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# Synthesis, spectroscopic characterization, molecular modeling and potentiometric studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,1-diaminobutane-Schiff base

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#### Abstract

Complexes of cobalt(II), nickel(II), copper(II) and zinc(II) of general composition  $[M(L)(H_2O)_2]$ .2H<sub>2</sub>O have been synthesized [L = N,N'-bis(2hydroxybenzylidene)-1,1-diaminobutane]. The elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, IR, UV, NMR, SEM, EDX, thermal and EPR spectral studies of the compounds led to the conclusion that the ligand acts as a tetradentate manner. The molar conductance of the complexes in fresh solution of DMSO lies in the range of 7.46–9.13  $\Omega^{-1}$  cm<sup>2</sup>mol<sup>-1</sup> indicating their nonelectrolytic behavior. On the basis of analytical and spectroscopic techniques, octahedral geometry of the complexes was proposed. The Schiff base acts as tetradentate ligand, coordinated through deprotonated phenolic oxygen and azomethine nitrogen atoms. The ligand field parameters were calculated for Co(II), Ni(II) and Cu(II) complexes and their values were found in the range reported for a octahedral structure. The molecular parameters of the ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes have been calculated. Protonation constants of Schiff base and stability constants of their binary metal complexes have been determined

potentiometrically in 50% DMSO–water media at 25 °C and ionic strength 0.10 M sodium perchlorate.

# *Keywords:* Schiff base; complexes; Spectroscopic; Protonation constants; SEM/EDX

#### 1. Introduction

Schiff bases represent one of the most widely utilized classes of ligands in metal coordination chemistry and the chemistry of Schiff bases is an area of increasing interest. Schiff bases are capable of forming coordinate bonds with many metal ions via azomethine or phenolic groups, and so they have been used for synthesis of metal complexes due to their easy formation and strong metalbinding ability. During recent years coordination compounds of biologically active ligands [1-3] have received much attention. Chelation causes drastic change in the biological properties of the ligands and also the metal moiety. It has been reported that chelation is the cause and cure of many diseases including cancer. A number of Schiff base complexes [4,5] have been tested for antibacterial activities and they have been found antibacterial [6], antifungal [7], anticancer [8], and herbicidal [9] activities. However, for the period of antibiotics using in clinical practice, steady growth of clinically significant bacteria tolerance to these preparations has been observed. This is likely to be an unavoidable process. Selection of resistant to antibiotic mutants is especially rapid in population of opportunistic pathogenic microorganism [10], which, in turn, often act as donors of resistance genes for particularly dangerous infections agents. Recently, the number of diseases, caused by multidrug resistant gram-

positive microorganism, has been continuously increasing. The ability of microorganism to become resistant to major therapies used against them has long been recognized and becomes increasing apparent [11]. Increasing antimicrobial resistance (AMR) presents major threats to public health because it reduces the effectiveness of antimicrobial treatment leading to increased morbidity, mortality and health care expenditure [12].

Thus, in this paper we synthesized a new tridentate Schiff base containing SNO donor atoms and its relevant nickel and palladium complexes. The Schiff base ligand and its complexes were characterized by the FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass, SEM, EDX, UV–Vis spectroscopy, elemental analysis, magnetic susceptibility, molar conductance and thermal analysis. The geometry of the complexes is characterized by means of spectral and magnetic measurements.

#### 2. Chemistry

#### 2.1. Materials and reagents

The metal salts and the reagents used in this work:  $NiCl_2.6H_2O$ , Co  $Cl_2.6H_2O$ ,  $CuCl_2.2H_2O$ ,  $ZnCl_2.2H_2O$ ,  $NH_4NO_3$ , salicylaldehyde and butanal were supplied from Aldrich and Fluka. The solvents used were purchased from Merck and used without further purification.

### 2.2. Instruments

Elemental analysis of ligand and its metal complexes were carried out using Perkin–Elmer elemental analyzer. Molar conductance of the complexes was measured using a coronation digital conductivity meter. IR spectra were recorded using Jasco FTIR- 410 spectrometer in KBr pellets from 200–4000 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded with Brucker 300 MHz spectrometer

using CDCl<sub>3</sub> for ligand and DMSO-d6 for Zn(II) complex with TMS as internal standard. DART-MS spectrum was recorded on a JEOLAccu TOF JMS mass spectrometer. Dry helium was used with 4 LPM flow rate for ionization at 350 °C. Magnetic moments were measured by Guoy method and corrected for diamagnetism of the component using Pascal's constants. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. ESR spectrum of the Cu(II) complex was recorded at 300 and 77 K in solid state using Varian, USA E-112 ESR spectrometer. Thermal studies were carried out using Q 600 SDT and Q 20 DSC thermal analyzer. XRD studies were carried out using Bruker AXS D8 advance configuration, X-ray diffractometer. SEM images were recorded in a Hitachi SEM analyzer. Energy Dispersive X-ray Analysis (EDX) (EDAX Falcon System) was conducted to analyze the presence of elements in the specimens that have been sputtered with carbon black.

#### 2.3. Synthesis of the ligand

To a mixture of salicylaldehyde (0.4 g, 3.27 mmol) and butanal (0.118 g, 1.64 mmol) was added  $NH_4NO_3$  (0.25 g, 3.27 mmol) in the presence of the  $NEt_3$  (1 ml) as a base by stirring in one portion. The mixture was stirred for a further 7 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, a yellow oily substance was obtained. Then, by dissolving the mixture in 2 ml MeOH and cooling overnight, a yellow solid precipitated. The solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N,N'-bis(2-hydroxybenzylidene)-1,1-diaminobutane (H<sub>2</sub>BHBDAB), was obtained in 96% yield (Scheme 1).



Scheme 1: Synthesis of Schiff base (H<sub>2</sub>BHBDAB).

