Mixed-Ligand Chelate Formation of Co(II), Ni(II), Cu(II) and Zn(II) Ions with Schiff Base as Main Ligand and Amino Acid as Co-Ligand

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Authors' contributions

This work was carried out in collaboration between all authors. Author MMEA supervision the laboratory work and wrote the protocol of the first draft of the manuscript and literature searches. Author AAM managed the data analysis and approved the final manuscript with the assistance of the first author. Author AME managed some laboratory techniques and some laboratory analysis. Author FSA preformed all the laboratory work and she is M. Sc student under the supervision of Prof. Dr. M.M. El-ajaily in collaboration with the other authors. Finally all authors read and approved the final manuscript.

| *Original Research Article* |

ABSTRACT

A bidentate NO type Schiff base ligand (L^1) has been obtained by the condensation reaction of 4-dimethylaminobenzaldehyde and 2-aminophenol and used as main ligand and *l*-Alanine as co-ligand (L^2), Four novel mixed ligand chelates of composition $[M(L^1L^2)(H_2O)_2].nH_2O$, where M represents, Co(II), Ni(II), Cu(II) and Zn(II) ions, in which n= 1, 1.7, 5 and 7 as sited later for chelates. The resulting Schiff base and the mixed ligand chelates were characterized by CHN elemental analysis, molar conductivity, magnetic moment, UV/Vis, IR, ^{1}H-NMR and mass spectra. All the obtained physiochemical data showed an octahedral structures.

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1. INTRODUCTION

It is well known that mixed ligand coordination complexes play an important role in biological systems [1]. Amino acids have special importance compared to other chemical compounds in the sense that they are regarded as the foundation stones of living organisms. Fostered by the crucial role of amino acids in our life, studying their structural, chemical and physical properties becomes very necessary to explain their behaviour and potential applications [2]. Cu(II) mixed ligand chelate with iminodiacetic and hippuric acids has been synthesized and investigated by using physicochemical techniques in terms; CHN elemental analyses, molar conductivity, magnetic moment measurements, IR and electronic spectra. The obtained data suggested the existence of an octahedral structure [3]. The mixed ligand chelates of some divalent transition metal ions derived from 4-chloroaniline with salicylaldehyde or benzaldehyde, also 2-aminophenol or 4-nitroaniline with 2-hydroxyacetophenone, as well as with 4, 4-dimethylaminobenzaldehyde have been synthesized and investigated by different physicochemical techniques. The synthesized mixed ligand chelates were assayed for antibacterial activity against some pathogenic bacteria. The mixed ligand chelates exhibited higher antibacterial activity than the free ligands because of chelation [4,5].

The present work aims to synthesis and characterize the structures of the mixed ligand chelates in which part of the ligands represents Schiff base. It is believed that this study would add to the present knowledge in coordination chemistry. The current experiment therefore, provides some scientific justification for the utilization of chemicals usefulness for the researchers in organic and inorganic chemistry field. So that, we describe the synthesis of four mixed ligand chelates and a Schiff base which used as main ligand with pure *l*-Alanine as co-ligand. Further research will be done to investigate the importance of these chelates in different chemical applications.

2. EXPERIMENTAL

2.1 Materials and Methods

All chemicals and reagents used in this investigation are of pure grade (BDH or Aldrich).

They include; 4-dimethylaminobenzaldehyde, 2-aminophenol, *l*-Alanine, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, DMSO, DMF, NH_4OH, ethanol and double distilled water. The Schiff base and the mixed ligand chelates were subjected to different physicochemical analyses such as, elemental analysis using 2400-CHN elemental analyzer. The molar conductivity of the chelates was measured in DMF solvent using digital conductivity meter CMD-650, at Chemistry Department, Benghazi University, Benghazi, Libya. The infrared spectra were carried out by using KBr disc technique with IFS-25 DPUS/IR spectrometer. Proton nuclear magnetic resonance spectra of the ligands and their Zn(II) chelate were recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and d^6DMSO as a solvent. The electronic spectra were measured in DMSO solvent by using a Perkin-Elmer lambda-4β spectrophotometer. The mass spectra also carried out by using Shimadzu QP-2010 Plus. All the micro analyses were done at Micro-analytical centre, Cairo University, Giza, Egypt.

