Synthesis and Characterization of Benzoic Acid 2-Salicylidene Complexes with Selected Metal Ions

Chemistry

KEYWORDS : transition metal complexes, spectral studies, Schiff base

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ABSTRACT

Salicylaldehyde was reacting with 2-amino benzoic acid to produce the Schiff base ligand benzoic acid 2-salicylidene (L) as a, which was identified by Microelemental Analysis, 1HNMR, FT-IR and UV-Vis spectroscopic techniques. Complexation of Schiff base ligand (L) with Co(II),Ni(II),Cu(II) and Zn(II) metal ions in 1:1 M:L ratio in aqueous ethanol at optimum pH yielded a series of neutral complexes with the general formula of [M(L)H2O]. Complexes were characterized by flame atomic absorption, Elemental Analysis (C, H, N), FT-IR and UV-Vis spectroscopic methods, as well as magnetic susceptibility and conductivity measurements. The nature of the complexes formed were studied following the mole ratio and continuous variation methods; Beer's law obeyed over a concentration range of 1.10-4 – 3.10-4 M. High molar absorbtivity of the complex solutions were observed. From the obtained data the tetrahedral structure was suggested for all prepared complexes.

Introduction

Schiff bases are a class of important compounds in medical and pharmaceutical field. They show biological activities including antibacterial(1-4), antifungal, anticancer(5-7) and herbicidal activities(8).Furthermore, Schiff bases are utilized as starting materials in the synthesis of industrial(9-11) and biological compounds(12,13). A large number of Schiff bases and their complexes have been studied for their interesting and important properties,e.g.; their ability to reversibly bind oxygen(14),catalytic activity in hydrogenation of olefins(15) and transfer of an amino group(16),photochromic properties(17) and complexing ability towards some toxic metals(18). The high affinity for the chelation of the Schiff bases towards the metal ions is utilized in preparing their solid complexes. The coordination chemistry of transition metal complexes of Schiff base ligands has been attracted much attention in recent years due the fact that the ligands around central metal ions in natural systems are unsymmetrical(19,20). The present paper reports the synthesis and characterization of Co(II),Ni(II),Cu(II) and Zn(II) complexes with Schiff base.

Experimental

Instrumentation

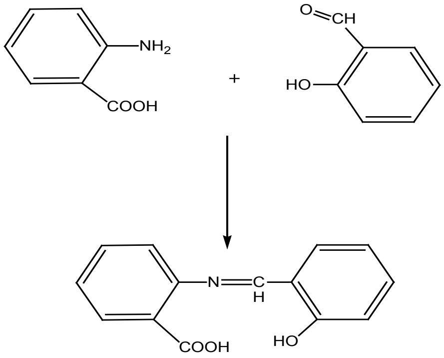
UV- Vis spectra were recorded on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer. IR- spectra were taken on a Shimadzu, FT-IR- 8400S Fourier Transform Infrared Spectrophotometer in the 4000- 400 cm^{-1} spectral region with samples prepared as KBr discs. Atomic absorption was obtained using a Shimadzu A.A-160A Atomic Absorption/Flame Emission Spectrophotometer. The ^{1}H-NMR spectra were recorded on a Brucker-300 MHz Ultra Shield spectrometer at the University of Al- al- Bayt using DMSO as the solvent and TMS as the reference. Microelemental analysis (C, H, N) were performed at the Al- al-Bayt University, Jordan, using Euro vector EA 3000A Elemental Analyser. Conductivities were measured for 10^{-3} M solutions of complexes in ethanol at 25°C using Philips PW- Digital Conductimeter. In addition, melting points were obtained using Stuart Melting Point Apparatus.

Materials and Reagents

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98% and zinc chloride 98.8% (Merck), Salicylaldehyde and 2-amino benzoic acid (B.D.H).All chemicals were of analytical grade used as suppliers without further purification.

Synthesis of Schiff base (L)

According to the general method(21) (0.26ml,1mmole) of salicylaldehyde was added to ethanolic solution of (0.34g,1mmole) of 2-amino benzoic acid. The solution mixture was stirred and refluxed for 2 hours, yellow crystalline precipitate observed. The resulting precipitate was filtered off, recrystallized from menthol and dried at 50 ^{0}C. The reaction is shown in Scheme 1, while Table 1 describes the physical properties and elemental analysis.



