

## Synthesis, Characterization and Magnetic Properties of $\mu$ -2-Nitroterephthalato Binuclear Iron(II) Complexes

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Four new binuclear iron(II) complexes bridged by 2-nitroterephthalato groups (NTPHA) and ended with 4,4'-dimethyl-2,2'-bipyridine (Me<sub>2</sub>-bpy), 2,9-dimethyl-1,10-phenanthroline (Me<sub>2</sub>-phen), 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), namely [Fe<sub>2</sub>(NTPHA)L<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (L = Me<sub>2</sub>-bpy, Me<sub>2</sub>-phen, Cl-phen, Br-phen), have been synthesized and characterized. Based on elemental analyses, magnetic moments (at room temperature), molar conductance measurements, and spectroscopic studies, extended NTPHA-bridged structures consisting of two iron(II) ions, each in a distorted octahedral environment are proposed for these complexes. The variable temperature magnetic susceptibilities of complexes [Fe<sub>2</sub>(NTPHA)(Me<sub>2</sub>-bpy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Fe<sub>2</sub>(NTPHA)(Me<sub>2</sub>-phen)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**) were measured over the range 4.2–300 K and the observed data were successfully simulated by the equation based on the spin Hamiltonian operator,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ , giving the exchange integrals  $J = -1.02 \text{ cm}^{-1}$  for (**1**) and  $J = -1.96 \text{ cm}^{-1}$  for (**2**). These results indicate the presence of a very weakly antiferromagnetic spin-exchange interaction between the iron(II) ions within each molecule. The influence of nitro substituent in the bridging ligand on magnetic interaction between the metal ions of this kind of complexes is also discussed.

**Key words:** 2-nitroterephthalato-bridge, binuclear iron(II) complexes, magnetism, synthesis

The study of long-range magnetic interactions of polynuclear transition metal complexes propagated by multiatom bridges has been an active field of research, with the aim of understanding fundamental factors governing the magnetic properties of transition-metal complexes, and to obtain some useful information about designing molecule-based ferromagnets and mimicking the active sites and functions of biological substances [1,2]. The benzene dicarboxylate dianions, due to their versatile bonding modes with metal ions and their peculiar structures, involving carboxylate groups that are non-coplanar with themselves and with the benzene ring, could be good candidates for the study of long-distance magnetic exchange interactions. Many polynuclear complexes containing the bridging phenyl dicarboxylate ligands have been synthesized and their magnetic properties have been studied [3–9]. It has been revealed by X-ray diffraction analyses [3–6,8] and variable temperature magnetic susceptibility investigation that long-range magnetic coupling can occur between the

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paramagnetic centers bridged by the phenyl dicarboxylate groups. However, to our knowledge, no 2-nitroterephthalato-bridged binuclear iron(II) complexes have been reported. Owing to the importance mentioned above and to understand the properties of this kind of complexes in magnetism, in this paper, we describe the syntheses and characterization of four new  $\mu$ -2-nitroterephthalato binuclear iron(II) complexes of general formula  $[\text{Fe}_2(\text{NTPHA})\text{L}_4](\text{ClO}_4)_2$  ( $\text{L} = \text{Me}_2\text{-bpy}$ ,  $\text{Me}_2\text{-phen}$ ,  $\text{Cl-phen}$ ,  $\text{Br-phen}$ ). The magnetic properties of the  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  (**1**) and  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  (**2**) have been studied to examine the effect of nitro substituent in the bridging ligand on magnetic interaction between the iron(II) ions. The results suggest that the nitro substituent in the bridging ligand will reduce antiferromagnetic exchange interactions between the metal ions.

## EXPERIMENTAL

**Materials:** Piperidinium 2-nitroterephthalate salt was synthesized by the literature method [4].  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the terminal ligands 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{-bpy}$ ); 2,9-dimethyl-1,10-phenanthroline ( $\text{Me}_2\text{-phen}$ ); 5-chloro-1,10-phenanthroline ( $\text{Cl-phen}$ ) and 5-bromo-1,10-phenanthroline ( $\text{Br-phen}$ ) were analytical grade and used as commercially obtained.

