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Synthesis, Spectral and Antiferromagnetic Interaction in Oxalato-Bridged Linear Trinuclear Oxovanadium(IV) Complexes

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Three new linear trinuclear oxovanadium(IV) complexes bridged by oxalato (ox) and end-capped with 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO_2phen); respectively, namely $[(VO)_3(ox)_2(bpy)_2]SO_4$ **(1)**, $[(VO)_3(ox)_2(phen)_2]SO_4$ **(2)** and $[(VO)_3(ox)_2(NO_2phen)_2]SO_4$ **(3)**, have been synthesized and characterized by elemental analyses, molar conductivity, magnetic measurements, IR, ESR and electronic spectral studies. It is proposed that these complexes have extended ox-bridged structures, consisting of three oxovanadium(IV) ions, each in a distorted square-pyramidal environment. Variable-temperature magnetic susceptibility measurements (4.2~300 K) of the complexes **(1)** and **(2)** revealed the occurrence of an intramolecular antiferromagnetic interaction between the oxovanadium(IV) ions through the oxalato-bridge within each molecule. The magnetic data have been also used to deduce the indicated structure. On the basis of spin Hamiltonian operator, $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$, the magnetic analyses were carried out for the two trinuclear complexes and the spin-coupling constants (J) were evaluated as –9.85 cm^{-1} for **(1)** and –10.16 cm^{-1} for **(2)**.

Key words: oxalato-bridge, oxovanadium(IV), trinuclear complexes, antiferromagnetic interaction

The coordination chemistry of vanadium is currently receiving much attention, owing to the discovery of vanadium as a biologically important metal [1–4] and the vanadoenzymes [5,6], as well as magnetism of polynuclear oxovanadium(IV) complexes [7]. It is known that vanadium has a significant role in many biological processes, and it is a constituent of living plants and animals and it has important effects for normal growth [8]. Besides their scientific significance, many of vanadium compounds are attractive as potential catalysts in biologal and industrial processes or their simple models [9,10]. Therefore, the studies of magnetic properties of polynuclear

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vanadium complexes are important, not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers, but also for gaining some insight into the electronic and geometric structure of metalloproteins and enzymes. These studies enable to correlate structure with biological function, and to obtaine useful information about designing and synthesizing molecule-based magnets and investigating the spin-exchange mechanism between paramagnetic metal ions [11–13].

Owing to their fundamental importance in the magnetic studies, much effort has been devoted to the development of multiatom bridging ligands that can afford magnetic interactions. Among 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 studied [14–18]. However, to the best of our knowledge, so far no linear trinuclear oxovanadium(IV) complexes with oxalato-bridge have been reported. Taking into account the above facts, it is of considerable interest to synthesize and study polynuclear oxovanadium(IV) complexes with bridging oxalato in order to understand better the magnetic properties of this important group of complexes.

In this work three new μ-oxalato-bridged trinuclear oxovanadium(IV) complexes of the general formula $[(VO)_3(ox)_2L_2]SO_4$ (L = bpy, phen or NO_2phen) were synthesized by using diammonium aquo*bis*(oxalato)oxovanadate(IV) hydrate, $(NH_4)_2VO(ox)_2 \cdot 2H_2O$, as bridging ligand. The cryomagnetic properties (4.2~300 K) of $[(VO)_3(ox)_2(bpy)_2]SO_4$ **(1)** and $[(VO)_3(ox)_2(phen)_2]SO_4$ **(2)** complexes were measured and studied in detail. At present, the three trinuclear oxovanadium(IV) complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic studies and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of these trinuclear oxovanadium(IV) complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Diammonium aquo*bis*(oxalato)oxovanadate(IV) hydrate, $(NH_4)_2VO(ox)_2 \cdot 2H_2O$, was synthesized according to the literature [19]. The terminal ligands 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 5-nitro-1,10-phenanthroline (NO_2phen) and $VOSO_4 \cdot 5H_2O$ were used as commercially obtained.