Scheme 1. Synthesis of the Schiff base Ligand (I).

Table 1. Physical Properties and Elemental Analysis of the Complexes.

Compounds	Color	M.P°C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	Reddish brown	182	74	-	69.70 (68.53)	4.56 (3.87)	5.81 (4.69)
[Co(L) H_2O]	Deep brown	220	67	18.67 (17.37)	53.16 (52.85)	3.48 (2.97)	4.43 (3.68)

[Ni(L) H_2O]	Yellowish green	>300	87	18.41 (18.02)	53.33 (52.59)	3.49 (3.11)	4.44 (3.65)
[Cu(L) H_2O]	Deep green	239	59	19.93 (19.55)	52.33 (50.01)	3.42 (2.86)	4.36 (3.94)
[Zn(L) H_2O]	Yellowish brown	217	79	20.19 (19.82)	52.17 (50.63)	3.41 (2.95)	4.34 (3.72)

Buffer Solution

Buffer solution, covering the pH range of 4-8, were prepared as 0.01 M solutions of ammonium acetate in distilled water. The required pH was obtained by the addition of either ammonia solution or glacial acetic acid.

Metal Salt Solutions

Solutions of (1.10^{-5}- 1.10^{-3} M) of the metal salt were prepared by dissolving appropriate weight of the metal salt in the buffer solutions.

Ligand Solution

Ligand solutions of (1.10^{-5}- 1.10^{-3} M) were prepared by dissolving a required weight of the ligand in ethanol.

Preparation of Metal Complexes (general procedure)

An ethanolic solution of the ligand (L) (0.5g,1mmol) was added gradually with stirring to the 0.246g, 0.246g,0.107g, and 0.070g of $CoCl_2.6H_2O$,$NiCl_2.6H_2O$,$CuCl_2.2H_2O$ and $ZnCl_2$ (1mmole) , respectively dissolved in the buffer solution with the required pH. The mixture was refluxed with constant stirring for about 1hour. The mixture was cooled at was formed, filtered and recrystillized from methanol.room temperature dark precipitate

Results and Discussion

The ligand was prepared by reaction of salicylaldehyde with 2-amino benzoic acid. Synthesized ligand (L) was characterized by ^{1}H-NMR, FT-IR, Elem.Anal. (C,H,N) and UV-Vis spectroscopic technique. The ^{1}HNMR spectrum of the benzoic acid 2-salicylidene in DMSO (Fig 1) shows multiplet signal at δ=6.915-8.097 ppm, which refers to aromatic protons(22). A signal at δ=12.233 ppm appears due to hydrogen atom of the carboxylic group(23). The signal at δ=9.833 ppm is assigned to δ hydrogen atom of the amine group and the signals at δ=6.630 ppm and δ=2.495 ppm referred to hydrogen of phenol group and DMSO-d_6 respectively (24).

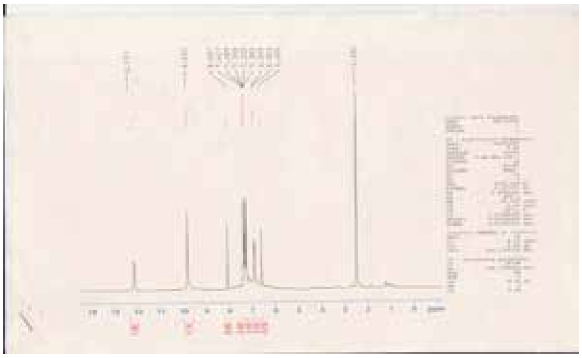


Figure 1. ^{1}H-NMR spectrum of the Schiff base ligand (L).

Interaction of the metal ions Co(II),Ni(II),Cu(II) and Zn(II) with the prepared ligand (L) has been studied in solution; an aqueous- ethanolic solution was always performed over wide molar concentration and acidity range. Colours of these mixed solutions were varied from brown or green.

Different range of molar concentrations (10^{-5}-10^{-3} M) of the mixed solutions, only concentrations in the range of 10^{-4} M obey the Lambert- Beer's law, and only these solutions showed intense colour. A calibration curve was fitted to data points in the range 1.10^{-4} – 3.10^{-4} M, which shows absorbance against molar concentration (Figure 2). Best fit straight lines were obtained with correlation factor of R> 0.998.

