

## Short Communication

# Physicochemical investigation on Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II) and VO(II)-3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino)propanoate systems

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### Abstract

The dissociation constants of 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino)propanoic acid (H<sub>2</sub>BP) and stability constants of its chelates with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II) and VO(II) have been determined by Calvin's extension of Bjerrum's method. Elemental analysis, molecular mass, magnetic, TGA and spectral data of the solid chelates were used to establish their stereochemistry.

**Key words:** 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino) propanoate, dissociation constants, and stability constants.

## 1. Introduction

A survey of the literature<sup>1-4</sup> reveals that no work has been done on the chelates of 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino) propanoic acid (H<sub>2</sub>BP). Therefore, both solid and solution-state studies on the chelates of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II) and VO(II) with H<sub>2</sub>BP are reported in the present communication.

## 2. Experimental

### 2.1 Synthesis of ligand (H<sub>2</sub>BP)

H<sub>2</sub>BP was synthesised by refluxing equimolar ethanolic solution of *o*-hydroxy benzophenone and  $\beta$ -alanine in the presence of piperidine as catalyst for 1–2 hours. The light yellow solution obtained was filtered hot, concentrated and cooled when yellow crystals were obtained. These were recrystallised from ethanol. M.P. 210°C. The purity was checked by TLC and the appearance of characteristic IR spectral frequencies.

### 2.2 Synthesis of solid chelates

The metal chelates were obtained as crystalline solid by refluxing ethanolic solutions of H<sub>2</sub>BP (0.01 M in 20.0 ml 80% ethanol) and metal nitrate (0.01 M in 10.0 ml 80% ethanol)

for 2–3 hours, in nitrogen atmosphere. These were recrystallised from suitable solvents. Their complexes with pyridine adducts were also synthesised.

### 2.3 Preparation of pyridine adducts

The hydrated metal chelates were warmed in distilled pyridine on a steam-bath and concentrated in a vacuum desiccator over calcium chloride, when coloured crystals of the pyridine adduct deposited. The crystals were separated, washed with little absolute alcohol and ether, dried and preserved in a vacuum desiccator.

## 3. Result and discussion

$pK_1$  and  $pK_2$  of  $H_2BP$  (Table I) as determined by interpolation at half  $\bar{n}$  values method<sup>5</sup> and algebraic method<sup>5</sup>, were found to fall with rise of temperature indicating that  $H_2BP$  was biprotic ligand. The formation curve<sup>5</sup> indicates that 1:1 and 1:2 chelate species were formed in solution. The refinement was done by correction term employing convergence formula, successive approximation and interpolation at various  $\bar{n}$  values<sup>6,7</sup>. The average values of their stabilities follow the order  $VO(II) > UO_2(II) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)$  which was in agreement with Irving-Williams rule<sup>8</sup>.

Free-energy change, enthalpy and entropy values are presented in Table I, which indicate endothermic nature of reactions and favourable formation of 1:1 chelates. In terms of Harned's equation<sup>9</sup>, the values of  $\theta$ ,  $pK_m^H$  and  $\Delta H$  were found to be 865.08, 0.1642 and 150.78, respectively. The  $\Delta H$  values obtained from Harned's equation and potentiometric studies were in satisfactory agreement with each other (Table I).

### 3.1 Solid chelates

Based on microelemental analysis and molecular mass determination (Table II) these chelates display 1:1 metal-ligand stoichiometry and hence their molecular formula may be represented by  $[M(BP)_nH_2O]$ , where M is the bivalent metal ion, (BP), the deprotonated  $H_2BP$  and n, the number of water molecules.

Pyrolysis (TGA) thermogram of hydrated chelates reveals that on gradual heating from room temperature to 700°C the hydrated salts were completely dehydrated and decomposed in the temperature range 180–780°C. Therefore, the thermogravimetric analysis along with the mass-loss curve of the metal chelates, the absence of water of crystallisation and the presence of three coordinated water molecules (for M = Co(II), Ni(II) and Cu(II)), two coordinated water molecules (for M = VO(II)) and one coordinated water molecule (for M = Zn(II) and Cd(II)) is inferred.