### 2.4. Synthesis of the metal complexes

All complexes were prepared (Scheme 2) by refluxing  $H_2BHBDAB$  (0.29 g, 1.0 mmol) and the hydrated metal salts (1.0 mmol), e.g. chloride, in 30 ml ethanol for 2–3 h. The resulting solid complexes were filtered while hot, washed with ethanol followed by diethyl ether and dried in vacuo over CaCl<sub>2</sub>.



Scheme 2. Synthesis of metal complexes Schiff base derived from H<sub>2</sub>BHBDAB with Co(II), Ni(II), Cu(II), and Zn(II) ions.

#### 2.5. Potentiometric titrations

Potentiometric measurements were made using a Metrohni 686 titroprocessor (Switzerland) equipped with a 665 Dosiniat. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications [13].

All Potentiometric measurements in this study were carried out in water-DMSO mixtures containing 50% DMSO because of low solubility of Schiff base and possible hydrolysis in aqueous solutions. The  $pk_w$  value in this medium was calculated to be 15.48.

#### 2.6. Procedure of potentiometric measurements

Potentiometric titrations were carried out at constant temperature and an inert atmosphere of nitrogen with  $CO_2$ - free standardized 0.1M NaOH in 40 ml solution containing 0.1M NaClO<sub>4</sub>:

(i)  $3.0 \times 10^{-3}$  M HNO<sub>3</sub> +  $1.5 \times 10^{-3}$  M Schiff base (for the protonation constant of the Schiff base );

(ii)  $3.0 \times 10^{-3}$  M HNO<sub>3</sub> +1.5 ×10<sup>-3</sup> M Schiff base + 7.5×10<sup>-4</sup> M metal (II or III) ions (for the stability constant of the complexes). The species formed were characterized by the general equilibrium process (1), whereas the formation constants for these generalized species are given by Eq. (2) (charges are omitted for simplicity).

$$pM + qL + rH \quad \overleftarrow{\qquad} \quad M_pL_qH_r \tag{1}$$
$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{2}$$

Where M, L, H stand for the metal ion, ligand and proton, respectively. The calculations were performed using the computer program MINIQUAD-75and were conducted on an IBM computer. The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models for the systems studied.

	Table 1. Thysical and elemental analysis data of the complexes									
Cpd.	M.F.	M.p.	Colour	Ele	mental analy	yses		$^{a}\Lambda_{m}$		
-	(M.Wt)	(°C)	[Yield %]	Fo	und (Calc.),	%				
				С	Н	Ν	Μ			
Ligand	H <sub>2</sub> BHBDAB	122-124	Yellow	72.82	6.71	9.39	-	_		
	$C_{18}H_{20}N_2O_2(296.36)$		[96]	(72.95)	(6.80)	(9.45)				
1	[Co(SBDAB)(OH <sub>2</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	182	Reddish	50.79	6.14	6.48	13.81	7.46		
	C <sub>18</sub> H <sub>26</sub> CoN <sub>2</sub> O <sub>6</sub> (425.34)		brown [77]	(50.83)	(6.16)	(6.59)	(13.86)			
2	[Ni(SBDAB)(OH <sub>2</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	188	Faint brown	50.83	6.12	6.47	13.77	9.13		
	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> NiO <sub>6</sub> (425.10)		[79]	(50.86)	(6.16)	(6.59)	(13.81)			
3	[Cu(SBDAB)(OH <sub>2</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	192	Dark brown	50.21	6.03	6.48	14.75	8.52		
	$C_{18}H_{26}CuN_2O_6(429.95)$		[82]	(50.28)	(6.10)	(6.52)	(14.78)			
4	[Zn(SBDAB)(OH <sub>2</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	177	Yellow	50.00	5.02	6.44	15.11	7.85		
	$C_{18}H_{26}N_2O_6Zn(431.79)$		[74]	(50.07)	(5.07)	(6.49)	(15.14)			

Table 1: Physical and elemental analysis data of the complexes

#### 2.7. Molecular modeling

The calculations using DMOL3 program were performed in Materials Studio package [14], which is designed for the realization of large scale density functional theory (DFT) calculations. DFT semi-core pseudo pods calculations (dspp) were performed with the double numerical basis sets plus polarization functional (DNP). The DNP basis sets are of comparable quality to 6–31G Gaussian basis sets [15]. Delley et al. showed that the DNP basis sets are more accurate than Gaussian basis sets of the same size [16]. The RPBE functional [17] is so far the best exchange–correlation functional [18], based on the generalized gradient approximation (GGA), is employed to take account of the exchange and correlation effects of electrons. The geometric optimization is performed without any symmetry restriction.

#### 3. Results and discussion

#### 3.1. The ligand (H<sub>2</sub>BHBDAB)

### 3.1.1. Elemental analyses

The novel Schiff base ( $H_2BHBDAB$ ) is prepared and subjected to elemental analyses, mass and IR spectral analyses. The results of elemental analyses (C, H, N) with molecular formula and the melting point are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula and the melting point is sharp indicating the purity of the prepared Schiff base. The structure of the Schiff base under study is as shown in Scheme 1.

#### 3.1.2. IR spectrum

The IR spectrum (Fig. S1., Table 2) of Schiff base ligand (H<sub>2</sub>BHBDAB) is given in synthetic procedures. Vibration bands with the wave numbers of 3386 cm<sup>-1</sup> (vO–H), 3075 cm<sup>-1</sup> (vC–H, Ar–H), 1623 cm<sup>-1</sup> (vC=N), 1565 cm<sup>-1</sup> (vC=C), 1212 cm<sup>-1</sup> (vC–O, Ar–O) was observed for Schiff base ligand (H<sub>2</sub>BHBDAB). The stretching frequency observed at 2850 cm<sup>-1</sup> in H<sub>2</sub>BHBDAB shows the presence of O–H…N intramolecular hydrogen bond (Figure 1) [19]. Schiff base ligand HL with strong band at 1212 cm<sup>-1</sup> possesses highest percentage of enolimino tautomer due to the stabilization of phenolic C–O bond [20].



