

## Oxovanadium(IV) Complexes of Macrocyclic Ligands Derived from 2,6-Dipicolinoyl Dihydrazine and $\beta$ -Diketones

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*The reactions of oxovanadium(IV) complexes of 2,6-dipicolinoyl dihydrazine (DPH) with  $\beta$ -diketones, viz., acetylacetone, propionylacetone and benzoylacetone have been studied. The reaction products, five-coordinate oxo-vanadium(IV) complexes of the type  $[VO(L)(H_2O)]$  (where L = macrocyclic ligand derived from 2,6-dipicolinoyl dihydrazine (DPH) and a  $\beta$ -diketone), have been characterized on the basis of elemental analyses, electrical conductance, magnetic susceptibility and spectral (infrared and electronic) data.*

### Introduction

The chemistry of oxovanadium(IV) complexes continues to be of unabated interest on account of the striking structural features presented by this class of compounds [1, 2]. The coordination number five is particularly of common occurrence in oxovanadium(IV) complexes [3–5]. However, there is hardly any known example of five-coordinate oxovanadium(IV) complexes of macrocyclic ligands. Recently, in a study of reactions of 2,6-dipicolinoyl dihydrazine with aldehydes, ketones, and  $\beta$ -diketones, we evaluated the template effect of zinc(II), cadmium(II), mercury(II), cobalt(II), nickel(II), copper(II) and zirconyl(IV) ions [6–9]. This work is now extended to study the role of oxovanadium(IV) cation in the cyclization of 2,6-dipicolinoyl dihydrazine (DPH) during its reactions with acetylacetone (AcAc), propionylacetone (PrAc) and benzoylacetone (BzAc).

### Experimental

All the chemicals and the solvents used were of the reagent grade.

The ligand dipicolinoyl dihydrazine (DPH) was synthesized as described earlier [10].

### Preparation of Oxovanadium(IV) Complexes of DPH

The complexes were prepared by the method reported earlier [11].

### Reactions of Oxovanadium(IV)-DPH Complexes with $\beta$ -Diketones

The following general method was adopted to study the reactions of  $\beta$ -diketones with oxovanadium(IV)-DPH complexes. Similar product was obtained in each case.

### Preparation of $[VO(DPH-Mac)(H_2O)]$ Complex (where DPH-Mac stands for a macrocycle derived from the DPH and a $\beta$ -diketone)

To the DPH complex (0.1 mol) in aqueous ethanol (50%, 25 ml) was added a  $\beta$ -diketone (0.1 mol) in ethanol (10 ml) and glacial acetic acid (5–7 ml). The reaction mixture was refluxed for 2–3 hr. A brown product formed was filtered, washed with ethanol (50%) and dried in an oven at 85 °C; yield: 60–70%.

### Analytical Procedures

The details of analytical procedures are the same as described earlier [12].

### Physical Measurements

Electrical conductance was measured on an Elico conductivity Bridge type CM 82T. The i.r. spectra were recorded on a Perkin Elmer-621 in KBr medium and electronic spectra in nujol mull were recorded on a visible Russian C $\Phi$ 10 and Perkin Elmer-4000A spectrophotometers. The magnetic susceptibilities of the complexes were determined by the Gouy's method using  $Hg[Co(NCS)_4]$  as calibrant.

### Results and Discussion

The reactions of two types of oxovanadium-DPH complexes [11], obtained at low (~4) and high (~8) pH having the molecular formulae  $[VODPH]$  and  $[VODPH]X_2$ , respectively, with  $\beta$ -diketones have been studied. The same type of product (I) is obtained in each case as evidenced by electrical

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conductance and spectral measurements. The formation of product (I) can be explained by assuming that in such reactions, the metal atom first dissociates from the coordinated ligand and then again with the formation of cyclic compound [13] since on treating  $\text{VOCl}_2$  with DPH in the presence of  $\beta$ -diketone, a similar product (I) is obtained.

The elemental analyses (Table I) of the reaction products reveal 1:1:1 metal to ligand to  $\beta$ -diketone stoichiometry. The complexes are non-conducting in dimethylformamide. Accordingly, these can be formulated as  $[\text{VO}(\text{DPH-Mac})\text{H}_2\text{O}]$ .

TABLE I. Analytical Data.

Complex	Calc. (Found) %			
	C	H	N	V
$\text{VO}(\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}_5)$	42.10 (41.84)	3.80 (2.89)	20.47 (20.23)	14.88 (14.46)
$\text{VO}(\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_5)$	43.82 (44.10)	4.21 (3.84)	19.66 (19.02)	14.23 (14.05)
$\text{VO}(\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_5)$	50.50 (49.84)	3.71 (2.97)	17.32 (16.84)	12.59 (11.93)
$\text{VO}(\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}_5)^{\text{a}}\text{Cl}_2$	42.59 (41.96)	3.96 (3.25)	14.61 (15.21)	10.69 (10.13)

<sup>a</sup>Pyrazole derivative (III).