Synthesis of $[(VO)_3(ox)_2(bpy)_2]SO_4$ (1): To a solution of $VOSO_4 \cdot 5H_2O$ (2.1 mmol, 531.5 mg) stirred in methanol (20 mL) was added successively dropwise a methanol/water (1:2) solution (15 mL) of $(NH_4)_2VO(ox)_2 \cdot 2H_2O$ (1.0 mmol, 315.1 mg) under nitrogen. The vigorous stirring was continued at room temperature (about 20 minutes). The resulting solution was then filtered to eliminate impurities. To the filtrate was added a methanol solution (20 mL) of bpy (2.0 mmol, 312.4 mg). The color of the solution turned from blue to brown-red immediately and a small amount of precipitate formed. The reaction mix-

ture was subsequently refluxed for *ca.* 12 h. After cooling to room temperature, brown-red microcrystals thus formed were collected by suction filtration, washed with methanol, water and diethyl ether several times, and dried over P_2O_5 under reduced pressure. It was recrystallized from a hot acetonitrile solution and the needle crystals were obtained. Yield, 518.3 mg (66%); m.p., 320.1°C. Anal. calc. for $(VO)_3C_{24}H_{16}N_4O_{12}S$ (M.W. 785.30): C, 36.71; H, 2.05; N, 7.13; VO, 25.57%. Found: C, 36.60; H, 2.12; N, 7.34; VO, 25.32%.

Synthesis of $[(VO)_3(ox)_2(phen)_2]SO_4$ (2): This complex was obtained as brown microcrystals by the same procedure as above, but by using phen instead of bpy. Recrystallization was carried out from DMF/ethanol (1:3) mixture and the needle crystals were collected. Yield, 625.0 mg (75%); m.p. 278.5°C. Anal. calc. for $(VO)_3C_{28}H_{16}N_4O_{12}S$ (M.W. 833.34): C, 40.36; H, 1.94; N, 6.72; VO, 24.10%. Found: C, 40.17; H, 2.12; N, 6.43; VO, 23.85%.

Synthesis of $[(VO)_3(ox)_2(NO_2phen)_2]SO_4$ (3): This complex was obtained as orange-red powder by the same procedure as complex **(1)**, but by using NO_2phen instead of bpy. Yield, 747.9 mg (81%); m.p. 248.2°C. Anal. calc. for $(VO)_3C_{28}H_{14}N_6O_{16}S$ (M.W. 923.34): C, 36.42; H, 1.53; N, 9.10; VO, 21.75%. Found: C, 36.20; H, 1.36; N, 9.39; VO, 21.53%.

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 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. ESR spectra were recorded with a JES-FEIXG ESR apparatus using an X-band and Mn-reference. Molar conductances were measured (in acetonitrile 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 [20] 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

Synthetic route and coordination environment of the trinuclear complexes: One of the best strategies to design and synthesize discrete polynuclear species is the "complex as ligand" approach, *i.e.*, using mononuclear complexes that contain potential donor groups capable of coordinating to another metal ion [21]. In this study, our aim was to obtain trinuclear oxovanadium(IV) complexes, therefore, this synthetic strategy was adopted. As the ligand complex we have selected, $(NH_4)_2VO(ox)_2 \cdot 2H_2O$, as a mononuclear fragment, because it can coordinate to another metal ion through oxalate oxygens to produce polynuclear complexes. Simultaneously, 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO_2phen) were used as the terminal ligands. Indeed, the elemental analytic data for the newly prepared complexes indicate that the reaction of $(NH_4)_2VO(ox)_2 \cdot 2H_2O$ with $VOSO_4 \cdot 5H_2O$ and the terminal ligand L (L = bpy, phen, NO_2phen) in *ca.* 1:2:2 mole ratio yielded the trinuclear complexes of the general formula $[(VO)_3(ox)_2L_2]SO_4$, as expected. These complexes are the first examples of trinuclear oxovanadium(IV) bridged by diammonium aquo*bis*(oxalato)oxovanadate(IV) hydrate. On the basis of the molar conductivity, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

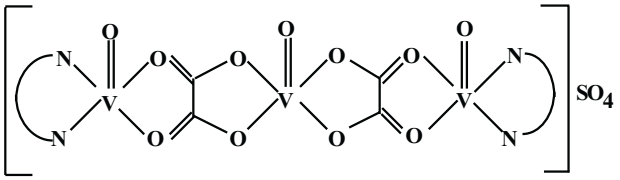

Figure 1. Suggested coordination environment of the complexes ($\overset{\frown}{N\ N}$ = bpy, phen, NO_2phen).