**Enol-Imine** 

**Keto-Amine** 

Fig. 1. Proposed structure of ligand (H<sub>2</sub>BHBDAB).



<sup>1</sup>H NMR spectrum (Figure S2, Table S1) of Schiff base was measured in a range of solvents, and the presence of a  ${}^{3}J(CHNH)$  coupling between the exchangeable and the olefinic proton, confirmed by decoupling, was interpreted as being due to the presence of the keto-amine tautomer. This coupling and  ${}^{1}J(NH)$  were measured in a range of solvents and, with a good reference value for this in a non tautomeric situation of 94 Hz, it is then possible to deduce a value for  ${}^{3}J(CHNH)$  for pure keto-amine tautomer of 11.6 Hz [21]. The <sup>1</sup>H NMR data for Schiff base ligand H<sub>2</sub>BHBDAB shows that the tautomeric equilibrium favors the enoimine in DMSO. The <sup>1</sup>H NMR data and coupling constant for the new Schiff base are listed in Table S1. The broad signal at  $\delta = 13.04$  ppm is assigned to the proton of the hydroxyl group. This peak is due to hydrogen bonded phenolic proton and the integration is generally less than 2.0 due to this intramolecular hydrogen bonding. Signal for the methine proton of the characteristic azomethine group for Schiff base, -N = C(H) was observed at 9. 33ppm. In the region of 7.06-8.25 ppm chemical shifts were assigned for hydrogen of the aromatic ring.

The <sup>13</sup>C NMR spectrum of the ligand (Figure S3, Table S1) is concordant with different types of magnetically non-equivalent carbons. The peak at 148.96 ppm is due to azomethine carbon (-CH=N-) [22].

### 3.1.4. UV–Visible spectrum

The electronic spectral data of H<sub>2</sub>BHBDAB ligand in ethanol and hexane shows absorption bands at 225 and 260 nm are assigned to  $\pi \rightarrow \pi^*$  transitions of the enol-imine tautomer of the Schiff base. The observed small hypsochromic shift of the 330 nm band in more polar solvents is typical to n  $\rightarrow \pi^*$  transitions of C=N group [23]. The maximum at 418 nm detected in

the EtOH solutions of HL ligand is assigned to  $n \rightarrow \pi^*$  transitions in dipolar zwitterionic or keto–imine tautomeric structures, respectively [23].

#### 3.1.5. Mass spectrum

The electron impact mass spectrum (Fig. S-4a) of the free ligand, confirms the proposed formula by showing a peak at 296 u corresponding to the ligand moiety [ $(C_{18}H_{20}N_2O_2)$  atomic mass 296u]. The series of peaks in the range, i.e. 64, 110 and 165 u, attributable to different fragments of the ligand. These data suggest the condensation of keto group with amino group.

#### 4. Complexes

### 4.1. Composition and structures of Schiff base complexes

The solid complexes are subjected to elemental analyses (C, H,N and metal content), infrared (IR), Mass (MS), electronic (UV-VIS.), nuclear magnetic resonance (<sup>1</sup>H–NMR), electron spin resonance (ESR), magnetic studies, molar conductance and ligand field parameters, to identify their tentative formulae of the molecular structures.

#### 4.1.1. Elemental analyses of the complexes

The results of elemental analyses, Table 1 are in good agreement with those required by the proposed formulae.

### 4.1.2. IR spectra and mode of bonding

In the absence of a powerful technique such as X-ray crystallography, IR spectra have proven to be the most suitable technique to give enough information's to elucidate the nature of bonding of the ligand to the metal

ion. The IR spectra of the free ligand and metal complexes were carried out in the range  $4000-200 \text{ cm}^{-1}$  (Fig. S1., Table 2).

complexes with their							
Compounds			*				
	v(OH)	v(CH=N)	v(C–O)	v(M–O)	v(M–N)	$\rho_r(H_2O)$	$\rho w(H_2O)$
H <sub>2</sub> BHBDAB	2677(br)	1597m	1337m,	_	-	_	—
			1278m				
1	—	1560m	1323m,	265m	239m	745m	618m
			1266m				
2	—	1575m	1316m,	274s	249m	782m	622m
			1265m				
3	_	1565m	1316m,	265m	2479m	850 m	618m
			1263m				
4	—	1570m	1315m,	278m	256s	798s	620s
			1264m				

**Table 2:** Important IR spectral (cm<sup>-1</sup>) bands of H<sub>2</sub>BHBDAB ligand and its complexes with their assignments.

The IR spectrum of the ligand shows a broad band at 2677 cm<sup>-1</sup>, which can be attributed to phenolic OH group. This band disappears in all complexes, which can be attributed to the involvement of phenolic OH in coordination. The involvement of deprotonated phenolic moiety in complexes is confirmed by the shift of v(C-O) stretching band observed at1337, 1278 cm<sup>-1</sup> in the free ligand to a lower frequency to the extent of  $\approx 15-25$  cm<sup>-1</sup> [24]. The shift of v(C-O) band at 1337, 1278 cm<sup>-1</sup>to a lower frequency suggests the weakening of v(C-O) and formation of stronger M–O bond. Another band appeared between 265 and 278 cm<sup>-1</sup>, which is assigned to the interaction of phenolic oxygen to the metal atom, i.e., the stretching vibrations v(M-O) [24]. A band corresponding to v(C=N) (azomethine linkage) appears at 1600 cm<sup>-1</sup> in the ligand. On complex formation, the IR band due to azomethine group shifts to the lower wave number (1560–1575 cm<sup>-1</sup>) which indicates that the nitrogen atom of azomethine groups are

coordinated to the metal atom. In the IR spectra of the complexes, a band is observed between 239 and 256 cm<sup>-1</sup> that is attributed to the v(M-N) stretching vibrations [25].

The band at  $1373-1380 \text{ cm}^{-1}$  in all the complexes is due to the  $v(CH_3)$  frequency, is not affected upon complexation. Furthermore, the aliphatic protons are not greatly affected upon complexation [26].