### Infrared Spectra

The important i.r. bands of the ligand and the complexes along with the tentative assignments are given in Table II. The free ligand [14] (DPH) shows the bands at 1690, 1510 and 1280  $\text{cm}^{-1}$  which may be assigned to amide-I ( $\nu\text{C}=\text{O}$ ), amide-II ( $\nu\text{CN} + \delta\text{NH}$ ) and amide-III ( $\nu\text{CN} + \delta\text{NH}$ ) vibrations, respectively. However, in the spectra of the reactions products these bands are observed at *ca.* 1690, 1490 and 1240  $\text{cm}^{-1}$ , respectively. The appearance of amide-I band rules out the possibility of enolization in the reaction products and further no shift in this band suggests the non-coordination of the amide-oxygen to the metal atom in the ketonic form [15]. A blue shift in the amide-II and amide-III bands and a red shift ( $\sim 20 \text{ cm}^{-1}$ ) in  $\delta\text{NCO}$  band in the complexes indicate the coordination of the deprotonated amide-nitrogen to the metal atom [16, 17]. The bands appearing at 450–460  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{V}-\text{N})$  vibrations.

The pyridine ring vibrations occurring at 1580 (8a, pyridine ring deformation), 610 (6a, an in-plane ring deformation) and 410  $\text{cm}^{-1}$  (16b, an out-of-plane ring deformation) in DPH, appear at *ca.* 1600, 630 and 425  $\text{cm}^{-1}$ , respectively, in the complexes. The spectrum of DPH shows an additional band at 990  $\text{cm}^{-1}$  due to ring breathing mode of the pyridine residue. It appears around 1020  $\text{cm}^{-1}$  in the com-

TABLE II. Important Infrared Spectral Bands ( $\text{cm}^{-1}$ ) of the Ligand and the Complexes along with Tentative Assignments.

Compound	$\nu(\text{OH})$	$\nu_{\text{asym}}(\text{NH})$	Amide I ( $\nu\text{C}=\text{O}$ )	$\nu(\text{C}=\text{N})$	8a	6a	16b	$\delta(\text{NCO})$	$\nu(\text{V}=\text{O})$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}-\text{py})$
DPH	—	3290s	1690s	—	1580s	610m	410m	730m	—	—	—
$[\text{VO}(\text{DPH-AcAc})(\text{H}_2\text{O})]$	3450	—	1685s	1630w	1600s	625w	420m	750m	960m	460m	255w
$[\text{VO}(\text{DPH-PrAc})(\text{H}_2\text{O})]$	3400m	—	1685s	1635w	1605s	630w	420m	755m	965m	465m	265m
$[\text{VO}(\text{DPH-BzAc})(\text{H}_2\text{O})]$	3500– 3200mb	—	1690s	1630w	1590s	630w	425m	755m	970m	465m	265m

TABLE III. Magnetic Moments and Electronic Spectral Data ( $\text{cm}^{-1}$ ).

Complex	Electronic Spectral Bands and Assignments			10Dq	$\mu_{\text{eff}}$ BM (300 K)
	$d_{xy} \rightarrow d_{yz}$	$d_{xy} \rightarrow d_{xz}$	$d_{xy} \rightarrow d_{x^2-y^2}$		
[VO(DPH-AcAc)(H <sub>2</sub> O)]	11700	15800	21200	15800	1.71
[VO(DPH-PrAc)(H <sub>2</sub> O)]	11000	15200	22800	15200	1.80
[VO(DPH-BzAc)(H <sub>2</sub> O)]	12500	16000	22100	16000	1.74

plexes. The upward shift in various pyridine ring vibrations indicates the coordination of pyridine-nitrogen to the metal [18]. The bands due to  $\nu(\text{V}-\text{py})$  are observed around  $260 \text{ cm}^{-1}$ .

The bands corresponding to  $\nu(\text{NH})$  and  $\delta(\text{NH}_2)$  vibrations are absent in the spectra of these complexes. However, a new weak band appears around  $1630 \text{ cm}^{-1}$  attributable to  $\nu(\text{C}=\text{N})$  vibration of the azomethine linkage [19]. The complexes show no characteristic band due to  $\nu(\text{C}=\text{O})$  vibration of  $\beta$ -diketone moiety. These observations indicate that both the ketonic groups of the  $\beta$ -diketone react with the terminal hydrazinic nitrogen atoms and the cyclization of the DPH complex takes place giving rise to a macrocyclic system. These complexes show additional bands in  $3300\text{--}3500$ ,  $1610\text{--}1620$ ,  $820\text{--}830$  and  $590\text{--}600 \text{ cm}^{-1}$  regions, assignable to  $\nu(\text{OH})$ ,  $\delta(\text{H}_2\text{O})$ ,  $\rho_z(\text{H}_2\text{O})$  and  $\rho_w(\text{H}_2\text{O})$  vibrations, respectively, due to coordinated water molecule [20]. The strong bands appearing in the vicinity of  $965 \text{ cm}^{-1}$  in these complexes are assigned to  $\nu(\text{V}=\text{O})$  vibrations. These values are consistent with the monomeric nature of the complexes.

