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Synthesis, Spectroscopic Characterization and Potentiometric Studies of a Tetradentate [N_2O_2] Schiff Base, N,N'-bis(2-hydroxybenzylidene)-1,1-diaminoethane and Its Co(II),Ni(II),Cu(II) and Zn(II) Complexes.

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The new complexes [M(BHBDAE)(H_2O)$_2$] (Co(II), Ni(II), Cu(II) and Zn(II); BHBDAE: N,N'-bis(2–hydroxybenzylidene)–1,1–diaminoethane) have been synthesized and characterized by IR, EPR, ^{1}H NMR, magnetic moment as well as electronic spectroscopy data. The stepwise formation of the complexes has been established in the pH region studied. The results show the formation of 1:1 complexes with amino acids. Protonation constants of Schiff base (H_2BHBDAE) and stability constants of their binary Co(II), Ni(II), Cu(II) and Zn(II) complexes have been determined potentiometrically in 50% DMSO–water media at 37°C and ionic strength 0.10 mol dm^{-3} sodium nitrate. The concentration distribution of the complexes in solution was evaluated.

Keywords: Schiff base; Complexes; Spectroscopic; Potentiometric studies; Stability constants;

1. INTRODUCTION

Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects [1]. These wide applications of Schiff bases have generated a great deal of interest in metal complexes. Schiff base–transition metal complexes are one of the most adaptable and thoroughly studied systems [2,3]. These complexes have also applications in clinical [4] and analytical fields [5]. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems [6]. Tetradentate Schiff base complexes are well known to form stable complexes, where the coordination takes place through the N_2O_2 donor set [7–9]. Schiff bases also offer opportunities for inducing substrate chirality, tuning metal-centered electronic factors and enhancing the solubility and stability of homogenous or heterogeneous catalysts [10]. Transition metals are involved in many biological processes which are essential to life process. The metals can coordinate with O- or N-terminals from proteins in a variety of models and play a crucial role in the conformation and function of biological macromolecules [11,12].

In the present article, our attention is focused on the synthesis, characterization and thermal behavior of a series of transition metal complexes of new Schiff base (H_2BHBDAE) derived from condensation of propanal and salicyaldehyde. 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.

2. EXPERIMENTAL

2.1 Materials, Instrumentation and materials

All complexes were synthesized from commercially available starting materials used without further purification [14]. Metal salts (Merck) were of analytical grade.

IR spectra were recorded in KBr pellets with an FTIR-Biorad 135 instrument in 200–4000 cm^{-1} range. Electronic spectra of the solids (380–1200 nm) were obtained by diffuse reflectance technique, using MgO as standard, with a VSU-2P Zeiss Jena instrument. ^{1}H NMR spectra were recorded on a Bruker Avance DPX250 spectrometer (working frequency 250 MHz) at 25 °C. Chemical shifts were measured in parts per million from internal standard TMS. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GC–MS Hewlett–Packard instrument in the Microanalytical Center, Cairo University. Magnetic susceptibility was measured with a Sherwood Scientific magnetic susceptibility balance at 297 K. The EPR measurements were performed on microcrystalline samples using a JEOL JES-ME upgrade spectrometer equipped with X- and K-band cavities (9.5 GHz and 24 GHz, respectively) and a Jeol system for low- and high-temperature experiments (80e550 K). Metlting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. pH measurements were carried out using 716 DMS Titrino Metrohm connected with 728 Metrohm Stirrer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II Analyzer.

2.2 Synthesis of N,N'-bis(2-hydroxybenzylidene)-1,1-diaminoethane (H_2BHBDAE)

To a mixture of salicylaldehyde (0.4 g, 3.27 mmol) and ethanal (0.072 g, 1.64 mmol) was added NH_4NO_3 (0.25 g, 3.27 mmol) in the presence of the NEt_3 (1ml) 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 2mL EtOH and cooling overnight, a yellow solid precipitated. The solid product was filtered off and washed with cold EtOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N,N'-bis(2-hydroxybenzylidene)-1,1-diaminoethane (H_2BHBDAE), was obtained in 93% yield, mp = 100-102°C; Anal. Calcd for C, H, N: C, 70.87; H, 5.51; N, 11.02; Found: C, 70.72; H, 5.46; N, 10.87.

2.3 Synthesis of the solid complexes

All complexes were prepared by refluxing **H_2BHBDAE** (0.35 g, 1.0 mmol) and the hydrated metal salts (1.0 mmol), e.g. chloride, in 30 ml ethanol for 3–4 h. The resulting solid complexes were filtered while hot, washed with ethanol followed by diethyl ether and dried in vacuo over $CaCl_2$.

