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Synthesis and Magnetic Studies of μ-Iodanilato-Bridged Iron(III)–Iron(III) Binuclear Complexes

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Four new μ-iodanilato-bridged binuclear iron(III) complexes have been prepared and identified: $[Fe_2(IA)L_4](ClO_4)_4$, where IA represents the dianion of iodanilic acid and L denotes 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (Cl-phen) or 5-nitro-1,10-phenanthroline (NO_2-phen). Based on elemental analyses, molar conductivity, magnetic moment of room-temperature measurements, IR and electronic spectra studies, these complexes are proposed to have extended IA-bridged structures consisting of two iron(III) ions, each in a distorted octahedral environment. The complexes $[Fe_2(IA)(bpy)_4](ClO_4)_4$ (**1**) and $[Fe_2(IA)(phen)_4](ClO_4)_4$ (**2**) were further characterized by variable temperature (4.2~300 K) magnetic susceptibility measurements 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 parameter $J = -6.9\ cm^{-1}$ for (**1**) and $J = -9.8\ cm^{-1}$ for (**2**). These results are commensurate with antiferromagnetic spin-exchange interaction between the two iron(III) ions within each molecule. The influence of halogen substituents in the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

Key words: iodanilato-bridged, iron(III)–iron(III), binuclear complexes, magnetism, synthesis

The studies of syntheses and magnetic exchange interactions of binuclear transition-metal complexes in view of the nature of bridge groups and stereochemical factors have received much attention in recent years [1–11]. Interest in this field is fundamental, not only for gaining some insight into the structural and electronic factors governing ferromagnetic interaction between para-magnetic centers, but also for obtaining some information about designing molecule-based magnets, and mimicking the structural and functional properties in biological systems.

In view of the effective bridged ability of chloranilate dianions (CA) and the growing interest in the synthesis of binuclear iron complexes, due to the discovery that the catalytic sites of a number of non-haem iron proteins contain diiron units [12,13], quite recently, we first utilized CA as a multi-atom bridge to synthesize and characterize the binuclear iron(III) complexes $[Fe_2(CA)L_4](ClO_4)_4$ and to study their magnetic properties [14]. As part of our systematic study on the effect of substituents in the

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bridging ligand on the magnetic interactions between iron(III) centres, the present paper is devoted to the synthesis, characterization and magnetism of four new iron(III) binuclear complexes using the dianion of iodanilic acid as bridging ligand: $[Fe_2(IA)L_4](ClO_4)_4$ [L = 1,10-phenanthroline (phen); 2,2′-bipyridine (bpy); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-nitro-1,10-phenanthroline (NO_2-phen)], where IA is dianion of iodanilic acid. The main results suggest that the different halogen substituents in the bridging ligand will have an effect on magnetic spin-exchange interactions between the iron(III) ions.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Iodanilic acid (H_2IA) was synthesized according to [15]; $Fe(ClO_4)_3 \cdot 6H_2O$; 1,10-phenanthroline (phen); 2,2′-bipyridine (bpy); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-nitro-1,10-phenanthroline (NO_2-phen) were used as commercially obtained.

Synthesis of iron(III) binuclear complexes: The methods used to prepare the complexes are virtually identical and are exemplified by $[Fe_2(IA)(bpy)_4](ClO_4)_4$. To a stirred absolute ethanol solution (20 cm^3) of iodanilic acid (1.0 mmol, 391.9 mg) was successively added dropwise an absolute ethanol solution (15 cm^3) of $Fe(ClO_4)_3 \cdot 6H_2O$ (2.0 mmol, 931.0 mg), followed by a solution of ethyl orthoformate (6 cm^3). Then, to the mixture was added an absolute ethanol solution (20 cm^3) of bpy (4.0 mmol, 624.7 mg). After the reaction mixture was boiled under reflux for *ca.* 8 h, the red-brown microcrystals thus obtained were filtered off, washed with ethanol, water and diethyl ether several times and dried over P_2O_5 under reduced pressure. Yields, colours and melting points of the complexes are collected in Table 1.

Table 1. Yields, colours and melting points (M.p) of the binuclear complexes.

Complex	Empirical Formula (Formula Weight)	Colour	Yield (%)	M.p (°C)
(1)	$Fe_2C_{46}H_{32}N_8O_{20}Cl_4I_2$ (1524.12)	red-brown	79	228
(2)	$Fe_2C_{54}H_{32}N_8O_{20}Cl_4I_2$ (1620.20)	brown	84	219
(3)	$Fe_2C_{54}H_{28}N_{12}O_{28}Cl_4I_2$ (1800.19)	light-brown	88	285
(4)	$Fe_2C_{54}H_{28}N_8O_{20}Cl_8I_2$ (1757.98)	pale-violet	75	162

(1) = $[Fe_2(IA)(bpy)_4](ClO_4)_4$, **(2)** = $[Fe_2(IA)(phen)_4](ClO_4)_4$,
(3) = $[Fe_2(IA)(NO_2\text{-phen})_4](ClO_4)_4$, **(4)** = $[Fe_2(IA)(Cl\text{-phen})_4](ClO_4)_4$.