Solubility of the trinuclear complexes: These trinuclear complexes are more soluble in acetonitrile, DMF and DMSO giving stable solutions at room temperature; whereas they are 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 three trinuclear complexes, the observed molar conductance values in acetonitrile solution at 25°C (in the 140~148 Ω^{-1} cm^2 mol^{-1} range) are given in Table 1. These values are indicative of 1:1 electrolytic nature [22], in accord with the presumed structure of the trinuclear complexes shown in Fig. 1. The trinuclear structure was further proved by the following results.

Infrared spectra:. Since the IR spectra of all the three trinuclear complexes are similar, discussion is confined to the most important vibration in 400~4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands of the trinuclear complexes and the mononuclear fragment $(NH_4)_2VO(ox)_2\cdot 2H_2O$, together with their assignments are given in Table 1. We here discuss selected infrared bands. It is noteworthy that the spectrum of the mononuclear complex $(NH_4)_2VO(ox)_2\cdot 2H_2O$ shows a broad band at 1715 cm^{-1} and a medium band at 790 cm^{-1}, which are attributed to ν(CO) and δ(CO) of a bidentate coordination mode of the oxalato group, respectively. However, the IR spectra of the three trinuclear oxovanadium(IV) complexes only exhibit bands corresponding to the typical of bridging coordination mode of oxalato ligand (*ca.* 1640 cm^{-1} [ν_{as}(CO)], 1340, 1320 cm^{-1} [ν_s(CO)]) [11,12], suggesting that the oxalato group of the mononuclear fragment coordinate with oxovanadium(IV) ions to form trinuclear complexes. On the other hand, the C–H deformation bands of aromatic ring of the end-capping ligands (bpy, phen, NO_2phen) are found in corresponding trinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the oxovanadium(IV) ions. The additional band observed at around 580 cm^{-1} due to ν(V–N) further supports this view. In addition, the band centered at *ca.* 1120 cm^{-1}, typical for a non-coordinated sulfate anion [23], was found for the trinuclear complexes. This is consistent with the conductance measurements and elemental analyses of these trinuclear complexes. Furthermore, the V=O stretching vibrations of all trinuclear complexes were observed near 990 cm^{-1}, indicating no intermolecular V=O···V=O bonding in these complexes [24], in accord with the following magnetic analysis.

Table 1. Molar conductances, effective magnetic moments and IR data for the trinuclear complexes.

Complex	Λ_M ($S \cdot cm^2 \cdot mol^{-1}$)	μ_{eff} (B.M.)	IR (cm^{-1})					
			ν_{as}(CO)	ν_s(CO)	ν(V–N)	ν(C–H)	$\nu(SO_4^{2-})$	ν(V=O)
(1)	142	1.55	1640	1342, 1325	582	856, 725	1120	985
(2)	140	1.53	1645	1340, 1328	585	850, 722	1125	988
(3)	148	1.50	1642	1343, 1320	580	852, 719	1123	983

(1) = $[(VO)_3(ox)_2(bpy)_2]SO_4$, **(2)** = $[(VO)_3(ox)_2(phen)_2]SO_4$, **(3)** = $[(VO)_3(ox)_2(NO_2phen)_2]SO_4$.

Table 2. ESR and electronic spectra of the trinuclear complexes.

