Polish J. Chem., **78**, 1–7 (2004) **INORGANIC CHEMISTRY**

Synthesis and Magnetic Properties of Dinuclear Oxovanadium(IV) Complexes Bridged by Tetracarboxylato Groups

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(Received July 4th, 2003)

Three novel μ-tetracarboxylato-bridged oxovanadium(IV) dinuclear complexes described by the overall formula $[(VO)_2(PMTA)L_2]$, where PMTA stands for the tetraanion of pyromellitic acid, and L denotes 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 1,10-phenanthroline (phen), respectively, have been synthesized and characterized by elemental analyses, molar conductivity and room-temperature magnetic moment measurements, IR, ESR and electronic spectral studies. It is proposed that these complexes have PMTA-bridged structures and consist of two oxovanadium(IV) ions, each in a square-pyramidal environment. The $[(VO)_2(PMTA)(bpy)_2]$ **(1)** and $[(VO)_2(PMTA)(phen)_2]$ **(2)** complexes were further characterized by variable temperature (4.2~300 K) magnetic susceptibility measurements and the observed data were fitted to the modified Bleaney-Bowers equation by the least-squares method, giving the exchange integral $J = -2.75$ cm^{-1} for **(1)** and $J = -3.91$ cm^{-1} for **(2)**. This result indicates that there is a weak antiferromagnetic spin-exchange interaction between the two VO^{2+} ions within each molecule.

Key words: μ-tetracarboxylato-bridge, oxovanadium(IV), dinuclear complex, magnetic properties

Recent years have witnessed a growing interest in the coordination chemistry of vanadium complexes [1–8]. The reason is probably 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 biological [9] and industrial [10] processes or their simple models. In particular, dinuclear oxovanadium(IV) complexes are receiving considerable attention, since the studies of the magnetism of dinuclear oxovanadium(IV) complexes is interesting in comparing with that of dinuclear copper(II) complexes [11], although both oxovanadium(IV) and copper(II) ions have only one unpaired electron in each of their 3d-shells.

In view of the bridging function of the tetracarboxylato group (PMTA), Chaudhuri *et al.* [12] first utilized PMTA as a multiatom bridge to synthesize the dinuclear copper(II) complex [LCu(μ-tetracarboxylato)CuL] · $4H_2O$ (L = 1,4,7-trimeth-

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yl-1,4,7-triazacyclononane). It has been revealed by the single crystal X-ray and magnetic analysis [12] that the long-range antiferromagnetic coupling could occur between the copper(II) ions bridged by the PMTA ligand although the Cu···Cu separation is 7.8 Å. Since then, many polynuclear complexes containing the bridging PMTA have been synthesized and their magnetic properties studied [13,14]. However, to the best of our knowledge, no tetracarboxylato-bridged dinuclear oxovanadium(IV) complexes have so far been reported. Owing to the importance mentioned above, it is of considerable interest to synthesize and study dinuclear oxovanadium(IV) complexes propagated by PMTA bridge in order to understand the feature and the molecular magnetism of this kind of complexes.

In this paper, three new dinuclear oxovanadium(IV) complexes bridged by tetracarboxylato group and end-capped with 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) or 1,10-phenanthroline (phen), respectively, namely $[(VO)_2(PMTA)(bpy)_2]$ **(1)**, $[(VO)_2(PMTA)(phen)_2]$ **(2)** and $[(VO)_2(PMTA)(Me_2bpy)_2]$ **(3)**, have been synthesized and characterized. The cryomagnetic properties of the complexes **(1)** and **(2)** were measured and studied in the temperature range 4.2~ 300 K, indicating that the spin coupling between oxovanadium(IV) ions through PMTA-bridge in both complexes **(1)** and **(2)** is antiferromagnetic.

EXPERIMENTAL

Materials: All the reagents used in the synthesis were of analytical grade. Pyromellitic acid (H_4PMTA), LiOH·H_2O, $VOSO_4\cdot 5H_2O$, 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) were used as commercially obtained.