2.2 Synthesis of Schiff Base

The Schiff base under investigation was synthesized by dissolving 4-dimethylamino-benzaldehyde (0.01mol;1.49 g) and same moles of 2-aminophenol in 50 ml of ethanol. The mixture was stirred magnetically at 60 °C for 2 hrs. Yellow crystals were formed, then filtered, washed several times with hot ethanol, dried and recrystallized from hot methanol to give pure crystals in excellent yield of 85%.

2.3 Synthesis of Mixed Ligand Chelates

A general procedure has been adopted for the synthesis of mixed ligand chelates in basic media. 25 ml of ethanolic solutions of 0.01 mole of the salts; $CoCl_2.6H_2O$; 2.38 g, $NiCl_2.6H_2O$; 2.37 g, $CuCl_2.2H_2O$; 1.705 g, $ZnCl_2$; 1.36 g; were added to the same volume of solutions of 0.01moles of Schiff base and *l*-Alanine. Few drops of ammonium solution were added to adjust the pH>9. The mixtures were refluxed for 3hrs. The obtained chelates were filtered, washed with hot ethanol and dried in deseccator over $CaCl_2$. The yields of the chelates were in the range 75.57- 85.93%.

3. RESULTS AND DISCUSSION

The reaction of the used ligands with the metal ions yielded chelates in $1:1:1[M:L^1:L^2]$ ratio as shown below:
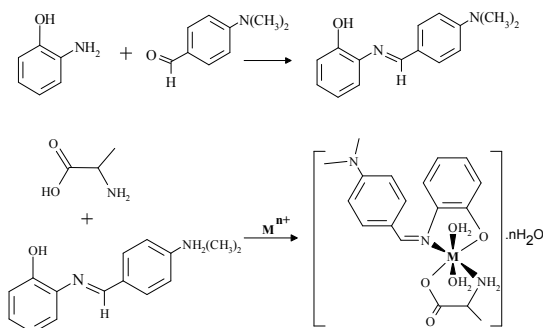
Where: M^{n+} = Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}, n= 1, 1.7, 5 and 7

3.1 Elemental Analysis and Molar Conductivity

The elemental analysis data and molar conductivity values of the synthesized mixed ligand chelates are shown in Table 1. The elemental analysis data exhibit the formation of $1:1:1[M:L^1:L^2]$ ratio, and the theoretical values of the chelates are in a good agreement with the obtained data. The purity of the Schiff base and mixed ligand chelates were tested by melting points, TLC and elemental analyses. The molar conductivity measurements of the mixed ligand chelates were carried out in DMF solvent and their values were taken as a good evidence for the presence of non-electrolytic nature [6].

3.2 Infrared Spectra

The infrared spectral data of the ligands and their mixed ligand chelates were listed in Table 2 and their spectra were given in Fig. 1. The infrared spectra of the synthesized mixed ligand chelates exhibit bands in the range of 3406-3420 cm^{-1} corresponding to the existence of water molecules as hydrated and coordinated [7]. Meanwhile, the same spectra show bands in the range of 1601-1608 cm^{-1} attributed to $\upsilon(HC=N)$ vibration, the lowering of these bands to low frequency comparing to the Schiff base (L^1) confirms the participation of this group in chelation through nitrogen atom [8]. The other coordination sites of which can take a part in coordination are NH_2 and $-CO_2$ groups, the strong evidence of sharing of these groups can be seen from the position of the bands at 3380 and 3088 cm^{-1}, respectively, in the spectrum of *l*-Alanine (L^2). The shifting of the $-NH_2$ group band to lower frequency in the spectra of the mixed ligand chelates suggest the involvement of this group in chelation via nitrogen atom [9]. The disappearance of $-CO_2$ group band of the *l*-Alanine in the spectra of the mixed ligand chelates indicates the participation of this group in bonding with the metal ions [10]. New bands in the range of 614-615 and 450-480 cm^{-1} which are not present in the free ligands are assigned to $\upsilon(M-O)$ and $\upsilon(M-N)$ vibrations and the appearance of these bands supports the involvement of oxygen and nitrogen atoms of the both ligands in chelation process [11].