Measurements: Analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer model 240. Metal contents were determined on ICP-4300 isoionic emission spectrophotometer. The results obtained point on formulae given in Table 1. The infrared spectra were recorded with a Nicolet FT-IR spectrophotometer model 470 in KBr pellets. The electronic spectra (DMF solution) were measured on a Varian Cary 300 spectrophotometer. Molar conductances were measured (in DMF solution) with a DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as the calibrant. Variable temperature magnetic susceptibilities (4.2~300 K) were measured using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [16] for all the constituent atoms and effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Coordination environment and general properties of the complexes: The elemental analytic data for the newly prepared complexes, listed in Table 1, indicate that the reaction of iodanilic acid (H_2IA) with $Fe(ClO_4)_3 \cdot 6H_2O$ and the terminal ligand L (L = bpy, phen, NO_2-phen, Cl-phen) in 1:2:4 mole ratio yielded the binuclear complexes of the general formula $[Fe_2(IA)L_4](ClO_4)_4$, as expected. These complexes are the first examples Fe(III)–Fe(III) bridged by IA. On the basis of the conductivity, room-temperature magnetic moment measurements, spectroscopic characterization (see Tables 2 and 3) and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

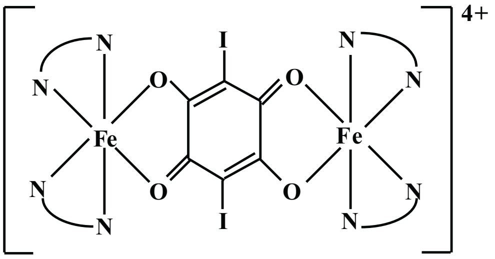

Figure 1. Coordination environment of the complexes (N⌒N = bpy, phen, NO_2-phen, Cl-phen).

These binuclear complexes are very soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature; moderately soluble in methanol and acetone, and practically insoluble in carbon tetrachloride, chloroform and benzene. The $[Fe_2(IA)(bpy)_4](ClO_4)_4$ **(1)** and $[Fe_2(IA)(phen)_4](ClO_4)_4$ **(2)** complexes can be recrystallized from 1:1 acetonitrile/ethanol and DMF/ethanol (1:2) mixture, respectively. In the solid state all the complexes are fairly stable in air, which facilitates physical measurements. For the four complexes, the observed molar conductance values in DMF solution at 25°C (310~320 $S \cdot cm^2 \cdot mol^{-1}$) are given in Table 2. These values are indicative of a 1:4 electrolytes [17], in accord with the presumed structure of the binuclear complexes shown in Fig. 1. The binuclear structure was further characterized on the basis of the following results.

Infrared spectra: In order to identify the binding mode of the ligand to the metal atom, the IR spectrum of the free ligand (H_2IA) was compared with the spectra of the binuclear iron(III) complexes. The most relevant IR absorption bands for the complexes, along with their assignments are shown in Table 2 and we will only discuss the selected infrared bands. In the IR spectra of the four complexes, a very strong peak at 1520~1530 cm^{-1} and a medium peak at 1380~1385 cm^{-1} is observed due to C=O stretching vibrations of the IA ligand. This agrees with D_{2h} symmetry for the IA ligand and suggests a bridging *bis*-bidentate coordination mode [9,10]. The *bis*-bidentate coordination modes of the bridging ligand have been revealed by X-ray diffraction analyses of analogous complexes [9,10]. The appearance of a new band at *ca.* 590

cm^{-1} due to υ(Fe–O) further confirms the coordinated nature of the IA ligand in these binuclear complexes. In contrast, the -N=C- vibrations for the terminal ligands (bpy, phen, NO_2-phen, Cl-phen) were shifted to higher frequencies in their binuclear complexes (1560~1568 cm^{-1}), suggesting that the N atoms of the terminal ligands coordinated with the metal ion. The additional band observed at around 475~480 cm^{-1} due to υ(Fe–N) further supports this view. In addition, a broad intense band centered at *ca.* 1100 cm^{-1} and a strong sharp band at *ca.* 630 cm^{-1}, typical for a non-coordinated perchlorate group [18,19], were observed for all binuclear complexes. This is consistent with the conductance data of the complexes.

Table 2. Physical data for the binuclear complexes.