Synthesis of $[(VO)_2(PMTA)(bpy)_2]$ (1): To a solution of 254.3 mg (1 mmol) of pyromellitic acid in methanol (20 mL) was added dropwise a methanol solution (20 mL) of 167.8 mg (4 mmol) of LiOH·H_2O under stirring at room temperature. The stirring was continued until the mixture became clear. The resulting solution was then filtered to eliminate impurities. To the filtrate was added a methanol solution (15 mL) of 762 mg (2.1 mmol) of $VOSO_4\cdot 5H_2O$ and 312.4 mg (2 mmol) of bpy in 20 mL methanol solution under N_2. The color of the solution changed immediately from green to pale-violet and a small amount of precipitate formed. The mixture was subsequently refluxed for *ca.* 12 h. After cooling to room temperature, violet microcrystals thus formed was filtered, washed with methanol, water and diethyl ether several times and dried with P_2O_5 under reduced pressure. Recrystallization was carried out from acetonitrile/ethanol (1:2) mixture. Yield, 452.6 mg (65%); m.p., 263.5°C. Anal. calc. for $(VO)_2C_{30}H_{18}N_4O_8$ (m.w. 696.38): C, 51.74; H, 2.61; N, 8.05; VO, 19.23%. Found: C, 52.01; H, 2.50; N, 8.27; VO, 19.01%.

Synthesis of $[(VO)_2(PMTA)(phen)_2]$ (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. Yield, 521.1 mg (70%); m.p., 188.9°C. Anal. calc. for $(VO)_2C_{34}H_{18}N_4O_8$ (m.w. 744.42): C, 54.86; H, 2.44; N, 7.53; VO, 17.98%. Found: C, 54.63; H, 2.57; N, 7.31; VO, 17.72%.

Synthesis of $[(VO)_2(PMTA)(Me_2bpy)_2]$ (3): This complex was obtained as red-violet microcrystals by the same procedure described as complex **(1)**, but by using Me_2bpy instead of bpy. Yield, 511.7 mg (68%); m.p., 281.8°C. Anal. calc. for $(VO)_2C_{34}H_{26}N_4O_8$ (m.w. 752.48): C, 54.27; H, 3.48; N, 7.45; VO, 17.79%. Found: C, 54.02; H, 3.35; N, 7.20; VO, 17.55%.

Physical measurements: Analyses for C, H and N were carried out on a Perkin-Elmer model 240 elemental analyser. Metal contents were determined by $KMnO_4$ volumetric titration. The infrared spectra were measured on a Shimadzu model 810 infrared spectrophotometer in KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. ESR spectra were recorded with a JES-FEIXG ESR apparatus using an X-band and Mn-reference. 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 (4~300 K) magnetic susceptibilities 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 by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism of the constituting atoms.

RESULTS AND DISCUSSION

Composition and coordination environment of the complexes: In this study, the PMTA-bridged dinuclear oxovanadium(IV) complexes were obtained by the reaction of H_4PMTA with $VOSO_4 \cdot 5H_2O$ and the terminal ligand L (L = bpy, Me$_2$bpy and phen) in methanol in the presence of a base. The use of $LiOH \cdot H_2O$ as the base gave good results because it and its salt ($LiClO_4$) formed in the reaction are all fairly soluble in methanol and the products are little contaminated with these inorganic materials. Indeed, elemental analytic data for the newly prepared complexes indicate that the reaction of PMTA with $VOSO_4 \cdot 5H_2O$ and L (L = bpy, Me$_2$bpy, phen) in *ca.* 1:2:2 mole ratio readily yielded the dinuclear complexes of the general formula [(VO)$_2$(PMTA)L$_2$], as expected. These compounds are the first examples of dinuclear oxovanadium(IV) complexes bridged by PMTA ligand. Based on the molar conductivity and magnetic moment at room-temperature measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes are presumed to have the coordination environment as shown in Fig. 1.

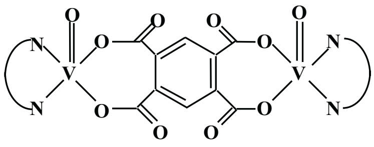

Figure 1. Proposed structure of the complexes ($\overset{\frown}{N\ N}$ = bpy, phen, Me$_2$bpy).

Solubility and molar conductances of the dinuclear complexes: All the dinuclear complexes are very soluble in DMSO, DMF, acetonitrile and acetone; moderately soluble in water, methanol, ethanol and practically insoluble in carbon tetrachloride, chloroform and benzene. For the three complexes, the molar conductance values in DMF solution at 25°C (see Table 2) fall in the range for non-electrolytes [16]. This is in agreement with the results of IR spectra.

