Structural, potentiometric and thermodynamic studies of hydroxybenzlidene and their metal complexes

Ashraf A. El-Bindary[a*], Sabry A. El-Korashy[b], Jehan A. Hasanen[b], Ibrahim M. El-Deen[c], M.A. Hussien[c], Shimaa M. Al-Sayed[b]

[a]Department of Chemistry, Faculty of Science, University of Damietta, Damietta 34517, Egypt.

[b]Department of Chemistry, Faculty of Science, University of Suez Canal, Ismailia, Egypt.

[c]Department of Chemistry, Faculty of Science, University of Port Said, Port Said, Egypt.

Abstract—A series of hydroxybenzlidene compounds p-[(2-hydroxybenzlidene) amino]- N,N-dimethyl aniline (HL_I), p-[(5-bromo-2-hydroxybenzlidene)amino]-N,N-dimethyl aniline (HL_{II}) and p-[(3,5-dibromo-2-hydroxybenzlidene)amino]-N,N-dimethyl aniline (HL_{III}) have been prepared and characterized by elemental analyses, ^{1}H NMR , mass spectroscopy and IR spectra. The IR spectral data indicate that, the compounds can exist in two resonance structures. Moreover, energy of HOMO & LUMO, HOMO–LUMO energy gap and electronic charge were calculated. In addition, absolute Electronegativities, chemical potentials, and absolute hardness have been calculated. Proton-ligand dissociation constants of hydroxybenzlidene compounds and metal-ligand stability constants of their complexes with bivalent (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) metal ions have been determined potentiometrically in 0.1 M KC1 and 30 % (v/v) methanol-water mixture. The influence of substituents on the dissociation and stability constants were examined on the basis of the electron repelling property of the substitiuent. The order of the stability constants of the formed complexes was found to be $Mn^{+2} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed.

Keywords — Hydroxybenzlidene, molecular parameters, potentiometry, thermodynamics.

*Corresponding Author: E-mail: abindary@yahoo.com; Tel.: +2 01114266996; Fax: +2 0572403868.

◆

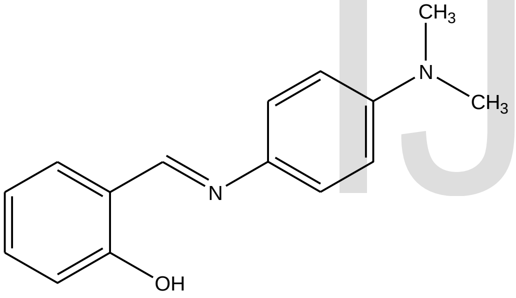
1 INTRODUCTION

Hydroxybenzlidene derivatives are a good series of ligands capable of binding metal ions leading to metal complexes with increasing properties [1]. The high stable potential of the complexes of hydroxybenzlidene derivatives in different oxidation states increased the application of these compounds in a wide range. Ligands with potential nitrogen and oxygen donors, such as hydroxybenzlidene and its derivatives are quite interesting which have gained special attention, not only because of the structural chemistry and their importance in medical chemistry, but also because these materials are used as drugs and they are reported to possess a wide variety of biological activities against bacteria and fungi [2,3]. They also have become a useful model for bioinorganic processes, which have many biochemical and pharmacological activities [4,5]. In continuation of our earlier work [6-9], we report herein the preparation and characterization of some hydroxybenzlidene derivatives. The geometrical structure of the ligands by HF method with 3-21G basis set was studied. The dissociation constant of the ligands (HL_I, HL_{II} and HL_{III}) and the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} at different temperatures were determined potentiometrically. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

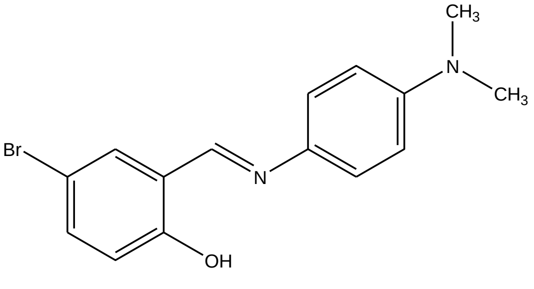
2 EXPERIMENTAL SECTION

2.1. Synthesis of the ligands

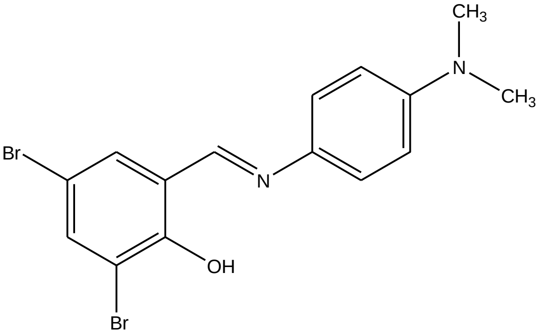
A mixture of p-N,N-dimethylamino aniline (0.01 mol) and aromatic aldehydes (2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde and 3,5-dibromo-2-hydroxybenzaldehyde) (0.01 mol) in ethanol (50 ml) was heated under reflux for 2 hr. The solid obtained after cooling was filtered off, dried and purified by recrystallization with ethanol to give ligands (HL_I, HL_{II} and HL_{III}), Fig. 1.



p-[(2-hydroxybenzlidene)amino]-N,N-dimethyl aniline (HL_I).



p-[(5-bromo-2-hydroxybenzlidene)amino]-N,N-dimethyl aniline (HL_{II}).



p-[(3,5-dibromo-2-hydroxybenzlidene)amino]-N,N- dimethyl aniline (HLIII).

Fig. 1. Structure of the ligands.

2.2. Measurements

All the compounds and solvents used were purchased from Alderich and Sigma. Elemental microanalyses of the separated ligands for C, H, and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The ^1H NMR spectrum was obtained by Bruker WP 300 MHz using DMSO-d_6 as the solvent and TMS as an internal reference. FT-IR spectra (KBr disks, 4000-400 cm^{-1}) by Jasco-4100 spectrophotometer. The molecular structures of the investigated compounds were optimized by HF method with 3-21G basis set.

