

## ACIDITY CONSTANT OF BENZALDEHYDE -2- HYDROXY AZINE AND ITS CHELATION WITH Cu (II), Co (II) AND Ni (II)

MOUSTAFA H. M. ABOU-EL-WAFA

Department of Chemistry, Faculty of Science at Qena, Egypt

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The acid dissociation constant of benzaldehyde-2-hydroxyazine ( $H_2A$ ) is determined spectrophotometrically in a series of universal buffer solutions (20% ethanol, v/v) of varying pH. Cu (II), Co (II) and Ni (II) complexes of  $H_2A$  have been prepared and characterized by elemental analysis, molar conductance, electronic and infrared spectra measurements. It is concluded that the ligand acts as bivalent ONNO tetradentate. The complexes are suggested to exhibit a distorted octahedral geometry.

**Key words:** Schiff base, Complexes of benzaldehyde-2-hydroxy azine, Acidity constant.

### Introduction

Due to wide use of Schiff bases in many biological applications, much work has been carried out on their chelating properties [1-5], acid-base equilibria [6-10] and electronic spectra [11,12]. Recently, a study on complexation of Schiff base, benzaldehyde-2-hydroxy azine with Cu (II), Co (II) and Ni (II) using potentiometric and conductometric techniques has been reported [7]. In the present work, it is aimed to estimate the acid dissociation constant of that ligand spectrophotometrically and to synthesis and character its solid complexes with Cu (II), Co (II) and Ni (II) using several tools e.g. elemental analyses, molar conductance, electronic and infrared spectral measurements.

### Experimental

**Schiff base preparation.** The Schiff base, benzaldehyde-2-hydroxy azine ( $H_2A$ ) was prepared by adding 0.1 mole of hydrazine hydrate to 0.2 mole of 2-hydroxy benzaldehyde in ethanol. The mixture was refluxed for half an hour, allowed to cool, filtered off and crystallised. The purity was checked by TLC and confirmed by elemental analysis and infrared spectra as given in Tables 1 and 2.

**Preparations of  $pK_a$  estimation.** Stock solution ( $1 \times 10^{-3}$  mol.  $dm^{-3}$ ) of  $H_2A$  was prepared by dissolving a known mass of the solid in ethanol, 0.2 ml of  $H_2A$  was added to 1.8 ml ethanol and completed to 10 ml using the modified universal buffer solutions [13]. The pH measurements were carried out using on Orion 501 digital ionalyzer accurate to  $\pm 0.01$  pH unit.

**Solid complexes.** The metal complexes were prepared by reacting one mole of hot ethanolic solution of metal salt ( $CoCl_2 \cdot 2H_2O$ ,  $NiCl_2 \cdot 6H_2O$  and  $CuCl_2 \cdot 2H_2O$ ) to one and/or two moles of ethanolic solution of the Schiff base  $H_2A$ . The mixture was refluxed for 3 hours, allowed to cool where a precipitate was formed. The structures were confirmed by elemental analysis and IR spectra (Tables 1, 2).

The absorption spectra were recorded on a Cecil 599 spectrophotometer using 1 cm matched silica cells. The infrared spectra of the ligand and its complexes were recorded on a Perkin-Elmer Spectrophotometer as KBr discs. Molar conductances were measured with a WPA, Saffron Walden CM 25 conductivity meter.

### Results and Discussion

**Spectrophotometric determination of the acid dissociation constant ( $pK_a$ ) of  $H_2A$ .** Fig. 1 shows the electronic spectra of  $H_2A$  in a series of universal buffer solutions of varying pH (7-11.5). The constructed absorbance-pH curve (Fig.2) is typical dissociation curve, supporting the acid-base equilibrium. The  $pK_a$  value was evaluated applying the half wave height and the limiting absorbance methods [14,15]. The obtained  $pK_a$  values are 10.45 and 10.10 respectively with a mean value  $10.28 \pm 0.17$  which in agreement with the value 10.55 reported [7] before using potentiometric technique.

TABLE I. ANALYTICAL AND PHYSICAL DATA OF LIGAND, L AND ITS COMPLEXES.

