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Synthesis, Characterization and Magnetic Properties of μ-Oxalato-Bridged Binuclear Iron(III) Complexes

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Four new oxalato-bridged iron(III)–iron(III) binuclear complexes have been synthesized and characterized, namely $[Fe_2(ox)_3L_2]$, where ox represents the oxalato dianions; L stands for 2,9-dimethyl-1,10-phenanthroline (Me_2-phen); 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen); diaminoethane (en) or 1,3-diaminopropane (pn), respectively. Based on elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR and electronic spectral studies, these complexes are proposed to have extended ox-bridged structure consisting of two iron(III) ions, each in an octahedral environment. The variable-temperature susceptibilities of $[Fe_2(ox)_3(Me_2\text{-phen})_2]$ (**1**) and $[Fe_2(ox)_3(Ph_2\text{-phen})_2]$ (**2**) complexes were measured and studied in the 4.2~300 K range. The magnetic coupling parameter is consistent with an antiferromagnetic exchange interaction between the iron(III) ions through the oxalato-bridged in both complexes (**1**) and (**2**). Based on the spin Hamiltonian operator, $\hat{H} = 2J\hat{S}_1 \cdot \hat{S}_2$, the exchange parameters (J) were evaluated as -4.85 cm^{-1} for (**1**) and J = -6.39 cm^{-1} for (**2**).

Key words: synthesis, oxalato-bridge, Fe(III)–Fe(III), binuclear complexes, magnetic properties

The studies on syntheses and magnetic properties of binuclear transition-metal complexes, in which spin coupling between paramagnetic metals is propagated by multiatom bridges, have been an active field of research in recent years [1–8]. Interest in this field is fundamental requirement, not only for gaining some insight into the electronic and geometric structure of metalloproteins and enzymes and thus correlating structure with biological function, but also for obtaining information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions. So far, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Amongst other more elaborate ligands employed in the study of magnetic interactions, the oxalato group, due to both its versatile bonding mode with metal ions and its remarkable ability to transmit electronic effects when acting as bridges between paramagnetic centers, has been shown to be an excellent multiatom bridging ligand in supporting magnetic exchange interactions. Several kinds of complexes bridged by the oxalato group have been synthesized and their magnetic properties

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studied [9–12]. Taking into account above facts, it is considerable interest to synthesize and study polynuclear complexes with bridging oxalato in order to gain some insight into the molecular magnetism of this kind of complexes. In this paper, we describe the synthesis and characterization of four new iron(III) binuclear complexes, $[Fe_2(ox)_3L_2]$, using potassium tris(oxalato)iron(III) as a polyatomic bridging ligand [L = 2,9-dimethyl-1,10-phenanthroline (Me_2-phen); 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen); diaminoethane (en) or 1,3-diaminopropane (pn); ox stands for oxalate dianions]. The magnetic properties of the complexes $[Fe_2(ox)_3(Me_2\text{-phen})_2]$ **(1)** and $[Fe_2(ox)_3(Ph_2\text{-phen})_2]$ **(2)** were studied.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Potassium tris(oxalato)iron(III) trihydrate ($K_3[Fe(ox)_3]\cdot 3H_2O$) and $Fe(ClO_4)_3\cdot 6H_2O$ were synthesized according to the literature [13,14]. The terminal ligands 2,9-dimethyl-1,10-phenanthroline (Me_2-phen); 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen); diaminoethane (en) or 1,3-diaminopropane (pn) were used as commercially obtained.

Synthesis of $[Fe_2(ox)_3(Me_2\text{-phen})_2]$ (1): To an absolute methanol solution (10 mL) of $Fe(ClO_4)_3\cdot 6H_2O$ (2.1 mmol, 970.8 mg) was successively added dropwise an absolute methanol solution (20 mL) of Me_2-phen (4.0 mmol, 833.0 mg), followed by a solution of ethyl orthoformate (9 mL) with vigorous stirring at room temperature. Then, to the mixture was added an absolute methanol solution (20 mL) of $K_3[Fe(ox)_3]\cdot 3H_2O$ (2.0 mmol, 982.5 mg). After stirring the mixture for *ca* 8 h in a darkness the violet-red microcrystals thus formed were filtered, washed with methanol, water and diethyl ether several times and dried over P_2O_5 under reduced pressure. It was recrystallized from a DMF/ethanol (1:1) mixture. Yield, 618 mg (78%); m.p. 277.1°C. Anal. calc. for $Fe_2C_{34}H_{24}N_4O_{12}$ (M.W. 792.28): C, 51.54; H, 3.05; N, 7.07; Fe, 14.10%. Found: C, 51.39; H, 3.18; N, 7.26; Fe, 14.32%.