The pH measurements were performed with a Metrohm 836 Titrando (KF & Potentiometric Titrator) equipped with a combined porolyte electrode. The pH–meter readings in the non–aqueous medium were corrected [10]. The electrode system was calibrated according to the method of Irving et al. [11]. All titrations have been carried out between pH 4.0 – 11.0 and under nitrogen atmosphere. The molecules were built with the Perkin Elmer Chem Bio Draw and optimized using Perkin Elmer ChemBio3D software [12]. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}) and HOMO–LUMO energy gap (ΔE) for the investigated molecules are calculated.

2.3. Potentiometry

A ligand solution (0.001 M) was prepared by dissolving an accurately weighted amount of the solid in methanol (Analar). Metal ion solutions (0.0001 M) were prepared from Analar metal chlorides in bidistilled water. Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free NaOH solution in 30 % (by volume) methanol-water mixture was used as titrant and standardized oxalic acid (Analar).

The apparatus, general conditions and methods of calculation were the same as in previous work [6-9]. The following mixtures (i) - (iii) were prepared and titrated potentiometrically at 298 K against standard 0.001 M KOH in a 30 % (v/v) methanol-water mixture:

(i) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 15 ml Methanol

(ii) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 10 ml Methanol + 5 ml 0.001 M ligand

(iii) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 10 ml Methanol + 5 ml 0.001 M ligand + 10 ml 0.0001 M metal chloride.

For each mixture, the volume was made up to 50 ml with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. The temperature was controlled to within ± 0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel.

3. Results and discussion

3.1. Structural of the ligands

Analytical data (Table 1) are in agreement with the proposed formulae of hydroxylbenzlidene compounds shown in Fig. 1.

The ^{1}H NMR spectra is a good tool to check the purity of organic compounds. The ^{1}H NMR spectra of the ligands (HL_I-HL_{III}) were carried out in DMSO-d^6 as a solvent. The phenolic OH proton appeared as a singlet at 9.96-9.89 ppm range. The proton of the HC=N appeared as a singlet in the range 8.92-8.81 ppm. The signals of aromatic protons appeared as a multiple within the range 6.80 - 7.80 ppm range. The peaks at 2.95-2.97 ppm range assigned to the terminal alkyl groups $N(CH_3)_2$.

Table 1. Analytical data of hydroxybenzlidene compounds[a].

Comp.[b]	Empirical formula	Colour	M.B (C°)	Calc. (Exp.) %		
				C	H	N
HL_I	$C_{15}H_{16}N_2O$	Yellow-orange	119	75.10 (75.00)	6.50 (6.66)	11.76 (11.66)
HL_{II}	$C_{15}H_{15}N_2OBr$	Yellow-orange	150	56.58 (56.60)	4.75 (4.71)	8.81 (8.80)
HL_{III}	$C_{15}H_{14}N_2OBr_2$	Red-brown	135	56.57 (56.81)	3.50 (3.55)	7.11 (7.07)

[a] Further studies with title ligands, using different metal, are in progress and will be published in due course.

[b] the analytical data agrees satisfactory with the expected formulae represented as given in Fig. 1 (see experimental). Air-stable, high melting temperature, colored, insoluble in water, but soluble in hot methanol, and coordinate solvent.

IR spectra exhibit a medium to strong band in the region 1625-1640 cm^{-1} which could be assigned to υC=N stretching vibration [1,2]. The investigation of Rossmey and Mecke [13] on deuterated phenolic derivatives showed that the higher frequency band would be related to δOH, whereas the band within 1100 cm^{-1} can be due to υC-OH. The higher value of the δOH may account for the existence of hydrogen bonding. Luttke [14] found that the -OH in hydroxy compounds suffered a blue shift when the OH group is involved in a hydrogen bond. Coggeshall [15] and El-Sonbati [16] found three kinds of bonded-OH structures on the basis of the frequencies: i) only the oxygen is in the bridge while the hydrogen is free, ii) a polymer chain is formed in which, both hydrogen and oxygen atoms participate in the hydrogen bond, iii) dimer associates are formed.

The IR spectral data exhibits a very strong band at 1585 ± 10 cm^{-1} is apparent and assignable to υC=C of the phenyl ring. The very interesting region is that in the frequency range 2800-3550 cm^{-1}. This is a characteristic region to the vibrational frequency of the -OH group at 2900 cm^{-1} of medium appearance and a broad at 3400 - 3550 cm^{-1}.

The mass spectrum of HL_I (Fig. 2) shows mass peaks at m/z 240, 223, 149, 120, 77 and 55. The first mass peak corresponds to the ligand and the second one proceed by loss of OH. The mass spectrum of HL_{II} shows mass peaks at m/z 319, 301, 223, 195, 159, 119, 77 and 55. The first mass peaks corresponds to the ligand, the second one proceed by loss of OH and the third proceed by loss of Br. The mass spectrum of HL_{III} shows mass peaks at m/z 398, 318, 198, 158, 121, 77 and 55. The first mass peak corresponds to the ligand and the second one proceed by loss of Br.

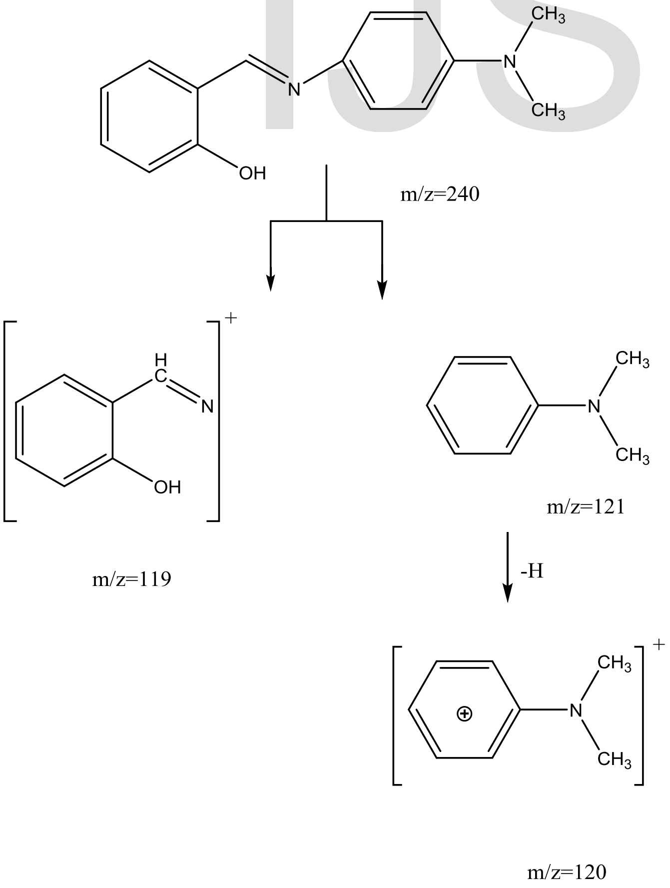


Fig. 2. Mass spectrum of the ligand (HL_{II}).

