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Synthesis, Characterization and Magnetism of Fe(II)–Pd(II)–Fe(II) Heterotrinuclear Complexes Bridged by Dioximato Groups

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Three new Fe(II)–Pd(II)–Fe(II) heterotrinuclear complexes with dioximato-bridge have been synthesized and identified as $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-bpy})_4]SO_4$ **(1)**, $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$ **(2)** and $[Fe_2Pd(\alpha\text{-FD})_2(Me\text{-phen})_4]SO_4$ **(3)**; where $(\alpha\text{-FD})^{2-}$ represents α-furildioximato; Me_2-bpy, Me_2-phen and Me-phen denote 4,4′-dimethyl-2,2′-bipyridine; 2,9-dimethyl-1,10-phenanthroline (Me_2-phen) and 5-methyl-1,10-phenanthroline (Me-phen). Based on elemental analyses, molar conductance measurements, IR and electronic spectral studies, these complexes are proposed to have extended dioximato-bridged structures and to consist of two iron(II) ions and a palladium(II) ion, in which the central palladium(II) ion has a square-planar environment and the end capped two iron(II) ions have a distorted octahedral environment. The magnetic properties of complexes $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-bpy})_4]SO_4$ **(1)** and $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$ **(2)** were investigated over the 4.2~300 K range and correspond to what is expected for an antiferromagnetic Fe(II)–Fe(II) pair with $S_{Fe(II)} = 2$ and $S_{Pd(II)} = 0$ (Pd^{2+} is a diamagnetic in a square-planar environment) local spins. The exchange integral (J) was evaluated as $J = -2.89$ for **(1)** and $J = -3.16$ for **(2)** based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$.

Key words: dioximato-bridge, iron(II), palladium(II), heterotrinuclear complexes, magnetism

Interest in bridged heteropolymetallic systems with different paramagnetic centers is fundamental requirement, not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers, but also for gaining some insight into the electron transfer pathway, mimicking the structural and functional properties in biological systems, and for obtaining useful information concerning the design and synthesis of molecule-based magnets [1–4]. Compared with the studies dealing with heteropolynuclear systems of 3d-transition metal ions, relatively few studies dealing with heterometal complexes containing 3d and 4d transition metal ions have been reported, especially for heterotrinuclear complexes of this kind.

In view of the effective bridging function of the oximato or dioximato groups, much work has been published on polynuclear complexes bridged by the deprotonated oximato or dioximato groups and their magnetic properties studied [4–10].

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The effective bridging function of the oximato or dioximato groups and the long-distance magnetic exchange interactions of these complexes have been revealed by single-crystal X-ray and magnetic analyses. However, to the best of our knowledge, so far, no iron(II)–palladium(II)–iron(II) heterotrinuclear complexes with extended dioximate bridges have been reported. Taking into account the above facts, it is of considerable interest to synthesize and study polynuclear complexes with bridging dioximate in order to gain some insight into the magnetic properties of this important group of complexes.

In this paper, three new iron(II)–palladium(II)–iron(II) heterotrinuclear complexes of the formula: $[Fe_2Pd(\alpha\text{-FD})_2L_4]SO_4$, where $(\alpha\text{-FD})^{2-}$ represents α-furildioximato and L denotes 4,4′-dimethyl-2,2′-bipyridine (Me_2-bpy); 2,9-dimethyl-1,10-phenanthroline (Me_2-phen) and 5-methyl-1,10-phenanthroline (Me-phen)], were synthesized and characterized. The magnetic properties of complexes $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$ **(1)** and $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$ **(2)** have been studied in detail. At present, these trinuclear complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic susceptibility and spectroscopic characterization clearly demonstrates the presence of exchange coupling between metal atoms, reveals certain electronic properties of the complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All reagents used in the synthesis were of analytical grade. The bis(α-furildioximato)palladium(II) complex, $[H_2[Pd(\alpha\text{-FD})_2]$ was prepared according to the literature methods [7,11]. $FeSO_4\cdot 7H_2O$; 4,4′-dimethyl-2,2′-bipyridine (Me_2-bpy); 2,9-dimethyl-1,10-phenanthroline (Me_2-phen) and 5-methyl-1,10-phenanthroline (Me-phen) were of analytical grade and used as commercially obtained.