Com-plex	ESR			UV (cm^{-1})/ε_{max} ($mol^{-1} \cdot cm^{-1} \cdot L$)				
	$g_\perp$	$g_{//}$	g_{av}	CT		$d_{xy} \rightarrow d_{xz, yz}$	$d_{xy} \rightarrow d_{z^2-y^2}$	$d_{xy} \rightarrow d_{z^2}$
(1)	2.027	2.128	2.061	35270(29120),	38730(31200)	13830(322)	18180(382)	23800(348)
(2)	2.036	2.143	2.072	34850(28300),	38590(32340)	13860(315)	18050(350)	23820(390)
(3)	2.030	2.132	2.064	35240(28600),	38820(31850)	13790(290)	18350(335)	24120(347)

Electronic spectra: The electronic spectra of the mononuclear fragment $(NH_4)_2VO(ox)_2 \cdot 2H_2O$ and the trinuclear oxovanadium(IV) complexes were studied and assigned on the basis of a careful comparison of the latter with the former. As shown in Table 2, the electronic spectra of the three trinuclear complexes in DMF solutions are similar. For all three trinuclear complexes, three weak absorption peaks in the 13790~13860, 18050~18350 and 23800~24120 cm^{-1} regions are observed, which may be assigned to d-d transitions of the oxovanadium(IV) ion in a five-coordinate, square-pyramidal environment (C_{4V}) [25]. In addition, two strong bands at 34850~35270 cm^{-1} and 38590~38820 cm^{-1} regions were also observed in the electronic spectra of the trinuclear 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.

ESR spectra: In order to obtain further structural information on these trinuclear complexes, the X-band ESR spectra of the three trinuclear oxovanadium(IV) complexes have been recorded in the polycrystalline state at room temperature. It is noted that the ESR spectra of the three trinuclear complexes are almost similar. The ESR spectrum of complex **(3)** is shown, as an example, in Figure 2. For trinuclear oxovanadium(IV) complexes, the antiferromagnetic interaction (*vide infra*) between the metal centres exhibits three molecular spins $S_T = 1/2$, 1/2 and 3/2, with S = 1/2 for the ground state. Trinuclear molecular (ground state S = 1/2) and trinuclear molecular (ground S = 1/2) couple to yield a spin singlet (S = 0) and a spin triplet (S = 1) [26], due to antiferromagnetic interaction between the molecules. As shown in Figure 2 for the three oxovanadium(IV) trinuclear complexes, a dissymmetric shape of upper and lower band at *ca.* 3200 G and a relatively weak half-field absorption (the intensity is about 1×10^{-3} times that of the band above) at *ca.* 1600 G are observed, which may be tentatively assigned to the allowed transition of $\Delta Ms = \pm 1$ and the $\Delta Ms = \pm 2$

spin-forbidden transition, respectively. The spectrum parameters can be derived from the room-temperature spectra by using g_3 and g_4 of Mn-reference and are summarized in Table 2. Thus, the above observations confirm a penta-coordinated complex with square-pyramidal geometry [27], and the existence of a magnetic interaction between oxovanadium(IV) ions for these trinuclear complexes [28]. This is in accord with the electronic spectra and the following magnetc studies.

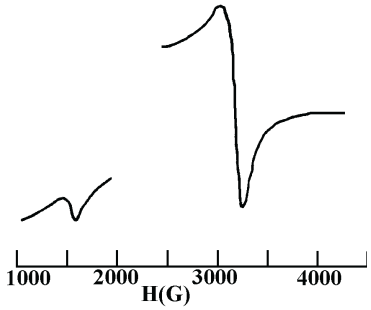

Figure 2. X-band ESR spectra of the complex **(3)** at room-temperature.

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, ESR, conductivity measurements and magnetic characterization (*vide infra*), these complexes are proposed to have an extended ox-bridged structure and to contain three oxovanadium(IV) ions, each in a distorted square-pyramidal environment, as shown in Figure 1. The plausible trinuclear structure of these complexes is further characterized by the following magnetic studies.

