Pergamon

PII: S0277-5387(97)00179-4

Polyhedron Vol. 16, No. 24, pp. 4379–4384, 1997
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0277-5387/97 $17.00+0.00

Synthesis, characterization and magnetic properties of novel μ-isophthalato oxovanadium(IV) binuclear complexes

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(Received 12 September 1996; accepted 1 May 1997)

Abstract—Four novel oxovanadium(IV) binuclear complexes have been synthesized, namely $[(VO)_2(IPHTA)(L)_2]SO_4$ (L denotes 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) and 5-nitro-1,10-phenanthroline (NO_2-phen)), where IPHTA is the isophthalate dianion. Based on elemental analyses, molar conductivity measurements, IR and electronic spectra studies, it is proposed that these complexes have IPHTA-bridged structures and consist of two vanadium(IV) atoms in a square-pyramidal environment. The complexes $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ (**1**) and $[(VO)_2(IPHTA)(bpy)_2]SO_4$ (**2**) were characterized by variable temperature magnetic susceptibility (4–300 K) and the data could be well fitted by the least-squares method to a susceptibility equation derived from the spin Hamiltonian operator, $\hat{H} = -2J\,\hat{S}_1 \times \hat{S}_2$. The exchange integral, J, was found to be $-26.8\ cm^{-1}$ for (**1**) and $-31.0\ cm^{-1}$ for (**2**). These results are commensurate with antiferromagnetic interactions between two oxovanadium(IV) ions within each molecule. The influence of different terminal ligands on magnetic interactions between the metals of this kind of complexes is also discussed. © 1997 Elsevier Science Ltd

Keywords: oxovanadium(IV), μ-isophthalato-bridge, binuclear complex, synthesis, characterization, magnetism.

The syntheses and magnetic exchange interactions of binuclear metal complexes propagated by multiatom bridges have been of current interest in recent years [1–7]. In view of the effective bridging function of isophthalate dianion (abbreviated as IPHTA), quite recently, we first utilized IPHTA as a multiatom bridge to synthesize and characterize the binuclear manganese(II) complexes [8]. It has been revealed by variable temperature magnetic susceptibility investigations that the long-range magnetic coupling could occur between the two Mn^{II} ions bridged by the isophthalato ligand. In order to assess comparatively the effects of IPHTA bridge upon the spin exchange between various metal ions, it was necessary to synthesize a series of binuclear complexes of essentially the same structure except for the metal ion. As an extension of that investigation, this paper deals with the synthesis and characterization of four new binuclear oxovanadium(IV) complexes using the dianion of isophthalic acid as bridging ligand, $[(VO)_2(IPHTA)(L)_2]SO_4$ (L = 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) and 5-nitro-1,10-phenanthroline (NO_2-phen)), where IPHTA is the isophthalate dianion. The magnetic properties of complexes $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ (**1**) and $[(VO)_2(IPHTA)(bpy)_2]SO_4$ (**2**) have also been studied. The main results suggest that the methyl substituents in terminal ligands will reduce antiferromagnetic spin-exchange interactions between the VO^{2+} ions because of their electronic releasing effect.

EXPERIMENTAL

Materials

Piperidinium isophthalate was synthesized by the literature method [4]. 2,2′-Bipyridine (bpy); 4,4′-

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dimethyl-2,2′-bipyridine (Me_2bpy); 1,10-phenanthroline (phen); 5-nitro-1,10-phenanthroline (NO_2-phen) were of analytical grade. They were purchased from the Beijing Chemical Company.

Synthesis of $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ (1)

To a methanol solution (10 cm^3) of piperidinium isophthalate (67.2 mg, 0.2 mmol) was added dropwise a methanol solution (10 cm^3) of $VOSO_4$ (65.2 mg, 0.4 mmol) and a solution of Me_2bpy (73.7 mg, 0.4 mmol) in methanol (10 cm^3) with stirring at room temperature. The mixture was further refluxed for 12 h to give yellow microcrystals, then the product was filtered off, washed with methanol and diethyl ether several times and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from an acetone/methanol (2 : 1) mixture. Yield: 0.105 g (69%). Found: C, 50.3; H, 3.6; N, 7.2; (VO), 17.5. Calc. for $(VO)_2C_{32}H_{28}N_4O_8S$ (m.w. 762.5): C, 50.4; H, 3.7; N, 7.4; (VO), 17.6%.

