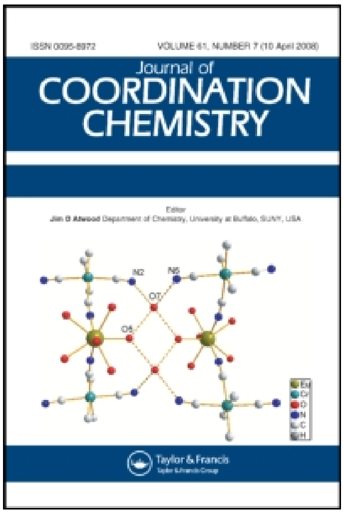

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HomoBinuclear Oxovanadium(IV) Complexes with Octaaza Macrocyclic Ligands Derived from Primary Diamines and 3,6-Dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione

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HOMOBINUCLEAR OXOVANADIUM(IV) COMPLEXES WITH OCTAAZA MACROCYCLIC LIGANDS DERIVED FROM PRIMARY DIAMINES AND 3,6-DIMETHYL/DIPHENYL-4,5-DIAZAOCTA-3,5-DIENE-2,7-DIONE

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The *in situ* reactions of 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione with diamines (ethylenediamine, *o*-phenylenediamine) in the presence of vanadyl salt yielded binuclear macrocyclic complexes of type $[(VO)_2mac](SO_4)_2$. Attempts to synthesize the corresponding metal-free macrocyclic ligands did not prove successful. The magnetic moment of the complexes decreases from *ca.* 1.73 (295 K) to 1.65 μ_B (91 K). The electronic spectra exhibit three bands at *ca.* 12 000–14 200, 18 200–19 500 and an intense band at *ca.* 30 000 cm^{-1}. The third band is probably due to a oxo → V(IV) charge-transfer transition. The infrared spectra indicate that the ligands coordinate through four aza nitrogen atoms to each V(IV). The fluid solution EPR spectra show an eight line pattern typical of a mononuclear VO(IV) compound and indicating the absence of VO...VO electron spin interaction. The electrochemical behavior of one complex with regards to oxidation has been studied by cyclic voltammetry in MeCN–MeOH solution.

Keywords: Oxovanadium(IV); Macrocycles; IR; EPR; Electronic spectra; Cyclic voltammetry

INTRODUCTION

Cyclic ligands species while are able to incorporate two metal ions offer the prospect of generating unusual electronic and chemical properties reflecting the proximity of the metal centers [1–3]. Binucleating macrocyclic ligands with similar and dissimilar coordination sites have been reported and the resulting bimetallic complexes often exhibit characteristic properties such as magnetic exchange between the adjacent metal ions or the tendency to undergo multi-electron redox reactions. These complexes are thermodynamically stabilized and kinetically retarded with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligands. Various macrocycles have been synthesized [4–10] as their metal complexes through

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the condensation of aromatic dialdehydes and primary diamines in the presence of metal ions as templates, and in most cases 2,6-diformyl-4-methylphenol is employed as the "head" unit for the macrocyclic framework. These complexes have been used extensively for studies on homo- and heterobinuclear and mixed valence complexes.

In this article, synthesis and characterization of octazamacrocyclic complexes of oxovanadium(IV), obtained by the template condensation reactions of 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione with primary diamines are reported.

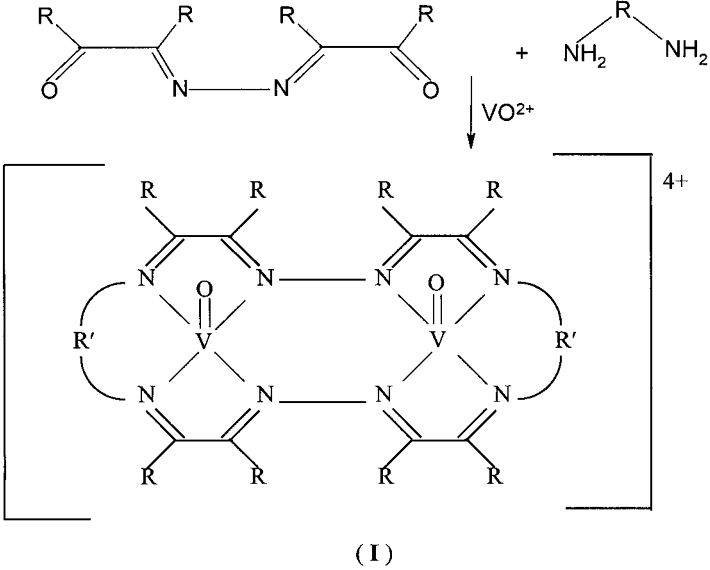
RESULTS AND DISCUSSION

The *in situ* reactions of 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione with diamines (ethylenediamine, *o*-phenylenediamine) in the presence of vanadium salt yielded new binuclear macrocyclic complexes (**I**), as given in Fig. 1.