The magnetic moment data (Table II) suggest an octahedral geometry for the Co(II), Ni(II), Cu(II) and VO(II) chelates and their pyridine adducts while a tetrahedral stereochemistry for the Zn(II) and Cd(II) chelates and also their pyridine adducts. The electronic spectral data (Table III) is also in agreement with this. It may be added that the Cu(II) chelate and its pyridine adducts seem to be having a distorted octahedral geometry due to Jahn-Teller distortion<sup>10</sup>.

IR spectral data as given in Table III indicate the presence of  $-OH$ ,  $-COOH$  and  $-C=N$  groups in the ligand. The phenolic<sup>11</sup>  $-OH$  and the carboxylic  $-OH$  were deproto-

**Table I**  
**Dissociation constants, average stability constants and thermodynamic parameters of bivalent metal chelates of 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino)propanoic acid [H<sub>2</sub>BP]**

Ligand/ Metal ion		Stability constants with deviation from theoretical values			log K°			(- $\Delta G^\circ$ ) K. Joule mole <sup>-1</sup>			( $\Delta H^\circ$ ) K. Joule mole <sup>-1</sup> at 35°C	( $\Delta S^\circ$ ) Joule deg <sup>-1</sup> mole <sup>-1</sup> at °C
		25°	35°	45°	25°	35°	45°	25°	35°	45°		
H <sub>2</sub> BP	pK <sub>1</sub>	8.54	8.18	7.65	—	—	—	107.45	106.86	104.12	156.96	162.66
	pK <sub>2</sub>	10.29	9.94	9.45								
VO(II)	log K <sub>1</sub>	11.30(± 0.02)	11.50(± 0.03)	11.90(± 0.04)	21.97	22.15	22.79	125.36	130.63	138.77	74.40	665.68
	log K <sub>2</sub>	9.70(± 0.04)	10.10(± 0.01)	10.35(± 0.02)								
UO <sub>2</sub> (II)	log K <sub>1</sub>	10.90(± 0.05)	11.22(± 0.02)	11.55(± 0.06)	21.11	21.55	22.10	120.46	127.09	134.57	89.82	704.25
	log K <sub>2</sub>	9.30(± 0.02)	9.50(± 0.03)	9.83(± 0.03)								
Cu(II)	log K <sub>1</sub>	10.30(± 0.02)	10.50(± 0.04)	10.75(± 0.03)	20.51	20.85	21.07	117.03	122.96	128.30	50.81	564.18
	log K <sub>2</sub>	8.83(± 0.06)	9.15(± 0.06)	9.42(± 0.05)								
Ni(II)	log K <sub>1</sub>	9.50(± 0.01)	9.82(± 0.06)	10.20(± 0.02)	18.42	18.60	18.95	105.11	109.69	115.39	48.09	512.22
	log K <sub>2</sub>	8.10(± 0.05)	8.45(± 0.04)	8.70(± 0.03)								
Co(II)	log K <sub>1</sub>	8.50(± 0.04)	8.80(± 0.03)	9.23(± 0.05)	17.25	17.56	17.90	98.43	103.56	108.99	58.97	527.76
	log K <sub>2</sub>	7.32(± 0.01)	7.63(± 0.05)	7.85(± 0.01)								
Zn(II)	log K <sub>1</sub>	8.27(± 0.03)	8.50(± 0.02)	8.83(± 0.03)	8.65	8.97	9.12	49.36	52.90	55.53	42.64	310.19
Cd(II)	log K <sub>1</sub>	7.45(± 0.03)	7.85(± 0.06)	8.15(± 0.04)	8.46	8.63	8.85	48.27	50.90	53.89	35.38	280.12

The deviations are given in parentheses.