Infrared spectra: The IR spectra taken in the region 4000~400 cm^{-1} provide some information regarding the mode of coordination in the complexes and were analysed in comparison with that of the free ligand (H_4PMTA). The most relevant IR absorption bands due to the complexes, together with their assignments, are shown in Table 1. It is noteworthy that the IR spectrum of pyromellitic acid shows a broad band near 1700 cm^{-1}, which is attributed to υ(C=O) of the carboxylic group. However, in the IR spectra of all complexes, this band had disappeared, accompanied by the appearance of two characteristic strong and broad bands at *ca*. 1620 cm^{-1} and 1380 cm^{-1} attributed to $\upsilon_{as}(CO_2^{-1})$ (1630~1618 cm^{-1}) and $\upsilon_s(CO_2^-)$ (1400~1370 cm^{-1}) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the $\upsilon_{as}(CO_2^-)$ and $\upsilon_s(CO_2^-)$ bands strongly suggests the end-to-end linking of the PMTA ligand in an equivalent way at both sites [5]. The appearance of a new band at 580~585 cm^{-1} due to υ(V–O) further confirms the coordinated nature of the carboxylate groups. Moreover, the coordination modes of carboxylate groups have often been diagnosed by the separation between $\upsilon_{as}(CO_2^-)$ and $\upsilon_s(CO_2^-)$. 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, these two bands were separated by *ca*. 230 cm^{-1} (see Table 1), suggesting an unidentate coordination mode for the four carboxylato groups of the PMTA ligand [17]. The unidentate coordination modes of the carboxylates in PMTA were supported by the crystal structure of the analogous complex [12] [LCu(μ-tetracarboxylato)CuL]·4H_2O (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). In addition, the –N=C– vibrations for the terminal ligands (bpy, Me$_2$bpy, phen) are present in the corresponding dinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinate with the metal ion. This view is further supported by the appearance of a band corresponding to the metal-nitrogen stretching vibration at 470~480 cm^{-1} in the complexes. In addition, the band centered at 1120 cm^{-1}, typical for a non-coordinated sulfate anion [18], was not found for the complexes. This is consistent with the conductance measurements and elemental analyses of the complexes. Furthermore, the V=O stretching vibrations of all complexes were observed near 990 cm^{-1}, indicating no intermolecular V=O···V=O bonding in these complexes [19], in accord with the following magnetic analysis.

Table 1. Physical data of the PMTA-bridged dinuclear oxovanadium(IV) complexes.

Complex	Λ_M (S·cm^2·mol^{-1})	μ_{eff} (B.M)	IR (cm^{-1})					
			$\upsilon_{as}(CO_2^-)$	$\upsilon_s(CO_2^-)$	υ(V–O)	υ(V=O)	υ(C=N)	υ(V–N)
(1)	4.0	2.43	1618	1380	582	990	1525	470
(2)	5.2	2.41	1630	1400	580	995	1510	473
(3)	4.8	2.30	1625	1370	585	992	1530	480

(1) = [(VO)$_2$(PMTA)(bpy)$_2$], **(2)** = [(VO)$_2$(PMTA)(phen)$_2$], **(3)** = [(VO)$_2$(PMTA)(Me$_2$bpy)$_2$].

Table 2. ESR and electronic spectra of the PMTA-bridged dinuclear complexes.

Complex	ESR			UV (cm^{-1})/ε_{max} (mol^{-1}·cm^{-1}·L)			
	$g_\perp$	$g_\parallel$	g_{av}	CT	$d_{xy}\rightarrow d_{xz,yz}$	$d_{xy}\rightarrow d_{x^2-y^2}$	$d_{xy}\rightarrow d_{z^2}$
(1)	2.02	2.13	2.06	31570 (29280)	13850 (320)	17900 (380)	24200 (372)
(2)	2.05	2.12	2.07	30820 (28900)	13920 (325)	18100 (356)	23850 (363)
(3)	2.04	2.15	2.08	32510 (28800)	13870 (312)	17860 (345)	25100 (338)

Electronic spectra: As shown in Table 2, the electronic absorption spectra of the three binuclear complexes in DMF solutions are similar. A strong absorption at *ca*. 30×10^3 cm^{-1} observed for all the complexes may be attributed to the charge-transfer absorption band [20]. Further investigation of these and similar systems are still required in order to obtain a detailed assignment for charge transfer. In addition, three weak absorption peaks in the 13850~13920, 17860~18100 and 23850~25100 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}) [20–23].

ESR spectra: In order to obtain further structural information of these dinuclear complexes, the X-band ESR spectra of the three dinuclear oxovanadium(IV) complexes have been recorded in the polycrystalline state at room temperature. It is noted that the ESR spectra of the three dinuclear complexes are almost similar and exhibit 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, which may be tentatively assigned to the allowed transition of $\Delta Ms = \pm1$ and the $\Delta Ms = \pm2$ 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 [24], and the existence of a magnetic interaction between two oxovanadium(IV) ions for these dinuclear complexes [25]. This is in accord with the electronic spectra and the following magnetic studies.