3.3 Proton Nuclear Magnetic Resonance Spectra of the Ligands and Zn(II) Chelate

The ^1HNMR spectra of the ligands and their Zn(II) mixed ligand chelate of the formula $[Zn(L^1L^2)(H_2O)_2].H_2O$ show signals in the range 2.50-8.70 ppm. The singlet obtained at 8.50 ppm due to HC=N group in the spectrum of L^1 [12]. The singles in the range of 6.76 -7.16 ppm are assigned to the presence of protons of the phenyl rings. The singlet at 8.70 ppm attributed to O-H group of the Schiff base. The methyl and DMSO solvent appeared at 2.50 and 2.01 ppm, respectively. The singlet at 8.40 ppm assigned to NH_2 group of the *l*-Alanine (L^2). The shifting of the singlet of NH_2 and HC=N groups during the chelation process indicate their participation in bonding with metal ions. Also the absence of –OH group supports the involvement of this group in complexation

3.4 Mass Spectra

The mass spectral fragmentations of the Schiff base, *l*-Alanine and their Ni(II) mixed ligand chelate are shown in Table 3, Scheme 1 and Fig. 2. The peak at m/z= 238 analogous to $C_{15}H_{14}N_2O^+$. Meanwhile, another peak at m/z = 195 is equivalent to the formula $C_{13}H_9NO^+$. The structure of $C_{12}H_7O^+$ is analogous to peak at m/z = 167.Whereas, the last peak at m/z = 64 is attributing this formula $C_5H_4^+$. The base peak of *l*-Alanine at m/z = 88 attributed to the original molecular weight. The peak at m/z = 46 corresponds to the loss of nitrogen and two carbon atoms and four hydrogen atoms from the compound. The loss of one oxygen, two hydrogen atoms give a peak at m/z = 28. The

spectrum of Ni(II) mixed ligand chelate shows a peak at m/z= 451, which is corresponding to the original molecular weight of the chelate. The peak at m/z = 408 can be assigned to $[Ni(C_{17}H_{19}NO) (H_2O)_2]^+$. The peak at m/z = 290 also assigned to $[Ni(C_{13}H_{15}NO_3)]^+$ ion. The peak at m/z =178 is assigned to $[NiC_9H_{13}]^+$. The final peak appeared at m/z = 53 is due to $C_4H_5^+$.

3.5 Electronic Spectra and Magnetic Moment

The electronic spectral results of the ligands and their mixed ligand chelates are shown in Table 2, and their spectra are shown in Fig. 3. The electronic spectral studies of the chelates of Co(II), Ni(II),Cu(II) and Zn(II) with Schiff base(L^1) and *l*-Alanine (L^2) ligands were carried out in DMSO solvent. The electronic spectra of the Schiff base and *l*-Alanine show π→π*(phenyl rings) and π→π* (HCN) transitions as shown in Table 2 [13]. The electronic spectral results of Co(II) chelate exhibit three bands at 300 nm (33333 cm^{-1}), 380 nm (26316 cm^{-1}) and 455 nm (21978 cm^{-1}) assigned to charge transfer,