All complexes are also display bands due to coordinated water molecules [27]. The bands in the range 745–850 cm<sup>-1</sup> and 618–622 cm<sup>-1</sup> appeared in the spectra of these complexes which may be assigned to  $\rho r(H_2O)$  and  $\rho w(H_2O)$  [27].

From the infrared spectra, it is apparent that, the chelation of the divalent or trivalent metal ions to the ligand occurs from the H<sub>2</sub>BHBDAB ligand through the oxygen atoms of the *ortho*-hydroxyl moiety and the nitrogen atom of the azomethine groups in the ligand. The coordinated water molecules satisfy the other coordination sites to complete the geometry of the central metal ion.

#### 4.1.3. Molar conductance measurements

The results given in Table 1 show that the Co(II), Ni(II), Cu(II) and Zn(II) complexes have a molar conductivity values in the range 7.46–9.13  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>, which indicates the non-ionic nature of these complexes and they are considered as non-electrolyte [28]. Thus the complexes may be formulated as [M(BHBDAB)(OH<sub>2</sub>)<sub>2</sub>]2H<sub>2</sub>O, where M= Co(II), Ni(II), Cu(II) and Zn(II), BHBDAB = ligand.

#### 4.1.4. NMR spectral data

Further evidence of the bonding mode of the ligand was also provided by the <sup>1</sup>H NMR spectra of the Schiff base ligand and their diamagnetic Zn(II) complex. The chemical shifts of different types of protons in the <sup>1</sup>H NMR spectra of the  $N_2O_2$  ligand and its complex are given in Table S1. <sup>1</sup>H NMR spectra of Zn(II) complex with H<sub>2</sub>BHBDAB is shown in Fig. S2 (a) and (b) as representative examples for the <sup>1</sup>H NMR data obtained for the prepared compounds.

The <sup>1</sup>HNMR spectra of the parent ligand H<sub>2</sub>BHBDAB showed singlet signal at very downfield in the region  $\delta$  13.04 ppm, which was attributed to one phenolic–OH proton. The OH signal disappears with addition of the D<sub>2</sub>O. The ligand also showed singlet at  $\delta$  9.33 ppm which was attributed to the azomethine (–CH=N–) proton. The <sup>1</sup>H NMR spectra of the ligand revealed multiplets at 7.06–8.25 ppm which was attributed to aromatic protons.

A comparison of <sup>1</sup>H NMR spectra of the free Schiff base ligand with that of the corresponding diamagnetic complex of Zn(II) revealed that the chemical shifts observed for the OH proton of the ligand has disappeared in Zn(II) complex (Fig. S2 (c) and (d)). The absence of –OH signal indicated deprotonation of the hydroxyl group of the Schiff base and confirmed the bonding of oxygen to the metal ion (C–O–M) and supports the FTIR findings. It is well-know that the <sup>1</sup>H NMR spectra can provide compelling evidence for the presence of either one or two azomethine groups. Indeed, the presence of only one sharp singlet for the –C(H)=N proton clearly indicated that the magnetic environment is equivalent for all such protons, suggesting the presence of a planar ligand in this complex.

In case of Zn(II) complex, the position of azomethine signal was shifted to upfield at 8.48 ppm in comparison with that of the free ligand, inferring coordination through the azomethine nitrogen atom of the ligand. This suggested deshielding of the azomethine proton and proved the coordination of the azomethine group to the central metal ion. No appreciable change is seen in the peak positions corresponding to aromatic ring and methyl protons in the complexes. The appearance of new signals at  $\delta$  1.29ppm and 3.33 ppm give strong evidence for the presence of the 3H of one methyl group and 8H of four water molecules, respectively.

In <sup>13</sup>C NMR of ligand (Table S1, Figure S3a) carbonyl carbon showed signal at 163.36 ppm, azomethine carbon at 158.38 ppm and aromatic carbons in between 150.02 and 114.97 ppm. The signals due to carbonyl and azomethine carbons were slightly shifted downfield in comparison to the corresponding signals of these groups in the ligand thereby confirming the complexation with zinc metal ion. It was observed that DMSO did not have any coordinating effect on the spectra of zinc complex (Table S1, Figure S-3b).

Moreover, the appearance of new signals at (175.68, 178.25) and (40.08, 39) ppm give strong evidence for the presence of the methylene and methyl groups, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of ligand H<sub>2</sub>BHBDAB and [Zn(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O mononuclear complex is given in Figs. S-2 and S-3.

#### 4.1.5. Mass spectra

ESI-Mass spectra of complexes  $[Co(BHBDAB)(H_2O)_2]2H_2O$  (Figure S–4b) and  $[Cu(BHBDAB)(H_2O)_2]2H_2O$  (Figure S–4c) were recorded. Complex

[Co(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>] 2H<sub>2</sub>O shows molecular ion peak m/z = 426 (M<sup>+</sup>+1), and base peak at m/z = 270. The base peak is attributed to the ligand (M<sup>+</sup>+1). Complex [Cu(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>] 2H<sub>2</sub>O shows molecular ion peak m/z = 430 (M<sup>+</sup>+1) and base peak at m/ z = 270. The base peak is attributed to the ligand (M<sup>+</sup>+1). Mass spectra of both the complexes are well agreed with the proposed structures of the complexes. Fragmentation of weakly coordinated water molecule/ion in ESI mass spectra is not unlikely. To confirm the presence of weakly hydrating and coordinating H<sub>2</sub>O molecules in the complexes, we carried out thermogravimetric analyses of complexes.

#### 4.1.6. Electronic and magnetic moment measurements

The Co(II) complex showed the magnetic moment  $5.08\mu$ B for complex (4) at room temperature where that of the usual octahedral complexes are 4.8–5.2 B.M [23-25]. The electronic spectrum of the Co(II) complex displays three bands at 13,684, 15,328 and 24,865 cm<sup>-1</sup>. These bands may be assigned to following transitions  ${}^{4}T_{1}g \rightarrow {}^{4}T_{2}g(F)$  ( $v_{1}$ ),  ${}^{4}T_{1}g \rightarrow {}^{4}A_{2}g(F)$  ( $v_{2}$ ) and  ${}^{4}T_{1}g \rightarrow {}^{4}T_{1}g(P)$  ( $v_{3}$ ), respectively. The position of bands suggest octahedral geometry of Co(II) complex [23].