Table 1. Physical and elemental analysis data of the complexes

Cpd.	M.F. (M.Wt)	M.p. (°C)	Colour [Yield %]	Elemental analyses Found (Calc.), %				
				C	H	N	M	$^a\Lambda_m$
1	$[Co(BHBDAE)(H_2O)_2]$ $C_{16}H_{18}CoN_2O_4$(361.26)	252	Reddish brown [68]	53.04 (53.19)	5.04 (5.02)	7.72 (7.75)	16.40 (16.31)	3.88
2	$[Ni(BHBDAE)(H_2O)_2]$ $C_{16}H_{18}N_2NiO_4$ (361.02)	234	Faint brown [72]	53.14 (53.23)	5.03 (5.03)	7.44 (7.76)	16.14 (16.26)	5.76
3	$[Cu(BHBDAE)(H_2O)_2]$ $C_{16}H_{18}CuN_2O_4$(365.87)	253	Dark brown [75]	53.73 (53.75)	4.96 (4.96)	7.53 (7.66)	17.37 (17.37)	4.25
4	$[Zn(BHBDAE)(H_2O)_2]$ $C_{16}H_{18}N_2O_4Zn$(367.74)	220	Yellow [63]	52.13 (52.26)	4.83 (4.93)	7.63 (7.62)	17.70 (17.79)	4.36

$^a\Lambda_m$ (molar conductance $\Omega^{-1}cm^2mol^{-1}$)

2.4 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 [15].

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.

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 $NaClO_4$:

(i) 3.0×10^{-3} M HNO_3 + 1.5×10^{-3} M Schiff base (for the protonation constant of the Schiff base);

(ii) 3.0×10^{-3} M HNO_3 +1.5×10^{-3} M Schiff base + 7.5×10^{-4} 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).

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \qquad (1)$$

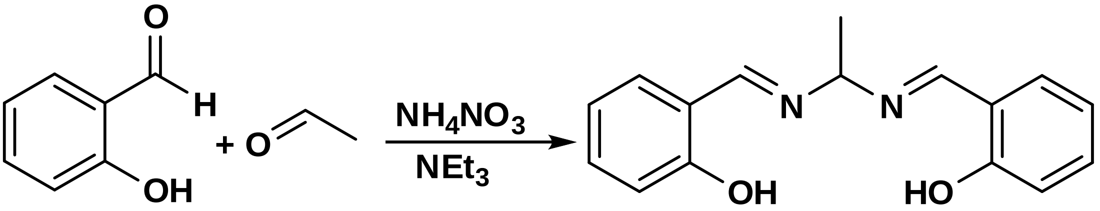
$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \qquad (2)$$

Where M, L, H stand for the metal ion, ligand and proton, respectively. The calculations were performed using the computer program MINIQUAD-75 and was 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.

3. RESULTS AND DISCUSSION

3.1. Characterization of ligand (H_2BHBDAE)

The novel Schiff base (**H_2BHBDAE**) 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.



Scheme 1. Synthesis of Schiff base (H_2BHBDAE)

The characteristic IR spectral data (Figure 2, Table 2) for H_2BHBDAE compound are presented in the experimental section. The band centered at about 2678 cm^{-1} are assigned to ν(O–H) in O–H·····N intramolecular (Figure 1) hydrogen-bonding fragment [16,17]. Very strong band centered at 1598 cm^{-1} are assigned to ν(C=N) stretching in H_2BHBDAE ligand.

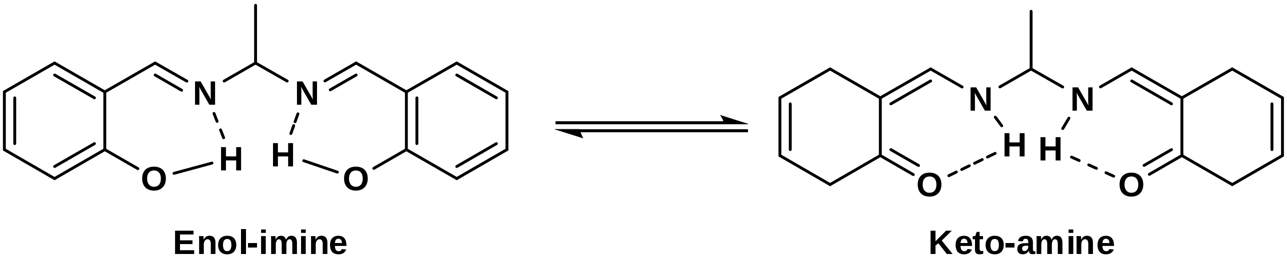


Figure 1. Proposed structure of ligand.