	Colour	Dcomp. Temp.°C	Molar* conduc.	Calc.(Found)%		
				C	H	N
$C_{14}H_{14}N_2O_2 \cdot L$	Yellow	210	—	69.99 (69.27)	5.04 (5.03)	11.66 (11.49)
$[(L-2H)_2Cu_2(2H_2O)_2]$	Brown	>360	7.40	49.77 (49.10)	4.18 (4.30)	8.30 (8.35)
$[(L-2H)_2Co_2(2H_2O)_2]$	Dark brown	>360	13.32	50.47 (49.90)	4.24 (4.28)	8.41 (8.30)
$[(L-2H)_2Ni_2(2H_2O)_2]$	Yellowish green	>360	11.84	50.50 (50.10)	4.24 (4.50)	8.41 (8.10)
$[(L-H)_2Cu(H_2O)_2]$	Yellowish green	>360	7.80	58.17 (57.90)	4.53 (4.70)	9.69 (10.01)
$[(L-2H)_2Co(H_2O)_2]$	Dark brown	>360	11.90	58.64 (59.22)	4.57 (4.60)	9.77 (9.80)
$[(L-H)_2Ni(H_2O)_2]$	Yellowish green	>360	8.90	58.66 (57.99)	4.57 (4.90)	9.74 (9.12)

\* In  $ohm^{-1} mole^{-1} m^2$ .



*Characterization of solid complexes of H<sub>2</sub>A.* The analytical data of the solid chelates indicate that 1:1 and 2:1 (L:M) are formed with the metal ions investigated (Table 1) and the ligand H<sub>2</sub>A is interacted in its dibasic form. Accordingly, the general formula for 1:1 chelates is suggested to be [(L-2H)<sub>2</sub>M<sub>2</sub>(2H<sub>2</sub>O)<sub>2</sub>] and (L-H)<sub>2</sub>M(H<sub>2</sub>O)<sub>2</sub>] for 2:1 where M= Cu (II), Co (II) and Ni (II). The molar conductance values of 10<sup>-3</sup> mol. dm<sup>-3</sup> solution of each of the different complexes in DMF are in accordance within the non-electrolytic [16] species (Table 1).

Assignment of the important IR bands is given in Table 2. The stretching vibration bands of the free two-OH groups of the ligand appeared as a broad band covering the range 3050-3340 m<sup>-1</sup>. This is in consistency with the expected involvement of these groups with the azomethine nitrogen through intramolecular hydrogen bonding [17]. On complexation this band disappeared and another band appeared in the region 3200-3400 cm<sup>-1</sup> indicating the presence of water molecules in such complexes which is supported by the results of microanalyses given in Table 1. Furthermore, the presence of water molecules in coordination sphere was verified by TGA where no loss of weight below 180°C was observed. The phenolic C-O stretching vibrations [18] appeared at 1275 cm<sup>-1</sup> in the spectra of ligand was found to have an appreciable shift (~30 cm<sup>-1</sup>) to lower frequency in the spectra of the corresponding metal chelates confirming its coordination to the metal.

The strong band appeared at 1620 cm<sup>-1</sup> in IR spectra of the ligand is assigned to the stretching vibration of the

TABLE 2. SOME INFRARED FREQUENCIES (CM<sup>-1</sup>) OF THE LIGAND, L AND ITS COMPLEXES.

	Frequency (Cm-1)				
	$\nu_{OH}$ and H <sub>2</sub> O	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{C-Ophenyl}$	$\nu_{M-N,M-O}$
Free ligand, L	3340*	1620	1510	1275	---
(L-2H) <sub>2</sub> -Cu <sup>+2</sup>	3275	1590b	1470	1250	675
(L-2H) <sub>2</sub> -Co <sup>+2</sup>	3400	1600b	1510	1245	655
(L-2H) <sub>2</sub> -Ni <sup>+2</sup>	3200	1610	1480	1250	690
(L-H) <sub>2</sub> -Cu <sup>+2</sup>	3250b	1605	1485	1275	680
(L-H) <sub>2</sub> -Co <sup>+2</sup>	3200b	1620	1540	1280	685
(L-H) <sub>2</sub> -Ni <sup>+2</sup>	3350b	1610	1535	1270	-

\*N-H...O bond, b=broad.

