

Synthesis and Magnetism of μ -Dioximato-Bridged Heterotrinnuclear Oxovanadium(IV)–Palladium(II)–Oxovanadium(IV) Complexes

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Four novel oxovanadium(IV)–palladium(II)–oxovanadium(IV) heterotrinnuclear complexes of the formula $[(VO)_2Pd(\alpha-FD)_2L_2]SO_4$, where $(\alpha-FD)^{2-}$ represents α -furildioximato and L denotes: 5-methyl-1,10-phenanthroline (Me-phen), 2,9-dimethyl-1,10-phenanthroline (Me₂-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen), have been synthesized and characterized by elemental analyses, molar conductance and magnetic moments of room-temperature measurements, IR and electronic spectral studies. It is proposed that these complexes have extended dioximato-bridged structures and consist of two oxovanadium(IV) and a palladium(II) ions, in which the central palladium(II) ion has a square-planar environment and the end capped two oxovanadium(IV) ions have a square-pyramidal environment. The magnetic properties of complexes $[(VO)_2Pd(\alpha-FD)_2(Me-phen)_2]SO_4$ (**1**) and $[(VO)_2Pd(\alpha-FD)_2(Me_2-phen)_2]SO_4$ (**2**) were investigated over the 4.2–300 K range and correspond to what is expected for an antiferromagnetic VO(IV)–VO(IV) pair with $S_{VO(IV)} = 1/2$ and $S_{Pd(II)} = 0$ (Pd^{2+} is a diamagnetic in a square-planar environment) local spins. The exchange integral (J) was evaluated as $J = -7.28 \text{ cm}^{-1}$ for (**1**) and $J = -6.19 \text{ cm}^{-1}$ for (**2**) based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$.

Key words: μ -dioximato-bridge, oxovanadium(IV), palladium(II), heterotrinnuclear complex, magnetism, synthesis

Interest in bridged transition-metal polynuclear complexes 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].

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 were studied [4–10]. The effective bridging function of the oximato or dioximato groups and the long-distance magnetic exchange interactions of these complexes have been revealed by sin-

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gle-crystal X-ray and magnetic analyses. However, to the best of our knowledge, so far no oxovanadium(IV)–palladium(II)–oxovanadium(IV) heterotrimeric complexes with extended dioximate bridges have been reported. In order to provide more examples of dioximate-bridged polynuclear complexes and to understand better the magnetic properties of this important group of complexes, this paper deals with the synthesis, characterization and magnetism of four new oxovanadium(IV)–palladium(II)–oxovanadium(IV) heterotrimeric complexes: $[(VO)_2Pd(\alpha-FD)_2L_2]SO_4$ [where $(\alpha-FD)^{2-} = \alpha$ -furildioximate; L = 5-methyl-1,10-phenanthroline (Me-phen); 2,9-dimethyl-1,10-phenanthroline (Me₂-phen); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen)]. The magnetic properties of complexes $[(VO)_2Pd(\alpha-FD)_2(Me-phen)_2]SO_4$ (**1**) and $[(VO)_2Pd(\alpha-FD)_2(Me_2-phen)_2]SO_4$ (**2**) have been measured and studied in the 4.2–300 K range.

EXPERIMENTAL

Materials: All reagents used in the synthesis were of analytical grade. The bis(α -furildioximate)palladium(II) $H_2[Pd(\alpha-FD)_2]$ complex was prepared according to the literature methods [7,11]. $VOSO_4 \cdot 5H_2O$; 5-methyl-1,10-phenanthroline (Me-phen); 2,9-dimethyl-1,10-phenanthroline (Me₂-phen); 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen) were of analytical grade and used as commercially obtained.

Synthesis of $[(VO)_2Pd(\alpha-FD)_2(Me-phen)_2]SO_4$ (1**):** To a solution of $H_2[Pd(\alpha-FD)_2]$ (0.109 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 $VOSO_4 \cdot 5H_2O$ (0.41 mmol, 0.104 g) and a solution of Me-phen (0.4 mmol, 0.078 g) in 15 mL of methanol. The mixture was boiled under reflux with stirring for 12 h to yield red-brown 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 MeCN/ethanol (1:3) mixture. Yield, 0.174 g (75%); m.p., 289.5°C.