The magnetic moment was measured which gave  $2.88\mu$ B, for complex (5), which lies in the range (2.9–3.3 $\mu$ B) of the Ni(II) octahedral complexes [23]. Electronic spectrum of Ni(II) complex displays bands at 14,369, 15,845 and 21,357 cm<sup>-1</sup> These bands may be assigned to  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)(v_{1})$ ,  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)(v_{2})$  and  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)(v_{3})$  transitions, respectively. It suggests octahedral geometry of Ni(II) complex [23].

The observed magnetic moment of the Cu(II) complex is 1.93 B.M., which confirms the octahedral structure of this complex [23, 25]. For octahedral

Cu(II) complex, the expected transition is  ${}^{2}B_{1}g \rightarrow {}^{2}A_{1}g$  with respective absorption at 15,398 cm<sup>-1</sup>. Due to Jahn–Teller distortions, Cu(II) complexes give a broad absorption between 600 and 700 nm.

#### 4.1.7. Ligand field parameters

Various ligand field parameters are calculated for the complexes (Table 3). The value of Dq in Co(II) complexes were calculated from transition energy ratio diagram using the  $v_3/v_2$  ratio [23]. The nephelauxetic parameter  $\beta$  was readily obtained by using the relation  $\beta =$ B (complex)/B (free ion), where B (free ion) for Ni(II) is 1045 cm<sup>-1</sup> and for Co(II) is 1120 cm<sup>-1</sup> [23]. The value of  $\beta$  lies in the range 0.48–0.98. These values indicate the appreciable covalent character of metal ligand  $\sigma$  bond. The *g* values are almost equal to free electron *g* value.

<b>C</b> 1		1						
Complex Ligand field parameters								
	$Dq (cm^{-1})$	B(cm <sup>-</sup> )	β	g	LFSE (kJ mol-1)			
[Co(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	302	683	0.48	1.99	45			
[Ni(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	954	1045	0.98		135			
[Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	_	_	_	1.97	_			

Table 3: Ligand field parameters of the complexes

### 4.1.8. EPR spectrum of Cu(II) complex

To obtain further information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complex. ESR spectrum of the copper complex (Fig. S-5) was recorded in the solid state. The spin Hamiltonian parameters of the complex was calculated and summarized in Table 4.

The spectrum of the Cu(II) complex exhibits two broad band with  $g \parallel = 2.18$ and  $g \perp 2.06$  so,  $g \parallel > g \perp > 2.0023$ , indicating that the unpaired electron of Cu(II) ion is localized in the  $dx^2 - y^2$  orbital. In axial symmetry, the g values are related to the G-factor by the expression  $G = (g||-2)/(g \perp -2) = 4$ . The G values of the Cu(II) complex are < 4 suggesting that the considerable exchange interaction in the solid state. Further, the shape of the ESR spectrum of Cu(II) complex indicates that the geometry around the Cu(II) ions are elongated octahedron. The lower value of  $\alpha^2$  (0.46) compared to  $\beta^2$ (1.04) in Cu(II) complex indicate that the covalent in-plane  $\sigma$ -bonding is more pronounced than the covalent in-plane  $\pi$ -bonding character.

The  $\alpha^2$  values for copper(II) complexes indicates a considerable covalencey in the bonding between the Cu(II) ion and the metal. In this study,  $\alpha^2$  is less than  $\beta^2$  indicating that in-plane  $\sigma$ -bonding is more covalent than in-plane  $\pi$ bonding. These ESR data showed that [29]:

- The value of  $A_{ll} \times 10^{-4}$  cm<sup>-1</sup> increases with increasing  $g_{ll}$  and  $\beta^2$ .
- The value of  $\alpha^2$  increases with increasing  $A_{ll} \times 10^{-4}$  (cm<sup>-1</sup>),  $g_{av}$  and  $\beta^2$ .
- $K^2_{ll}$  and  $K^2_{\perp}$  increase with increasing  $g_{ll}$  and  $g_{\perp}$ .

 $A_{\parallel}^{a}$ G ${\rm B_1}^2$  $K^2$  $K^2 \perp$ Complex  $\alpha^2$  $\beta^2$ K2 g⊥ gav  $g_{\parallel}$ 38.34 6.28 0.52 0.16 0.27 Cu 2.18 2.02 2.075 0.46 1.04 1.5 0.65 <sup>a</sup> values in  $10^{-4}$  (cm<sup>-1</sup>).

#### Table 4: ESR spectral data of the Cu(II) complex

#### 4.1.9. Kinetics of thermal decomposition

In order to characterize the metal complexes more fully in terms of thermal stability, their thermal behaviors were studied. In the present investigation, the correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formula of the complexes. The TGA curves are given in Fig. S–6. The weight losses for each complex are calculated within the corresponding temperature ranges.

The [Cu(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>]2H<sub>2</sub>O complex (Figure S-6) with the molecular formula [C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>Cu] is thermally decomposed in four successive steps. The first estimated mass loss 8.42% (calculated mass loss = 8.46%) within the temperature range 57-182 °C can be attributed to the loss of two hydrated water fragment. The DTG curve gives an exothermic peak at 203 °C (the maximum peak temperature). The second estimated mass loss of 8.41% (calculated mass loss = 8.46%) within the temperature range 182-317°C could be attributed to the liberation of two coordinated water fragment. The DTG curve gives an exothermic peak at 324 °C (the maximum peak temperature). The third estimated mass loss 24.42% (calculated mass loss = 24.44%) within the temperature range 317-581 °C can be attributed to the loss of  $(C_7H_5O)$  fragment. The DTG curve gives an exothermic peak at 568 °C (the maximum peak temperature). The fourth step occurs within the temperature range 581-796 °C with an estimated mass loss 40.27% (calculated mass loss = 40.29%), which is reasonably accounted for the loss of rest of the ligand molecule  $(C_{11}H_{13}N_2)$ , leaving CuO as residue with total estimated mass loss of 81.52% (calculated mass loss = 81.65%). The DTG curve gives an exothermic peak at 661 °C (the maximum peak temperature).