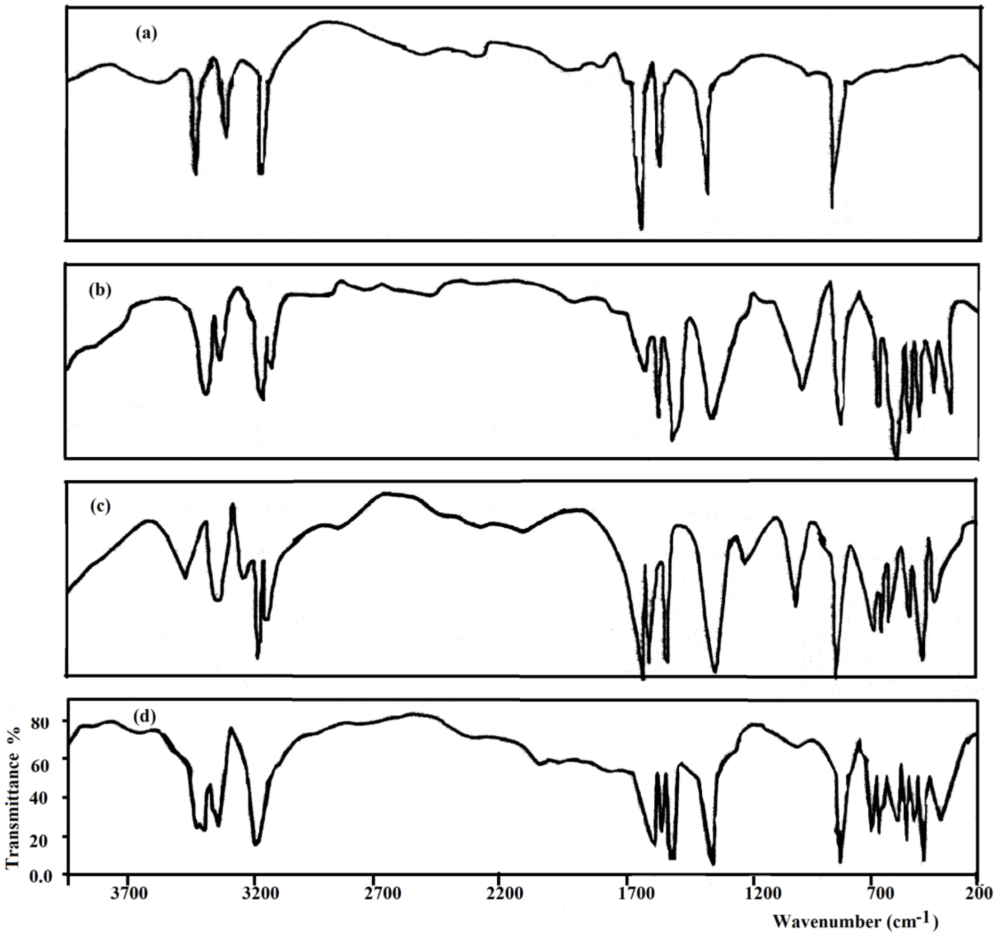


Figure 2. FT–IR spectrum of: (a) H_2BHBDAE ligand, (b) [Co(BHBDAE)(H_2O)$_2$], (c) [Cu(BHBDAE)(H_2O)$_2$]and (d) [Zn(BHBDAE)(H_2O)$_2$].

The NMR spectra of Schiff base ligand H_2BHBDAE (Table 3) were recorded in $CDCl_3$ at room temperature. The ^{1}H NMR spectral data of the ligand H_2BHBDAE showed a sharp singlet at 8.82 ppm assignable to protons of the azomethine group (–CH=N–). Multiplet in the range 6.82–7.87 ppm is due to protons of the benzene ring. A sharp singlet in the downfield region at 15.03 ppm is attributed to hydroxyl protons.

The electronic spectral data of **H_2BHBDAE** ligand (in ethanol and hexane) are presented in Table 4. The wavelength of the absorption bands appeared in the UV region in both solvents is practically identical. From the relatively higher intensity the bands at 223 and 264 nm are assigned to $\pi\rightarrow\pi^*$ transitions of the enol-imine tautomer of the SB. The observed small hypsochromic shift of the 334 nm band in more polar solvents is typical to $n\rightarrow\pi^*$ transitions of C=N group [18]. The maximum at 420 nm detected in the EtOH solutions of **H_2BHBDAE** ligand is assigned to $n\rightarrow\pi^*$ transitions in dipolar zwitterionic or keto-imine tautomeric structures, respectively [19].

The electron impact mass spectrum (Figure 3) of the free ligand, confirms the proposed formula by showing a peak at 268 u corresponding to the ligand moiety [($C_{16}H_{16}N_2O_2$) atomic mass 268 u]. The series of peaks in the range, i.e. 66, 123 and 165 u, attributable to different fragments of the ligand. These data suggest the condensation of keto group with amino group.

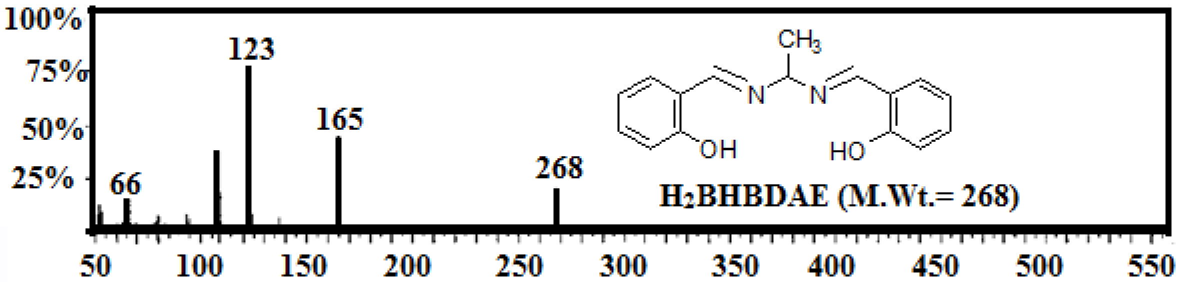


Figure 3. Mass spectrum of ligand, H_2BHBDAE.