Complex	Λ_M ($S\cdot cm^2\cdot mol^{-1}$)	μ_{eff} (B.M.)	IR (cm^{-1})				
			υ(C=O)	υ(Fe–O)	υ(Fe–N)	υ(C=N)	$\upsilon(ClO_4^-)$
(1)	315	8.28	1382, 1522	590	480	1560	1100, 625
(2)	318	8.30	1380, 1530	588	473	1568	1100, 630
(3)	310	8.18	1385, 1520	580	478	1562	1095, 630
(4)	320	8.22	1380, 1525	592	475	1565	1098, 628

Table 3. Electronic spectral bands and assignments of the complexes.

Complex	UV (nm)			
	CT	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$	$^6A_{1g} \rightarrow {}^4E_g(G)$
(1)	515	850	535	380
(2)	500	852	530	382
(3)	508	848	540	380
(4)	512	850	532	385

Electronic spectra: In order to obtain further structure information on these binuclear complexes, the electronic spectra of the ligand (H_2IA) and iron(III)–iron(IIII) binuclear complexes were studied and assigned on the basis of a careful comparison of the latter with the former. As shown in Table 3, the electronic spectra of the four complexes in DMF solutions are similar. All exhibit three very weak absorptions ($\varepsilon <$ 0.1) in the 848~852, 530~540 and 380~385 nm regions. The number, position and assignment (see Table 3) of these d-d bands are commensurate with a six-coordinated octahedral geometry [20]. In addition, a broad band at about 500~515 nm was also observed in the electronic spectra of the complexes. It is attributed to charge-transfer bands arising from IA ligand, as expected for *p*-benzoquinones [21], further supporting a bridging *bis*-bidentate coordination proposed for IA.

Based on the above discussion, and the crystal structure study of the analogous compounds [9,10], we conclude that these complexes have an extended IA-bridged structure and contain two iron(III) ions, in which the IA ligand bridges in a *bis*-bidentate fashion, and each iron(III) ion is in a six-coordinated octahedral environment, as shown in Fig. 1. It should be pointed out that the direct and forceful evidence for the above assumption may come from X-ray crystallography studies. Unfortunately, all our efforts to grow crystals of these binuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, the plausible binuclear structure of these complexes is supported by the following magnetic studies.

Magnetic studies: The observed magnetic moment per binuclear complex at room temperature, shown in Table 2, is less than the spin-only value (8.37 B.M) for binuclear iron(III) ($S = 5/2$) complexes in the absence of an exchange interaction. This result reflects that both iron(III) ions of the binuclear complexes are in the $S = 5/2$ ground state and suggests the presence of an antiferromagnetic spin-exchange interaction in these complexes [22]. In order to obtain further information on the structure of the complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for complexes [Fe$_2$(IA)(bpy)$_4$](ClO$_4$)$_4$ **(1)** and [Fe$_2$(IA)(phen)$_4$](ClO$_4$)$_4$ **(2)**. The results are shown in Fig. 2 in the form of the χ_M, μ_{eff} *versus* T plots, χ_M being the molar magnetic susceptibility, μ_{eff} the effective magnetic moment and T the absolute temperature. From Fig. 2 we noted that the magnetic behavior of the two complexes is similar. When the temperature is lowered, the curve of the effective magnetic moment decreases steadily in the 30~ 300 K region, but decre-

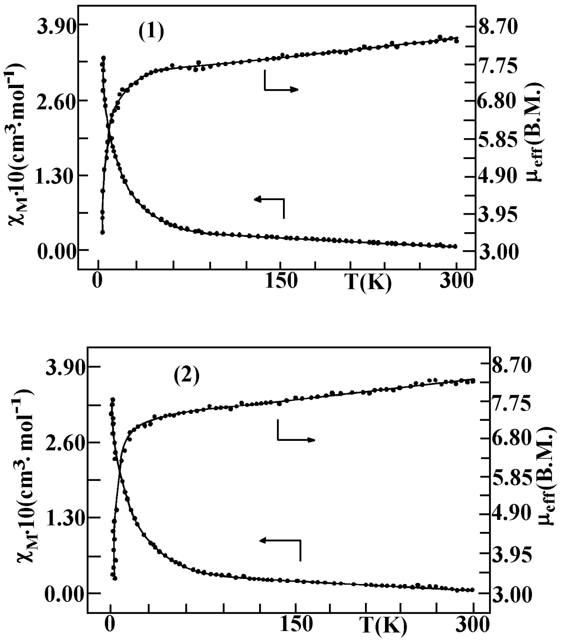

Figure 2. Temperature variation of χ_M (lower curves) and μ_{eff} (upper curves) for the complexes [Fe$_2$(IA)(bpy)$_4$](ClO$_4$)$_4$ **(1)** and [Fe$_2$(IA)(phen)$_4$](ClO$_4$)$_4$ **(2)**. The curves are based on equation (1) using the magnetic parameters given in the text. (•), experimental data; (–), calculated curve as described in the text.