**Synthesis of  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  (**1**):** To a solution of piperidinium 2-nitroterephthalate salt (417 mg, 1 mmol) stirred in methanol (15 mL) was successively added a solution of  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (726 mg, 2 mmol) in methanol (20 mL) and  $\text{Me}_2\text{-bpy}$  (737 mg, 4 mmol) in the same solvent (20 mL) under  $\text{N}_2$ . The reaction mixture was subsequently refluxed for *ca.* 6 h. After cooling to room temperature, violet microcrystals thus formed were collected by suction filtration, washed with methanol and diethyl ether several times, and dried over  $\text{P}_2\text{O}_5$  under reduced pressure. Recrystallization was carried out from a hot acetone solution. Yield, 943 mg (75%), m.p., 199.6°C. Anal. calcd for  $\text{Fe}_2\text{C}_{56}\text{H}_{51}\text{N}_9\text{O}_{14}\text{Cl}_2$  (M.W. 1256.67): C, 53.52; H, 4.09; N, 10.03; Fe, 8.89%. Found: C, 53.47; H, 4.12; N, 10.19; Fe, 8.75%.

**Synthesis of  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  (**2**):** This complex was obtained as blue microcrystals by the same procedure and the same amounts of reagents as above but by using  $\text{Me}_2\text{-phen}$  (833 mg, 4 mmol) instead of  $\text{Me}_2\text{-bpy}$ . 1096 mg (81%) of this complex was yielded and crystallized from an DMF/ethanol (1:3) mixture, m.p., 185.9°C. Anal. calcd for  $\text{Fe}_2\text{C}_{64}\text{H}_{51}\text{N}_9\text{O}_{14}\text{Cl}_2$  (M.W. 1352.76): C, 56.82; H, 3.80; N, 9.32; Fe, 8.26%. Found: C, 56.70; H, 3.72; N, 9.14; Fe, 8.09%.

**Synthesis of  $[\text{Fe}_2(\text{NTPHA})(\text{Cl-phen})_4](\text{ClO}_4)_2$  (**3**):** This compound was prepared as described for complex (**1**), except that  $\text{Cl-phen}$  (858.6 mg, 4 mmol) was used instead of  $\text{Me}_2\text{-bpy}$  and the same amount of ethanol instead of methanol. The pale-green microcrystals obtained were recrystallized from a hot acetonitrile solution. Yield, 1172 mg (85%), m.p., 192.6°C. Anal. calcd for  $\text{Fe}_2\text{C}_{56}\text{H}_{31}\text{N}_9\text{O}_{14}\text{Cl}_6$  (M.W. 1378.32): C, 48.80; H, 2.27; N, 9.15; Fe, 8.10%. Found: C, 48.69; H, 2.34; N, 8.95; Fe, 8.27%.

**Synthesis of  $[\text{Fe}_2(\text{NTPHA})(\text{Br-phen})_4](\text{ClO}_4)_2$  (**4**):** This complex was obtained as a greenish yellow powder by the same procedure and the same amounts of reagents as above but by using  $\text{Br-phen}$  (1036.4 mg, 4 mmol) instead of  $\text{Me}_2\text{-bpy}$ . Yield, 1369 mg (88%), m.p., 217.1°C. Anal. calcd for  $\text{Fe}_2\text{C}_{56}\text{H}_{31}\text{N}_9\text{O}_{14}\text{Cl}_2\text{Br}_4$  (M.W. 1556.13): C, 43.22; H, 2.01; N, 8.10; Fe, 7.18%. Found: C, 43.37; H, 2.19; N, 8.24; Fe, 7.01%.

**Physical measurements:** Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined by EDTA titration. IR spectra were recorded with a NICOLET FT-IR 5DX spectrometer using KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities (4–300 K) were measured using a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [10] for all the constituent atoms and effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ , where  $\chi_{\text{M}}$  is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

## RESULTS AND DISCUSSION

**Composition and general properties of the complexes:** Elemental analyses and physical data (Table 1) indicated that the reaction of NTPHA with  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the terminal ligand L (L =  $\text{Me}_2\text{-bpy}$ ,  $\text{Me}_2\text{-phen}$ ,  $\text{Cl-phen}$ ,  $\text{Br-phen}$ ) in 1:2:4 mole ratio yielded binuclear complexes of general formula  $[\text{Fe}_2(\text{NTPHA})\text{L}_4](\text{ClO}_4)_2$ , as expected. In the solid state all the complexes are fairly stable in air so as to allow physical measurements. For the four complexes, the molar conductance values in acetonitrile solution (see Table 1) fall in the expected for 1:2 electrolytes range [11], indicating that the two perchlorate anions lie outside the coordination sphere. All the complexes can be soluble in some organic solvents, such as DMF, DMSO and acetonitrile; moderately are soluble in methanol, ethanol, acetone and water; and practically insoluble in carbon tetrachloride, chloroform and benzene. The binuclear complexes were further characterized on the basis of the following results.