Synthesis of $[(VO)_2(IPHTA)(bpy)_2]SO_4$ (2)

This complex was obtained as yellow microcrystals by the same procedure but by using bpy instead for Me_2bpy. It was recrystallized from hot acetone. Yield: 0.102 g (72%). Found: C, 47.7; H, 2.7; N, 8.1; (VO), 19.2. Calc. for $(VO)_2C_{28}H_{20}N_4O_8S$ (m.w. 706.4): C, 47.6; H, 2.9; N, 7.9; (VO), 19.0%.

Synthesis of $[(VO)_2(IPHTA)(phen)_2]SO_4$ (3)

This complex was obtained as orange microcrystals by the same procedure as above but by using phen instead of Me_2bpy. Yield: 0.121 g (80%). Found: C, 51.0; H, 2.7; N, 7.6; (VO), 18.0. Calc. for $(VO)_2C_{32}H_{20}N_4O_8S$ (m.w. 754.5): C, 50.9; H, 2.7; N, 7.4; (VO), 17.8%.

Synthesis of $[(VO)_2(IPHTA)(NO_2\text{-phen})_2]SO_4$ (4)

This complex was prepared as described for $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$, except that NO_2-phen was used instead of Me_2bpy. Dark-yellow microcrystals were obtained. Yield: 0.144 g (85%). Found: C, 45.7; H, 2.4; N, 10.3; (VO), 16.1. Calc for $(VO)_2C_{32}H_{18}N_6O_{12}S$ (m.w. 844.5): C, 45.5; H, 2.2; N, 10.0; (VO), 15.9%.

Measurements

Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer elemental analyser, Model 240. Metal contents were determined by $KMnO_4$ volumetric titration. The infrared spectra were measured on a Shimadzu infrared spectrometer 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. The 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 at the Institute of Physics, Chinese Academy of Sciences, using a vibrating sample magnetometer Model CF-1 (sensitivity $m = 10^{-4}$ e.m.u.). Diamagnetic corrections were made with Pascal's constants [9] for all the constituent atoms and the effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828\,(\chi_M T)^{1/2}$, where χ_M = susceptibility, T = temperature.

RESULTS AND DISCUSSION

On the basis of elemental analyses and physical data (Table 1) for the complexes, it seems reasonable to assume that the reaction of IPHTA with $VOSO_4$ and bpy, Me_2bpy, phen or NO_2-phen yielded the binuclear complexes of the general formula $[(VO)_2(IPHTA)(L)_2]SO_4$ (L = bpy, Me_2bpy, phen and NO_2-phen, respectively). These complexes are very soluble in DMF, DMSO and acetone; moderately soluble in acetonitrile and water, 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 complexes, the molar conductance values in DMF solution (see Table 1) fall in the expected range for 1 : 1 electrolytes [10], indicating that the sulphate anion is situated outside the metal coordination sphere.

Infrared spectra

The mode of bonding of the VO^{2+} ion to the ligand was investigated by IR spectroscopy. The most relevant IR absorption bands due to the complexes along with their assignments are shown in Table 1. In the IR region of the spectra the complexes exhibited two characteristic strong and broad bands in the 1700–1300 cm^{-1} region, attributed to the asymmetrical stretching vibrations $\nu_{as}(CO_2^-)$ (1585–1600 cm^{-1}) and the symmetrical stretching vibrations $\nu_s(CO_2^-)$ (1415–1425 cm^{-1}) of the coordinated carboxylate groups. Compared with the $\nu_{as}(CO_2^-)$ (1610 cm^{-1}) and $\nu_s(CO_2^-)$ (1405 cm^{-1}) stretching vibrations of free ligand IPHTA, the asymmetrical stretching vibrations of the carboxylato groups have shifted towards lower frequencies in the binuclear complexes. However, the symmetrical stretching vibrations of the carboxylato groups have shifted to higher frequencies in the binuclear complexes. This shift implies that the coordination reaction has taken place. The absence of any splitting of the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ bands strongly suggests the end-to-end linking of the isophthalato

Table 1. Physical data for the complexes

Complex	Λ_M (S cm^2 mol^{-1}) (DMF)	IR (cm^{-1})						μ_{eff} (μ_B)^a 296 K, per dimer unit
		$\nu_{as}(CO_2^-)$	$\nu_s(CO_2^-)$	$\Delta(\nu_{as}$—$\nu_s)$	$\nu(SO_4^{2-})$	ν(N=C)	ν(V=O)	
(1)	75	1595	1420	175	1120	1529	995	2.30
(2)	68	1585	1420	165	1119	1520	990	2.29
(3)	82	1590	1415	175	1125	1535	996	2.36
(4)	85	1600	1425	175	1121	1540	998	2.34

^{a} Refers to values of μ_{eff} measured by Gouy's method.