Synthesis of $[(VO)_2Pd(\alpha-FD)_2(Me_2-phen)_2]SO_4$ (2**):** This complex was obtained as pale-red microcrystals by the same procedure and the same amount of reagents as above but by using Me₂-phen instead of Me-phen. It was recrystallized from a hot acetonitrile solution. Yield, 0.195 g (82%), m.p., 236.1°C.

Synthesis of $[(VO)_2Pd(\alpha-FD)_2(Cl-phen)_2]SO_4$ (3**):** This complex was obtained as a brown powder by the same procedure and the same amounts of reagents as above but by using Cl-phen instead of Me-phen. Yield, 0.192 g (80%); m.p., 311.0°C.

Synthesis of $[(VO)_2Pd(\alpha-FD)_2(Br-phen)_2]SO_4$ (4**):** This red-orange compound was prepared as described for complex (**1**), except that Br-phen was used instead of Me-phen. Yield, 0.222 g (86%); m.p., 327.8°C.

The analyses confirmed the compositions.

Measurements: 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 the calibrant. Variable temperature magnetic susceptibilities were measured using a magnetometer Model MPMS/C. Diamagnetic corrections were made with Pascal's constants [12] for all the constituent atoms and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism of the constituting atoms.

RESULTS AND DISCUSSION

Synthesis and coordination environment of the trinuclear complexes: One strategy for the synthesis of heteropolynuclear complexes is to use a complex as a “ligand” that contains a potential donor group capable of coordinating to other metal ions [4,13,14]. In our synthetic approach to dioximato-bridged VO(IV)–Pd(II)–VO(IV) trinuclear complexes, $H_2[Pd(\alpha-FD)_2]$ 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 $H_2[Pd(\alpha-FD)_2]$ with $VOSO_4 \cdot 5H_2O$ and terminal ligands L (L = Me-phen, Me₂-phen, Cl-phen, Br-phen) in *ca* 1:2:2 mole ratio readily yielded the heterotrinuclear complexes of the general formula $[(VO)_2(\alpha-FD)L_2]SO_4$, as expected. They are the first examples of oxovanadium(IV)–palladium(II)–oxovanadium(IV) heterotrinuclear complexes doubly bridged by oximate. In the solid state all these complexes are fairly stable in air. Based on the molar conductivity and magnetic moments of room-temperature measurements, spectroscopic characterization and the magnetic studies (*vide infra*) the complexes are presumed to have the coordination environment as shown in Figure 1.

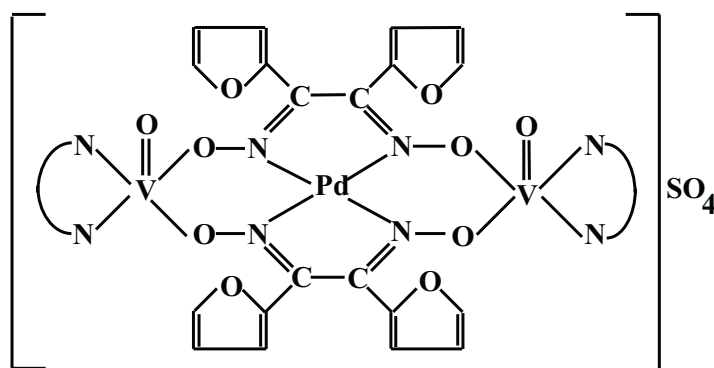


Figure 1. Proposed structure of the trinuclear complexes ($\overset{\curvearrowright}{N}$ N = Me-phen, Me₂-phen, Cl-phen, Br-phen).