Synthesis of $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-bpy})_4]SO_4$ (1): To a solution of $H_2[Pd(\alpha\text{-FD})_2]$ (0.1.09 g, 0.2 mmol) stirred in methanol (20 mL) was added successively a solution of triethylamine (2 mL). The stirring was continued at room temperature (about 30 minutes). Then to the resulting solution was added a methanol solution (10 mL) of $FeSO_4\cdot 7H_2O$ (0.41 mmol, 0.114 g) and a solution of Me_2-bpy (0.8 mmol, 0.147 g) in 20 mL of methanol under N_2 at room temperature. After the reaction mixture was stirred for 8 h to yield pale-blue microcrystals, which were filtered, washed with methanol and diethyl ether several times and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from a hot acetonitrile solution. Yield, 0.214 g (72%); m.p., 187.5°C.

Synthesis of $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$ (2): This complex was obtained as blue microcrystals by using the same procedure and the same amount of reagents as above but with Me_2-phen instead of Me_2-bpy. It was recrystallized from DMF/ethanol (1:2) mixture. Yield, 0.279 g (88%); m.p., 201.6°C.

Synthesis of $[Fe_2Pd(\alpha\text{-FD})_2(Me\text{-phen})_4]SO_4$ (3): This pale-green compound was prepared as described for complex **(1)**, except that Me-phen was used instead of Me_2-bpy. Yield, 0.238 g (78%); m.p., 231.9°C. Chemical analyses confirmed the compositions indicated.

Physical measurements: Analyses for C, H and N were carried out on a Perkin-Elmer elemental analyser model 240. Metal contents were determined on an ICP-9000 isoionic emission spectrophotometer. 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 (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 a calibrant. Variable temperature magnetic susceptibilities were measured using a Quantum Design MPMS-5 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [12] 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 magnetic susceptibility per molecule corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Synthesis and coordination environment of the heterotrinuclear complexes: One strategy for the synthesis of heteropolynuclear complexes is to use a complex as a "ligand" that contains potential donor groups capable of coordinating to other metal ions [4,13,14]. In our synthetic approach to dioximato-bridged Fe(II)–Pd(II)–Fe(II) trinuclear complexes, $H_2[Pd(\alpha\text{-FD})_2]$ mononuclear complex was used as the "complex ligand", because it can coordinate to another metal ion through the deprotonated dioximate oxygens to afford trinuclear complexes doubly bridged by oximate groups [10,15,16]. Indeed, the analytical data for the newly prepared complexes have indicated that the reaction of $H_2[Pd(\alpha\text{-FD})_2]$ with $FeSO_4\cdot 7H_2O$ and the terminal ligands L (L = Me_2-bpy, Me_2-phen and Me-phen) in *ca.* 1:2:4 mole ratio readily yielded the heterotrinuclear complexes of the general formula $[Fe_2Pd(\alpha\text{-FD})_2L_4]SO_4$, as expected. They are the first examples of iron(II)–palladium(II)–iron(II) heterotrinuclear complexes doubly bridged by oximate. In the solid state all these complexes are fairly stable in air, thus allowing physical measurements to be made. Based on the molar conductivity measurements, spectroscopic characterization and the magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Figure 1.

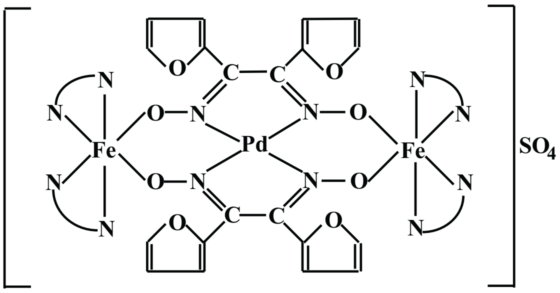

Figure 1. Proposed structure of the trinuclear complexes ($\overset{\frown}{N\ N}$ = Me_2-bpy, Me_2-phen, Me-phen).