All the complexes are soluble in some organic solvents, but attempts to obtain single crystals suitable for X-ray structure determination have been unsuccessful. However, based on the composition of these complexes, the infrared, ESR and electronic spectra, magnetic moments at room temperature and molar conductivity measurements, the results of variable-temperature susceptibilities, and the crystal structure of the analogous complex [12] [LCu(μ-tetracarboxylato)CuL]$\cdot 4H_2O$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), it is reasonable to suppose that these complexes have an extended PMTA-bridged structure, in which each carboxylic group is bound to the oxovanadium(IV) ion in a monodentate fashion through only one oxygen atom, yielding two seven-membered rings. Each vanadium(IV) atom is in a five-coordinated, square-pyramidal environment (Fig. 1).

Magnetic properties: The observed magnetic moment per dinuclear complex at room temperature, shown in Table 1, is less than the spin-only value (2.45 μ_B) for dinuclear oxovanadium(IV) complexes in the absence of exchange interaction. This suggests the presence of an antiferromagnetic spin-exchange interaction in these complexes [26]. 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 example, and the results are shown in Fig. 2 in the form of the effective magnetic moment (μ_{eff}) *versus* the absolute temperature (T). From Fig. 2 it can be seen that the curves of the μ_{eff}~T of the two complexes are similar. When the temperature is lowered, the curve of μ_{eff}~T exhibits a continuous decrease. This magnetic behavior is typical for a weak antiferromagnetic interaction

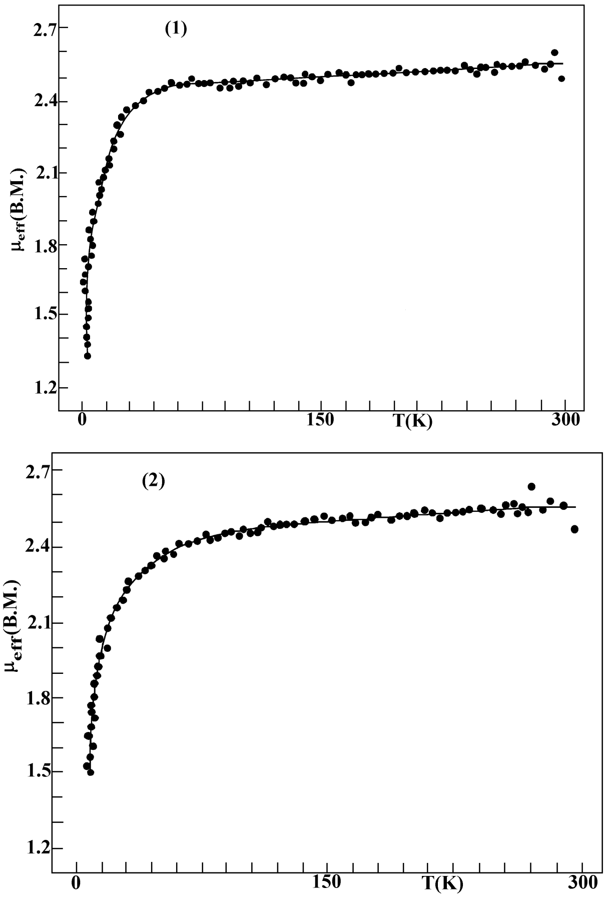

Figure 2. Temperature variation of μ_{eff} for complexes $[(VO)_2(PMTA)(bpy)_2]$ **(1)** and $[(VO)_2(PMTA)(phen)_2]$ **(2)**. The curve is based on Eq. (1) using the magnetic parameters given in the text. (•), experimental data, (–), calculated curves as described in text.

between the metal 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 intramolecular antiferromagnetic spin-exchange interaction through the PMTA bridge [26].

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 [27], which includes the fraction of a small amount of uncoupled oxovanadium(IV) impurity (ρ) based on the Heisenberg operator ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, $S_1 = S_2 = 1/2$):

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

where χ_M denotes the molecular susceptibility per dinuclear complex, N_α is the temperature-independent paramagnetism and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-squares fits to the experimental data were obtained with equation (1) for complexes **(1)** and **(2)**. The determined magnetic parameters and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{calc} - (\chi_M)_{obs})^2/\Sigma(\chi_M)_{obs}$ are: $J = -2.75$ cm^{-1}, $g = 2.05$, $\rho = 0.002$, $F = 8.1 \times 10^{-4}$, $N_\alpha = 0$ for **(1)**; $J = -3.91$ cm^{-1}, $g = 2.07$, $\rho = 0.005$, $F = 7.9 \times 10^{-4}$, $N_\alpha = 0$ for **(2)**. These results indicate that the complexes are essentially dinuclear and undergo weak antiferromagnetic spin-exchange interaction between the VO^{2+} ions within each molecule. 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 [28].

Acknowledgments

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

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