$^4T_1g(F)→^4T_2g(F)$ and $^4T_1g(F)→^4T_1g(P)$ transitions, respectively. An octahedral geometry was suggested for the chelate. The intensity of the obtained bands and the magnetic moment value (4.98 BM), support the structure [14]. The electronic spectrum of d^8 electronic configuration of Ni(II) chelate displays two bands at 298 nm (33557 cm^{-1}) and 339 nm (29499 cm^{-1}) which could be due to $^3A_2g(F)→^3T_2g(F)$ and $^3A_2g(F)→^3T_1g(P)$ transitions. The nature of the bands and the magnetic moment of the chelate (3.05 BM) confirm the existence of an octahedral geometry [15]. For Cu(II) chelate, the spectrum exhibits three bands as shown in Table 2, assigned to charge transfer with respect to $^2Eg→^2T_2g$ transitions. Based on the magnetic moment value (1.56 BM) and the nature of the bands, an octahedral structure was proposed for this chelate [16]. The spectrum of Zn(II) chelate shows three bands at 315 nm (31746 cm^{-1}), 385 nm (25974 cm^{-1}) and 435 nm (22989 cm^{-1}) assigned to the presence of charge transfer transitions. The intensity of the bands and diamagnetic character of the chelate suggest the existence of an octahedral structure [17].
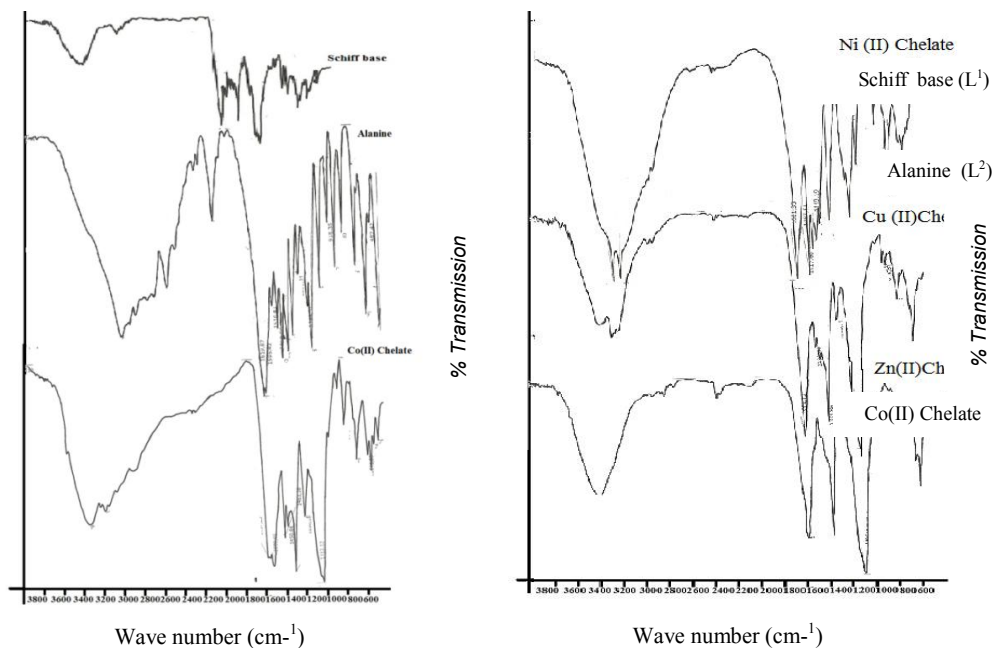

Fig. 1. Infrared spectra of the ligands and their chelates

Table 1. Elemental analyses (CHN) and some physical properties of the chelates

Compounds	M. Wt	Color	Yield (%)	C% calc.	C% exp.	%H calc.	%H exp.	%N calc.	%N exp.	µ* (BM)	Λ*
Schiff base (L^1)	240	Bright yellow	85.93	75.00	74.76	6.60	4.84	11.67	11.15	-	-
[CoL^{1}L^2(H$_2$O)$_2$].7H$_2$O	548	Burnt umber	76.45	39.50	39.08	3.84	2.95	7.68	7.68	4.98	6.18
[NiL^{1}L^2(H$_2$O)$_2$].1.7H$_2$O	451	Moderate olive	75.57	47.89	47.66	6.21	6.09	9.31	9.03	3.05	5.21
[CuL^{1}L^2(H$_2$O)$_2$].5H$_2$O	514	Brown black	78.83	42.02	41.99	4.08	2.88	8.17	10.18	1.56	3.55
[ZnL^{1}L^2(H$_2$O)$_2$].H$_2$O	446	Orange lake	81.85	48.43	47.83	4.70	4.69	9.42	11.63	-	7.17

