

PHYSICO-CHEMICAL STUDIES ON VANADYL COMPLEXES OF SOME TRIDENTATES

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The vanadyl complexes of the type $[\text{VO.L}(\text{H}_2\text{O})_2]$ were synthesised with 3-(α -benzoylmethyl-benzylideneimino) propanoic acid (H_2BP), O-(α -benzoylmethyl-benzylideneimino) benzoic acid (H_2BB) and (α -benzoylmethyl-benzylideneimino)benzene sulphonic acid (H_2BBS). These complexes have been studied potentiometrically in aqueous medium ($\mu = 0.1, 0.05$ and 0.01 M NaClO_4) at $25^\circ, 35^\circ$ and 45°C . The solid chelates have also been synthesised and characterised by elemental analysis, molecular weight, magnetic, conductance and spectral techniques.

Keywords : Vanadyl Complexes of Biprotic Tridentates.

INTRODUCTION

THE vanadyl complexes of H_2BP , H_2BB and H_2BBS , obtained by the interaction of dibenzoyl methane with β -alanine, anthranilic acid and orthanilic acid, respectively have not been studied (Hodgson, 1975). These ligands containing acidic ($-\text{COOH}$ or $-\text{SO}_3\text{H}$) and azomethine ($-\text{C}=\text{N}$) groups are structurally similar and are thus expected to behave as biprotic tridentates.

EXPERIMENTAL

The ligand and their solid VO(II)-chelates were prepared by the procedure reported (Gupta *et al.*, 1979a) earlier. The apparatus and the reagents employed were the same as described (Gupta *et al.*, 1979b) earlier.

Calvin-Bjerrum $p\text{H}$ -titration techniques as used by Irving and Rossotti was adopted to study the proton-ligand stability constants of the H_2BP and $\text{H}_2\text{BB-VO(II)}$ complexes whereas Bjerrum method was followed in the case of $\text{H}_2\text{BBS-VO(II)}$ complex. The ligands were titrated with standard alkali in absence and in the presence of the metal-ion at $25^\circ, 35^\circ$ and 45°C .

RESULTS AND DISCUSSION

Dissociation constants of H_2BP , H_2BB and H_2BBS and stability constants ($\log K_1$ and $\log K_2$) of their vanadyl complexes at $25^\circ, 35^\circ$, and 45°C are summarised in Table I. The stability constants increase with increase in temperature suggesting that high temp. is favourable for complexation.

The free energies of formation are all negative and the values are more negative at higher temperatures. It shows that complex formation is a spontaneous process

TABLE I

Dissociation constants of H₂BP, H₂BB and H₂BBS and stability constants of their VO(II) complexes

Ligand/Complex	Dissociation/stability constants	Average values		
		25°	35°	45°
H ₂ BP	log K_1^H	9.35	9.05	8.70
	log K_2^H	7.10	6.90	6.50
H ₂ BB	log K_1^H	9.60	9.22	9.00
	log K_2^H	7.30	7.00	6.72
H ₂ BBS	p K_1	3.26	2.98	2.64
	p K_2	10.20	9.89	9.69
VO(II)—H ₂ BP	log K_1	8.89	9.25	9.40
	log K_2	8.42	8.45	8.50
VO(II)—H ₂ BB	log K_1	5.71	5.76	5.81
	log K_2	4.16	4.34	4.50
VO(II)—H ₂ BBS	log K_1	12.35	12.55	12.83
	log K_2	9.59	9.79	10.14

and that higher temperature favours complexation. ΔS values are positive suggesting favourable entropy changes for complex formation.

As reported (Harned & Ehlera, 1933; Harned & Embree, 1935; and Harned & Kazanjian, 1936) earlier, in terms of Harned's relation, the values of θ (the temp. at which K^H is minimum) and pK_m^H (pK^H at $t = 0$) for H₂BP, H₂BB and H₂BBS are 372.8° and 2.24; 632° and 3.54; 417.7° and 3.43, respectively. ΔH values calculated from Harned's and Gibbs-Helmoltz equations were also found to be similar for all the ligands.