(1) : $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$.

(2) : $[(VO)_2(IPHTA)(bpy)_2]SO_4$.

(3) : $[(VO)_2(IPHTA)(phen)_2]SO_4$.

(4) : $[(VO)_2(IPHTA)(NO_2\text{-}phen)_2]SO_4$.

ligand in an equivalent way at both sites [5]. Moreover, the coordination modes of carboxylate groups have often been diagnosed by the separation between $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$. That is, bidentate carboxylate groups show a separation smaller than 200 cm^{-1}, whereas unidentate carboxylate groups show a separation larger than 200 cm^{-1}. Thus, for the present complexes, the observed $\nu_{as}(CO_2^-) - \nu_s(CO_2^-)$ values of 175–180 cm^{-1} call for a bidentate bonding mode of the carboxylate groups of the IPHTA ligand [11]. The bidentate coordination modes of the carboxylates in IPHTA were supported by the crystal structure of analogous complex [6] $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$ (TPHA : terephthalate dianion, Fig. 1). The —N=C< stretching vibrations for the terminal ligands (bpy, Me$_2$bpy, phen, NO$_2$-phen) are shifted to higher frequencies (1520–1540 cm^{-1}) in their binuclear complexes. In addition, a band centered at *ca.* 1120 cm^{-1}, typical for a non-coordinated sulphate anion [12], were observed for all binuclear complexes. This is consistent with the conductance data of the complexes. The V=O stretching vibrations of all complexes were observed near 990–998 cm^{-1}, indicating no intermolecular V=O ··· V=O ··· bonding in these complexes [13].

Electronic spectra

As shown in Table 2, the electronic absorption spectra of the four complexes in DMF solutions are similar to each other. For all four binuclear complexes, three electronic spectral bands are observed in the 12,500–12,300, 16,400–15,300 and 23,800–23,000 cm^{-1} regions. The number, position and assignment of d–d bands in the spectra of these complexes are commensurate with a five-coordinate square pyramidal geometry [13–15].

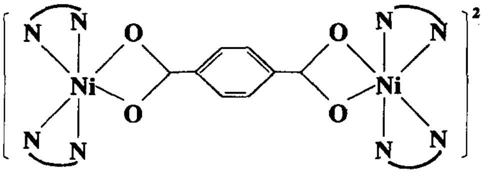

Fig. 1. Chemical structure of the complex cation $[Ni_2(TPHA)(bpy)_4]^{2+}$ ($\overset{\frown}{NN}$ = bpy).

All our efforts to grow large crystals of these oxovanadium(IV) complexes suitable for X-ray structure determination have so far been unsuccessful. However, based on the composition of these complexes, infrared spectra, electronic spectra, conductivity measurements, magnetic data (*vide infra*) and the crystal structure of analogous complex [6], these complexes are proposed to have a plausible coordination environments as shown in Fig. 2.

It should be pointed out that for the present complexes another tetranuclear structure with two of their binuclear units bridged by four carboxylates, with two carboxylates between each pair of vanadiums on neighbouring binuclear fragments may be also possible due to the versatile bonding modes of isophthalate dianions. But for the plausible tetranuclear oxovanadium(IV) complexes, the molar conductance values in DMF solution should fall in the expected range (130–170 S cm^2 mol^{-1}) for 1 : 2 electrolytes [10]. This is not consistent with the conductance data (68–85 S cm^2 mol^{-1}) observed of the present binuclear complexes. But, because the possibility of dissociation of tetranuclear oxovanadium(IV) complexes in solution cannot be completely ruled out, the conductance data may not refer to those present in the solid. However, the binuclear structure is supported by the magnetic characterization (*vide infra*). Thus, at this stage, it seems more reasonable to assume that these oxovanadium(IV) complexes have the coordination environment as shown in Fig. 2.