$Λ* = Ω^{-1}cm^2mol^{-1}$, µ*= magnetic moment

Table 2. Infrared and electronic spectral data of the ligands and their chelates

Ligand/Chelate	υ$_{COO}$	υ$_{OH}$	υ$_{NH2}$	υ$_{C=N}$	υ$_{M-O}$	υ$_{M-N}$	nm (cm^{-1})
Schiff Base (L^1)	-	3337	-	1588	-	-	375(26667)
Alanine (L^2)	3088	3676	3380	-	-	-	234(42735),333(30030)
[CoL^{1}L^2(H$_2$O)$_2$].7H$_2$O	-	3406	-	1601	614	450	300(33333),380(26316),455(21978)
[NiL^{1}L^2(H$_2$O)$_2$]1.7H$_2$O	-	-	3319	1602	614	440	298(33557),339(29499)
[CuL^{1}L^2(H$_2$O)$_2$].5H$_2$O	-	3420	3319	1601	615	480	345(28985),370(27027),424(23529)
[ZnL^{1}L^2(H$_2$O)$_2$].H$_2$O	-	3410	-	1608	615	466	315(31746),385(25974),435(22989)

Table 3. Mass spectral fragmentation of the ligands and their Ni(II) chelate

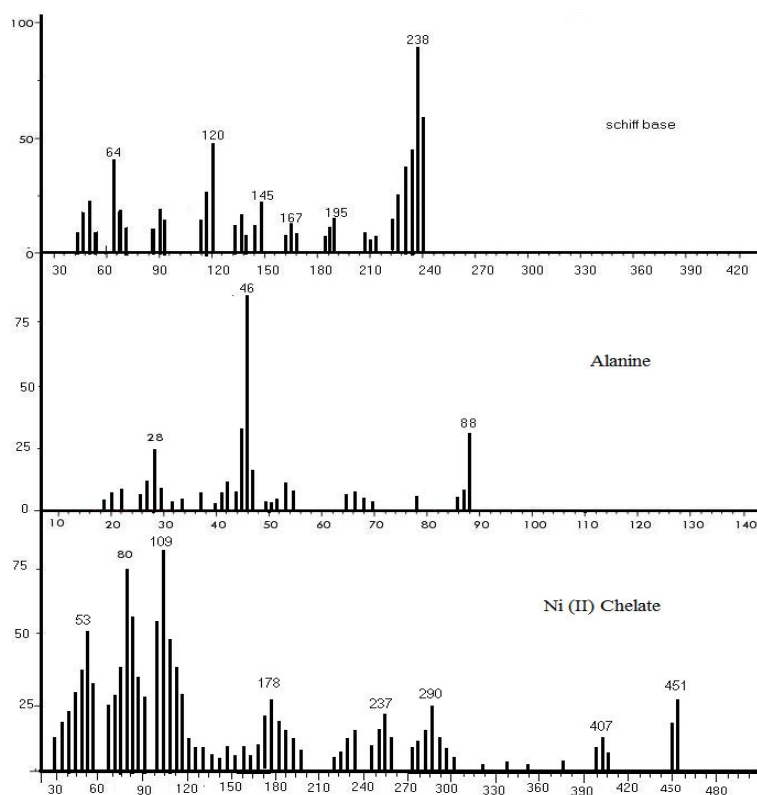| Compound	Fragmented ions	m/z values
C$_{15}$H$_{16}$N$_2$O(L^1)	C$_{15}$H$_{16}$N$_2$O	240
	C$_{15}$H$_{14}$N$_2$O$^+$	238
	C$_{13}$H$_9$NO$^+$	195
	C$_{12}$H$_7$O$^+$	167
	C$_5$H$_4$$^+$	64
C$_3$H$_6$NO$_2$ (L^2)	C$_3$H$_6$NO$_2$	88
	CH$_2$O$_2$$^+$	46
	CO$^+$	28
Ni[(L^1)(L^2)(H$_2$O)$_2$].1.7H$_2$O	[Ni(C$_{18}$H$_{20}$N$_3$O$_3$)(H$_2$O)$_2$]1.7H$_2$O	451
	[Ni(C$_{17}$H$_{19}$NO)(H$_2$O)$_2$]$^+$	407
	[Ni(C$_{13}$H$_{15}$NO$_3$)]$^+$	290
	[NiC$_9$H$_{13}$]$^+$	178
	[C$_8$H$_{13}$]$^+$	109
	[C$_4$H$_5$]$^+$	53