3.2. Characterization of metal complexes

3.2.1. Elemental analyses of the complexes

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

3.2.2. 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 cm^{-1} (Table 2).

Table 2. Important IR bands of H_2BHBDAE ligand and its complexes with their assignments.

Compounds	**assignments**						
	ν(OH)	ν(CH=N)	ν(C–O)	ν(M–O)	ν(M–N)	$\rho_r(H_2O)$	**$\rho w(H_2O)$**
H_2BHBDAE	2678(br)	1600m	1333m, 1273m	–	–	–	–
1	–	1575m	1312m, 1261m	660m	450s	795s	**604s**
2	–	1570m	1310m, 1258m	670s	457m	832m	**630m**
3	–	1570m	1308m, 1248m	674s	455m	789s	**623m**
4	–	1565m	1318m, 1252m	675m	460m	845m	**606m**

The IR spectrum of the ligand shows a broad band at 2678 cm^{-1}, 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 at 1333, 1273 cm^{-1} in the free ligand to a lower frequency to the extent of 15–25 cm^{-1} [21]. The shift of *v*(C–O) band at 1333, 1273 cm^{-1} to a lower frequency suggests the weakening of *v*(C–O) and formation of stronger M–O bond. Another band appeared between 662 and 674 cm^{-1}, which is assigned to the interaction of phenolic oxygen to the metal atom, i.e., the stretching vibrations *v*(M–O) [21]. A band corresponding to ν(C=N) (azomethine linkage) appears at 1600 cm^{-1} in the ligands. On complex formation, the IR band due to azomethine group shifts to the lower wave number (25–35 cm^{-1}) 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 450 and 460 cm^{-1} that is attributed to the *v*(M–N) stretching vibrations [22].

The band at 1375–1376 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 [23].

The bands in the range 745–845 cm^{-1} and 600–630 cm^{-1} appeared in the spectra of these complexes which may be assigned to ρr(H_2O) and ρw(H_2O) [24].

From the infrared spectra, it is apparent that, the chelation of the divalent or trivalent metal ions to the ligand occurs from the H_2BHBDAE ligands through the two oxygen atoms of the resorcinol moiety and the two 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.

3.2.3. 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 3.88–5.76 Ω^{-1} mol^{-1} cm^{2}, which indicates the non-ionic nature of these complexes and they are considered as non-electrolyte [25]. Thus the complexes may be formulated as [M(BHBDAE)(H_2O)$_2$] respectively [where M= Co(II), Ni(II), Cu(II) and Zn(II), BHBDAE = ligand.

3.2.4. ^{1}Hnuclear magnetic resonance spectra

The ^{1}H NMR spectra of a DMSO-d_6 solution of H_2BHBDAE ligand (H_2BHBDAE) and Zn(II) complex show well resolved signals as expected (Table 3). The spectrum of H_2BHBDAE (Figure 2a) shows triplet at 4.94 ppm (t, 1H, $NC\underline{H}N$), triplet at 0.92 ppm (t, 3H, $C\underline{H}_3$), multiple at 6.82–7.92 ppm (m, 8H, Ar-H), singlet at 8.82 ppm (s, 2H, $C\underline{H}$=N), singlet at 15.03 ppm (s, 2H, $O\underline{H}$). The ^{1}H NMR spectra of both the complexes show the resonance with expected integrated intensities. In both complexes, no signal is recorded for phenolic hydrogen in the 12–13.5 ppm region, as in the case of ligand (H_2BHBDAE). This indicates deprotonation of the *ortho*-hydroxyl group on complexation. The shift to higher field of the $C\underline{H}$=N– proton signal which appears in the free ligand at δ 8.95 ppm (s, 2H) for Zn(II) complex, respectively [26], suggesting the coordination to the metal ions via the azomethine nitrogen. The signal observed at 3.35 ppm with an integration corresponding to four protons in case of Zn(II) complex was assigned to two coordinate water molecules.

Table 3. ^{1}HNMR spectral data of H_2BHBDAE ligand and its Zn(II) complex.

Compound	Chemical shift, δ(ppm)	Assignment
H_2BHBDAE	4.94	**s, 1H, NCHN**
	0.92	**t, 3H, CH_3**
	6.82–7.92	**m, 8H, Ar-H**
	8.82	**s, 2H, CH=N**
	15.03	**2H, OH**
[Zn(BHBDAE)(OH_2)$_2$]	4.92	**s, 1H, NCHN**
	0.92	**t, 3H, CH_3**
	6.69–7.88	**m, 8H, Ar-H**
	8.95	**s, 2H, CH=N**
	3.35	**m, 4H, Coordinate water**

3.2.5. Mass spectra

The FAB mass spectra of Co(II), Ni(II), Cu(II) and Zn(II) Schiff-base complexes**(1-4)**, respectively, have been recorded. All the spectra exhibit parent peaks due to molecular ions (M^+). The proposed molecular formula of theses complexes was confirmed by comparing their molecular formula weights with m/z values. The molecular ion (M^+) peaks obtained for various complexes are as follows: **(1)** m/z = 361 (Cobalt(II)complex), **(2)** m/z = 361 (Nickel(II)complex) **(3)** m/z = 365 (Copper(II) complex) **(4)** m/z = 367(zinc(II)complex). This data is in good agreement with the proposed molecular formula for these complexes i.e. [M(BHBDAE)(H_2O)$_2$] respectively [where M= Co(II), Ni(II), Cu(II) and Zn(II), BHBDAE = ligand. This confirms the formation of the Schiff–base complexes frame.