Solubility and molar conductance of the trinuclear complexes: These trinuclear complexes are very soluble in DMSO, DMF, acetone and acetonitrile; moderately soluble in water and ethanol, and practically insoluble in carbon tetrachloride, chloroform and benzene. For the three complexes, the molar conductance values in DMF solution at 25 °C (Table 1) fall in the expected range for 1:1 electrolytes [17], in accord with the presumed structure of the complexes shown in Figure 1. The heterotrinuclear structures were further supported by the following results.

Infrared spectra: The IR spectra taken in the region 4000~400 cm^{-1} using KBr pellets provide some information regarding the mode of coordination in the trinuclear complexes and were analyzed in comparison with that of the mononuclear fragment $H_2[Pd(\alpha\text{-FD})_2]$. The relevant IR absorption bands of the complexes and their assignments are listed in Table 1. We discuss here selected infrared bands only. It is noteworthy that the spectrum of bis(α-furildioximato)palladium(II), $H_2[Pd(\alpha\text{-FD})_2]$ mononuclear complex exhibits a broad IR band at 2300~2700 cm^{-1}, which may be assigned to the ν(OH) vibration of the hydrogen bonded N–OH···O–N group [18,19]. However, in the IR spectra of all trinuclear complexes, this band had disappeared, and is accompanied by the appearance of a new band at 470~480 cm^{-1}, due to ν(Fe–O), indicating that the dioxime protons have been completely removed [4]. The medium strong band at 1270~1280 cm^{-1} in the trinuclear complexes is assignable to the N–O stretching vibrating. In fact, $H_2[Pd(\alpha\text{-FD})_2]$ mononuclear complex exhibits two or more bands of medium intensity at *ca.* 1220 cm^{-1} and 1090 cm^{-1}, assignable to the N–O stretches [18,20,21]. The second N–O IR absorption was not observed in the present trinuclear complexes because of the superposition of the band originating from the sulfate anion. On the other hand, in the spectra of trinuclear complexes, the ν(C=N) vibration is assigned to the intense band at *ca.* 1600 cm^{-1}. This vibration is situated at a significantly higher frequency than that for the corresponding bis(α-furildioximato)palladium(II) complex, where it is found at 1565 cm^{-1}. This is in accord with the concept that upon trinuclear complexes formation, the positively charged $[(C_{20}H_{12}N_4)Pd]^{2+}$ unit stabilized the negative charge on the oxygen of the oximate function, thus increasing the double bond character of the C=N bond, which is expressed as a frequency rise [6]. In addition, all the trinuclear complexes show a broad band centered at *ca.* 1120 cm^{-1}, which is typical for a non-coordinated sulfate anion [22]. This is consistent with the conductance data of the heterotrinuclear complexes. Furthermore, the C–H deformation bands of aromatic ring of the end-capping ligands (Me_2-bpy, Me_2-phen and Me-phen) are found in corresponding trinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the metal ion. The additional band observed at 450~462 cm^{-1}, due to ν(Fe–N), supports further this view.

Table 1. Physical data for the trinuclear complexes.

Complexes	Λ_M (Scm^2mol^{-1})	IR (cm^{-1})						UV (10^3 cm^{-1})	
		ν(N–O)	ν(Fe–O)	ν(Fe–N)	ν(C=N)	ν(SO_4^{2-})	ν(C–H)	d-d	CT
(**1**)	76	1276	510	470	1618	1118	842, 724	11.2, 22.3	37.1, 40.2
(**2**)	79	1270	520	478	1620	1120	840, 720	11.1, 22.7	36.8, 41.3
(**3**)	72	1274	512	480	1615	1125	845, 721	11.4, 22.5	37.0, 40.8

(**1**) = $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-bpy})_4]SO_4$, (**2**) = $[Fe_2Pd(\alpha\text{-FD})_2(Me_2\text{-phen})_4]SO_4$, (**3**) = $[Fe_2Pd(\alpha\text{-FD})_2(Me\text{-phen})_4]SO_4$.