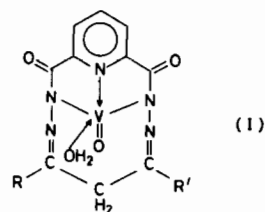
#### Magnetic Moments and Electronic Spectra

The magnetic moments of the oxovanadium macrocyclic complexes (Table III) lie in the 1.71–1.80 BM range at room temperature. These values are well within the range reported for vanadyl(IV) complexes with one unpaired electron [1, 12].

The electronic spectra recorded in Nujol mull are given in Table III. Three bands are observed in the regions  $11000\text{--}12500$ ,  $15200\text{--}16000$  and  $21200\text{--}23000 \text{ cm}^{-1}$ . These spectra resemble those of other five-coordinate oxovanadium(IV) complexes involving nitrogen and oxygen donor atoms [5, 12, 21, 22]. Several schemes [1, 2] have been advanced to interpret the electronic spectra of vanadyl(IV) complexes. These schemes predict a three band spectrum for five-coordinate complexes possessing the effective  $C_{4v}$  symmetry of a square pyramid. Recently, Wasson *et al.* [22] have reported an energy level scheme:  $d_{xy} < d_{yz} < d_{xz} < d_{x^2-y^2} < d_{z^2}$  to interpret the electronic spectra of distorted five-coordinate square pyramidal oxovanadium(IV) com-

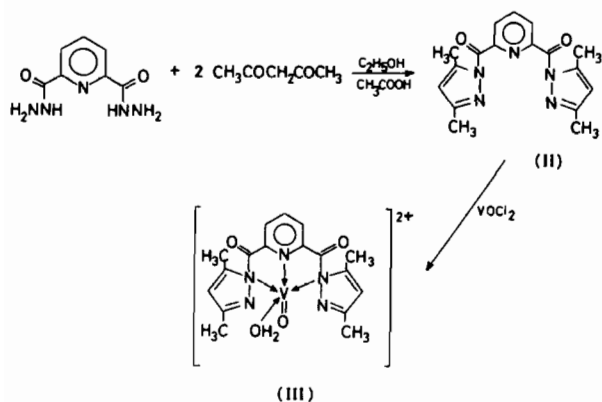
plexes. This scheme is similar to one proposed by Ballhausen and Gray [23], except for the splitting of  $d_{xz}$  and  $d_{yz}$  levels. Accordingly, the bands observed for the present complexes can be assigned to  $d_{xy} \rightarrow d_{yz}$  ( $11000 \text{ cm}^{-1}$ ),  $d_{xy} \rightarrow d_{xz}$  ( $16000 \text{ cm}^{-1}$ ) and  $d_{xy} \rightarrow d_{x^2-y^2}$  ( $23000 \text{ cm}^{-1}$ ) transitions. The second band in the electronic spectra of the complexes corresponds [3] to the 10 Dq. In addition to these bands, two more bands are observed at *ca.*  $36,000$  and  $40,000 \text{ cm}^{-1}$ . The first band may be assigned to  $\pi \rightarrow \pi^*$  transition of the azomethine linkage ( $>\text{C}=\text{N}$ ) formed by the condensation of the hydrazinic groups with carbonyl groups of a  $\beta$ -diketone and the latter to  $n \rightarrow \pi^*$  transition of the pyridine ring in resonance with the  $\text{C}=\text{O}$  group. The appearance of the former band ( $\pi \rightarrow \pi^*$  transition) due to azomethine linkage further supports the formation of macrocyclic systems.

Thus on the basis of these studies, the structure of the oxovanadium macrocyclic complex can be depicted as (I).



where	R	R'	$\beta$ -diketone
	CH <sub>3</sub>	CH <sub>3</sub>	AcAc
	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub>	PrAc
	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	BzAc

However, a different product (III) is obtained when vanadyl(IV) chloride is treated with the condensation product (II) of dipicolinoyl dihydrazine and acetylacetone as indicated by the conductance and spectral properties of this complex. This complex (III) behaves as a 1:2 electrolyte in dimethylformamide and appears to be a complex of a pyrazole derivative as shown by the following sequence of reactions:



It appears that the presence of oxovanadium(IV) cation induces the cyclization and this metal template effect is 'kinetic' in nature as an undesired product (II) is obtained in the absence of this oxovanadium cation [24]. This observation is similar to one observed with Zn(II), Cd(II), Hg(II) [8] and ZrO(IV) [6].

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