3.2.6. Magnetic susceptibility, electronic, ligand field parameter and EPR spectra

The Co(II) complex showed the magnetic moment 5.32μB for complex (**2**) at room temperature where that of the usual octahedral complexes are 4.8–5.2 B.M [24]. The electronic spectrum of the Co(II) complex displays three bands at 13,655, 15,155 and 25,008 cm^{-1}. These bands may be assigned to following transitions ${}^4T_1g \rightarrow {}^4T_2g(F)$ (ν_1), ${}^4T_1g \rightarrow {}^4A_2g(F)$ (ν_2) and ${}^4T_1g \rightarrow {}^4T_1g(P)$ (ν_3), respectively. The position of bands suggest octahedral geometry of Co(II) complex [21]. The various ligand field parameters were calculated (Table 4) for the cobalt(II) complex. The value of Dq has been calculated from Orgel energy level diagrams using the ν_3/ν_1 ratio [24]. The value for B (free ion) is 1122 cm^{-1}. The value of β indicates that the covalent character of metal ligand σ-bond is low (Table 4).

The magnetic moment was measured which gave 3.18 μB, for complex (**3**), which lies in the range (2.9–3.3μB) of the Ni(II) octahedral complexes [24]. Electronic spectrum of Ni(II) complex displays bands at 14,370, 15,796 and 21,455 cm^{-1} (Fig. 5d) These bands may be assigned to ${}^3A_2g(F) \rightarrow {}^3T_2g(F)(\nu_1)$, ${}^3A_2g(F) \rightarrow {}^3T_1g(F)(\nu_2)$ and ${}^3A_2g(F) \rightarrow {}^3T_1g(P)(\nu_3)$ transitions, respectively. It suggests octahedral geometry of Ni(II) complex [21]. The value of Dq has been calculated (Table 4) by using Orgel energy level diagrams using the v_3/v_1 ratio [21]. The value for B (free ion) is 1042 cm^{-1}. The value of β indicates [24] that the covalent character of metal ligand σ bond is low.

The observed magnetic moment of the Cu(II) complex is 2.04 B.M., which confirms the octahedral structure of this complex [21, 24]. The electronic spectrum of the Cu(II) complex gave a band at 12,503, 15,348 and 17,,853 cm^{-1}, these bands may be assigned to $^2B_1g\rightarrow{}^2B_2g$, $^2B_1g\rightarrow{}^2A_1g$ and $^2B_1g\rightarrow{}^2Eg$ transitions, respectively, another band observed at 21,300 cm^{-1} suggesting the existence of a transition from dxy, dz^2 and dxz, dyz transfer to the antibonding and half-filled dx^2−dy^2 level which is consistent with an octahedral configuration.

The complex exhibit an anisotropic EPR spectra characteristic for hexagonal geometry of copper(II) complex [24]. The anisotropic *g*- values have been calculated by Kneubuhl's methods [27] and by methods reported earlier [28] viz. $G= (g_\perp -2)/(g_\parallel-2)$, which measures the exchange interaction between the copper centers in polycrystalline samples, have been calculated. The calculated *g*-values are reported in Table 4. According to Hathaway [29-32], if $G > 4$, the inter-exchange interaction between the Cu(II) centers will be negligible, but a value of $G < 4$, indicates considerable exchange interaction in the solid complexes. The calculated *G*-value for the complex, under study is larger than 4, suggesting that there is no interaction between the copper centers. The g_{av} was calculated to be 2.0425.Thus the results suggested that, the Cu(II) complex (Table 4) possess distorted octahedral geometry.