Synthesis of $[Fe_2(ox)_3(Ph_2\text{-phen})_2]$ (2): This complex was obtained as red-brown microcrystals by the same procedure and the same amounts of reagents as above, but by using Ph_2-phen instead of Me_2-phen. Recrystallization was carried out from a hot acetonitrile solution. Yield, 894.9 mg (86%); m.p. 308.3°C. Anal. calc. for $Fe_2C_{54}H_{32}N_4O_{12}$ (M.W. 1040.57): C, 62.33; H, 3.10; N, 5.38; Fe, 10.73%. Found: C, 62.15; H, 2.97; N, 5.11; Fe, 10.52%.

Synthesis of $[Fe_2(ox)_3(en)_2]$ (3): This complex was obtained as pale-violet powder by the same procedure and the same amounts of reagents as above, but by using en instead of Me_2-phen. Yield, 248 mg (50%); m.p. 197.3°C. Anal. calc. for $Fe_2C_{10}H_{16}N_4O_{12}$ (M.W. 495.96): C, 24.22; H, 3.25; N, 11.30; Fe, 22.52%. Found: C, 24.10; H, 3.09; N, 11.51; Fe, 22.36%.

Synthesis of $[Fe_2(ox)_3(pn)_2]$ (4): This violet compound was prepared as described for complex **(1)**, except that pn instead of Me_2-phen. Yield, 324.9 mg (62%); m.p. 231.6°C. Anal. calc. for $Fe_2C_{12}H_{20}N_4O_{12}$ (M.W. 524.0): C, 27.51; H, 3.85; N, 10.69; Fe, 21.32%. Found: C, 27.32; H, 3.66; N, 10.42; Fe, 21.14%.

Measurements: Analyses for C, H and N were carried out on a Perkin-Elmer elemental analyzer model 240. Metal contents were determined by EDTA titration. The infrared spectra were measured on a Shimadzu infrared spectrophotometer model 810 in KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 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 [15] 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

Synthesis and coordination environment of the binuclear complexes: One of the strategies to design and synthesize polynuclear complexes is to use mononuclear complexes which contain potential donor groups for another metal ion. In this study, we have adopted this synthetic method to prepare Fe(III)–Fe(III) binuclear complexes. For this purpose, $K_3[Fe(ox)_3]\cdot 3H_2O$ was chosen, because it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes. Indeed, the elemental analytic data for the newly prepared complexes indicate that the reaction of $K_3[Fe(ox)_3]\cdot 3H_2O$ with $Fe(ClO_4)_3\cdot 6H_2O$ and the terminal ligand L (L = Me_2-phen, Ph_2-phen, en, pn) in *ca* 1:1:2 mole ratio yielded the binuclear complexes of the general formula $[Fe_2(ox)_3L_2]$, as expected. On the basis of the molar conductivity, room-temperature magnetic moment measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

General properties of the binuclear complexes: 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. In the solid state all the complexes are fairly stable in air so as to allow physical measurements. For the four binuclear complexes, the molar conductance in DMF solution at 25°C (see Table 1) falls in the expected range for a non-electrolyte [16], in accord with the the presumed structure of the binuclear complexes shown in Figure 1. The binuclear structure was further proved by the following results.

Infrared spectra: In order to clarify the mode of bonding, the IR spectra of the mononuclear fragment $K_3[Fe(ox)_3]\cdot 3H_2O$ and the binuclear iron(III) complexes were studied and assigned on the basis of a careful comparison of the latter with the former. The most relevant IR absorption bands due to the complexes along with their

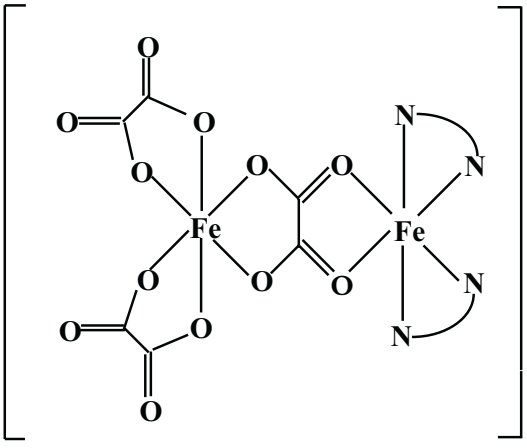

Figure 1. Coordination environment of the complexes ($\overset{\frown}{N\,N}$ = Me_2-phen, Ph_2-phen, en, pn).