**Infrared spectra:** The IR spectra taken in the region  $4000\sim 400\text{ cm}^{-1}$  using KBr pellets provide some information regarding the mode of coordination in the complexes and were studied and assigned on the basis of a careful comparison of the latter with the former. The selected IR absorption bands for the complexes, along with their assignments are shown in Table 1. The spectrum of 2-nitroterephthalic acid shows a broad bands near  $1710\text{ cm}^{-1}$ , attributed to  $\nu(\text{C}=\text{O})$  of the carboxylic groups. However, in the IR spectra of all complexes, this band disappeared, and is accompanied by the appearance of two characteristic strong and broad bands at *ca.*  $1580\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$ , attributed to  $\nu_{\text{as}}(\text{CO}_2)$  ( $1580\sim 1590\text{ cm}^{-1}$ ) and  $\nu_{\text{s}}(\text{CO}_2)$  ( $1400\sim 1420\text{ cm}^{-1}$ ) 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 end-to-end linking of the 2-nitroterephthalato ligand in an equivalent way at both sites [5]. This fact may be attributed to the coordination of the carboxylate oxygens to the Fe(II) ions. The appearance of a new band at  $510\sim 520\text{ cm}^{-1}$  due to  $\nu(\text{Fe}-\text{O})$  further confirms the coordinated nature of the carboxylate groups. According to the literature [12], the coordination modes of carboxylate groups have been determined by a separation  $\nu_{\text{as}}(\text{CO}_2)$  and  $\nu_{\text{s}}(\text{CO}_2)$ , *i.e.*, bidentate coordination modes of carboxylate groups show a separation smaller  $200\text{ cm}^{-1}$ , whereas unidentate coordination modes of carboxylate groups show a larger separation. Thus, for the present complexes, these two bands were separated by *ca.*  $160\text{ cm}^{-1}$  (see Table 1), suggesting a bidentate coordination mode for both carboxylate groups of the NTPHA ligand. The bidentate coordination modes of the carboxylates in bridging ligand (NTPHA) have been revealed by X-ray diffraction analysis of the analogous bridging ligand  $\mu$ -terephthalato nickel(II) binuclear complex  $[\text{Ni}_2(\text{TPHA})(\text{bpy})_4](\text{ClO}_4)_2$  [8]. On the other hand, the  $-\text{N}=\text{C}-$  stretching vibrations for the terminal ligands ( $\text{Me}_2\text{-bpy}$ ,  $\text{Me}_2\text{-phen}$ ,  $\text{Cl-phen}$ ,  $\text{Br-phen}$ ) are shifted to higher frequencies ( $1500\sim 1520\text{ cm}^{-1}$ ) in their binuclear complexes, suggesting that the N atoms of the terminal ligands coordinated with the Fe(II) ion. The additional band observed at  $450\sim 455\text{ cm}^{-1}$  due to  $\nu(\text{Fe}-\text{N})$  also supports this view. In addition, a broad and intense band centered at *ca.*  $1100\text{ cm}^{-1}$ , and a strong sharp band at *ca.*  $630$

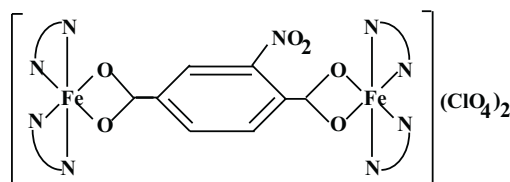
$\text{cm}^{-1}$ , typical for a non-coordinated perchlorate group [13], were observed for all binuclear complexes. This is consistent with the conductance data of the binuclear complexes.

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

Complex	$\Lambda_M$ ( $\text{s cm}^2 \text{ mol}^{-1}$ )	$\mu_{\text{eff}}$ B.M.	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )						$\lambda_{\text{max}}$ ( $10^3 \text{ cm}^{-1}$ )	
			$\nu_{\text{as}}(\text{CO}_2^-)$	$\nu_{\text{s}}(\text{CO}_2^-)$	$\nu(\text{ClO}_4^-)$	$\nu(\text{C}=\text{N})$	$\nu(\text{Cr}-\text{N})$	$\nu(\text{Cr}-\text{O})$	d-d	CT
(1)	290	6.91	1570	1400	1099, 630	1520	450	520	11.40	29.5
(2)	280	6.92	1580	1415	1095, 625	1510	452	510	11.39	30.0
(3)	275	6.88	1585	1420	1100, 630	1518	450	512	11.42	29.8
(4)	288	6.80	1590	1420	1098, 630	1500	455	515	11.45	30.3