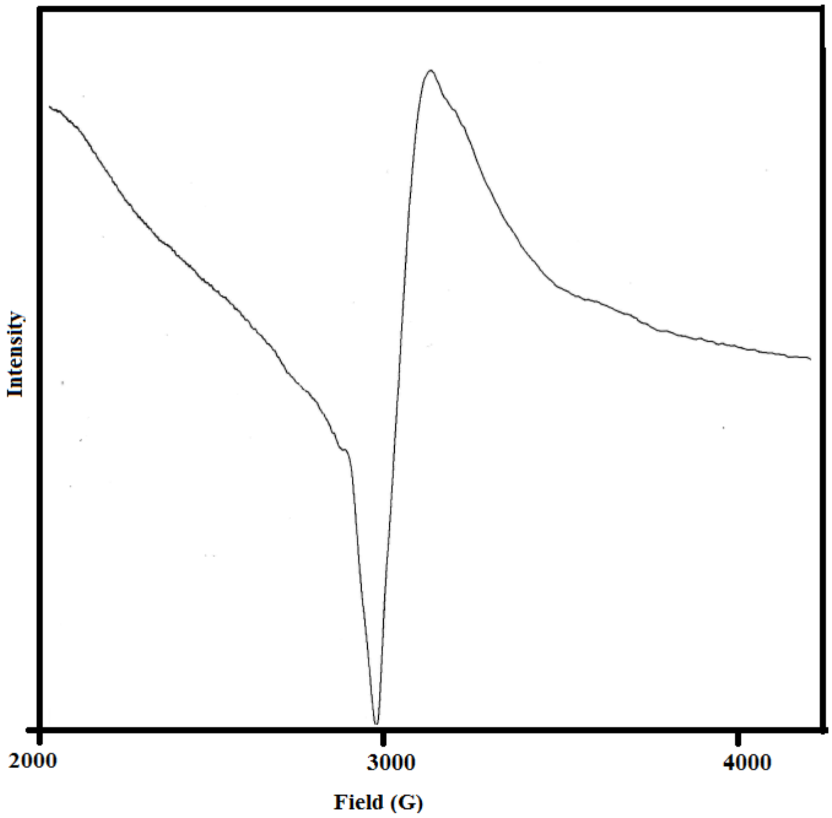


Figure 4. X-Band esr spectra in the solid state at 25 °C of the [Cu(BHBDAE)(H_2O)$_2$] complex.

The Zn(II) complex is diamagnetic as expected and its geometry is most probably octahedral similar to the Co(II), Ni(II) and Cu(II) complexes of the H_2BHBDAE ligand.

Table 4. EPR and Ligand field parameters of the complexes

Complex	**Ligand field parameters**				**EPR**		
	Dq (cm^{-1})	β	β	LFSE (kJ mol^{-1})	$g_{\|\|}$	$g_{\perp}$	g_{iso}
[Co(BHBDAE)$(OH_2)_2$]	303	684	0.65	46	–	–	–
[Ni(BHBDAE)$(OH_2)_2$]	953	765	0.78	138	–	–	–
[Cu(BHBDAE)$(OH_2)_2$]	–	–	–	–	**2.11**	**2.04**	**2.09**

3.2.7. Potentiometric studies

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 [33]. This fact would affect reproducibility of our experiments. However, DMSO–water 50:50% mixture has only a small hygroscopic character.

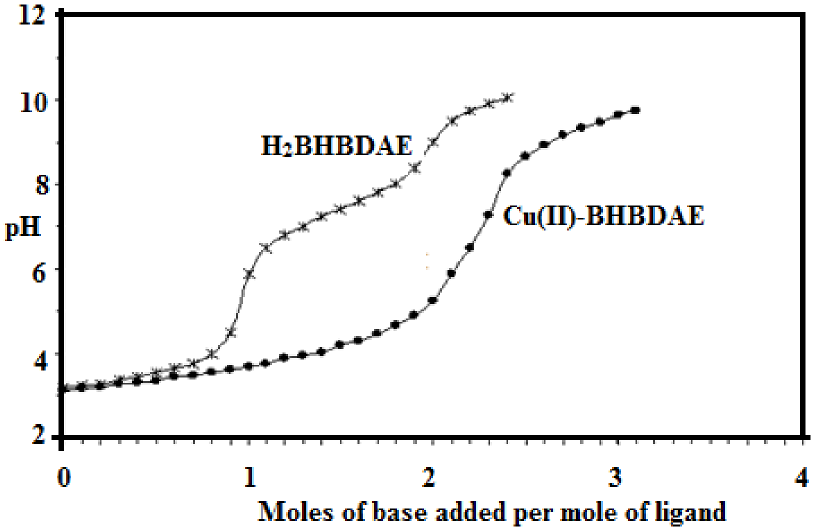


Figure 5. Potentiometric titration curve of the H_2BHBDAE and Cu(II)- BHBDAE system.

The stoichiometric protonation constants of the investigated Schiff base H_2BHBDAE was determined in 50% DMSO–water at 25°C and these constants are tabulated in Table 6. As the titration curve of the ligand (H_2BHBDAE) in Figure 5, 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 Figure 6 and 7.

