaction of PMTA with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and L (L = $\text{Me}_2\text{-bpy}$, phen, Cl-phen, Br-phen) in *ca.* 1:2:4 mole ratio yielded the binuclear complexes of the general formula $[\text{Fe}_2(\text{PMTA})\text{L}_4]$. These compounds are the first examples of binuclear iron(II) complexes bridged by PMTA. Based on the molar conductivity and magnetic moment at room-temperature measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

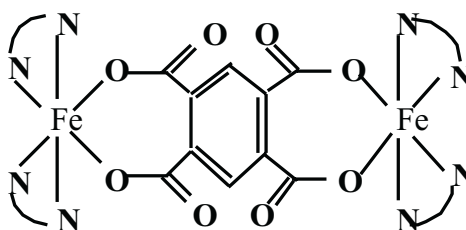


Figure 1. Plausible coordination environment of the binuclear complexes (N N = $\text{Me}_2\text{-bpy}$, phen, Cl-phen, Br-phen).

General properties and molar conductance of the binuclear complexes: All the binuclear complexes are sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene, but are soluble in acetone, acetonitrile, DMF and DMSO to give stable solutions at room temperature. In the solid state all the complexes are fairly stable in air, thus allowing measurements to be made. For the four complexes, the molar conductance values in DMF solution (see Table 1) show that all complexes are non-electrolytes [14]. This is consistent with the measured IR data.

Table 1. Physical data of the PMTA binuclear iron(II) complexes.

Complex	Λ_M ($\text{s}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	μ_{eff} (B.M)	IR ^a (cm^{-1})				UV $\nu(10^3 \text{ cm}^{-1})/\epsilon_{\text{max}}(\text{mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{L})$		
			$\nu_{\text{as}}(\text{CO}_2^-)$	$\nu_{\text{s}}(\text{CO}_2^-)$	$\nu(\text{Fe-O})$	$\nu(\text{C=N})$	$\nu(\text{Fe-N})$	d-d	CT
(1)	4.0	6.90	1610 s,br	1380 s,br	520 w	1525 m	450 w	11.40 (30)	29.6 (29700)
(2)	5.2	6.88	1630 s,br	1400 s,br	510 w	1510 m	452 w	11.45 (21)	29.9 (21580)
(3)	4.5	6.75	1620 s,br	1375 s,br	518 w	1520 m	450 w	11.41 (20)	30.8 (28900)
(4)	4.8	6.78	1625 s,br	1370 s,br	515 w	1523 m	460 w	11.42 (22)	31.1 (28800)

^a_s = strong, m = medium, w = weak, br = broad.

(1) = $[\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]$, (2) = $[\text{Fe}_2(\text{PMTA})(\text{phen})_4]$, (3) = $[\text{Fe}_2(\text{PMTA})(\text{Cl-phen})_4]$,

(4) = $[\text{Fe}_2(\text{PMTA})(\text{Br-phen})_4]$

Infrared spectra: IR spectra taken in the region 4000–400 cm^{-1} provide some information regarding the mode of coordination in the complexes and were analysed in comparison with that of the free ligand (H_4PMTA). The most relevant IR absorption bands due to the complexes, together with their assignments, are shown in Table 1. The IR spectrum of pyromellitic acid shows a broad band near 1700 cm^{-1} , which is attributed to $\nu(\text{C}=\text{O})$ of the carboxylic group. However, in the IR spectra of all complexes, this band had disappeared, accompanied by the appearance of two characteristic strong and broad bands at *ca.* 1620 cm^{-1} and 1380 cm^{-1} attributed to $\nu_{\text{as}}(\text{CO}_2^-)$ (1630–1610 cm^{-1}) and $\nu_{\text{s}}(\text{CO}_2^-)$ (1400–1370 cm^{-1}) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$ bands strongly suggests the end-to-end linking of the PMTA ligand in an equivalent way at both sites [5]. The appearance of a new band at 510–520 cm^{-1} , due to $\nu(\text{Fe}-\text{O})$, further confirms the coordinated nature of the carboxylate groups. Moreover, the coordination modes of carboxylate groups have often been diagnosed by the separation between $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$. That is, bidentate carboxylate groups show a separation smaller than 200 cm^{-1} , whereas unidentate carboxylate groups show a separation larger than 200 cm^{-1} . Thus, for the present complexes, these two bands were separated by *ca.* 230 cm^{-1} (see Table 1), suggesting an unidentate coordination mode for the four carboxylate groups of the PMTA ligand [15]. The unidentate coordination modes of the carboxylates in PMTA were supported by the crystal structure of the analogous complex [6] $[\text{LCu}(\mu\text{-tetracarboxylato})\text{CuL}]\cdot 4\text{H}_2\text{O}$ ($\text{L} = 1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane}$). In addition, the $-\text{N}=\text{C}-$ vibrations for the terminal ligands ($\text{Me}_2\text{-bpy}$, phen, Cl-phen, Br-phen) are present in the corresponding binuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the metal ion. This view is further supported by the appearance of a band corresponding to the metal-nitrogen stretching vibration at 450–460 cm^{-1} in the complexes. Furthermore, the band centered at 1100 cm^{-1} , typical for $\nu(\text{Cl}-\text{O})$ stretching of the perchlorate group [16], was not found. This is consistent with the conductance measurements and elemental analyses.