**Table II**  
**Yield, molecular mass, elemental analysis and magnetic moments of the hydrated metal chelates of H<sub>2</sub>BP and their pyridine adducts**

Ligand/chelates (Yield %)	Molecular mass		Elemental analysis (%)						$\mu_{\text{eff}}$ B.M. at 308°K				
	Found	Calc.	Water		C		H			N		Metal	
			Found	Calc.	Found	Calc.	Found	Calc.		Found	Calc.	Found	Calc.
[C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ] (75)	260	269	—	—	71.27	71.38	5.45	5.58	5.11	5.20	—	—	—
[VO(C <sub>16</sub> H <sub>13</sub> NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ] (80)	356 (480)	370 (492)	9.67	9.73	51.82 (63.32)	51.90 (63.42)	4.53 (4.51)	4.60 (4.68)	3.70 (8.40)	3.78 (8.54)	18.00 (13.55)	18.09 (13.61)	1.75 (1.80)
[Cu(C <sub>16</sub> H <sub>13</sub> NO <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ] (89)	371 (554)	384 (567)	14.00	14.04	49.85 (65.40)	49.93 (65.55)	4.85 (4.79)	4.94 (4.93)	3.54 (9.75)	3.64 (9.87)	16.47 (11.07)	16.52 (11.20)	2.10 (2.16)
[Ni(C <sub>16</sub> H <sub>13</sub> NO <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ] (70)	368 (549)	379 (573)	14.12	14.22	50.45 (66.01)	50.57 (66.11)	4.93 (4.83)	5.00 (4.98)	3.60 (9.86)	3.69 (9.95)	15.40 (10.25)	15.46 (10.43)	3.20 (3.21)
[Co(C <sub>16</sub> H <sub>13</sub> NO <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ] (79)	370 (552)	380 (563)	14.17	14.21	50.42 (66.00)	50.54 (66.08)	4.95 (4.80)	5.00 (4.97)	3.54 (9.82)	3.68 (9.95)	15.40 (10.33)	15.51 (10.47)	5.10 (5.18)
[Zn(C <sub>16</sub> H <sub>13</sub> NO <sub>2</sub> )(H <sub>2</sub> O)] (51)	345 (400)	350 (411)	5.05	5.14	54.70 (61.14)	54.79 (61.25)	4.20 (4.25)	4.28 (4.38)	3.90 (6.71)	4.00 (6.81)	18.54 (15.73)	18.66 (15.90)	—
[Cd(C <sub>16</sub> H <sub>13</sub> NO <sub>3</sub> )(H <sub>2</sub> O)] (58)	385 (440)	397 (458)	4.45	4.58	48.25 (54.81)	48.31 (54.97)	3.62 (3.80)	3.77 (3.93)	3.47 (6.00)	3.52 (6.11)	28.20 (24.42)	28.28 (24.52)	—

The values in the parentheses are those of the pyridine adducts.

Table III

The electronic and IR spectral data of bivalent metal chelates of 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino)propanoic acid [H<sub>2</sub>BP]

Ligand/ Metal ion	Electronic spectra		IR spectra (cm <sup>-1</sup> )									
	Absorption bands (cm <sup>-1</sup> )	Assignments	$\nu$ C=N	$\nu$ C-O	$\nu$ OH Phenolic	$\nu$ O-H of carbo- xylic group	$\nu$ C-O of carbo- xylic	$\nu$ COOH	$\nu$ SCOO	$\nu$ asCOO	$\nu$ M-N	$\nu$ M-O
[H <sub>2</sub> BP]	—	—	1630	1320	3350	1650	1710	1750	—	—	—	—
Co(II)	8,400 17,050 20,800	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	1610	1330	—	—	—	—	1435	1578	480	360
Ni(II)	14,650 25,600	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	1607	1335	—	—	—	—	1432	1575	485	368
Cu(II)	12,509	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	1603	1338	—	—	—	—	1437	1576	492	375
VO(II)	11,925 20,100	<sup>2</sup> B <sub>2</sub> → <sup>2</sup> E <sub>1</sub> → <sup>2</sup> B <sub>1</sub>	1600	1340	—	—	—	—	1440	1580	500	380