The complexes are polycrystalline solids and the elemental analyses agree with the formulation (**I**). Attempts are being made to grow single crystals of the complexes suitable for X-ray analysis but so far, no success has been achieved. The complexes are ionic in nitrobenzene.

Magnetic Properties

The spin orbit coupling for the oxovanadium(IV) complexes is positive and magnetically dilute oxovanadium(IV) complexes should exhibit magnetic moments very close to the spin only value, $1.73\,\mu_B$ as expected for a $S = 1/2$ system. Binuclear oxovanadium(IV) species generally exhibit an antiferromagnetic exchange interaction due to direct overlap of the unpaired electron in the d_{xy} orbital, a few instances of



(I)

R = CH_3 or C_6H_5 ; R' =$(CH_2)_2$ or *o*-C_6H_4

FIGURE 1 Synthetic route for macrocyclic complexes.

ferromagnetic exchange coupling are known [11]. The magnetic susceptibility measurements of all macrocyclic compounds at variable temperature have been carried out between 295 and 91 K. In this temperature range, there is a very small but definite change of magnetic moment per vanadium. The magnetic moment decreases from *ca.* 1.73 (295 K) to *ca.* 1.65 μ_B (91 K), indicating slight interaction between two vanadium centers. If the two magnetically equivalent oxovanadium(IV) centers are totally non-interacting, then the magnetic moments should remain constant throughout. A plot of X_M^{-1} *vs* $1/T$ gave a linear fit with the Weiss constant $\theta = -4.0$ to 3.0 K, also indicating that there may be intra or intermolecular exchange interactions. In phenoxo-, alkoxo- or hydroxo- bridged dimeric oxovanadium(IV) complexes for which a singlet ground state has been reported, direct overlap of the d_{xy} orbital is considered to be the dominant magnetic exchange pathway [13,14]. Recently, some sulfato- bridged oxovanadium(IV) complexes have been reported [12] in which the antiferromagnetic exchanges depend upon the distance between the two metal centers, polarizability of the donor atom, electron density modulating behavior of the auxiliary ligands or bridging groups and geometric distortion of the coordination sphere. Nag *et al.* reported [7–9] similar magnetic behavior for oxovanadium(IV) complexes with tetra-aminodiphenol macrocyclic ligands. For these complexes, exchange parameters were evaluated but must be considered tentative because for such weak interactions reliable estimation is not possible.

Electronic Spectra

The electronic spectra of oxovanadium(IV) complexes having a square pyramidal or a distorted octahedral structure are most often interpreted in terms of the energy level scheme proposed by Ballhausen and Gray [15]. Usually, three optical bands are observed, assigned to $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xy}, d_{yz})$ (ν_1), $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ (ν_2) and $^2B_2(d_{xy}) \rightarrow {}^2A_1(d_z{}^2)$ (ν_3). The ν_3 band is often obscured by intense change-transfer absorptions in the u.v. region. The nujol mull spectra of the complexes (Table I), reported in this article, exhibit two bands at *ca.* 12000–15800, 18200–19500 cm^{-1} and a band at *ca.* 30000 cm^{-1}, probably due to an oxo → vanadium(IV) charge-transfer transition admixed with the $d_{xy} \rightarrow d_{z^2}$ (ν_3) transition.

TABLE I Magnetic moments and electronic spectral bands of oxovanadium complexes with octaaza macrocyclic ligands

Complexes	μ_{eff} (μ_B)		*Electronic spectral bands* (cm^{-1})		
	(295 K)	(91 K)	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$ + *charge transfer*
$[(VO)_2MOE](SO_4)_2$	1.73	1.68	12000	18500	30000
$[(VO)_2POE](SO_4)_2$	1.72	1.65	13500	19500	29500
$[(VO)_2MOP](SO_4)_2$	1.70	1.65	14200	18200	29800
$[(VO)_2POP](SO_4)_2$	1.74	1.66	15800	19000	29600

where, MOE = Macrocyclic ligand derived from 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and ethylenediamine.
POE = Macrocyclic ligand derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and ethylenediamine.
MOP = Macrocyclic ligand derived from 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine.
POP = Macrocyclic ligand derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine.