Electronic spectra: In order to obtain further information on the mode of bonding of the Fe(II) ion to the ligand, the electronic spectra of these binuclear complexes were measured in DMF solutions. As shown in Table 1, the electronic absorption spectra of the four complexes in DMF solution are similar. For all four complexes a weak intensity band ($\epsilon = 20\text{--}30 \text{ mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{L}$) in the 11400–11450 cm^{-1} region is observed, which may reasonably be assigned to the ${}^5\text{T}_{2\text{g}} \rightarrow {}^5\text{E}_{\text{g}}$ transition and is characteristic of a high spin octahedral configuration around iron(II) ion [17]. In addition, a strong absorption ($\epsilon > 10^4 \text{ mol}^{-1}\cdot\text{cm}^{-1}\cdot\text{L}$) at *ca.* $30 \times 10^3 \text{ cm}^{-1}$ found for all the complexes may be attributed to the charge-transfer absorption band [18]. Further investigation of these and similar systems are still required in order to obtain a detailed assignment for charge transfer.

All the complexes are soluble in some organic solvents, but attempts to obtain single crystals suitable for X-ray structure determination have been unsuccessful. However, based on the composition of these complexes, the infrared and electronic

spectra, magnetic moments at room-temperature and molar conductivity measurements, as well as the results of variable-temperature susceptibilities, which we will discuss later, and the crystal structure of the analogous complex [6], it is reasonable to suppose that these complexes have an extended PMTA-bridged structure, in which each carboxylic group is bound to the iron(II) ion in a monodentate fashion through only one oxygen atom, yielding two seven-membered rings. Each iron(II) ion is in a distorted octahedral environment (Figure 1).

Magnetic properties: The observed magnetic moment per complex at room temperature, shown in Table 1, is slightly less than the spin-only value (6.93 B. M.), calculated from the equation, $\mu_{\text{eff}} = (\mu_{\text{Fe(II)}}^2 + \mu_{\text{Fe(II)}}^2)^{1/2}$, in the absence of an exchange interaction for the present binuclear iron(II) ($S_1 = S_2 = 2$) complexes. This result reflects that both iron(II) ions of the binuclear complexes are in the $S = 2$ ground state and suggests the presence of a weak antiferromagnetic spin-exchange interaction in these complexes [18]. In order to obtain further structural information, variable temperature (4.2–300 K) magnetic susceptibility data were collected for $[\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]$ (**1**) and $[\text{Fe}_2(\text{PMTA})(\text{phen})_4]$ (**2**) complexes. The results are shown in Fig. 2 in the form of plots $\chi_{\text{M}}T$ vs. T , where χ_{M} and T denote magnetic susceptibility per molecule and temperature, respectively. From Fig. 2 it can be seen that the magnetic behavior of the two complexes is similar. When the temperature is lowered, the curve of the $\chi_{\text{M}}T$ vs. T exhibits a continuous decrease, with $\chi_{\text{M}}T = 5.95 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ (6.90 B.M.) (**1**) and $\chi_{\text{M}}T = 5.92 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ (6.88 B.M.) (**2**) at 300 K and the extrapolated value very close to zero when T approaches zero. This is typical for an intramolecular antiferromagnetic interaction between high-spin iron(II) ions with a molecular spin singlet ground state. In other words, the iron(II) ions within the two complexes do not present any spin transition. Thus, as noted above, the observed magnetic behavior clearly demonstrates that the iron(II) ions are high-spin in the