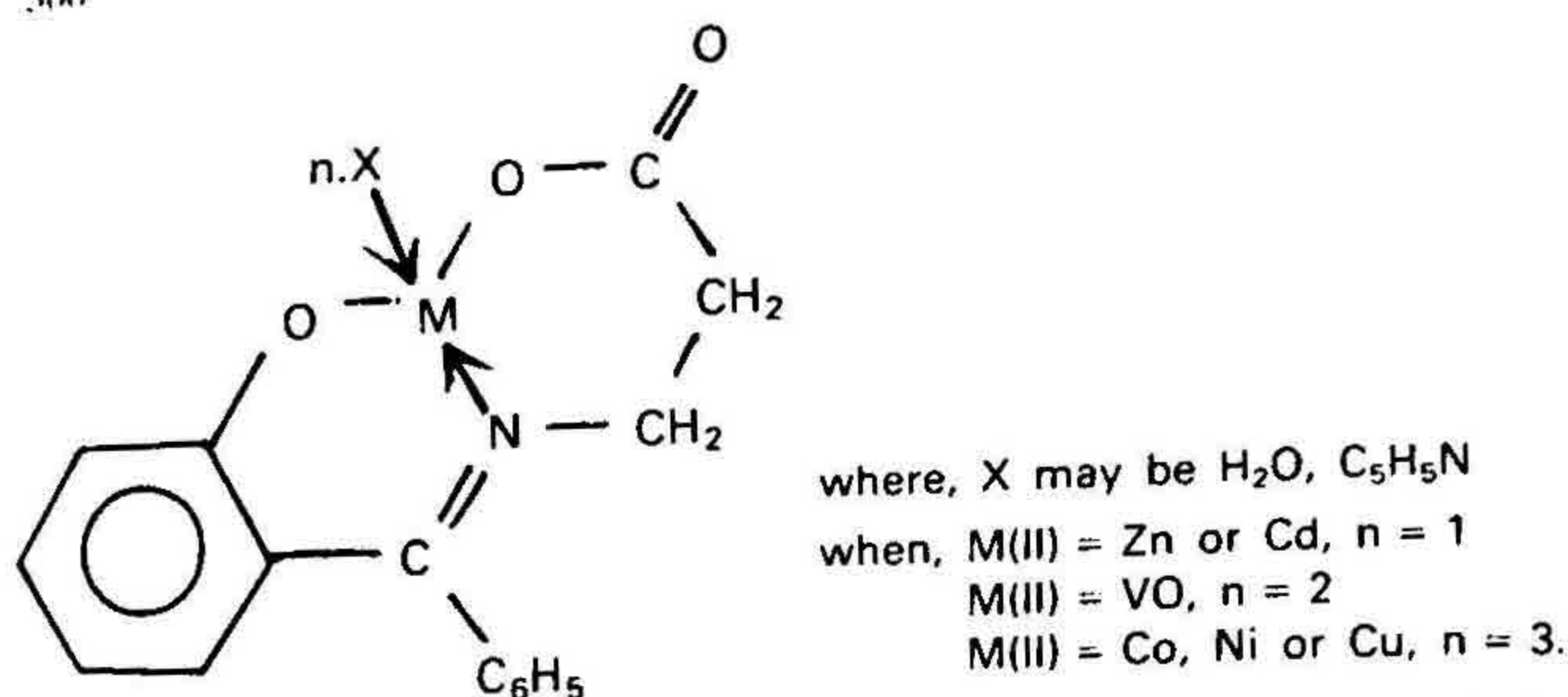


FIG. 1. Bivalent metal chelates of 3-(N- $\alpha$ -phenyl, 2-hydroxy benzylideneimino) propanoic acid [H<sub>2</sub>BP].

nated on chelation. The  $\nu >C=N$  was lowered to  $1600\text{ cm}^{-1}$  suggesting its participation in complexation. The appearance of new bands in the ranges  $500\text{--}480\text{ cm}^{-1}$  and  $380\text{--}360\text{ cm}^{-1}$  suggests  $\nu M-N$  and  $\nu M-O^{12}$  bonding, respectively in the chelates.

Based on the above evidences the structures of the chelates may be represented as shown in fig. 1.

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