Infrared Spectra

The infrared spectra of all macrocyclic complexes of V(IV) show a band at *ca.* 930–950 cm^{-1}. This frequency is at the low end of the range 930–1040 cm^{-1}, reported for a large set of oxovanadium complexes [16]. It has been reported that the V=O stretching frequency is susceptible to a number of influences such as electron donation from basal plane ligand atoms, solid state effects and the nature of the anion. It has also been mentioned that electron-withdrawing groups attached to ligands cause a lowering of the ν(V=O) frequency. The complexes also show bands at *ca.* 1620–1600 cm^{-1} and 430–415 cm^{-1} assignable to ν(C=N) and ν(V–N) vibrations, respectively. The presence of an ionic sulfate group in the complexes is confirmed by the appearance of three bands at *ca.* 1140–1130 (ν_3), 960–950 (ν_1), and 620–600 cm^{-1} (ν_4). The absence of a ν_2 band and nonsplitting of ν_3 band indicate that T_d symmetry is retained. However, the presence of ν_1, otherwise forbidden, indicates that there is some deformation of the $SO_4{}^{-2}$ ion.

ESR Spectra

In the solid state, the ESR spectra of compounds show a single absorption with $g \approx 1.97$. The fluid solution (MeCN–MeOH) spectra at room temperature shows an eight line pattern, typical of a mononuclear oxovanadium (IV) compound (^{51}V; $I = 7/2$) with $g_{\text{iso}} \approx 1.975$ and $A_{\text{iso}} \approx 0.008\,\text{cm}^{-1}$. Clearly, an intramolecular VO···VO electron spin interaction is absent otherwise a fifteen-line hyperfine pattern would have been observed. Further, the frozen solution spectra show the species to be square pyramidal with the unpaired electron in an orbital of mostly d_{xy} character (ligand along x and y axes). Such complexes have $g_{\|} < g_{\perp}$ and $A_{\|} > A_{\perp}$ (Table II). The spectra rule out dissociation in solution.

Electrochemistry

The electrochemical behavior of only one complex ($R = C_6H_5$; $R' = (CH_2)_2$) with regard to its oxidation has been studied by cyclic voltammetry (cv) in MeCN–MeOH (4 : 1) solution. The complex undergoes two successive oxidation processes. The first couple ($VO^{IV}VO^{IV} \rightarrow VO^{IV}VO^{V}$) at 0.440 V *vs* Ag–AgCl is fully reversible ($\Delta E_p = 60$ mv) while the second ($VO^{IV}VO^{V} \rightarrow VO^{V}VO^{V}$) at 0.65 v is nearly reversible ($\Delta E_p = 85$ mv, scan rate v = 100 mv s^{-1}). The coproportionation constant, Kc, obtained from the relation $Kc = 10^{\Delta E_{1/2}}/0.0591$ is 4.1×10^2. It may be mentioned that molecules containing

TABLE II ESR parameters of oxovanadium complexes with octaaza macrocyclic ligands in frozen (MeCN–MeOH) solutions

Complexes	g_{av}	$g_{\|}$	$g_{\perp}$	A_{av}	$A_{\|}$	$A_{\perp}$
$[(VO)_2MOE](SO_4)_2$	1.979	1.952	1.991	87	161	50
$[(VO)_2POE](SO_4)_2$	1.974	1.950	1.986	88	161	52
$[(VO)_2MOP](SO_4)_2$	1.969	1.948	1.979	87	160	50
$[(VO)_2POP](SO_4)_2$	1.972	1.950	1.980	90	165	52

where, MOE = Macrocyclic ligand derived from 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and ethylenediamine.
POE = Macrocyclic ligand derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and ethylenediamine.
MOP = Macrocyclic ligand derived from 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine.
POP = Macrocyclic ligand derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine.

two chemically equivalent totally noninteracting reversible redox sites give $Kc = 4$. However, for most commonly observed cases, Kc is greater than 4. In the present case, two electron transfer was expected but the occurrence of two closely spaced redox couples ($\Delta E_{1/2} = 0.21$ v) suggests that removal of an electron from the second metal center is relatively more difficult than the first. It may be possible that the differences exist in their bond angles [9]. The slight geometrical differences facilitate easier oxidation of one vanadium(IV) center with respect to the other.