Fig. 2. Mass spectra of the ligands and their Ni(II) chelate
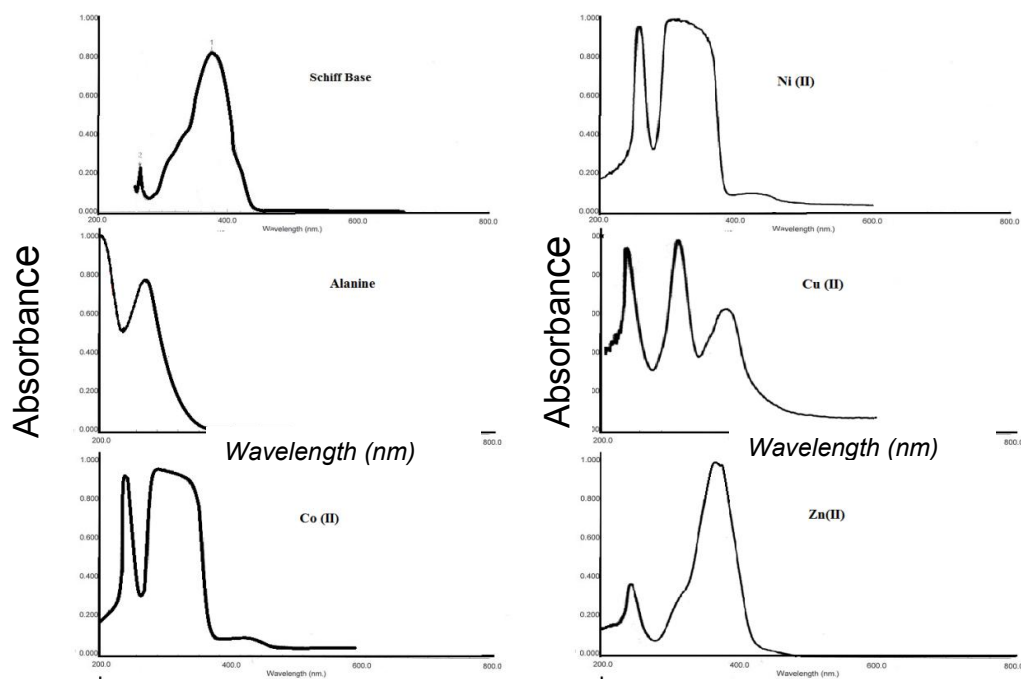
Fig. 3. Electronic spectra of the ligands and their chelates