Electronic spectra: In order to obtain further structural information on these trinuclear complexes, the electronic spectra of the trinuclear complexes in DMF solutions were measured at room temperature. Since the electronic spectra of the three complexes are similar to each other, the discussion is confined to the most important of the structure. As shown in Table 1, for all three trinuclear complexes, two strong absorption bands in 36800~37100 and 40200~40800 cm^{-1} range are observed, which may be attributed to the charge-transfer transitions. These transitions are thought to be d-$\pi_{oximate}$ in character. In addition, two weak absorption peaks in the visible range are also observed (see Table 1). The band at 22300~22700 cm^{-1} is due to $^1B_{1g} \rightarrow {}^1A_{1g}$ transition of the palladium(II) ion in a square-planar environment, whilst the band appearing in the 11100~11400 cm^{-1} region may reasonably be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition and is characteristic of a high-spin octahedral configuration around iron(II) ion [23,24].

All our efforts to grow crystals of these heterotrinuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, based on the magnetic and spectroscopic data (*vide infra*), it is reasonable to suppose that these complexes are proposed to have an extented dioximato-bridged structure containing a palladium(II) ion and two iron(II) ions, in which the central palladium(II) ion has a square-planar environment and the end capped two iron(II) ions have a distorted octahedral environment as shown in Figure 1. The plausible structure is further proved by the following magnetic studies.

Magnetic properties: Being interested in the magnetic behavior of the complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for complexes **(1)** and **(2)**, by way of examples and the results are shown in Figure 2 in the form of plots $\chi_M T$ *vs.* T, where χ_M and T denote magnetic susceptibility per molecule and absolute temperature, respectively. From Figure 2 it can be seen that the magnetic behavior of the two complexes is similar. The curve of $\chi_M T$ *vs.* T exhibits a continuous decreases upon cooling down, with $\chi_M T = 6.28$ $cm^3mol^{-1}K$ for **(1)** and $\chi_M T = 6.16$ $cm^3mol^{-1}K$ for **(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 spins in the whole temperature range and antiferromagnetically coupled through the dioximato-bridge within the trinuclear complexes [25].

Because the central palladium(II) ion with a square-planar environment (see Figure 1) is diamagnetic, from the viewpoint of magnetism, the trinuclear complexes can be considered as a homobinuclear iron(II)–iron(II) system. In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic susceptibility data were analyzed 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 antiferromagnetic and positive for a ferromagnetics interaction. For the iron(II)–iron(II) ($S_1 = S_2 = 2$) system, the molar magnetic susceptibility is given by