Magnetic properties

The observed magnetic moment per binuclear complex at room temperature shown in Table 1 is less than

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

Complexes	Band maxima (cm^{-1}) and assignments $d_{xy} \rightarrow d_{xz,yz}$	 $d_{xy} \rightarrow d_{x}^2-y^2$	 $d_{xy} \rightarrow d_z^2$
$[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$	12,400	15,400	23,100
$[(VO)_2(IPHTA)(bpy)_2]SO_4$	12,300	15,300	23,800
$[(VO)_2(IPHTA)(phen)_2]SO_4$	12,500	16,300	23,000
$[(VO)_2(IPHTA)(NO_2\text{-}phen)_2]SO_4$	12,500	16,400	23,600

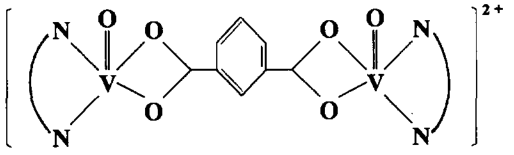

Fig. 2. Plausible coordination environments of the complexes (N͡N = bpy, Me_2bpy, phen, NO_2-phen).

the spin-only value (2.45 μ_B) for binuclear oxovanadium(IV) complexes in the absence of exchange interaction. This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes [16]. Being interested in the magnetic behaviour of the complexes, variable temperature (4–300 K) magnetic moments and magnetic susceptibility were further measured for complexes (**1**) and (**2**) and shown in Fig. 3. From Fig. 3, it is evident that the magnetic moments decrease steadily with decreasing temperature, implying the existence of an antiferromagnetic spin-exchange interaction within each molecule [17]. This is consistent with the room-temperature magnetic moments data of the complexes. In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic susceptibility data were analysed by the modified Bleaney-Bowers equation [18], which includes the fraction of a small amount of uncoupled oxovanadium(IV) impurity (ρ):

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

where χ_M is the molecular susceptibility per binuclear complex, $2J$ (in the spin Hamiltonian $\hat{H} = -2J\,\hat{S}_1 \times \hat{S}_2$) is the singlet–triplet splitting or exchange integral, $N\alpha$ is the temperature-independent paramagnetism and the remaining symbols have their usual meanings. As shown in Fig. 3, good least-squares fits to the experimental data were obtained with eq. (1) for complexes (**1**) and (**2**). The magnetic parameters thus determined and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma(\chi_M)_{abs}$ are: $J = -26.8\ cm^{-1}$, $g = 2.01$, $\rho = 0.005$, $F = 5.2 \times 10^{-6}$ for (**1**); $J = -31.0\ cm^{-1}$, $g = 2.08$, $\rho = 0.003$, $F = 4.8 \times 10^{-6}$ for (**2**). These results indicate that the complexes are essentially binuclear and undergo a moderately strong antiferromagnetic spin-exchange interaction between the VO^{2+} ions within each molecule.

The present complexes $[(VO)_2(IPHTA)(bpy)_2]SO_4$ and $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ have the same extended IPHTA-bridge structures and their IR and electronic spectra are also similar. The only difference between $[(VO)_2(IPHTA)(bpy)_2]SO_4$ and $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ is that there are four methyl substituents in the terminal ligands for the latter. However, its presence led to the exchange parameter J for complex $[(VO)_2(IPHTA)(bpy)_2]SO_4$ is larger (absolute value) than for complex $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$. This magnetic behaviour is very similar with that of analogous nickel(II) complexes $[Ni_2(IPHTA)(Me_2bpy)_4](ClO_4)_2$ ($-J = 12.5\ cm^{-1}$) and $[Ni_2(IPHTA)(bpy)_4](ClO_4)_2$ ($-J = 17.8\ cm^{-1}$) previously reported [19]. The results suggest that the methyl substituents in terminal ligands will reduce antiferromagnetic spin-exchange interactions between metal ions. The influence of substituents in the terminal ligands on magnetic interactions between metal ions may be explained as follows: Two substituents ($—CH_3$) in terminal ligand (Me_2bpy) molecule are electron-repelling groups which may have effects on both electronic and molecular structures [20]. The steric effects of the methyl substituents will lead to loss of planarity in the bridging system, so as to decrease interaction between VO^{2+} ions. On the other hand, methyl is an electron repelling group, which will cause increases in the electron density of the metal ions. The addition of electron density to the metal ion increases the electron–electron repulsion and raises the metal orbital levels. This in turn will lead to a larger energy gap between the metal and the bridged orbitals and lower delocalization of the metal orbitals towards the oxygen atoms of the bridge, so as to decrease the antiferromagnetic interactions.