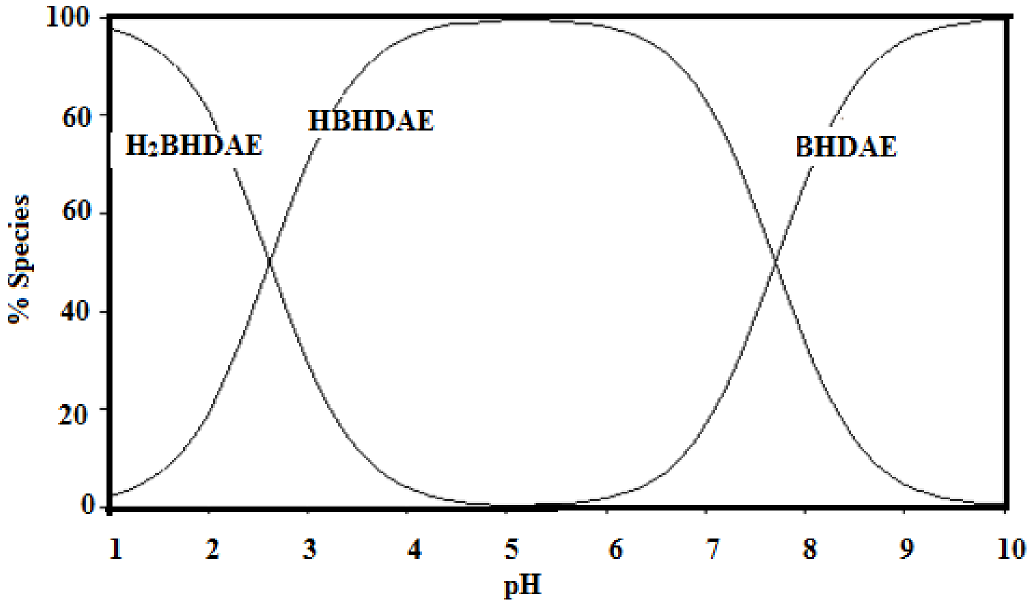


Figure 6. Species distribution diagram for the systems $H_2BHBDAE$ as a function of pH.

The potentiometric titration curves of the Cu(II)–$H_2BHBDAE$ system, taken as a representative, are given in Figure 5. The titration curve of the Cu(II)–$H_2BHBDAE$ complex is lowered from that of the free Schiff base($H_2BHBDAE$) curve, indicating formation of Cu(II) complex by displacement of protons. 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 BHBDAE (110), CuL_2 (120) and Cu(HBHBDAE) (111) complexes. The stability constants of their complexes are given in Table 5. The concentration distribution for the Cu(II) complex, taken as a representative, is given in Figure 7. The Cu–BHBDAE complex starts to form at pH value 4, reaching a maximum concentration (88.61%). On the other hand, CuL complex concentration was found to increase with increasing the pH and becomes predominant (95.14%) at pH=10.2. Protonated complex (CuH BHBDAE) 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 [34] and by Irving and Williams [35] for 3d transition metal ions. 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 [36].

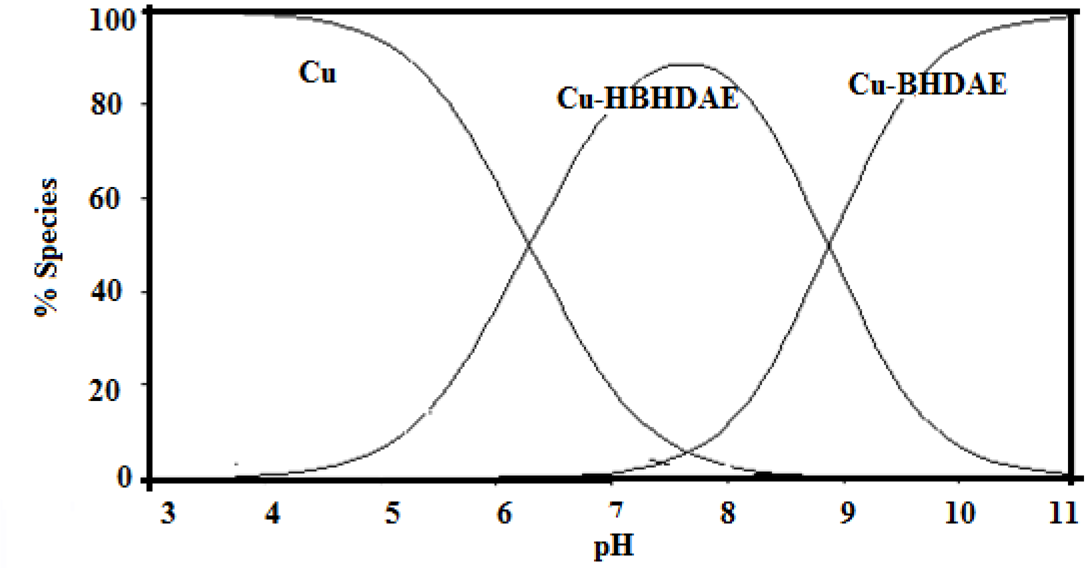


Figure 7. Species distribution diagram for the systems Cu(II)-BHBDAE as function of pH.