3.2. Molecular parameters

The selected geometrical structures of the investigated ligands are calculated by optimizing their bond lengths and bond angles. The calculated molecular structures for ligands (HL_I-HL_{III}) are shown in Fig. 3. The selected geometric parameters are listed in Tables 2-4. The surfaces of frontier molecular orbital theory (FMOs) are shown in Fig. 4.

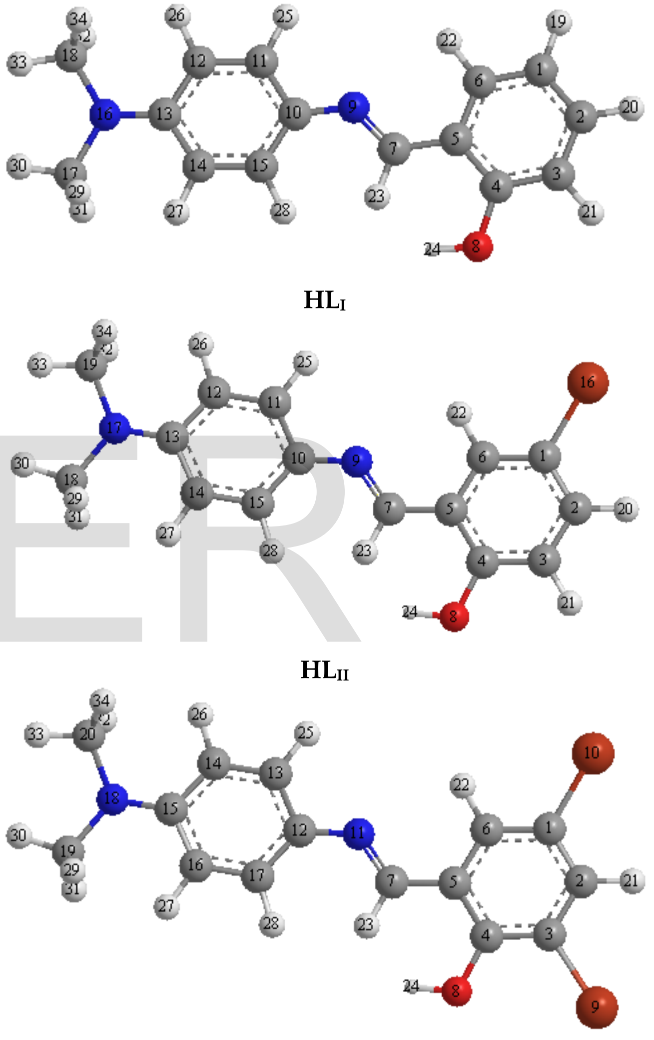


Fig. 3. The calculated molecular structures of the investigated ligands.

The HOMO–LUMO energy gap, ΔE, which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller is the value of ΔE, the more is the reactivity of the compound [17,18]. The calculated quantum chemical parameters are given in Table 5. Additional parameters such as ΔE, absolute Electronegativities, χ, chemical potentials, Pi, absolute hardness, η, absolute softness, σ, global electrophilicity, ω [19-21], global softness, S, and additional electronic charge, ΔN_{max}, have been calculated according to the following equations [22]:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (3)$$

$$\sigma = 1/\eta \quad (4)$$

$$Pi = -\chi \quad (5)$$

$$S = \frac{1}{2\eta} \quad (6)$$

$$\omega = Pi^2 / 2\eta \quad (7)$$

$$\Delta N_{\max} = -Pi/\eta \quad (8)$$

The values of the HOMO–LUMO energy gap, ΔE, for HL_I, HL_{II} and HL_{III} are calculated and found to be 0.1823, 0.1819 and 0.1856 a.u., respectively, so the ligand HL_{II} more stable and highly reactive than ligand HL_I and ligand HL_{III}.