Magnetic properties: The observed magnetic moment per oxovanadium(IV) ion of the trinuclear complexes at room temperature, shown in Table 1, is less than the spin-only value (1.73 B.M), which suggests the presence of an antiferromagnetic spin-exchange interaction in these complexes. Being interested in the magnetic behavior of these complexes, variable-temperature (4.2~300 K) magnetic susceptibility data were further collected for complexes $[(VO)_3(ox)_2(bpy)_2]SO_4$ **(1)** and $[(VO)_3(ox)_2(phen)_2]SO_4$ **(2)**, and the results are shown in Figure 3 in the form of plots of χ_M *vs.* T and μ_{eff} *vs.* T. From Figure 3 it is evident that the curve of the effective magnetic moment (μ_{eff}) decreases steadily when the temperature is lowered, indicating the operation of intramolecular antiferromagnetic interaction through the ox-bridge within both trinuclear 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 the oxovanadium(IV) ions through the ox-bridges within each trinuclear unit.

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic susceptibility data were analyzed on the basis of a symmetrical linear trinuclear oxovanadium(IV) complex derived from a spin-Hamiltonian

operator, $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$, assuming that the exchange integrals between the neighboring oxovanadium(IV) ions are identical ($J_{12} = J_{23} = J$) and the integral between the terminal oxovanadium(IV) ions is zero ($J_{13} = 0$) [29,30].

$$\chi_M = \frac{N\beta^2 g^2}{4kT}\left[\frac{1 + 10\exp(-J/kT) + \exp(-2J/kT)}{1 + 2\exp(-J/kT) + \exp(-2J/kT)}\right] \quad (1)$$

where χ_M denotes the magnetic susceptibility per trioxovanadium(IV), and the remaining symbols have their usual meanings. As shown in Figure 3, good least-square fits to the experimental data were obtained with equation (1) for complexes $[(VO)_3(ox)_2(bpy)_2]SO_4$ **(1)** and $[(VO)_3(ox)_2(phen)_2]SO_4$ **(2)**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{calc} - (\chi_M)_{obs})^2/\Sigma(\chi_M)_{obs}$ are: J = –9.85 cm^{-1}, g = 2.06, $F = 2.6\times10^{-4}$ for **(1)** and J = –10.16 cm^{-1}, g = 2.07, $F = 1.9\times10^{-4}$ for **(2)**. The results (negative and small J value) indicate that these complexes are essentially trinuclear and undergo weak antiferromagnetic spin-exchange interaction between the oxovanadium(IV) ions within each molecule.

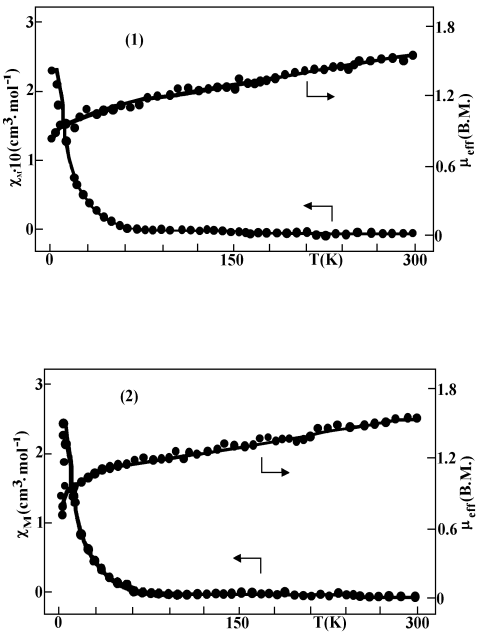

Figure 3. Plots of molar magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) *vs*. T for $[(VO)_3(ox)_2(bpy)_2]SO_4$ **(1)** and $[(VO)_3(ox)_2(phen)_2]SO_4$ **(2)** complexes. The point denotes the experimental data, the solid line represents the best least-squares fit to the experimental data using the parameters given in the text.

These small J values of complexes **(1)** and **(2)** may be brought out mainly by the geometry structures of the complexes and the properties of the bridged-ligand [11].

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