Solubility and molar conductances 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 four 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: IR spectra taken in the region 4000–200 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 $\text{H}_2[\text{Pd}(\alpha\text{-FD})_2]$. The relevant IR absorption bands of the complexes and their assignments are shown in Table 1. We discuss here selected infrared bands only. The spectrum of bis(α -furildioximato)palladium(II) $\text{H}_2[\text{Pd}(\alpha\text{-FD})_2]$ mononuclear complex exhibits a broad IR band at 2300–2700 cm^{-1} , which may be assigned to the $\nu(\text{OH})$ vibration of the hydrogen bonded $\text{N-OH}\cdots\text{O-N}$ group [18,19]. However, in the IR spectra of all trinuclear complexes, this band had disappeared, and is accompanied by a new band at 470–480 cm^{-1} , due to $\nu(\text{V-O})$, indicating that the dioxime protons have been completely removed [4]. The medium strong band at *ca* 1270–1285 cm^{-1} in the trinuclear complexes is assignable to the N–O stretching vibrating. In fact, $\text{H}_2[\text{Pd}(\alpha\text{-FD})_2]$ 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 $\nu(\text{C=N})$ 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 1560 cm^{-1} , in accord with the concept that upon trinuclear complexes formation, the positively charged $[(\text{C}_{20}\text{H}_{12}\text{N}_4)\text{Pd}]^{2+}$ 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]. 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 trinuclear complexes. In addition, the V=O stretching vibrations of all trinuclear complexes were observed near 990–997 cm^{-1} , indicating no intermolecular $\text{V=O}\cdots\text{V=O}$ bonding in these complexes [23]. Furthermore, the C–H deformation bands of aromatic ring of the end-capping ligands (Me-phen, Me₂-phen, Cl-phen, Br-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 around 365–390 cm^{-1} due to $\nu(\text{V-N})$ further supports this view.

Table 1. Physical data for the trinuclear complexes.

Complexes	Λ_M ($\text{S cm}^2 \text{ mol}^{-1}$)	IR (cm^{-1})							μ_{eff} (B.M.)
		$\nu(\text{N-O})$	$\nu(\text{V-O})$	$\nu(\text{V-N})$	$\nu(\text{C=N})$	$\nu(\text{SO}_4^{2-})$	$\nu(\text{C-H})$	$\nu(\text{V=O})$	
(1)	72	1275	470	384	1615	1122	845.728	992	2.42
(2)	70	1280	472	390	1610	1120	844.722	995	2.41
(3)	78	1285	480	365	1619	1124	842.726	997	2.36
(4)	75	1278	475	378	1620	1120	840.720	990	2.39

(1): $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me-phen})_2]\text{SO}_4$, (2): $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-phen})_2]\text{SO}_4$,
 (3): $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Cl-phen})_2]\text{SO}_4$, (4): $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Br-phen})_2]\text{SO}_4$.

Electronic spectra: In order to obtain further structural information of these trinuclear complexes, the electronic spectra of the trinuclear complexes in DMF solutions were measured at room temperature. Since the electronic spectra of the four complexes are similar to each other, the discussion is confined to the most important part of the structure. As shown in Table 2, for all four trinuclear complexes, two strong absorption bands in 36900~37500 and 40520~41200 cm^{-1} ranges are observed, which may be attributed to the charge-transfer transition. These transitions are thought to be $d-\pi_{\text{oximate}}$ in character. In addition, four weak absorption peaks in the visible range are also observed (see Table 2). The band at 22490~22800 cm^{-1} is due to ${}^1B_{1g} \rightarrow {}^1A_{1g}$ transition of the palladium(II) ion in a square-planar environment, whilst the remaining three bands, appearing in the 13800~14500, 17900~18200 and 25730~25860 cm^{-1} region, may be assigned to d-d transitions of oxovanadium(IV) ion in a five-coordinate, square-pyramidal environment (C_{4v}) [23,24].

Table 2. Electronic spectra bands (cm^{-1}) and assignments of the trinuclear complexes.