Bond lengths (Å)		Bond angles (°)	
C(18)-H(34)	1.114	H(34)-C(18)-H(33)	105.711
C(18)-H(33)	1.112	H(34)-C(18)-H(32)	111.368
C(18)-H(32)	1.114	H(34)-C(18)-N(16)	111.44
C(17)-H(31)	1.114	H(33)-C(18)-H(32)	105.691
C(17)-H(30)	1.112	H(33)-C(18)-N(16)	110.866
C(17)-H(29)	1.114	H(32)-C(18)-N(16)	111.467
C(15)-H(28)	1.101	H(31)-C(17)-H(30)	105.706
C(14)-H(27)	1.102	H(31)-C(17)-H(29)	111.365
C(12)-H(26)	1.102	H(31)-C(17)-N(16)	111.451
C(11)-H(25)	1.106	H(30)-C(17)-H(29)	105.697
O(8)-H(24)	0.968	H(30)-C(17)-N(16)	110.862
C(7)-H(23)	1.097	H(29)-C(17)-N(16)	111.46
C(6)-H(22)	1.103	C(18)-N(16)-C(17)	120.552
C(3)-H(21)	1.104	C(18)-N(16)-C(13)	119.685
C(2)-H(20)	1.103	C(17)-N(16)-C(13)	119.762
C(1)-H(19)	1.103	H(27)-C(14)-C(15)	114.784
C(10)-C(15)	1.345	H(27)-C(14)-C(13)	121.824
C(14)-C(15)	1.344	C(15)-C(14)-C(13)	123.392
C(13)-C(14)	1.35	C(14)-C(13)-C(12)	114.176
C(12)-C(13)	1.35	C(14)-C(13)-N(16)	122.946
C(11)-C(12)	1.343	C(12)-C(13)-N(16)	122.877
C(10)-C(11)	1.346	H(26)-C(12)-C(13)	122.235
C(1)-C(6)	1.341	H(26)-C(12)-C(11)	114.871
C(5)-C(6)	1.349	C(13)-C(12)-C(11)	122.894
C(4)-C(5)	1.354	H(28)-C(15)-C(10)	122.046
C(3)-C(4)	1.346	H(28)-C(15)-C(14)	116.283
C(2)-C(3)	1.34	C(10)-C(15)-C(14)	121.67
C(1)-C(2)	1.339	H(25)-C(11)-C(12)	117.965
N(16)-C(18)	1.487	H(25)-C(11)-C(10)	119.814
N(16)-C(17)	1.487	C(12)-C(11)-C(10)	122.221
C(13)-N(16)	1.283	C(15)-C(10)-C(11)	115.646
N(9)-C(10)	1.27	C(15)-C(10)-N(9)	128.23
C(7)-N(9)	1.268	C(11)-C(10)-N(9)	116.124
C(4)-O(8)	1.363	C(10)-N(9)-C(7)	127.507
C(5)-C(7)	1.352	H(23)-C(7)-N(9)	117.121
		H(23)-C(7)-C(5)	117.834
		N(9)-C(7)-C(5)	125.045
		H(22)-C(6)-C(1)	116.36
		H(22)-C(6)-C(5)	121.745
		C(1)-C(6)-C(5)	121.896
		H(24)-O(8)-C(4)	111.008
		C(6)-C(5)-C(4)	118.507
		C(6)-C(5)-C(7)	120.057
		C(4)-C(5)-C(7)	121.435
		C(5)-C(4)-C(3)	118.929
		C(5)-C(4)-O(8)	122.795
		C(3)-C(4)-O(8)	118.276
		H(21)-C(3)-C(4)	119.091
		H(21)-C(3)-C(2)	118.755

Table 2. The selected geometric parameters for HL_I.

Table 3. The selected geometric parameters for HL_{II}.

Bond lengths (Å)	Bond angles (°)

C(19)-H(34)	1.114	H(34)-C(19)-H(33)	105.702
C(19)-H(33)	1.112	H(34)-C(19)-H(32)	111.366
C(19)-H(32)	1.114	H(34)-C(19)-N(17)	111.455
C(18)-H(31)	1.114	H(33)-C(19)-H(32)	105.703
C(18)-H(30)	1.112	H(33)-C(19)-N(17)	110.864
C(18)-H(29)	1.114	H(32)-C(19)-N(17)	111.451
C(15)-H(28)	1.102	H(31)-C(18)-H(30)	105.699
C(14)-H(27)	1.102	H(31)-C(18)-H(29)	111.364
C(12)-H(26)	1.102	H(31)-C(18)-N(17)	111.448
C(11)-H(25)	1.106	H(30)-C(18)-H(29)	105.703
O(8)-H(24)	0.968	H(30)-C(18)-N(17)	110.869
C(7)-H(23)	1.097	H(29)-C(18)-N(17)	111.458
C(6)-H(22)	1.103	C(19)-N(17)-C(18)	120.551
C(3)-H(21)	1.104	C(19)-N(17)-C(13)	119.684
C(2)-H(20)	1.103	C(18)-N(17)-C(13)	119.765
C(10)-C(15)	1.345	H(27)-C(14)-C(15)	114.78
C(14)-C(15)	1.344	H(27)-C(14)-C(13)	121.828
C(13)-C(14)	1.35	C(15)-C(14)-C(13)	123.392
C(12)-C(13)	1.35	C(14)-C(13)-C(12)	114.182
C(11)-C(12)	1.343	C(14)-C(13)-N(17)	122.937
C(10)-C(11)	1.346	C(12)-C(13)-N(17)	122.88
C(1)-C(6)	1.342	H(26)-C(12)-C(13)	122.239
C(5)-C(6)	1.35	H(26)-C(12)-C(11)	114.869
C(4)-C(5)	1.353	C(13)-C(12)-C(11)	122.892
C(3)-C(4)	1.346	H(28)-C(15)-C(10)	122.049
C(2)-C(3)	1.34	H(28)-C(15)-C(14)	116.29
C(1)-C(2)	1.339	C(10)-C(15)-C(14)	121.661
N(17)-C(19)	1.487	H(25)-C(11)-C(12)	117.97
N(17)-C(18)	1.487	H(25)-C(11)-C(10)	119.818
C(13)-N(17)	1.282	C(12)-C(11)-C(10)	122.212
C(1)-Br(16)	1.894	C(15)-C(10)-C(11)	115.66
N(9)-C(10)	1.27	C(15)-C(10)-N(9)	128.221
C(7)-N(9)	1.268	C(11)-C(10)-N(9)	116.119
C(4)-O(8)	1.363	C(10)-N(9)-C(7)	127.524
C(5)-C(7)	1.352	H(23)-C(7)-N(9)	117.085
		H(23)-C(7)-C(5)	117.879
		N(9)-C(7)-C(5)	125.036
		H(22)-C(6)-C(1)	117.397
		H(22)-C(6)-C(5)	120.833
		H(20)-C(2)-C(3)	119.652
		H(20)-C(2)-C(1)	121.5
		C(3)-C(2)-C(1)	118.848
		C(6)-C(1)-C(2)	119.632
		C(6)-C(1)-Br(16)	120.592
		C(2)-C(1)-Br(16)	119.775
		C(1)-C(6)-C(5)	121.77
		H(24)-O(8)-C(4)	111.161
		C(6)-C(5)-C(4)	118.592
		C(6)-C(5)-C(7)	120.131

Table 4. The selected geometric parameters for HL$_{III}$.