**Electronic spectra:** 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 ( $\epsilon = 15\text{--}20 \text{ mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{L}$ ) in the  $11390\text{--}114500 \text{ cm}^{-1}$  region is observed, which may reasonably be assigned to the  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition and is characteristic of a high spin octahedral configuration around iron(II) ion [14]. 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 [15]. 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 above discussion and the crystal structure study [8] on the  $[\text{Ni}_2(\text{TPHA})(\text{bpy})_4](\text{ClO}_4)_2$  complex, we conclude that these complexes have an extended 2-nitroterephthalato-bridged structure and contain two iron(II) ions, in which the NTPHA ligand bridges in a *bis*-bidentate fashion and each iron(II) ion is in a six-coordinated octahedral environment, as shown in Fig. 1. The plausible binuclear structure is further improved by the following magnetic studies.



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

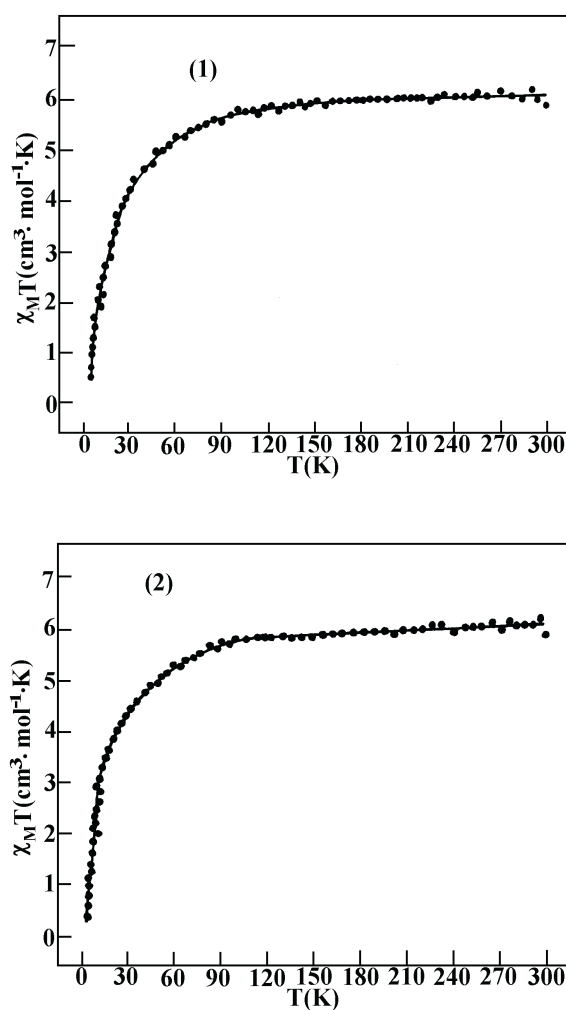
**Magnetic studies:** The observed magnetic moment per complex at room temperature, shown in Table 1, is slightly less than the spin-only value (6.93 B. M.), which is calculated from the equation,  $\mu_{\text{eff}} = (\mu_{\text{Fe(II)}}^2 + \mu_{\text{Fe(II)}}^2)^{1/2}$ , in the absence of an exchange 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 weak antiferromagnetic spin-exchange interaction in these complexes [15]. In order to obtain further structural information, variable temperature (4.2–300 K) magnetic susceptibility data were collected for  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  (**1**) and  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  (**2**) complexes. The results are shown in Fig. 2 in the form of plots  $\chi_{\text{M}}T$  vs.  $T$ , where  $\chi_{\text{M}}$  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 are similar. When the temperature is lowered, the  $\chi_{\text{M}}T$  vs.  $T$  dependence exhibits a continuous decrease, with  $\chi_{\text{M}}T = 5.97 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$  (6.91 B.M.) (**1**) and  $\chi_{\text{M}}T = 5.99 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$  (6.92 B.M.) (**2**) at 300 K and an extrapolated value very close to zero when  $T$  approaches zero. This phenomenon 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 whole temperature range and antiferromagnetically coupled through the NTPHA bridge within each binuclear complex [15–17].