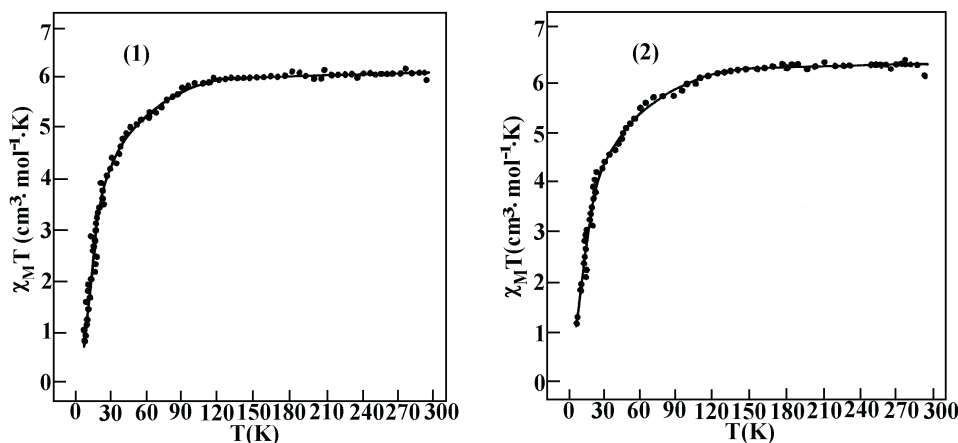


Figure 2. $\chi_{\text{M}}T$ versus T plot for the complexes $[\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]$ (**1**) and $[\text{Fe}_2(\text{PMTA})(\text{phen})_4]$ (**2**). The curves are based on Eq. (1) using the magnetic parameters given in the text. (•), experimental data. (—), calculated curves as described in the text.

whole temperature range and antiferromagnetically coupled through the PMTA bridge within each binuclear complex [19].

In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic analyses were carried out by the spin Hamiltonian for isotropic binuclear magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$), where the exchange integral J is negative for an antiferromagnetic interaction and positive for a ferromagnetic one. For the iron(II)–iron(II) ($S_1 = S_2 = 2$) system, the molar magnetic susceptibility is given by:

$$\chi_M = \frac{2N\beta^2 g^2}{KT} \left[\frac{A}{B} \right] (1 - \rho) + \frac{0.75g^2}{T} \rho + N\alpha \quad (1)$$

where $A = 30 + 14\exp(8x) + 5\exp(14x) + \exp(18x)$, $B = 9 + 7\exp(8x) + 5\exp(14x) + 3\exp(18x) + \exp(20x)$, with $x = -J/KT$, χ_M is the molecular susceptibility per binuclear complex, $N\alpha$ is the temperature-independent paramagnetism ($N\alpha = 100 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$), ρ stands for the impurity with $S = 2$, and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-square fits to the experimental data were obtained with (1) for complexes **(1)** and **(2)**. The magnetic parameters thus determined and the agreement factor F , defined here as $F = \sum[(\chi_{M\text{obs.}} - (\chi_{M\text{calc.}})]^2 / \sum(\chi_{M\text{obs.}}$, are: $J = -1.09 \text{ cm}^{-1}$, $g = 2.18$, $\rho = 0.002$, $F = 1.6 \times 10^{-5}$ for **(1)**; and $J = -1.18 \text{ cm}^{-1}$, $g = 2.19$, $\rho = 0.003$, $F = 2.7 \times 10^{-5}$ for **(2)**. In order to investigate further the zero-field splitting of the iron(II) ion effects upon the quality of the fitting, we also attempted to introduce the local anisotropy of the iron(II) ion in the calculation of χ_M . This anisotropy splits the excited states in the zero field. Unfortunately, we did not get any improvement of the fitting. This fact indicates that the zero-field splitting of the excited state is evidently weaker than the intramolecular spin exchange and can be neglected. These results indicate that the complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the iron(II) ions within each molecule. The weak antiferromagnetic behavior for these systems may result mainly from the geometric structures of the complexes and the properties of the bridge ligand [20].

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