Bond lengths (Å)		**Bond angles (°)**	
C(20)-H(34)	1.114	H(34)-C(20)-H(33)	105.698
C(20)-H(33)	1.112	H(34)-C(20)-H(32)	111.363
C(20)-H(32)	1.114	H(34)-C(20)-N(18)	111.451
C(19)-H(31)	1.114	H(33)-C(20)-H(32)	105.702
C(19)-H(30)	1.112	H(33)-C(20)-N(18)	110.87
C(19)-H(29)	1.114	H(32)-C(20)-N(18)	111.458
C(17)-H(28)	1.102	H(31)-C(19)-H(30)	105.7
C(16)-H(27)	1.102	H(31)-C(19)-H(29)	111.365
C(14)-H(26)	1.102	H(31)-C(19)-N(18)	111.451
C(13)-H(25)	1.106	H(30)-C(19)-H(29)	105.708
O(8)-H(24)	0.968	H(30)-C(19)-N(18)	110.872
C(7)-H(23)	1.097	H(29)-C(19)-N(18)	111.446
C(6)-H(22)	1.103	C(20)-N(18)-C(19)	120.546
C(2)-H(21)	1.103	C(20)-N(18)-C(15)	119.689
C(12)-C(17)	1.345	C(19)-N(18)-C(15)	119.765
C(16)-C(17)	1.344	H(27)-C(16)-C(17)	114.783
C(15)-C(16)	1.35	H(27)-C(16)-C(15)	121.824
C(14)-C(15)	1.35	C(17)-C(16)-C(15)	123.393
C(13)-C(14)	1.343	C(16)-C(15)-C(14)	114.181
C(12)-C(13)	1.346	C(16)-C(15)-N(18)	122.945
C(1)-C(6)	1.341	C(14)-C(15)-N(18)	122.874
C(5)-C(6)	1.349	H(26)-C(14)-C(15)	122.238
C(4)-C(5)	1.355	H(26)-C(14)-C(13)	114.871
C(3)-C(4)	1.349	C(15)-C(14)-C(13)	122.891
C(2)-C(3)	1.342	H(28)-C(17)-C(12)	122.054
C(1)-C(2)	1.339	H(28)-C(17)-C(16)	116.284
N(18)-C(20)	1.487	C(12)-C(17)-C(16)	121.662
N(18)-C(19)	1.487	H(25)-C(13)-C(14)	117.968
C(15)-N(18)	1.282	H(25)-C(13)-C(12)	119.815
N(11)-C(12)	1.27	C(14)-C(13)-C(12)	122.216
C(7)-N(11)	1.268	C(17)-C(12)-C(13)	115.656
C(1)-Br(10)	1.895	C(17)-C(12)-N(11)	128.234
C(3)-Br(9)	1.901	C(13)-C(12)-N(11)	116.11
C(4)-O(8)	1.365	C(12)-N(11)-C(7)	127.598
C(5)-C(7)	1.353	H(23)-C(7)-N(11)	116.856
		H(23)-C(7)-C(5)	118.042
		N(11)-C(7)-C(5)	125.102
		H(22)-C(6)-C(1)	117.286
		H(22)-C(6)-C(5)	121.001
		C(1)-C(6)-C(5)	121.713
		H(24)-O(8)-C(4)	111.817
		C(6)-C(5)-C(4)	118.886
		C(6)-C(5)-C(7)	119.642
		C(4)-C(5)-C(7)	121.472
		C(5)-C(4)-C(3)	118.714
		C(5)-C(4)-O(8)	121.732
		C(3)-C(4)-O(8)	119.554
		C(4)-C(3)-C(2)	121.972
		C(4)-C(3)-Br(9)	120.681

HOMO **LUMO**

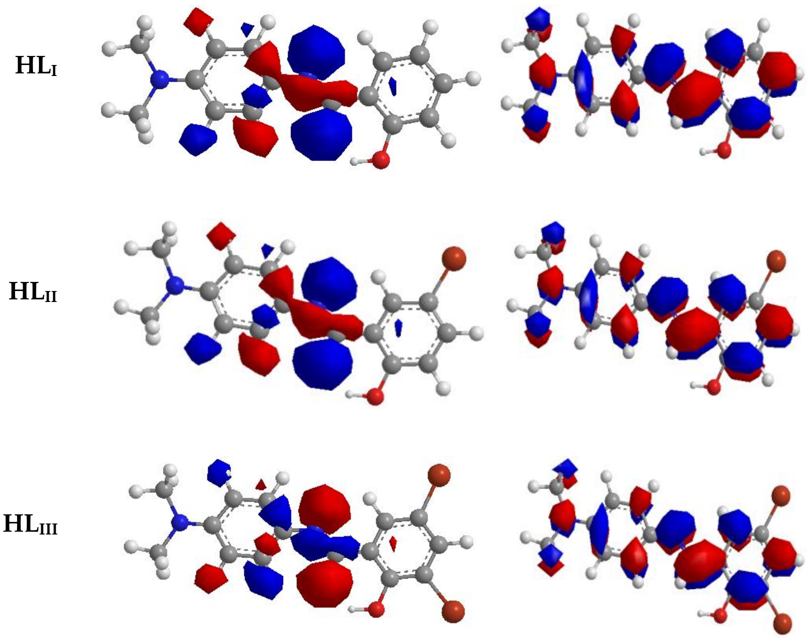


Fig. 4. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the ligands.

Table 5. The calculated quantum chemical parameters of the investigated ligands (HL$_I$, HL$_{II}$ and HL$_{III}$).