assignments are given in Table 1. We will only discuss here the selected infrared bands. It is noteworthy that the spectrum of the mononuclear complex $K_3[Fe(ox)_3]\cdot 3H_2O$ only shows typical of a bidentate coordination mode of the oxalato group. However, the IR spectra of the four binuclear complexes exhibit bands corresponding to the bidentate oxalato ligand (*ca* 1715, 1680, 1650 cm^{-1} [$\nu_{as}(CO)$]; 790 cm^{-1} [$\delta(CO)$]) and also the bridging oxalato ligand (*ca* 1640 cm^{-1} [$\nu_{as}(CO)$]; 1360, 1320 cm^{-1} [$\nu_s(CO)$]) [11,12], suggesting that the oxalato group of the mononuclear fragment coordinate with iron(III) to form binuclear complexes. This is in accord with the presumed structure shown in Figure 1. On the other hand, the –N=C– or $–NH_2$ vibrations for the terminal ligands (Me_2-phen, Ph_2-phen, en, pn) were found in corresponding binuclear complexes (see Table 1), indicating that the N atoms of the terminal ligands coordinated with the metal ion. The additional band observed at around 480 cm^{-1} due to ν(Fe–N) further supports this view. In addition, the band centered at 1100 cm^{-1}, typical for ν(Cl–O) stretching of the perchlorate group [17,18], was not found for the binuclear complexes, which coincides with the non-electrolyte nature and elemental analyses of these binuclear complexes.

Electronic spectra: As shown in Table 2, the electronic spectra of the four binuclear complexes in DMF solutions are similar. For all four complexes, three very weak absorptions were observed. The assignments (see Table 2) of these d-d bands are commensurate with a six-coordinated octahedral geometry [19]. In addition, a strong band at 315~328 nm was also observed in the electronic spectra of the complexes, which may be attributed to charge-transfer bands. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer.

In spite of our many attempts, single crystals suitable for X-ray crystallography have not yet been obtained for these complexes. However, based on the composition of these complexes, their infrared spectra, electronic spectra, conductivity measurements and magnetic characterization (*vide infra*), these complexes are proposed to have an extended ox-bridged structure and to contain two Fe(III) ions bridged by the oxalato group, each iron(III) ion has a distorted octahedral coordinated environment, as shown in Figure 1. The plausible binuclear structure of these complexes is further characterized by the following magnetic studies.

Table 1. Molar conductances, effective magnetic moments and IR data (cm^{-1}) for the complexes.

Complex	Λ_M[a]	μ_{eff}[b]	ν(ox) (bidentate)		ν(ox) (bridging)				
		(B.M.)	$\nu_{as}(CO)$	$\delta(CO)$	$\nu_{as}(CO)$	$\nu_s(CO)$	ν(Fe–N)	ν(C=N)	$\nu(NH_2)$

lowered, but sharply decrease below *ca* 30 K. This behavior is characteristic for a weak antiferromagnetic interaction between the two iron(III) ions through the ox-bridge within each binuclear complexes. Thus, as noted above, the observed magnetic behavior both at room-temperature and variable-temperature clearly demonstrates the operation of a weak intramolecular antiferromagnetic spin-exchange interactions between high-spin iron(III) ions through the the ox-bridge within each binuclear unit [21]. 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 [22–24], the contribution of the intermolecular interaction and the zero-field splitting are evidently weaker than the intramolecular spin exchange and can be neglected.

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic analysis was carried out using 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):

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

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

where χ_M denotes the molecular susceptibility per binuclear complex, and the remaining symbols have their usual meanings. As shown in Figure 2, good least-square fits to the experimental data were obtained with equation (1) for complexes **(1)** and **(2)**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \sum[(\chi_M)_{calc} - (\chi_M)_{obs}]^2/\sum(\chi_M)_{obs}$ are: $J = -4.85\ cm^{-1}$, $g = 2.01$, $\rho = 0.003$, $F = 7.8\times10^{-5}$ for **(1)**; $J = -6.39\ cm^{-1}$, $g = 2.03$, $\rho = 0.004$, $F = 6.6\times10^{-5}$ for **(2)**. The results (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 magnetic behavior of the present complexes is similar with those of other relevant oxalato-bridged binuclear complexes previously reported [25,26]. It is known that the exchange interaction between the transition metal ions propagated by the oxalate bridge is strongly dependent on the geometry around the metal ions and the bridging mode of the oxalate anion. The geometry of the metal ion exerts a marked influence on the magnetic exchange interaction. Thus, the weak antiferromagnetic behavior for these systems may be brought out mainly by the geometry structures of the complexes and the properties of the bridged ligand [1]. 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.

Acknowledgments

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