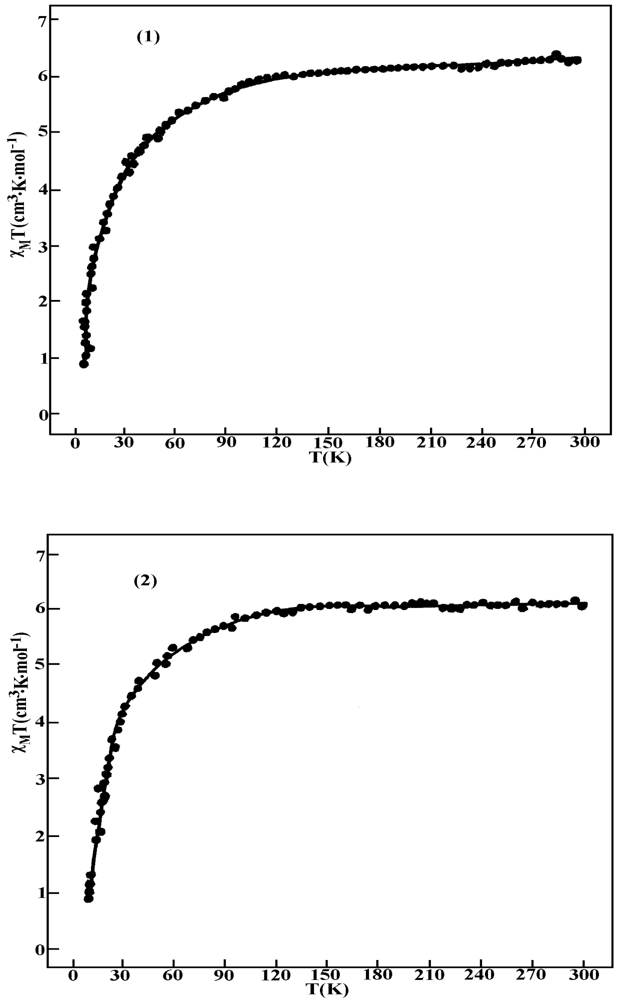

Figure 2. Temperature variation of $\chi_M T$ for complexes $[Fe_2Pd(\alpha\text{-}FD)_2(Me_2\text{-}bpy)_4]SO_4$ (**1**) and $[Fe_2Pd(\alpha\text{-}FD)_2(Me_2\text{-}phen)_4]SO_4$ (**2**). The curves are based on Eq. (1) using the magnetic parameters given in the text. (•), experimental data; (-), calculated curves as described in the text.

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

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 N_α is the temperature-independent paramagnetism ($N_\alpha = 100\times10^{-6}$ $cm^3 \cdot mol^{-1}$), ρ stands for the impurity with $S = 2$ and the remaining symbols have their usual meanings. As shown in Figure 2, good least-squares 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 $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$ are: $J = -2.89\ cm^{-1}$, $g = 2.18$, $\rho = 0.003$, $F = 6.9\times10^{-5}$ for **(1)**; and $J = -3.16\ cm^{-1}$, $g = 2.20$, $\rho = 0.004$, $F = 8.3\times10^{-5}$ 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 splits 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 negligible. These results indicate that the trinuclear complexes undergo weak antiferromagnetic spin-exchange interaction between the two terminal iron(II) ions through dioximate-bridge within each molecule. The small and negative J values observed for the two complexes can be rationalized by the following reasons. (*i*) Based on the method of magnetic orbital interaction between the two adjacent paramagnetic ions, as proposed by Kahn [26,27], considering the symmetry of the $[Fe(N_4O_4)Fe]$ skeleton of the dioximate bridging network close to C_{2V} (for the definition of X and Y coordinates, see Figure 3), the four unpaired electrons of the iron(II) ion occupy the $d_{x^2-y^2}$, d_{z^2}, d_{yz} and d_{xz} orbitals [28], which transform as $a_1(d_{x^2-y^2}$ and $d_{z^2})$, $a_2(d_{yz})$ and $b_2(d_{xz})$ irreducible representations of the C_{2V} point group, respectively. According to the point group theory, $<a_1|a_1> \neq 0$, $<a_2|a_2> \neq 0$, $<b_2|b_2> \neq 0$, therefore, the antiferromagnetic interaction between the two terminal iron(II) ions should be observed. (*ii*) Since the distance between the two iron(II) ions in these trinuclear complexes is long, the small J values (absolute value) are reasonable.

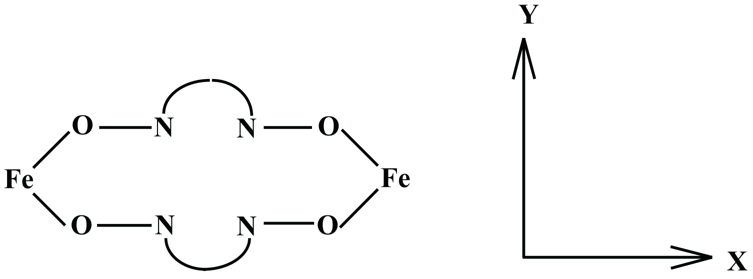

Figure 3. The structure of the Fe(II)–Fe(II) skeleton.

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