ases sharply below 30 K. This phenomenon is typical for a weak antiferromagnetic interaction between iron(III) ions within each molecule and is consistent with the room-temperature magnetic moment data for the complexes. Thus, as noted above, the observed magnetic behavior both at room-temperature and variable-temperature clearly demonstrates the operation of an intramolecular antiferromagnetic spin-exchange interactions between high-spin iron(III) ions through the IA-bridge within each binuclear unit [23,24]. The rapid decrease of the magnetic moment in the low temperature range may be attributed to an intermolecular antiferromagnetic interaction and/or a zero-field splitting of the iron(III) ion. As can be seen in other cases [25–27], the contribution of the intermolecular interaction and the zero-field splitting are evidently weaker than the intramolecular spin exchange and can be negligible.

To understand quantitatively the magnitude of the spin-exchange interaction, the magnetic susceptibilities data were analysed by the spin Hamiltonian for isotropic binuclear magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$), where the exchange parameter J is negative for an antiferromagnetic interaction and positive for a ferromagnetic. For the iron(III)–iron(III) ($S_1 = S_2 = 5/2$) system, the molar magnetic susceptibility is given by equation (1), which includes the fraction of a small amount of uncoupled iron(III) impurity (ρ):

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[\frac{A}{B}\right](1-\rho) + \frac{2.19g^2}{T}\rho \tag{1}$$

$$A = \exp(2J/kT) + 5\exp(6J/kT) + 14\exp(12J/kT) + 30\exp(20J/kT) + 55\exp(30J/kT)$$
$$B = 1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT) + 9\exp(20J/kT) + 11\exp(30J/kT)$$

where χ_M denotes the molecular susceptibility per binuclear complex, 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 $F = [(\chi_M)_{calc} - (\chi_M)_{obs})^2/\Sigma(\chi_M)_{obs}$ are: $J = -6.9$ cm^{-1}, $g = 2.01$, $\rho = 0.004$, $F = 8.9\times10^{-5}$ for (1); $J = -9.8$ cm^{-1}, $g = 2.03$, $\rho = 0.002$, $F = 7.2\times10^{-5}$ for **(2)**. The negative and small J values indicate that the complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the iron(III) ions within each molecule. The antiferromagnetic behavior for these systems may be brought out mainly by the geometry structures of the complexes and the properties of the bridged ligand [4]. In addition, the very good agreement factor (F) also indicates that the contribution of the intermolecular interaction and the zero-field splitting is evidently weaker than the intramolecular spin exchange and can be neglected.

If we compare the J values with those previously reported for the analogous μ-chloranilato binuclear iron(III) complexes [14] $[Fe_2(CA)(L)_4](ClO_4)_4$ [where CA = the dianion of chloranilic acid, L = bpy and phen], we obtained the following results for the magnetic interactions: $[Fe_2(CA)(bpy)_4](ClO_4)_4$ ($J = -2.1$ cm^{-1}) <

$[Fe_2(IA)(bpy)_4](ClO_4)_4$ (J = –6.9 cm^{-1}); $[Fe_2(CA)(phen)_4](ClO_4)_4$ (J = –5.8 cm^{-1}) < $[Fe_2(IA)(phen)_4](ClO_4)_4$ (J = –9.8 cm^{-1}). In fact, these complexes have similar bridging ligands and the same terminal ligands, thus their IR and electronic spectra are also similar. The only difference between $[Fe_2(CA)(L)_4](ClO_4)_4$ and $[Fe_2(IA)(L)_4](ClO_4)_4$ (L = bpy, phen) is that there are different substituents on hydranilic acid, that is, there are two chlorine substituents (Cl) in the former case and two iodine substituents (I) in the latter, which may have effects on the electronic structure of the bridged groups. The results suggest that the different halogen substituents on hydranilic acid will have an effect on magnetic interactions between the metals ions of this kind of complexes. This magnetic behavior may be explained as consequence of the greater electronegativity of the chloro substituents compared to the iodic substituents, which leads to a decrease in the available electron density of CA ligand compared to IA ligand. 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 [4]. Since the electronegativity of iodine atom is smaller than that of chlorine atom, the energy gap between d orbitals of the metal ions and the highest occupied molecular orbitals of the bridging ligand [28] in the present complexes is smaller than that of complexes $[Fe_2(CA)(L)_4](ClO_4)_4$ (L = bpy, phen). This will, in turn, lead to larger delocalization of the d electrons towards the bridging oxygen atoms in the present complexes, compared to that of the CA-bridged binuclear iron(III) complexes, so as to increase the antiferromagnetic interaction in iodanilato-bridged binuclear iron(III) complexes [4]. This would explain the difference in J values for these complexes.

Further studies are currently underway in our laboratory to elucidate the effect of the different substituents in bridging ligand on the magnetic interaction.

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