Compound	HL$_I$	HL$_{II}$	HL$_{III}$
HOMO (a.u)	-0.2917	-0.2913	-0.2905
LUMO (a.u)	-0.1094	-0.1094	-0.1049
ΔE (a.u)	0.1823	0.1819	0.1856
χ (a.u)	0.2005	0.2004	0.1977
η (a.u)	0.0912	0.0909	0.0928
σ (a.u)$^{-1}$	10.9703	10.9945	10.7753
Pi (a.u)	-0.2005	-0.2004	-0.1977
S (a.u)$^{-1}$	5.4852	5.4972	5.3876
ω (a.u)	0.2205	0.2207	0.2106
ΔN$_{max}$	2.1997	2.2029	2.1305

3.3. Potentiometric studies

The average number of the protons associated with ligands (HL$_I$, HL$_{II}$ and HL$_{III}$) at different pH values, $\bar{n}_A$, was calculated from the titration curves of the acid in the absence and presence of ligands by applying the following equation:

$$\bar{n}_A = Y \pm \frac{(V_1 - V_2)(N^o + E^o)}{(V^o - V_1)TC^o_L} \qquad \textbf{(9)}$$

where Y is the number of available protons in ligands (HL$_I$, HL$_{II}$ and HL$_{III}$) (Y=1) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, $V°$ is the initial volume (50 cm^3) of the mixture, TC°$_L$ is the total concentration of the reagent, N° is the normality of sodium hydroxide solution and E° is the initial concentration of the free acid. Thus, the formation curves ($\bar{n}_A$ *vs.* pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that hydroxybenzlidene has one ionizable proton (the enolized hydrogen ion of the hydroxyl group in the benzene ring, pK^H). Different computational methods were applied to evaluate the dissociation constant [23]. Three replicate titrations were performed; the average values obtained are listed in Table ~~5~~ 6. The completely protonated form of ligands (HL$_I$, HL$_{II}$ and HL$_{III}$) has one dissociable proton, that dissociates in the measurable pH range. The deprotonation of the hydroxyl group most probably results in the formation of stable intramolecular H–bonding with nirtogen atom. Such an interaction decreases the dissociation process, *i.e.* increases the pK^H value [24]. An inspection of the results in Table 6 reveals that the pK^H values of HL$_I$ and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents [25]. The Br and two Br derivatives (HL$_{II}$ and HL$_{III}$) have a higher acidic character (lower pK^H value). This is quite reasonable because the presence of Br and two Br groups (i.e. an electron withdrawing effect) will lead the electron density by their high acidic character found in the ligands (HL$_{II}$ and HL$_{III}$).

Table 6. Thermodynamic function of Hydroxybenzlidene-

compounds in 30% (v/v) methanol-water mixture and 0.1 M KCl at different temperatures.

Compound	T/K	Dissociation constant pK^H	Free energy change (kJ mol^{-1}) ΔG	Enthalpy change (kJ mol^{-1}) ΔH	Entropy change (J mol^{-1} K^{-1}) $-\Delta S$
HL_I	298	10.50	60.92	95.70	197.89
	308	10.45	62.63		196.97
	318	10.40	63.92		196.15
HL_{II}	298	9.60	55.70	86.16	180.97
	308	9.54	57.17		179.91
	318	9.51	58.45		179.41
HL_{III}	298	9.30	53.95	76.59	175.54
	308	9.26	55.50		174.86
	318	9.22	56.67		174.15

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}_A$) *vs*. the free ligands exponent (pL), according to Irving and Rossotti [26]. The average number of the reagent molecules attached per metal ion, $\bar{n}$, and free ligands exponent, pL, can be calculated using eqs. 10 and 11:

$$\bar{n} = \frac{(V_3 - V_2)(N^o + E^o)}{(V^o - V_2).\bar{n}_A.TC^o_M} \qquad \textbf{(10)}$$

and

$$pL = \log_{10} \frac{\sum_{n=o}^{n=J} \beta^H_n \left(\frac{1}{[H^+]}\right)^n}{TC^o_L - \bar{n}.TC^o_M} . \frac{V^o + V_3}{V^o} \qquad \textbf{(11)}$$

where TC°_M is the total concentration of the metal ion present in the solution, β^H_n is the overall proton-reagent stability constant. V_1, V_2 and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively. These curves were analyzed and the successive metal-ligand stability constants were determined using different computational methods [27,28]. The values of the stability constants (log K_1 and log K_2) are given in Table 7.

Table 7. Stepwise stability constants for for the complexation of hydroxybenzlidene compounds in 30% (v/v) methanol-water mixture and 0.1 M KCl at different temperatures.

Comp.	M^{n+}	298 K		308 K		318 K	
		log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
HL_I	Mn^{2+}	3.54	2.84	3.83	3.13	4.01	3.21
	Co^{2+}	3.72	3.02	3.97	3.27	4.12	3.32
	Ni^{2+}	3.87	3.17	4.09	3.39	4.22	3.62
	Cu^{2+}	4.00	3.30	4.30	3.60	4.51	3.71
	Zn^{2+}	3.91	3.20	4.10	3.41	4.39	3.69
HL_{II}	Mn^{2+}	3.36	2.66	3.55	2.85	3.70	3.11
	Co^{2+}	3.51	2.81	3.79	3.09	3.92	3.30
	Ni^{2+}	3.66	2.96	3.82	3.12	4.30	3.50
	Cu^{2+}	3.80	3.11	4.04	3.34	4.22	3.40
	Zn^{2+}	3.71	3.01	3.94	3.24	4.10	3.30
HL_{III}	Mn^{2+}	3.19	2.49	3.33	2.63	3.51	2.91
	Co^{2+}	3.34	2.64	3.57	2.87	3.72	3.01
	Ni^{2+}	3.49	2.79	3.69	2.99	3.82	3.01
	Cu^{2+}	3.62	2.92	3.80	3.10	4.01	3.40
	Zn^{2+}	3.51	2.81	3.70	3.01	3.99	3.30

The following general remarks can be pointed out:

(i) The maximum value of n was ≈ 2 indicating the formation of 1:1 and 1:2 (metal: ligand) complexes only.

(ii) The metal ion solution used in the present study was very dilute (2×10^{-5} M); hence there was no possibility of formation of polynuclear complexes [29,30].

(iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [31].

(iv) In most cases, the color of the solution after complex formation was observed to be different from the color of the ligand at the same pH.

(v) For the same ligand at constant temperature, the stability of the chelates increases in the order $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ [32-34]. This order largely reflects the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion [35] and the crystal field stabilization energies [35]. The greater stability of Cu^{2+} complexes is produced by the well-known Jahn-Teller effect [36].