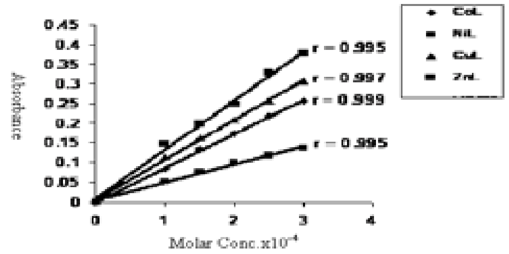


Figure 2. Linear correlation between molar concentration and absorbance.

The optimal concentration was chosen for complex solutions, and it was observed that the absorption maximum (λ_{max}) remained the same at different pH values. The influence of pH was also studied in the pH range of 4-8, and the absorbance- pH curves for each metal ion measured at λ_{max} are plotted in Figure 3. Figure 3 shows selective pH-absorbance curves. The plateaus of the curves represent the completion of the reaction and consequently represent the optimum pH value.

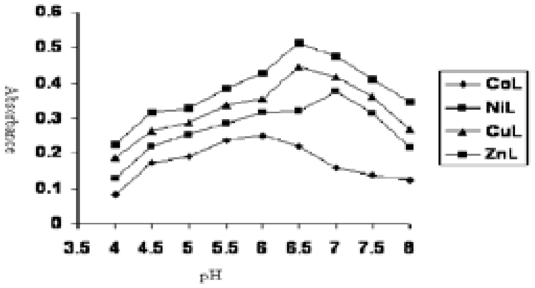


Figure 3. Effect of pH on absorbance (λ_{max}) for complexes.

The composition of complexes formed in solutions has been established by mole ratio and job methods. In both cases the results reveal a 1:1 metal to ligand (L) ratio. A selected plot is presented in Figure 4.

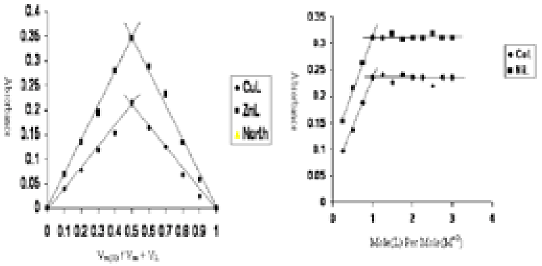


Figure 4. Mole ratio and Job methods for complexes’ solutions.

Table 2 summarizes the results obtained, as well as conditions for the preparation of the complexes.

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligand (L) with the aqueous solution of the metal ions at the optimum pH and in a M:L ratio of 1:1. The result of C.H.N analysis and the metal content of these complexes were in good agreements with the calculated values.

The molar conductance of 10^{-3} M in ethanolic solutions of these complexes indicated their non- electrolytic nature;(25) data are presented in Table 2. The UV-Vis spectra of the prepared complexes dissolved in ethanol (10^{-3} M) have been measured and the data obtained are included in Table 2. The large bathochromic shift of the absorption maximum (λ_{max}), assigned to (π- π^*) transition of the ligand (L), suggests the involvement of the ligand (L) in the bond formation with the metal ion.

The effective magnetic moments (Table 2) of the complexes lie in the range (1.83-4.62) B.M. This value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry. In case of Zn^{II} complex because of filled-d orbital, therefore the magnetic moment (μ=0) is diamagnetic (26).

Table 2. Condition for the preparation of complexes, and the data of UVV-Vis and conductance measurements.