Complexes	UV/ ϵ_{max} ($\text{L cm}^{-1} \text{mol}^{-1}$)				
	CT	${}^1B_{1g} \rightarrow {}^1A_{1g}$	$d_{xy} \rightarrow d_{xz,yz}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{z^2}$
$[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me-phen})_2]\text{SO}_4$	37500, 40600 (29500) (31420)	22800 (210)	14500 (125)	17900 (178)	25860 (191)
$[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-phen})_2]\text{SO}_4$	36900, 41200 (28900) (29450)	22750 (215)	14270 (150)	18050 (128)	26150 (182)
$[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Cl-phen})_2]\text{SO}_4$	37100, 40520 (30580) (31750)	22580 (198)	13870 (142)	18150 (170)	25900 (214)
$[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Br-phen})_2]\text{SO}_4$	36970, 41180 (29880) (28630)	22490 (240)	13920 (165)	18200 (180)	25730 (217)

In spite of our many efforts, single crystals suitable for X-ray crystallography have not been obtained. However, based on the above discussion, it is reasonable to suppose that these complexes have an extended dioximate-bridged structure containing a Pd^{2+} ion and two VO^{2+} ions, in which the central palladium(II) ion has a square-planar environment and the end capped two oxovanadium(IV) ions have a square-pyramidal environment, as shown in Figure 1. The plausible structure is further proved by magnetic studies.

Magnetic properties: The observed magnetic moment per trinuclear complex at room temperature, shown in Table 1, is less than the spin-only value (2.45 B.M), implying an operation of an antiferromagnetic spin-exchange interaction in these complexes [25]. 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)**, and shown in Figure 2 in the form of the $\chi_{\text{M}}T$ versus T plot, χ_{M} being the molar magnetic susceptibility. From Figure 2 it can be seen that the curves of $\chi_{\text{M}}T-T$ of the two complexes are similar. When the temperature is lowered, the curve of the $\chi_{\text{M}}T-T$ exhibits a continuous decrease from 0.732 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (2.42 B.M.) for **(1)** and 0.726

$\text{cm}^3 \text{mol}^{-1} \text{K}$ (2.41 B.M.) for **(2)** at 300 K to $0.189 \text{ cm}^3 \text{mol}^{-1} \text{K}$ **(1)** at 4.48 K and $0.215 \text{ cm}^3 \text{mol}^{-1} \text{K}$ **(2)** at 6.05 K. This phenomenon is typical for an antiferromagnetic interaction between VO^{2+} ions within each molecule. Thus, as noted above, the observed magnetic behavior, both at room-temperature and variable-temperature, clearly demonstrates the operation of an antiferromagnetic spin-exchange interaction within each molecule.

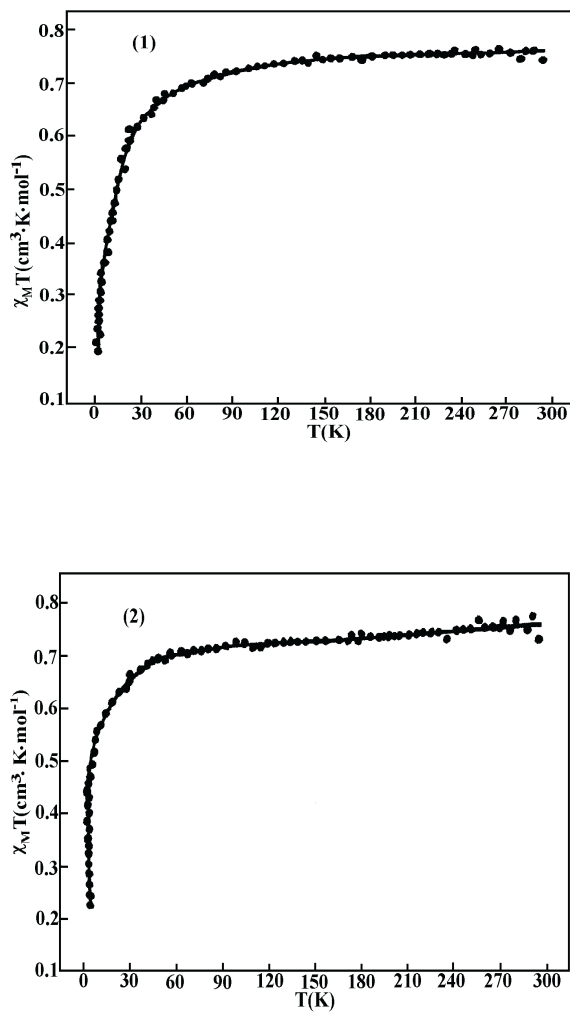


Figure 2. Temperature variation of $\chi_M T$ for complexes $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me-phen})_2]\text{SO}_4$ **(1)** and $[(\text{VO})_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-phen})_2]\text{SO}_4$ **(2)**. The curves are based on Eq. (1) using the magnetic parameters given in the text. (), experimental data, (—), calculated curves.