An inspection of the results in Table 7 reveals that the stability constant values of the complexes of HL_{I}, HL_{II} and HL_{III} are influenced by the inductive or mesomeric effect of the substituents. This behavior correlates with the effect of substitution on the phenyl ring as follows:

(i) The high stability of HL_{I} complexes can be attributed to the no presence of groups relative to the phenolic group.

(ii) The low stability of HL_{II} complexes can be attributed to the presence of the Br group (i.e. an electron withdrawing effect), in the p-position relative to the phenolic group. This is caused by the negative indicative effect of the Br group, which decreases its ability for chelation, and therefore the stability of the complexes.

(iii) The lowest stability of HL_{III} complexes can be attributed to the presence of the two Br groups (i.e. an electron withdrawing effect), in the o- and p-position relative to the phenolic group. This is caused by the negative indicative effect of the two Br group, which decreases its ability for chelation, and therefore the stability of the complexes.

(iv) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order: $HL_{III} < HL_{II} < HL_{I}$.

3.4. Effect of temperature.

The dissociation constant (pK^{H}) for the ligands as well as the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} have been evaluated at (298 , 308, 318) K, and are given in Tables 8-10, respectively. The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^{H} or log K *vs.* 1/T using the graphical representation of van't Hoff eqs. 12 and 13:

$$\Delta G = -2.303\ RT \log K = \Delta H - T\,\Delta S \qquad \textbf{(12)}$$

or

$$\log K = (-\Delta H\ /\ 2.303\ R)(1/T) + (\Delta S / 2.303\ R) \qquad \textbf{(13)}$$

where R gas constant = 8.314 $J.mol^{-1}.K^{-1}$, K dissociation constant for the ligand stability and T temperature (K)

From the ΔG and ΔH values one can deduce the entropy ΔS using the well known relationship:

$$\Delta S = (\Delta H - \Delta G)\ /\ T \qquad (14)$$

All thermodynamic parameters of the dissociation process of HL_{I} – HL_{II} are recorded in Tables 6, 8-10. From these results the following conclusions can be made:

(i) The pK^{H} values decrease with increasing temperature, i.e., the acidity of the ligands increases, independent of the nature of the substituent.

(ii) A positive value of ΔH indicates that the process is endothermic [37].

(iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous [38].

(iv) The dissociation processes for the compounds have negative values of ΔS due to increased order as a result of the solvation processes.

Table 8. Thermodynamic functions for the complexation of HL_{I}

in 30 % (v/v) methanol-water mixture.

M^{n+}	*T*/K	Free energy change (kJ mol^{-1})		Enthalpy change (kJ mol^{-1})		Entropy change (J mol^{-1} K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	20.20	16.20	42.71	33.76	211.11	167.67
	308	22.53	18.46			211.82	169.54
	318	24.42	19.55			211.10	167.63
Co^{2+}	298	21.23	17.23	36.37	27.40	193.29	149.78
	308	23.41	19.28			194.11	151.58
	318	25.09	20.21			193.27	149.74
Ni^{2+}	298	22.08	18.09	31.83	39.00	180.91	191.59
	308	24.12	19.99			181.66	191.55
	318	25.69	21.92			180.90	191.59
Cu^{2+}	298	22.82	18.83	46.34	40.95	232.09	200.63
	308	25.36	21.23			232.79	201.91
	318	27.46	22.83			232.08	200.61
Zn^{2+}	298	22.31	18.26	43.43	44.37	220.61	210.16
	308	24.18	20.11			219.52	209.35
	318	26.73	22.47			220.64	210.18

Table 9. Thermodynamic functions for the complexation of HL_{II} in 30 % (v/v) methanol-water mixture.

M^{n+}	*T*/K	Free energy change (kJ mol^{-1})		Enthalpy change (kJ mol^{-1})		Entropy change (J mol^{-1} K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	19.17	15.18	30.87	40.74	167.94	187.65
	308	20.94	16.81			168.22	186.85
	318	22.53	18.94			167.93	187.62
Co^{2+}	298	20.03	16.03	37.33	44.51	192.48	203.15
	308	22.35	18.22			193.77	203.66
	318	23.87	20.09			192.45	203.14
Ni^{2+}	298	20.88	16.89	57.73	48.76	263.80	220.29
	308	22.53	18.40			260.57	218.04
	318	26.18	21.31			263.87	220.34
Cu^{2+}	298	21.68	17.75	38.15	26.46	200.78	148.36
	308	23.83	19.70			201.21	149.88
	318	25.69	20.70			200.77	148.33
Zn^{2+}	298	21.17	17.17	35.44	26.46	189.95	146.44
	308	23.24	19.11			190.50	147.96
	318	24.96	20.09			189.94	146.41

Table 10. Thermodynamic functions for the complexation of HL_{III} in 30 % (v/v) methanol-water mixture.

M^{n+}	*T*/K	Free energy change (kJ mol^{-1})		Enthalpy change (kJ mol^{-1})		Entropy change (J mol^{-1} K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Mn^{2+}	298	18.20	14.21	28.98	37.95	158.33	175.03
	308	19.64	15.51			157.85	173.58
	318	21.37	17.72			158.34	175.07
Co^{2+}	298	19.06	15.06	34.54	33.64	179.86	163.44
	308	21.05	16.93			180.50	164.18
	318	22.65	18.33			179.85	163.43
Ni^{2+}	298	19.91	15.92	30.00	20.13	167.48	120.96
	308	21.76	17.63			168.04	122.60
	318	23.26	18.33			167.47	120.93
Cu^{2+}	298	20.66	16.66	35.34	43.41	187.90	201.59
	308	22.41	18.28			187.50	200.31
	318	24.42	20.71			187.91	201.62
Zn^{2+}	298	20.03	16.03	43.43	44.35	212.96	202.63
	308	21.82	17.75			211.86	201.63
	318	24.29	20.09			212.98	202.65

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Tables 8-10. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then he considered as the sum of two contributions: (a) release of H_2O molecules, and (b) metal-ligand bond formation. Examination of these values shows that:

(i) The stepwise stability constant (log K_1 and log K_2) for ligand complexes increases with increasing temperature, i.e., its stability constants increase with increasing the temperature.

(ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process.

(iii) The ΔH values are positive, meaning that these processes are endothermic.

(iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favorable.