TABLE 3. ELECTRONIC SPECTRAL DATA OF THE LIGAND, L AND ITS COMPLEX SOLUTION IN DMF.  
max. (max. x10<sup>3</sup> mole<sup>-1</sup> cm<sup>2</sup>)

Ligand, L	1:1 Complexes			1:2 Complexes		
	Cu (II)	Co (II)	Ni (II)	Cu (II)	Co (II)	Ni (II)
---	444b (0.76)	394 (6.50)	408b (5.45)	420sh (3.48)	450vb (2.00)	446b (5.23)
358(10.60)	-	365b (6.15)	-	-	-	-
298(10.35)	-	-	-	-	-	-

b = broad, vb = very broad and sh = shoulder.

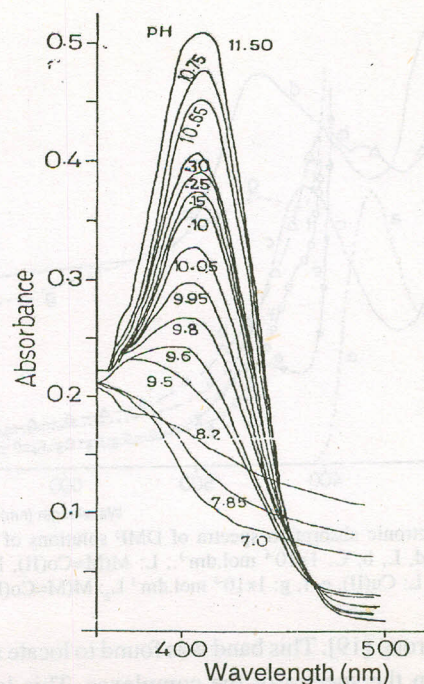


Fig. 1. Electronic absorption spectra of 2x10<sup>-5</sup> mol. dm<sup>-3</sup> of benzaldehyde-2-hydroxy azine in universal buffer solutions (20% ethanol, v/v).

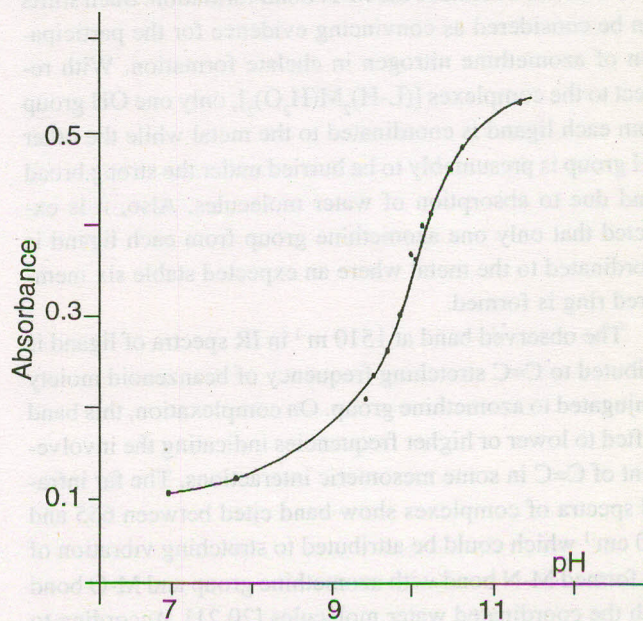


Fig. 2. Absorbance- pH curve for benzaldehyde-2-hydroxy azine.