The thermodynamic activation parameters (Table 5) of decomposition processes of the metal (Co(II), Ni(II), Cu(II) and Zn(II)) complexes namely

activation energy  $(E^*)$ , entropy  $(\Delta S^*)$  and Gibbs free energy change of the decomposition  $(\Delta G^*)$  were evaluated graphically by employing three methods, Coats–Redfern [30] (CR), Horowitz–Metzger [31] (HM), and Piloyan–Novikova [32] (PN). From the results obtained, the following remarks can be pointed out:

- (1) The high values of the energy of activation, Ea of the complexes reveal the high stability of such chelates due to their covalent bond character [33].
- (2) The positive sign of  $\Delta G$  for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound, and all the decomposition steps are non spontaneous processes. Also, the values of the activation,  $\Delta G$  increases significantly for the subsequent decomposition stages of a given complex. This is due to increasing the values of T $\Delta S$  significantly from one step to another which overrides the values of  $\Delta H$  [34–36].
- (3) The negative  $\Delta S$  values for the decomposition steps indicate that all studied complexes are more ordered in their activated states [37].

Table 5

Kinetic parameters of [Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O:								
Compound	Stage	TG range	DTGA	А	Ea	$\Delta H^*$	$\Delta S^*$	$\Delta G^*$
		(°C)	peak	$(S^{-1})$	(kJ/mol)	(kJ/mol)	(kJ/mol	(kJ/mol)
			(°C)		· · · ·	· · · · ·	K)	
Using Coast–Redfern equation								
[Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	1st	57-182	203	$45.62 \times 10^5$	134.58	123.47	-0.018	137
	2nd	182-317	324	$23.65 \times 10^{7}$	147.20	136.02	-0.035	156
	3rd	317-581	568	$45.38 \times 10^{9}$	155.89	152.46	-0.047	188
	4th	581-796	661	$47.77 \times 10^{11}$	168.78	172.38	-0.056	247
Using Horowitz–Metzger equation								
[Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	1st	57-182	203	$45.6 \times 10^5$	134.48	123.43	-0.015	136
	2nd	182-317	324	$23.62 \times 10^{7}$	147.18	136.08	-0.034	157
	3rd	317-581	568	$45.31 \times 10^{9}$	155.84	152.42	-0.048	189
	4th	581-796	661	$47.69 \times 10^{11}$	168.79	172.33	-0.054	248

Using Piloyan-Novikova equation

[Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	1st	57-182	203	45.66×10 <sup>5</sup>	134.33	123.43	-0.017	139
	2nd	182-317	324	$23.78 \times 10^{7}$	147.34	136.09	-0.034	157
	3rd	317-581	568	$45.47 \times 10^{9}$	155.78	152.46	-0.044	190
	4th	581-796	661	$47.89 \times 10^{11}$	168.64	172.29	-0.053	249

#### 4.1.10. Powder XRD

Single crystals of the complexes could not be prepared to get the XRD and hence the powder diffraction data were obtained for structural characterization. Structure determination by X-ray powder diffraction data has gone through a recent surge since it has become important to get to the structural information of materials, which do not yield good quality single crystals. The indexing procedures were performed using (CCP4, UK) CRYSFIRE program [24,38] giving tetragonal crystal system for [Co(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>]2H<sub>2</sub>O (Fig. S-7a) having M(9) = 11, F(6) = 8, cubic crystal system for [Ni(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>]2H<sub>2</sub>O (Fig. S-7b) having M(6) = 13, F(6) = 7 and tetragonal crystal system for [Cu(BHBDAB)(H<sub>2</sub>O)<sub>2</sub>]2H<sub>2</sub>O (Fig. S-7c) having M(6) = 19, F(6) = 8, as the best solutions. Their cell parameters are shown in Table 6.

Table 6.	Crystallographic data	for the Schiff base	complexes
C 1	Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub>	O, Ni(BHBDAB)(H <sub>2</sub> O)	$)_2$ ]2H <sub>2</sub> O and
	Co(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub>	<u>0</u> .	
Data	Cu(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	Ni(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	Co(BHBDAB)(H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O
Empirical formula	$C_{18}H_{26}CuN_2O_6$	$C_{18}H_{26}N_2NiO_6$	$C_{18}H_{26}CoN_2O_6$
Formula weight(g/mol)	429.95	425.10	425.34
Wavelength(Å)	1.53998	1.53998	1.53998
Crystal system	Tetragonal	Cubic	Triclinic
Space group	P4/m	P4/m	P4/m
Unit cell dimensions(Å,°	)		
a(Å)	8.200418	16.1048	7.301458
$b(\text{\AA})$	8.200417	16.1048	7. 301458

$c(^{\circ})$	16.022610	16.1048	7.301458
$\alpha(\circ)$	90	90	90
β(°)	90	90	90
$\gamma(^{\circ})$	90	90	90
Volume (Å <sup>3</sup> )	1097.63	5168.52	856.46
(Calc.) density $(g/cm^{-3})$	1.91976	1.23	1.84
2θ range	13.22–56.38	16.18-64.75	12.48-68.08
Limiting indices	$0 \le h \le 3, 0 \le k \le 1, 1 \le l \le 7$	3≤ <i>h</i> ≤10, 1≤ <i>k</i> ≤6, 3≤ <i>l</i> ≤10	$2 \le h \le 8, 1 \le k \le 8, 0 \le l \le 2$
Z	2	6	6
Rf	0.0000799	0.000015	0.0000682
Temperature (K)	298	298	298

#### 4.1.11. SEM and EDX spectra

A representative scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) analysis results of the residue obtained from thermal decomposition of all complexes are shown in Fig. 2. They provide insights on the surface morphology and the composition.