4. Conclusions

The ligands of hydroxybenzlidene compounds have been synthesized and characterized using spectroscopic techniques. The molecular structures of the investigated compounds (HL_{I}, HL_{II} and HL_{III}) are optimized. The values of the HOMO–LUMO energy gap, ΔE, for HL_{I}, HL_{II} and HL_{III} are calculated and found to be 0.1823, 0.1819 and 0.1856 a.u., respectively, dependent on the nature of the substituent. The proton-ligand dissociation constant of (HL_{I}, HL_{II} and HL_{III}) and metal-ligand stability constants of their complexes with metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) were determined at different temperatures. The stability constants of the formed complexes increases in the order $Mn^{+2} < Co^{+2} < Ni^{2+} < Zn^{2+} < Cu^{2+}$. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable.

References

[1] A.M. Burger, G. Kaur, M.C. Alley, J.G. Supko, L. Malspeis, M.R. Grever, E.A. Sausville, J. Cancer Res. 55 (1995) 2794-2799.

[2] N.M. Hosny, M.A. Hussien, F.M. Radwan, N. Nawar, Spectrochim. Acta A 132 (2014) 121-129.

[3] T. Hidaka, K. Hosoe, I. Katsumi, T. Yamashita, K. Watanabe, J. Pharm. Pharmacol. 38 (1986) 244–247.

[4] A.A.R. Silva, A.J.S. Góes, L.T. Limaand, M.B.S. Maia, J. Chem. Pharmaceut. Bull. 51 (2003) 1351-1355.

[5] M. Brvar, A. Perdih, V. Hodnik, M. Renko, G. Anderluh, R. Jerala, T. Solmajer, J. Bioorg. Med. Chem. 20 (2012) 2572–2580.

[6] A.A. El-Bindary, A.Z. El-Sonbati, M.A. Diab, M.K. Abd El-Kader, J. Chem. art. no. 682186 (2013).

[7] A.A. El-Bindary, A.Z. El-Sonbati, E.H. El-Mosalamy, E.M. El-Santawy, Spectrochim. Acta A 57 (2001) 2359–2365.

[8] T.M. El-Gogary, A.A. El-Bindary, A.S. Hilali, Spectrochim. Acta A 58 (2002) 447–455.

[9] A.A. El-Bindary, A.Z. El-Sonbati, M.A. Diab, E.E. El-Katori, H.A. Seyam, Int. J. Adv. Res. 2 (2014) 493–502.

[10] R.G. Bates, M. Paabo, R.A. Robinson, J. Phys. Chem. 67 (1963) 1833–1838.

[11] H.M. Irving, M.G. Miles, L.D. Pettit, Anal. Chim. Acta 38 (1967) 475–488.

[12] N.A. El-Ghamaz, M.M. Ghoneim, A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.K. Abd El-Kader, J. Saudi Chem. Soc. (DOI: 10.1016/j.jscs.2014.03.010).

[13] G. Rossmey and R. Mecke, Z. Electrochem. 59 (1956) 866-874.

[14] S. Califan and W. Luttke, Z. Phys. Chem. 5 (1955) 240-251.

[15] N.D. Coggeshall, J. Am. Chem. Soc. 69 (1947) 1620-1624.

[16] M.A. Diab, A.Z. El-Sonbati, Polym. Deg. Stab., 29 (1990) 271-277.

[17] T.A. Yousef, G.M. Abu El-Reash, M. Al-Jahdali, E.R. El-Rakhawy, J. Mol. Struct. 1053 (2013) 15-21.

[18] G. Gao, C. Liang, Electrochim. Acta 52 (2007) 4554-4559.

[19] R.G. Pearson, J. Org. Chem. 54 (1989) 1423-1430.

[20] P. Geerlings, F. DeProft, W. Langenaeker, Chem. Rev. 103 (2003) 1793-1873.

[21] P.K. Chattaraj, S. Giri, J. Phys. Chem. A 111 (2007) 11116-11121.

[22] D. Kivelson, R. Niemen, J. Chem. Phys. 35 (1961) 149-155.

[23] H. Irving, H.S. Rossotti, J. Chem. Soc. 76 (1954) 2904–2910.

[24] I. Shehatta, A.A. El-Bindary, Thermochim. Acta A 237 (1994) 357–368.

[25] A.A. Al-Sarawy, A.A. El-Bindary, A.Z. El-Sonbati, T.Y. Omar, Chem. Pap. 59 (2005) 261–266.

[26] H. Irving, J. Rossotti, J. Chem. Soc. (1953) 3397-3405.

[27] F.J.C. Rossotti, H.S. Rossotti, Acta Chem. Scand. 9 (1955) 1166–1176.

[28] M.T. Beck, I. Nagybal, Chemistry of complex equilibrium, Wiley, New York, 1990.

[29] P. Sanyal, G.P. Sengupta, J. Ind. Chem. Soc. 67 (1990) 342–346.

[30] S. Sridhar, P. Kulanthaip, P. Thillaiarasu, V. Thanikachalam, G.J. Manikandan, World J. Chem. 4 (2009) 133–140.

[31] V.D. Athawale, V.J. Lele, Chem. Eng. Data 41 (1996) 1015–1019.

[32] G.A. Ibañez, G.M. Escandar, Polyhedron 17 (1998) 4433–4441.

[33] W.U. Malik, G.D. Tuli, R.D. Madan, Selected Topics in Inorganic Chemistry, 3rd Edition, Chand S. & Company LTD, New Delhi, 1984.

[34] G.C. Mohamed, M.M. Omar, A. Ibrahim, Eur. J. Med. Chem. 44 (2009) 4801-4812.

[35] F.R. Harlly, R.M. Burgess, R.M. Alcock, Solution Equilibria, p. 257. Ellis Harwood, Chichester, 1980.

[36] L.E. Orgel, p. 55, Methuen, London, 1966.

[37] K.D. Bhesaniya, S. Baluja, J. Mol. Liq. 190 (2014) 190-195.

[38] A. Bebot-Bringaud, C. Dange, N. Fauconnier, C. Gerard, J. Inorg. Biochem. 75 (1999) 71–78.