All the solid complexes were found paramagnetic as suggested by their magnetic moments (Table II). It is apparent from the magnetic moments of these compounds that there is no metal-metal bonding and hence no spin-exchange occurs and they exist as monomers. This fact is also supported by their molecular weights (Table II) obtained ebulliometrically in dioxan.

Thermogravimetric analysis suggests a weight-loss between 130–185° corresponding to two water molecules. On heating further between 400–450°, a sudden weight-loss suggests the formation of metallic oxides.

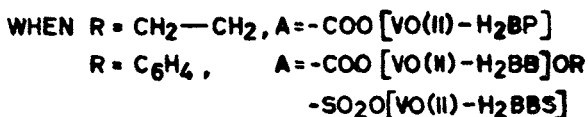
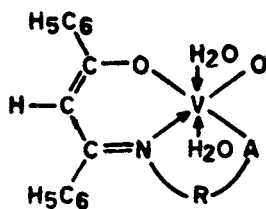
Based on the elemental analysis and molecular weight data the hydrated metal chelates display 1 : 1 (metal-ligand) stoichiometry and possess the composition [VO.L.(H₂O)₂].

The absorption spectra of all the vanadyl complexes in donor and non-donor solvents exhibit two bands in the narrow ranges 11500–11900 cm⁻¹ ($\epsilon = 110$ –130

TABLE II

Thermodynamic parameters, magnetic moment and molecular weight of the vanadyl complexes

Complex	$-\Delta G$ (k.J/mole)			ΔH K.J/mole	ΔS J/deg/ mole	μ_{eff} B.M. at 308 °K	Mol. wt. Found (Calcd.)
	25°	35°	45°				
VO(II)—H ₂ BP	104.84	111.72	117.18	56.28	94.50	1.64	387 (394)
VO(II)—H ₂ BB	57.16	62.58	62.65	21.84	265.44	1.68	432 (444)
VO(II)—H ₂ BBS	125.58	132.30	140.25	95.34	742.56	1.67	468 (480)

FIG. 1. Vanadyl complexes of H₂BP, H₂BB and H₂BBS (tridentates).

mole⁻¹ cm⁻¹) and 20000–22000 cm⁻¹ ($\epsilon = 150$ –170 mole⁻¹ cm⁻¹), assignable to the transitions $dx_y \rightarrow dx_z$, dy_z and $dx_y \rightarrow dx^2 - y^2$.

In the I. R. spectra of H₂BP, H₂BB and H₂BBS five bands were observed in the ranges 3360–3380, 2570–2890 or 1080–1100, 1680–1690, 1635–1650 and 1600–1610 cm⁻¹ which correspond to ν_{OH} , ν_{COOH} or ν_{SO_3H} , $\nu_{C=O}$, $\nu_{C=C}$ and $\nu_{C=N}$, respectively. The spectra of the complexes show absorption characteristics of the aromatic ligands; ν_{as} COO (at 1600–1620 cm⁻¹ as compared to 1730 cm⁻¹ in the free ligand) and ν_s COO (1440–1460 cm⁻¹) for coordinated carboxylate groups were observed in the VO(II) chelates of H₂BP, H₂BB. In the complexes the $\nu_{C=N}$ is lowered to 1580–1570 cm⁻¹ suggesting involvement of azomethine nitrogen in chelation. The $\nu(VO)$ mode of the complexes occurs in the region 915–990 cm⁻¹ and this is in the usual range observed for the oxovanadium complexes (Selbin, 1966).

The band in the range 410–485 cm⁻¹ and 510–530 cm⁻¹ suggest M-N and M-O bonding in the chelates. Bands in the region 3320–3160 cm⁻¹ appearing in the spectra of complexes may be due to ν_{OH} mode of coordinated water molecules. This assignments is further supported by the presence of new bands around 1620, 765–855 and 555–650 cm⁻¹ assignable to bending, rocking and wagging modes of coordinated water (Nakamoto, 1970).

Similarity in the nature of the VO(II) complexes under study may be due to similarity in the position of azomethine nitrogen in β -position to the $-\text{COOH}$ or $-\text{SO}_2\text{OH}$ groups. This view is also supported by Kubo *et al.* (1963). Based on above evidences the VO(II)-chelates may display an octahedral stereochemistry as shown in Fig. 1.

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