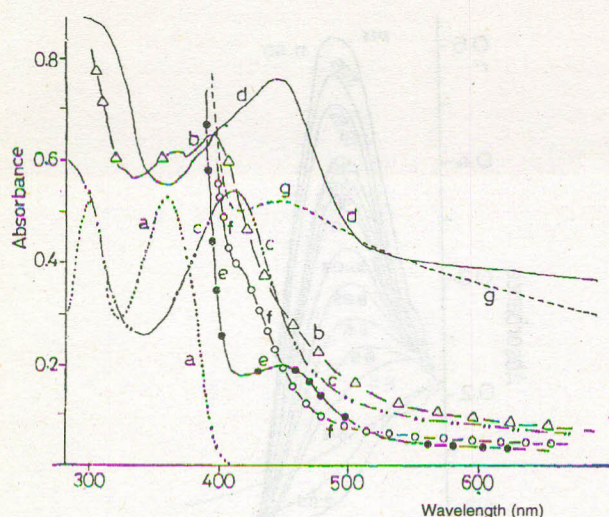
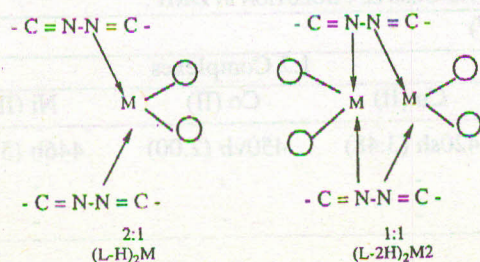


Fig. 3. Electronic absorption spectra of DMF solutions of a:  $1 \times 10^{-4}$  mol.  $\text{dm}^{-3}$  ligand, L, b, c:  $1 \times 10^{-4}$  mol.  $\text{dm}^{-3}$ ; L; M(M=Co(II), Ni(II)), d:  $1 \times 10^{-3}$  mol.  $\text{dm}^{-3}$  L; Cu(II), e, f, g:  $1 \times 10^{-4}$  mol.  $\text{dm}^{-3}$  L<sub>2</sub>; M(M=Co(II), Cu(II), Ni(II)).

azomethine group [19]. This band was found to locate at lower frequencies in the spectra of the complexes. This lowering may be tentatively be attributed to a lowering of the C=N band order as a result of the M-N bond formation. Such shifts can be considered as convincing evidence for the participation of azomethine nitrogen in chelate formation. With respect to the complexes  $[(L-H)_2M(H_2O)_2]$ , only one OH group from each ligand is coordinated to the metal while the other OH group is presumably to be buried under the strong broad band due to absorption of water molecules. Also, it is expected that only one azomethine group from each ligand is coordinated to the metal where an expected stable six membered ring is formed.

The observed band at  $1510 \text{ cm}^{-1}$  in IR spectra of ligand is attributed to C=C stretching frequency of benzenoid moiety conjugated to azomethine group. On complexation, this band shifted to lower or higher frequencies indicating the involvement of C=C in some mesomeric interactions. The far infrared spectra of complexes show band cited between  $655$  and  $690 \text{ cm}^{-1}$  which could be attributed to stretching vibration of the formed M-N bond with azomethine group and M-O bond with the coordinated water molecules [20,21]. According to the discussed results, it can be assumed that the ligand acts as dibasic tetradentate as shown in the structural diagram.



The UV-Visible electronic spectra of DMF solutions of the free ligand and its 1:1 and 2:1 complexes are shown in Fig. 3. The  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values of different absorption bands observed are listed in Table 3. The band at 298 nm in the spectrum of ligand can be assigned [22] to the TT-TT\* transitions of the benzenoid moiety of the ligand. The band at 358 nm is assigned to an intramolecular charge transfer transition taking place within the Schiff base molecule [12]. A similar assignment of this band was described by Jaff *et al.* [23]. In the spectra of complexes, the observed band in the wavelength range 365-450 nm can be ascribed [24] to an intramolecular charge transfer transition liable to take place within the complexed Schiff base molecule (i.e. L → MCT). This assignment is supported from the fact that this type of electronic transition is expected to be easier in the complexed ligand due to the positive charge of coordination metal ion. Furthermore, in all the recorded spectra of the complexes, the longer wavelength side of charge transfer band is associated with a long tail to near infrared region which can be attributed to a d-d electronic transition within the coordinated metal ion. This behaviour may suggest a hexacoordinated configuration with low symmetry components in the ligand field, i.e. distorted octahedral geometry [24]. This suggestion can be substantiated by the observed brown colour of these complexes (Table 1) where it was reported that most octahedral complexes are pink, reddish or brown [24].

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