m/z = 88 → m/z = 46 → m/z = 28

m/z = 240 → m/z = 238

m/z = 195 → m/z = 167 → m/z = 64

m/z = 451 → 1.7H$_2$O → m/z = 408

m/z = 290 → m/z = 178 → m/z = 109 → m/z = 53
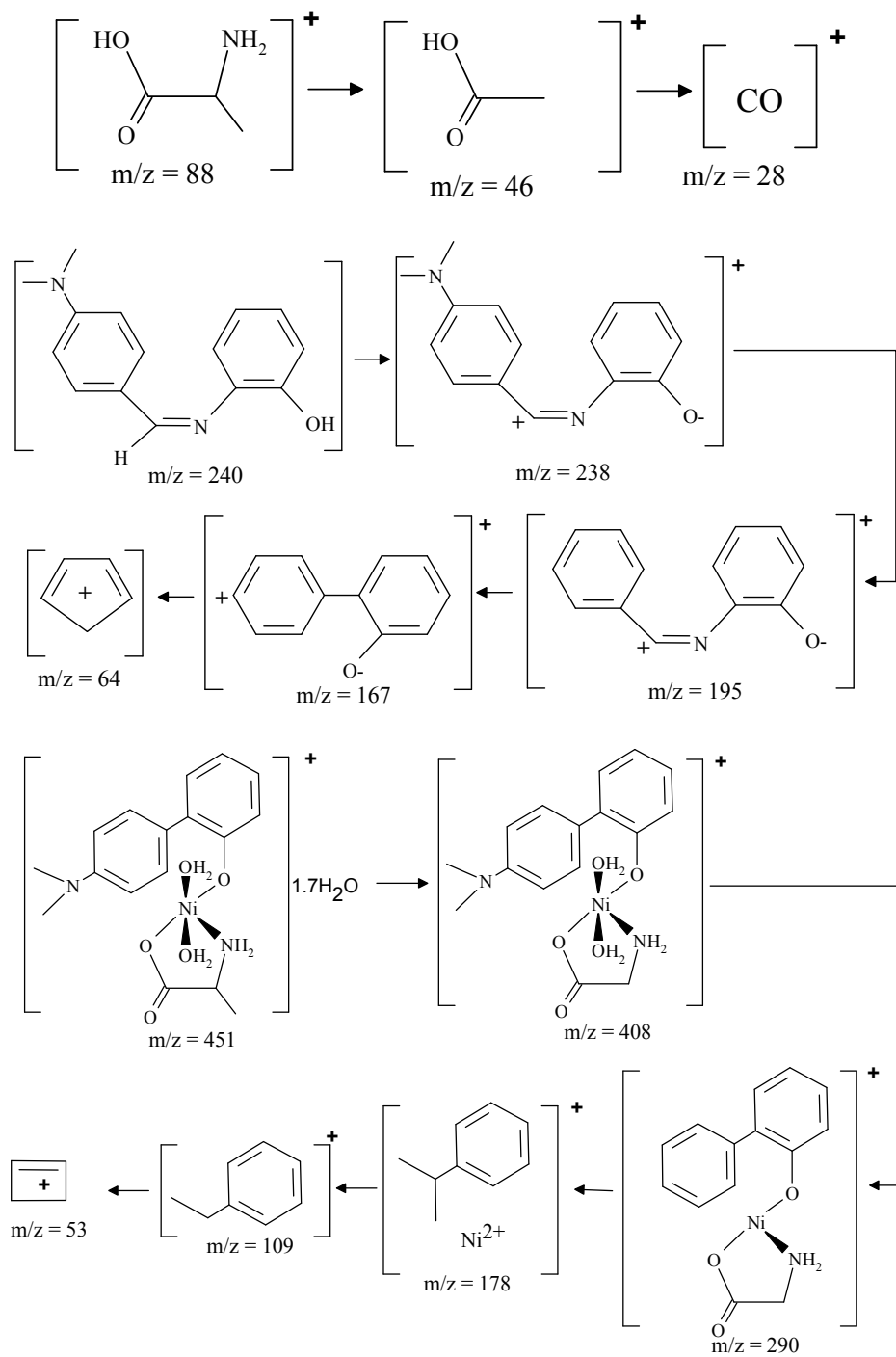
Scheme 1. Mass fragmentations of the ligands and their Ni(II) mixed ligand chelate

235

4. CONCLUSION

The obtained Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand chelates were synthesized and characterized by using several physical techniques, CHN elemental analysis, molar conductivity, magnetic moments, infrared, proton nuclear magnetic resonance spectra of the ligands and Zn(II) chelate has been preformed to justify the chemical structure of ligands situation, electronic and mass spectroscopes. The mass spectral fragmentations of the Schiff base, *l*-Alanine and Ni(II) mixed ligand chelate also conducted to show the importance of chelation of the ligands with different characters. All the experimental data confirm the existence of an octahedral geometry for all chelates as cited before. The differences in the chemical behavior of the chelates aim to investigate the applications in chemical and biological fields.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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