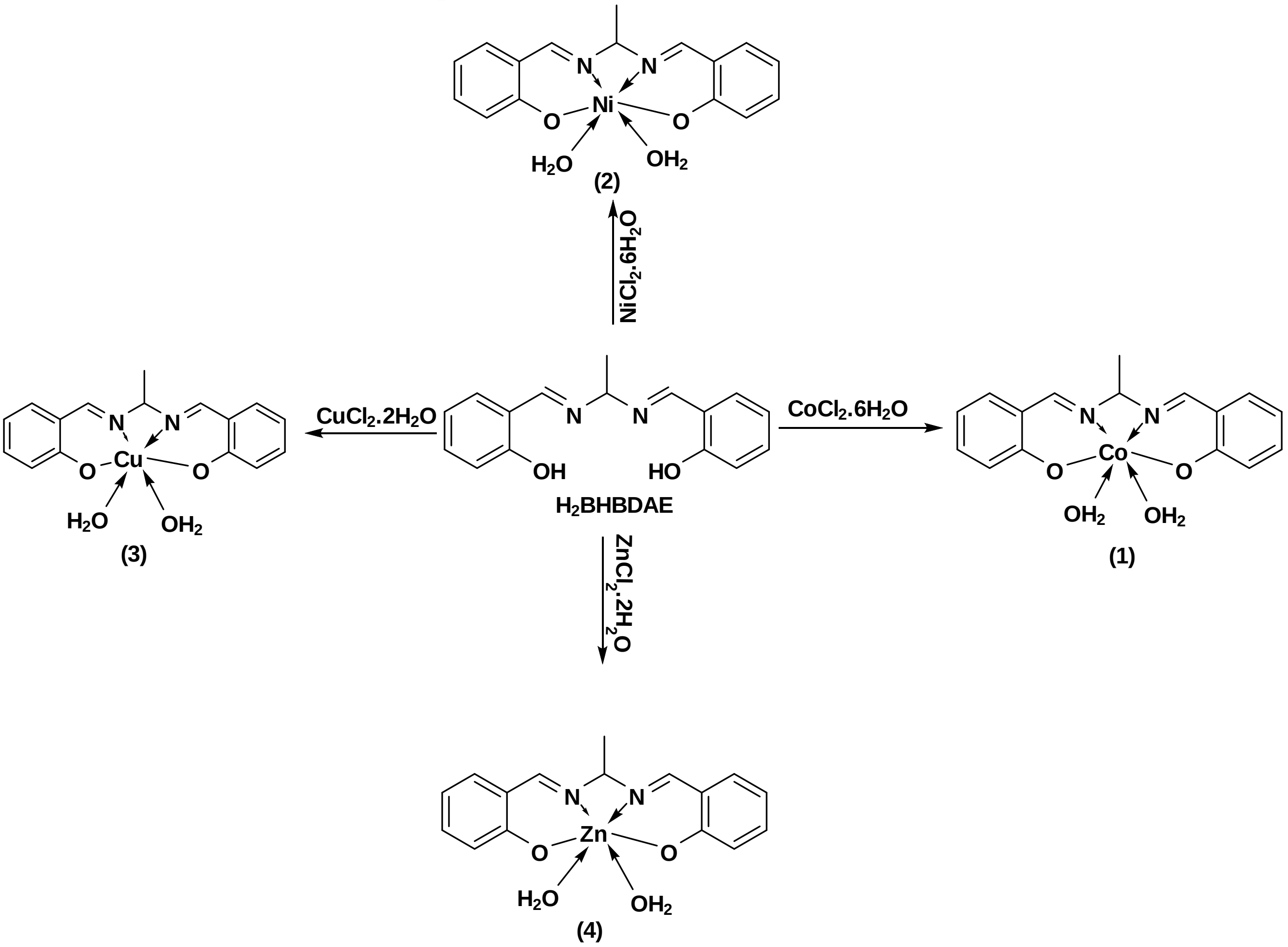
Table 5. Formation constants of the metal complexes.

System	p	q	r[a]	Log β [b]	S[c]
H_2BHBDAE	0	1	1	9.06(0.01)	**3.6×10^{-9}**
	0	1	2	10.68(0.02)	
Cu(II)	1	1	0	4.87(0.01)	**6.8×10^{-9}**
	1	2	0	10.54(0.03)	
	1	1	1	15.87(0.03)	
Co(II)	1	1	0	3.43(0.04)	**9.7×10^{-7}**
	1	2	0	7.24(0.06)	
	1	1	1	15.44(0.02)	
Ni(II)	1	1	0	3.72(0.03)	**7.4×10^{-8}**
	1	2	0	6.26(0.05)	
	1	1	1	15.89(0.02)	
Zn(II)	1	1	0	3.12(0.01)	**9.8×10^{-8}**
	1	2	0	6.26(0.06)	
	1	1	1	14.36(0.02)	

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

4. CONCLUSION

The structures of the complexes of H_2BHBDAE with Co(II), Ni(II), Cu(II) and Zn(II) ions are confirmed by the elemental analyses, IR, ^{1}H NMR, molar conductance, magnetic moment, UV–VIS., mass, ESR and thermal analyses data. Therefore, from the IR spectra, it is concluded that H_2BHBDAE behaves as a Schiff base tetradentate ligand with two N_2O_2 sites coordinating to the metal ions via the two azomethine N and deprotonated two phenolic–O. From the molar conductance data of the complexes (Λ_m), it is concluded that the complexes of H_2BHBDAE ligand are considered as non-electrolytes. The ^{1}H NMR spectra of the free ligand shows that the OH signal, appeared in the spectrum of H_2BHBDAE ligand at 15.03 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. On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral geometry is suggested for the investigated complexes. The Potentiometric data for the system consisting of H_2BHBDAE ligand and Co(II), Ni(II), Cu(II) and Zn(II) ions showed the formation of 1:1 complexes. The concentration distribution curves of the various complex species existing in solution were evaluated. The structure of the complexes is shown in Scheme 2.



Scheme 2. Syntheses of metal complexes Schiff base derived from H_2BHBDAE with Co(II), Ni(II), Cu(II) and Zn(II) ions.

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