Acknowledgements—This project was supported by Shandong Province Youth Science Fund and the National Natural Science Foundation of China.

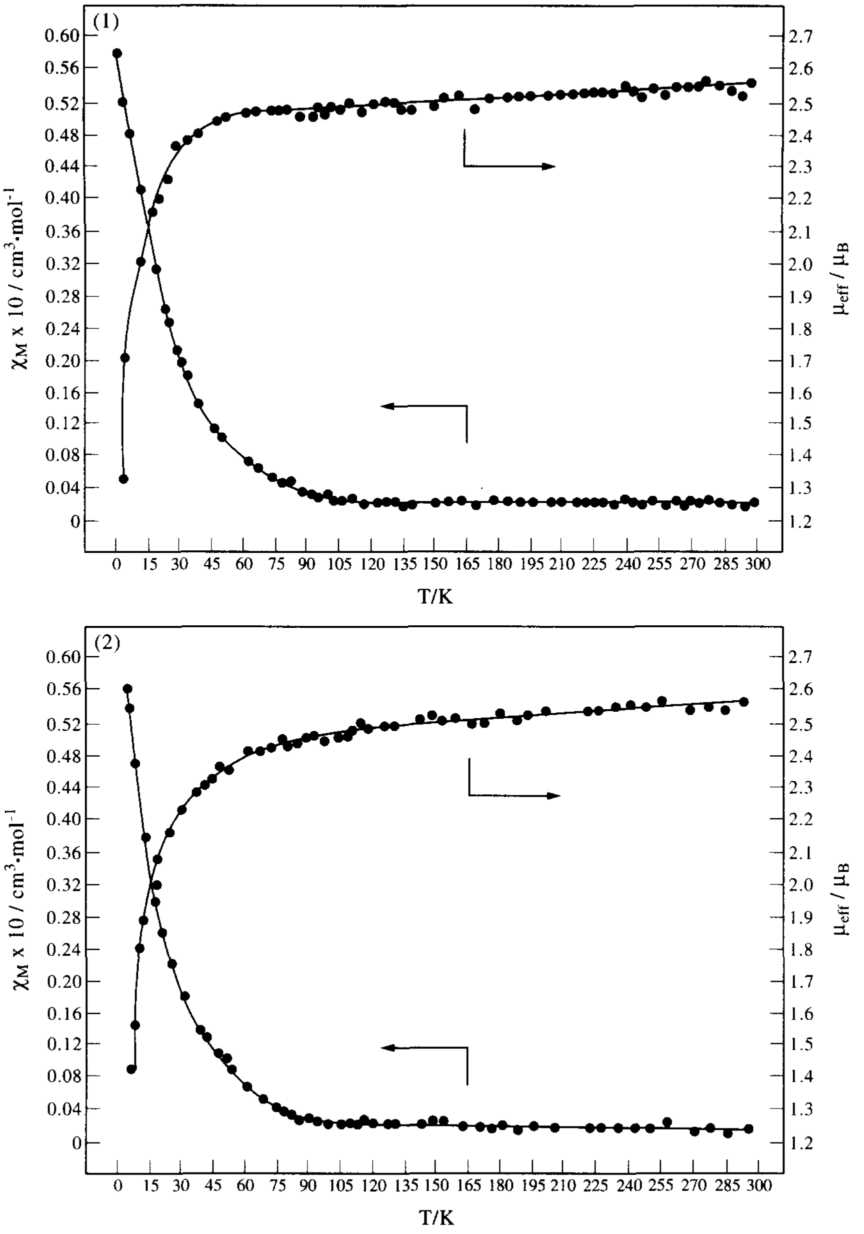

Fig. 3. Temperature variation of χ_M (lower) and μ_{eff} (upper) for complexes $[(VO)_2(IPHTA)(Me_2bpy)_2]SO_4$ (**1**) and $[(VO)_2(IPHTA)(bpy)_2]SO_4$ (**2**). The curve is based on eq. (1) using the magnetic parameters given in the text. (●), experimental data ; (—), calculated curves as described in the text.

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