The SEM micrographs of ligand and its complexes are shown in Fig. 5a–d. The Co(II) complex shows bar like structure. The Ni(II) complex shows faceted microcrystal. Agglomerated morphology was seen for the Cu(II) complex. For Zn(II) complex bar with layered structure was present. The EDX spectra show that the residues majorly consist of metal (cobalt, nickel and copper) and oxygen with some traces of sulfur.





Fig. 2. SEM and EDX spectra for (a) Co(II), (b) Ni(II), (c) Cu(II) and (d) Zn(II) complexes(a-d), respectively.

#### 5. Potentiometric studies

#### 5.1. Protonation constants of H<sub>2</sub>BHBDAB

The study of complex formation by the studied Schiff base cannot be carried out in aqueous solution because of the nature of the compounds involved. These metal complexes as well as the ligand themselves are insoluble in water. This solvent has been most widely used for potentiometric determination of stability constants. The mixture DMSO–water 50: 50% was the chosen solvent for our study. In such a medium, the studied Schiff base and their metal complexes are soluble giving stable solutions. The use of this mixed solvent has some advantages over pure DMSO. Thus, pure DMSO is very hygroscopic and controlling its water content is difficult [39]. This fact would affect reproducibility of our experiments. However, DMSO–water 50:50% mixture has only a small hygroscopic character.

The stoichiometric protonation constants of the investigated Schiff base HL was determined in 50% DMSO–water at 25°C and these constants are tabulated in Table 7. As the titration curve of the ligand in Figure 3, it can be seen that there are two end –points at a = 1 and a = 2. According to the results obtained from this titration curve it can be concluded that the Schiff base have two protonation constants. The highest values due to the protonation of phenolic oxygen while the other value due to the imine nitrogen proton. The concentration distribution diagram of the protonated forms of the ligand are shown in Figures 3 and 4.

1 abic 7.10	main			mpiezes.	
System	р	q	r <sup>a</sup>	$Log \beta^{b}$ S	lc
H <sub>2</sub> BHBDABB	0	1	1	8.96(0.01) 4	$2 \times 10^{-9}$
	0	1	2	11.74(0.02)	
Cu(II)	1	1	0	4.88(0.01) 6	$6.4 \times 10^{-9}$
	1	2	0	10.24(0.03)	
	1	1	1	15.43(0.03)	
Co(II)	1	1	0	3.66(0.04)	$3.5 \times 10^{-7}$
	1	2	0	7.87(0.06)	
	1	1	1	15.74(0.02)	
Ni(II)	1	1	0	3.32(0.03)	$5.8 \times 10^{-8}$
	1	2	0	6.44(0.05)	
	1	1	1	15.98(0.02)	
Zn(II)	1	1	0	3.12(0.01) 7	$4 \times 10^{-8}$
	1	2	0	6.33(0.06)	
	1	1	1	14.36(0.02)	

Table 7: Formation constants of the metal complexes.

<sup>*a*</sup>*p*, *q* and *r* are the stoichiometric coefficients corresponding to metal ion, ligand and  $H^+$ , respectively; <sup>*b*</sup>Standard deviations are given in parentheses; <sup>*c*</sup>Sum of square of residuals .



Fig. 3. Potentiometric titration curve of the  $H_2BHBDAB$  and Cu(II)- BHBDAB system.



Fig. 4. Concentration distribution diagram of H<sub>2</sub>BHBDABB ligand system.

### 5.2. Stability constants of complexes

The concentration distribution for the Cu(II) complex, taken as a representative, is given in Fig. 5 and the stability constants of their complexes are given in Table 7. The formation constants were determined by fitting potentiometric data on the basis of possible composition models. The selected model with the best statistical fit was found to consist of Cu BHBDAB (110) and Cu(HBHBDAB) (111) complexes. The Cu–BHBDAB complex starts to form at pH value 4, reaching a maximum concentration (89.68%). On the other hand, CuL complex concentration was found to increase with increasing the pH and becomes predominant (96.23%) at pH=10.2. Protonated complex (Cu–HBHBDAB) species have been found to be most favored at lower pH values.

The results show that the stability of the metal chelates follows the order Co<Ni<Cu>Zn. This order is in good agreement with that found by Mellor and Naley [40] and by Irving and Williams [41] for 3d series. The classic sharp maximum for the Cu(II) complex is due to the stabilizing contribution of the Jahn–Teller effect With respect to increasing electronegativity of the metals, the electronegativity difference between metal atom and donor atom of the ligand will decrease, hence the metal-ligand bond would have more covalent character which may result in greater stability of the metal chelates [42].



Fig. 5. Concentration distribution of various species as a function of pH in the Cu–BHBDABB system.

6. Molecular modeling

6.1. Molecular modeling of Schiff-base ligand (H<sub>2</sub>BHBDAB) and its metal complexes

The ligand attains different types of tautomers which are the di-keto, the keto-enol and the di-enol forms. The molecular structures along with atom numbering, electron density, HOMO, LUMO and hydrogen bonds of the Schiff-base ligand (H<sub>2</sub>BHBDAB) Tautomers are shown in structures (1, S8-S9), respectively, where the same characters are presented for the metal complexes by the structures (2, S10- S 12). Comparison between the bond lengths and bond angles of tautomers of the ligand and also, between the diketo form with the Co(II), Ni(II), Cu(II) and Zn(II) complexes are listed in the supplementary materials (Tables S2–S5), respectively. The molecular parameters: total energy, binding energy, dipole moment, HOMO, LUMO and  $\Delta E_{Gap}$  were calculated for the Schiff-base ligand forms (Table S6) and the same data for the di-keto form of ligand and the metal complexes were represented in Table 9. Using these data one can conclude the following remarks:

- The total and binding energy for the ligand tautomers are equal but the values of the dipole moment, HOMO and LUMO are different according to their stability.
- Also, the values of the bond angles and lengths varied significantly.
- The di-enol form of the Schiff-base ligand reveals intra-molecular hydrogen bonds of the type (O-H---N)with a bond length 1.698 Å and 150.186° bond angle.
- C(4)-O(9), N(8)-C(10), C(10)-N(11) and C(14)-O(19) bond lengths of the ligand were enlarged in complexes due to participation in coordination.
- The bond angles of the di-keto Schiff-base moiety (H<sub>2</sub>BHBDAB) are altered somewhat upon coordination; the largest change affects C(5)-

C(4)-O(9), C(7)-N(8)-C(10),N(8)-C(10)-N(11), C(10)-N(11)-C(12) and C(13)-C(14)-O(19) angles. The previous angles are reduced or increased on complex formation due to complexation[43].

- The bond angles N(8)-C(10)-N(11) and C(13)-C(14)-O(19) of the ligand changed from 111.744° and 122.781° to 93.271°-97.591° and 125.458°-126.853° due to the formation of N(8)-M-N(11) and N(11)-M-O(19), respectively [44].
- The strongest coordinated bond is that formed by Ni<sup>II</sup> ion and the azomethine nitrogen atoms then the carbonyl group as M-N(11), M-N(8), M-O(19) and M-O(9).
- The stable bonds of the complexes can be arranged according to their lengths asNi-N(11)>Co-N(8)> Co-N(11)> Ni-O(19)> Co-O(9)> Co-O(19)> Ni-N(8)> Cu-N(8) >Cu-O(19)> Cu-O(9) > Zn-O(19)>Zn-O(9)> Zn-N(8)>Zn-N(11) and Zn-O(9), respectively.
- The lower HOMO energy values show that molecules donating electron ability is the weaker. On contrary, the higher HOMO energy implies that the molecule is a good electron donor. LUMO energy presents the ability of a molecule receiving electron [45].



**Structure 1:** The molecular structure, electron density, HOMO and LUMO of the di-keto form of the Schiff-base ligand.

Compound	Total energy (kcal/mol)	Binding energy (kcal/mol)	Dipole moment (D)	HOMO (ev)	LUMO (ev)	лЕ <sub>Gap</sub>
Di-keto form	$-6.013 \times 10^{5}$	-4661.664	2.995	-4.662	-2.778	1.884
L-Co <sup>II</sup>	$8.013 \times 10^{5}$	-5152.872	6.511	-4.754	-2.570	2.184
L-Ni <sup>II</sup>	$-8.181 \times 10^{5}$	-5141.531	4.256	-4.754	-2.697	2.057
$L-Cu^{II}$	$-8.362 \times 10^{5}$	-5063.889	5.022	-4.007	-2.646	1.361
L-Zn <sup>II</sup>	-8.563×10 <sup>5</sup>	-5033.265	3.671	-4.814	-2.471	2.343



HOMO LUMO Structure 2: The molecular structure, electron density, HOMO and LUMO of the Co(II) complex.

#### Table 9

Comparison between the energetic data ligand and its metal complexes

7-Conclusion

The structures of the complexes of H<sub>2</sub>BHBDAB with Co(II), Ni(II), Cu(II) and Zn(II) ions are confirmed by the elemental analyses, IR, <sup>1</sup>H NMR, molar conductance, magnetic moment, UV–VIS., mass, ESR and thermal analyses data. Therefore, from the IR spectra, it is concluded that  $H_2BHBDAB$  behaves as a Schiff base tetradentate ligand with two  $N_2O_2$ sites coordinating to the metal ions via the azomethine N and deprotonated phenolic–O. From the molar conductance data of the complexes ( $\Lambda_m$ ), it is concluded that the complexes of H<sub>2</sub>BHBDAB ligand are considered as nonelectrolytes. The <sup>1</sup>H NMR spectra of the free ligand shows that the OH signal, appeared in the spectrum of H<sub>2</sub>BHBDAB ligand at 15.04 ppm completely disappeared in the spectra of its Zn(II) complex indicating that the OH proton is removed by the chelation with Zn(II) ion. The ionization constants of the investigated H<sub>2</sub>BHBDAB ligand have been determined potentiometrically. The complex formation equilibria were investigated to ascertain the composition and stability constants of the complexes. The concentration distribution diagrams of the complexes were evaluated. Geometry optimization and conformational analysis have been performed and the perfect agreement with spectral studies allows for suggesting the exact structure of all studies complexes. The stability of complexes was explained and kinetic parameters (Ea, A,  $\Delta$ H,  $\Delta$ S and  $\Delta$ G) of all the thermal decomposition stages have been evaluated using Coats-Redfern and Horowitz-Metzger methods. On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral geometry is suggested for the investigated complexes. The structure of the complexes is shown in Scheme 2.

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#### **Figure captions**

- Fig. 1. Proposed structure of ligand (H<sub>2</sub>BHBDAB).
- Fig. 2. SEM and EDX spectra for (a) Co(II), (b) Ni(II), (c) Cu(II) and (d) Zn(II) complexes(a-d), respectively.
- Fig. 3. Potentiometric titration curve of the H<sub>2</sub>BHBDAB and Cu(II)-BHBDAB system.
- Fig. 4. Concentration distribution diagram of H<sub>2</sub>BHBDABB ligand system.
- Fig. 5. Concentration distribution of various species as a function of pH in the Cu–BHBDABB system.

# Synthesis, spectroscopic characterization, molecular modeling and potentiometric studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,1-diaminobutane-Schiff base

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► Novel Schiff's base complexes were synthesized. ► The complexes are characterized by different spectroscopic techniques. ► The complexes have different varieties of geometrical struct res. Schiff's base form complexes with M (II) ions through  $N_2O_2$  donation. ► Protonation equilibria were calculated for Schiff base 50% (v/v) DMSO–water solution.

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