Compounds	Optimum pH	Optimum Molar Conc. x 10^{-4}	M:L Ratio	(λ nm)	ABS	ϵ_{max} (L.mol^{-1}.cm^{-1})	Λ_m (S.cm^2.mol^{-1}) In Absolute ethanol
Ligand(L)	-	-	-	345	1.813	1813	-
				384	1.532	1532	
[Co(L) H_2O]	6	2.5	1:1	304	1.488	1488	4.62
				470	0.567	567	
				669	0.134	134	
				832	0.064	64	
[Ni(L) H_2O]	7	2	1:1	304	1.765	1765	3.06
				410	1.799	1799	
				645	0.045	45	
				738	0.056	56	
[Cu(L) H_2O]	6.5	2	1:1	337	1.397	1397	1.83
				421	0.559	559	
[Zn(L) H_2O]	6.5	2	1:1	311	1.487	1487	Dia

The UV-Vis spectrum of an ethanolic solution of the ligand 10^{-3} M shows two peaks at 345 nm and 384 nm which was assigned to (p – p*) and (n – p*) electronic transitions(27,28). The spectrum of Co(II) complex showed peak at 304 nm due to charge transfer. Other three peaks at 470 nm, 669 nm and 832 nm were found to be caused by (d-d) electronic transition type ${}^4A_{2(F)} \rightarrow {}^4T_{1(P)}$, ${}^4A_{2(F)} \rightarrow {}^4T_{1(F)}$ and ${}^4A_{2(F)} \rightarrow {}^4T_{2(F)}$ respectively(29). The spectrum of Ni(II) complex appeared absorption peak at 304 nm was related to charge transfer, then other three peaks at 410 nm, 645 nm and 738 nm were assigned to electronic transition type ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$, ${}^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ and ${}^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively(30). The spectrum of Cu(II) complex gave absorption peak at 337 nm due to charge transfer. The peak at 421 nm was caused by electronic transition(31) ${}^2T_2 \rightarrow {}^2E$ .The spectrum of Zn(II) complex showed absorption peak at 311 nm due to charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened, this is a good result for tetrahedral complex.(32)

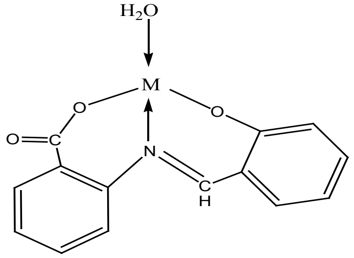
In order to study the bonding mode of the ligand (L) with the metal ions, the FT-IR spectra of the free ligand (L) and the prepared complexes have been compared, and the data was tabulated in Table 3. The IR spectrum of the ligand (L) exhibited broad bands at 3375 cm^{-1} and 3271 cm^{-1} were assigned to stretching vibration of ν(OH) of carboxyl and phenol group(33,34). The disappearance of these bands in the spectra of all complexes indicated the engagement of these bands in the coordination with metal ion. Strong band at 1680 cm^{-1} in the ligand spectrum ascribed to azomethine group(35,36), suffered a great change to lower frequency was observed on complexation with metal ion. The characteristic bands in the ligand spectrum at 1618 cm^{-1} and 1570 cm^{-1} which were assigned to the asymmetric and symmetric of ν(COO) stretching(37). Since a great change in the intensity and in position to lower frequency were also observed in the spectra of all complexes. The presence of coordination water in the spectra of all complexes(38) were suggested by the very broad absorption around (3412-3421)cm^{-1}. The new bands observed at (420-563) cm^{-1} are tentatively assigned to ν(M-N) and ν(M-O) (Metal-Ligands) stretching bands(39,40).

Table 3. The main experimental wavenumber of the ligand and their complexes (in cm^{-1}).

Compounds	$\upsilon(H_2O)$	υ(OH)	υ(C=N)	υ_{as}(COO) + υ_s(COO)	υ(M-N)	υ(M-O)
Ligand(L)	-	3375 br. 3271 sho.	1680 s.	1618 s. 1570 sho.	-	-
[Co(L) H_2O]	3410 br.	-	1612 sh.	1583 s. 1533 s.	526 w.	472 w.
[Ni(L) H_2O]	3414 br.	-	1635 sho.	1616 sh. 1543 sh.	528 w.	489 w.
[Cu(L) H_2O]	3421 br.	-	1612 sho.	1591 sh. 1539 sh.	468 w.	420 w.
[Zn(L) H_2O]	3412 br.	-	1616 sho.	1593 s. 1543 s.	563 w.	486 w.

br = broad, s= strong, , sh = sharp, w = weak, as=asymmetric , s=symmetric

According to the results obtained, a tetrahedral structure has been tentatively suggested to these complexes (Scheme 1).



M^{+2}= Co,Ni,Cu and Zn

Scheme 1

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