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 (1),

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

where  $A = 30 + 14\exp(8x) + 5\exp(14x) + \exp(18x)$ ,  $B = 9 + 7\exp(8x) + 5\exp(14x) + 3\exp(18x) + \exp(20x)$ ,  $x = -J/KT$ , and  $\chi_{\text{M}}$  is the molecular susceptibility per binuclear complex,  $N\alpha$  is the temperature-independent paramagnetism ( $N\alpha = 100 \times 10^{-6} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ ),  $\rho$  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 Eq. (1) for complexes (**1**) and (**2**). The magnetic parameters thus determined and the agreement factor  $F$ , defined here as  $F = \Sigma[(\chi_{\text{M}})_{\text{obs.}} - (\chi_{\text{M}})_{\text{calc.}}]^2 / \Sigma(\chi_{\text{M}})_{\text{obs.}}$  are:  $J = -1.02 \text{ cm}^{-1}$ ,  $g = 2.19$ ,  $\rho = 0.002$ ,  $F = 7.8 \times 10^{-5}$  for (**1**); and  $J = -1.96 \text{ cm}^{-1}$ ,  $g = 2.16$ ,  $\rho = 0.003$ ,  $F = 7.5 \times 10^{-5}$  for (**2**). In order to investigate further 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  $\chi_{\text{M}}$ . 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 negligible. These results in-



**Figure 2.** Temperature dependence of  $\chi_M T$  for the complexes  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  (**1**) and  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  (**2**). The curve is based on Eq. (1) using the parameters given in the text. (•), experimental data; (-), calculated curve as described in the text.

dicates that the complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the iron(II) ions within each molecule.

We have previously investigated the magnetic behavior of the analogous binuclear iron(II) complexes  $[\text{Fe}_2(\text{TPHA})\text{L}_4](\text{ClO}_4)_2$  [where  $\text{TPHA}$  = terephthalate dianions,  $\text{L} = \text{Me}_2\text{-bpy}$  and  $\text{Me}_2\text{-phen}$ ] [19], and obtained the following results for the magnetic interactions:  $[\text{Fe}_2(\text{TPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  ( $J = -2.15 \text{ cm}^{-1}$ ) >  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-bpy})_4](\text{ClO}_4)_2$  ( $J = -1.02 \text{ cm}^{-1}$ );  $[\text{Fe}_2(\text{TPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  ( $J = -3.28 \text{ cm}^{-1}$ ) >  $[\text{Fe}_2(\text{NTPHA})(\text{Me}_2\text{-phen})_4](\text{ClO}_4)_2$  ( $J = -1.96 \text{ cm}^{-1}$ ). In fact, these complexes have the same skeletal structure and the same terminal ligands, and their IR and electronic

spectra are also similar. The main difference between  $[\text{Fe}_2(\text{TPHA})\text{L}_4](\text{ClO}_4)_2$  and  $[\text{Fe}_2(\text{NTPHA})\text{L}_4](\text{ClO}_4)_2$  ( $\text{L} = \text{Me}_2\text{-bpy}$  and  $\text{Me}_2\text{-phen}$ ) is that there is one nitro substituent in the bridging ligands in the latter, which may have effects on both electronic and molecular structures [18]. The steric effects of the nitro substituent will lead to less of planarity in the bridging system, so as to decrease interaction between the iron(II) ions. On the other hand, it is well known that the delocalization of the d electrons of the metal towards the bridging atom is one of the main factors affecting the magnetic exchange interaction, while the delocalization extent is determined by the energy gap between the d orbital and bridged atom orbital [20]. Since the nitro is an electron-withdrawing group which causes decrease in the electron density of the bridged group, the reduction of electron density on the bridged group decreases the electron-electron repulsion and reduces the bridged orbital levels. In other words, the energy gap between d orbitals and the bridged orbital in the present complexes is larger than that of complexes  $[\text{Fe}_2(\text{TPHA})\text{L}_4](\text{ClO}_4)_2$  ( $\text{L} = \text{Me}_2\text{-bpy}$  and  $\text{Me}_2\text{-phen}$ ). This, in turn, will lead to smaller delocalization of d electron towards the oxygen atoms of the bridge in the present complexes than that of complexes  $[\text{Fe}_2(\text{TPHA})\text{L}_4](\text{ClO}_4)_2$  ( $\text{L} = \text{Me}_2\text{-bpy}$  and  $\text{Me}_2\text{-phen}$ ), so as to decrease the antiferromagnetic interaction in the present complexes. This would explain the difference in J values for these complexes.

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