Because the center palladium(II) ion with a square-planar environment (see Figure 1) is diamagnetic, from the view point of magnetism, the trinuclear complexes can be considered as a homodinuclear oxovanadium(IV)–oxovanadium(IV) system. In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic analysis was carried out using the modified Bleaney-Bowers susceptibility equation [26], which includes the fraction of a small amount of uncoupled oxovanadium(IV) impurity (ρ) based on the Heisenberg spin-exchange operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where the exchange parameter J is negative for antiferromagnetic and positive for ferromagnetic interaction. The mole susceptibility of the oxovanadium(IV)–oxovanadium(IV) ($S_1 = S_2 = 1/2$) system is given by:

$$\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1}(1 - \rho) + (2N\beta^2g^2/kT)/\rho + N_\alpha \quad (1)$$

where χ_M denotes the molecular susceptibility per binuclear complex, N_α is the temperature-independent paramagnetism and the remaining symbols have their usual meanings. As shown in Figure 2, good least-squares fit to the experimental data were obtained with (1) for complexes **(1)** and **(2)**. The determined magnetic parameters and the agreement factor F , defined here as $F = \sum[(\chi_M)_{\text{calc}} - (\chi_M)_{\text{obs}}]^2 / \sum(\chi_M)_{\text{obs}}$ are: $J = -7.28 \text{ cm}^{-1}$, $g = 2.02$, $\rho = 0.004$, $F = 1.9 \times 10^{-5}$ and $N_\alpha = 0$ for **(1)**; $J = -6.19 \text{ cm}^{-1}$, $g = 2.04$, $\rho = 0.005$, $F = 2.7 \times 10^{-5}$ and $N_\alpha = 0$ for **(2)**. These results indicate that the trinuclear complexes undergo a weak antiferromagnetic spin-exchange interaction between the two terminal oxovanadium(IV) ions through dioximate-bridge within each molecule. The small and negative J values, observed for the two complexes, can be rationalized on the basis of the method of magnetic orbital interaction between the two adjacent paramagnetic ions, as proposed by Kahn [27,28]. Considering the symmetry of the $[\text{VO}(\text{N}_4\text{O}_4)\text{VO}]$ skeleton of the dioximate bridging network close to C_{2v} (for the definition of X and Y coordinates, see Figure 3), the one unpaired electron of the terminal oxovanadium(IV) ions occupies the $d_{x^2-y^2}$ orbital, which transforms as a_1 irreducible representation of the C_{2v} point group. According to the point group theory, $\langle a_1 | a_1 \rangle \neq 0$, therefore, the antiferromagnetic interaction between the two terminal oxovanadium(IV) ions should be observed. In addition, because the distance between the two oxovanadium(IV) ions in these trinuclear complexes is long, the small J values are reasonable.

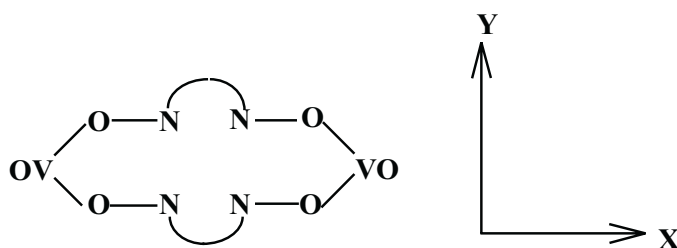


Figure 3. The structure of the VO(IV)–VO(IV) skeleton.

Acknowledgments

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