EXPERIMENTAL

Oxovanadium(IV) sulfate was an Aldrich sample and was gravimetrically estimated as the oxide. Estimation of carbon, hydrogen, and nitrogen was done at CDRI, Lucknow. Details of physical measurements have been described earlier [17,18]. The compound 3,6-dimethyl-4,5-diaazaocta-3,5-diene-2,7-dione was prepared as reported in the literature [19].

Preparation of Oxovanadium (IV) Complex with the Macrocyclic Ligand Derived from 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and Ethylenediamine

To a hot solution of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione (20 mmol) in acetonitrile (25 mL), a solution of $VOSO_4 \cdot 5H_2O$ (20 mmol) in methanol (20 mL) was added, slowly. The mixture was stirred for 30 min and ethylenediamine (20 mmol) was added. This resulted in a red solution which slowly changed to brown. The solution was refluxed for 12 h which resulted in the formation of dark brown precipitate. The mixture was cooled to room temperature and filtered. The precipitate was washed by stirring in hot CH_3CN, filtered and then washed with ether and dried *in vacuo*. Yield 55%.

A similar procedure was adopted for the synthesis of the oxovanadium(IV) complex with the macrocyclic ligand derived from -3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine. For the sake of brevity, these reactions along with analytical data of the products are summarized in Table III.

Preparation of Oxovanadium (IV) Complex with the Macrocyclic Ligand Derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and Ethylenediamine

3,6-Diphenyl-4,5-diazaocta-3,5-diene-2,7-dione (20 mmol) was dissolved in 20 mL of acetonitrile and to this, were added ethylenediamine (20 mmol) and a methanolic solution (20 mL) of oxovandium (IV) sulfate (20 mmol) resulting in a dark brown solution. The mixture was refluxed for 8 h, cooled, concentrated and filtered to give a brown precipitate. The precipitate was washed with ether and dried *in vacuo*. Yield 62%.

A similar procedure was adopted for the synthesis of oxovanadium(IV) complex with the macrocyclic ligand derived from 3,6-diphenyl-4,5-diazaocta-3,5-diene-2,7-dione and *o*-phenylenediamine. The details of these reactions along with analytical data of the products are summarized in Table III.

TABLE III Preparation, physical properties and analytical data of oxovanadium(IV) complexes with macrocyclic ligands derived from a primary diamine and 3,6-dimethyl/diphenyl 4,5-diazaocta-3,5-diene-2,7-dione

Reactants (molar ratio)	*Solvent*	*Refluxing time* (h)	*Product color, yield* (%)	*Decomp. temp.* (°C)	*Analysis* (%) *Found* (Calcd.)			
					C	*H*	*N*	*V*
$VOSO_4 \cdot 5H_2O$ + MDDD + en (1 : 1 : 1)	CH_3CN+CH_3OH	12	$[(VO)_2(MOE)](SO_4)_2$ green, 55	> 250	33.6 (33.8)	4.2 (4.5)	15.4 (15.8)	14.2 (14.3)
$VOSO_4 \cdot 5H_2O$ + MDDD + phen (1 : 1 : 1)	CH_3CN + CH_3OH	10	$[(VO)_2(POE)](SO_4)_2$ brown, 50	232	59.6 (59.7)	4.0 (4.0)	9.1 (9.3)	8.3 (8.4)
$VOSO_4 \cdot 5H_2O$ + PDDD + en (1 : 1 : 1)	CH_3CN + CH_3OH	8	$[(VO)_2(MOP)](SO_4)_2$ brown, 62	210	41.6 (41.7)	3.9 (4.0)	13.7 (13.9)	12.5 (12.6)
$VOSO_4 \cdot 5H_2O$ + PDDD + phen (1 : 1 : 1)	CH_3CN + CH_3OH	6	$[(VO)_2(POP)](SO_4)_2$ brown, 60	> 250	62.6 (62.7)	3.6 (3.7)	8.4 (8.6)	7.8 (7.8)

where, MDDD = 3,6-dimethyl 4,5-diazaocta-3,5-diene-2,7-dione; PDDD = 3,6-diphenyl 4,5-diazaocta-3,5-diene-2,7-dione; en = ethylenediamine; phen = *o*-phenylenediamine; MOE = Macrocyclic ligand derived from MDDD and en; POE = Macrocyclic ligand derived from MDDD and phen; MOP = Macrocyclic ligand derived from PDDD and en; POP = Macrocyclic ligand derived from PDDD and phen.

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