

Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Benzothiazol-2-yl-(4-chloro-benzylidene)-amine.

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Abstract: The Benzothiazol-2-yl-(4-chloro-benzylidene)-amine was prepared by the reaction of 2-aminobenzothiazole with 4-chlorobenzaldehyde, the prepared ligand was identified by Micro elemental Analysis, FT.IR and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with the following selected metal ions (Co(II), Ni(II), Cu(II) and Zn(II)) in aqueous ethanol with a 1:2 M:L ratio, yielded a series of complexes of the general formula $[M(L)_2Cl_2]$. The prepared complexes were characterized using flame atomic absorption, (C.H.N) Analysis, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. From the obtained data the octahedral structure was suggested for all prepared complexes.

Keywords: spectral studies, complexes, transition metals.

I. Introduction

Schiff base derivatives attract significant interest and occupy an important role in the development of coordination chemistry⁽¹⁾. Complexes of Schiff base with most transition metal ion has been studied in several area^(2,3). Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards various metals^(4,5). Designing a suitable polydentate Schiff base ligand to combine with a metal ion along with pseudohalide anion has opened a choice⁽⁶⁾ Recently, the complexes of Schiff base ligands have been investigated for their interesting important applications, such as biological, biochemical, analytical, antimicrobial, antibacterial, anticancer, antitumor and antifungal activity⁽⁷⁻¹⁰⁾. The present paper reports the synthesis and characterization of new Co(II), Ni(II), Cu(II) and Zn(II) complexes with .

II. Experimental

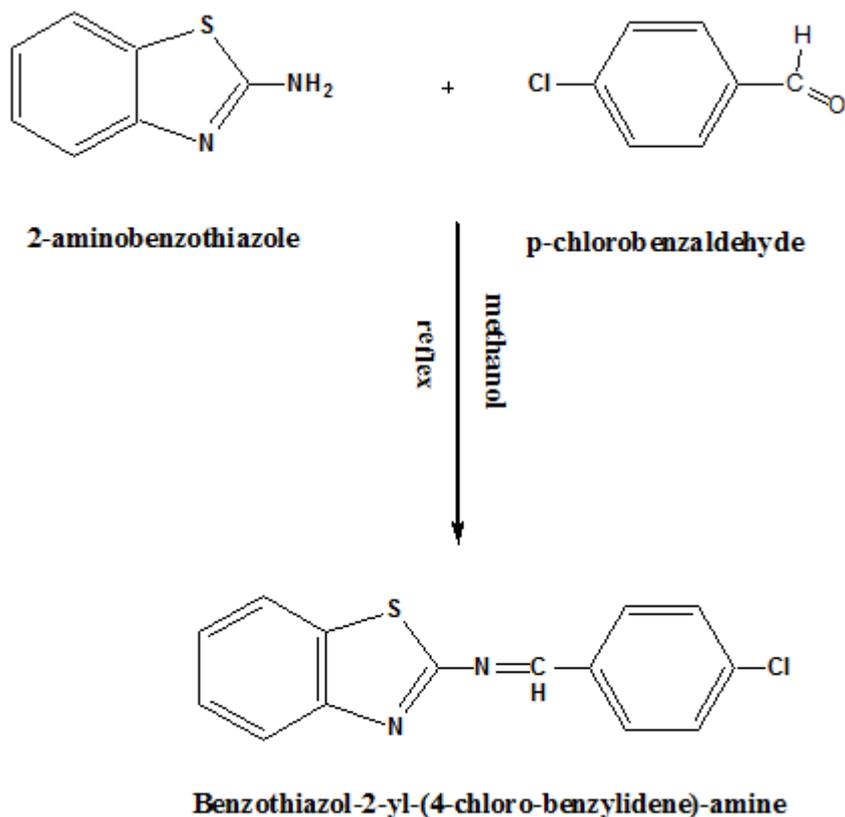
Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-160 A) Ultra Violet-Visible Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-8400 S) Fourier Transform Infrared. Spectrophotometer (4000-400) cm^{-1} with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-160A) Atomic Absorption/Flame Emission Spectrophotometer. Microelemental analysis (C.H.N) was performed in the central service laboratory, College of Education for pure Sciences/Ibn Al-haitham by using (Euro EA 3000 Elemental Analyzer). Conductivities were measured for 10^{-3}M of complexes in ethanol at 25°C by using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.6) instrument at 25°C . In addition, melting points were obtained by using (Melting Point Apparatus).

III. Materials

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 98.8% (Merck), 2-aminobenzothiazole and 4-chlorobenzaldehyde (B.D.H).

Synthesis of Schiff base (L)⁽¹¹⁾ (0.140g, 1mmole) of 4-chlorobenzaldehyde was added to methanolic solution of 0.150g, 1mmole) of 2-aminobenzothiazole. The solution mixture was stirred and refluxed for 3 hours, yellow crystalline precipitate observed. The resulting precipitate as filtered off recrystallized from menthol and dried at 50°C . The preparation method of the ligand (L) is represented in scheme-1.



(Schem-1): Preparation Method of the Ligand (L)

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.118g, 0.118g, 0.084g and 0.065g (1mmole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 respectively was added gradually with stirring to ethanolic solution (0.273g, 2mmol) of the ligand by using stichiometric amount (1:3) Metal to Ligand molar ratio. The mixture was refluxed with constant stirring for 3 hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from ethanol.

IV. Results and Discussion

The ligand was prepared by condensation reaction between 4-chlorobenzaldehyde and 2-aminobenzothiazole. The ligand was sparingly soluble in water but soluble in organic solvents such as DMSO and DMF, stable toward air and moisture. Synthesized ligand (L) was characterized by FT-IR, Elem. Anal. (C, H, N) and UV-Vis spectroscopic technique. The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions in a (M:L) of (1:2). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-1) includes some physical properties and elemental analysis.

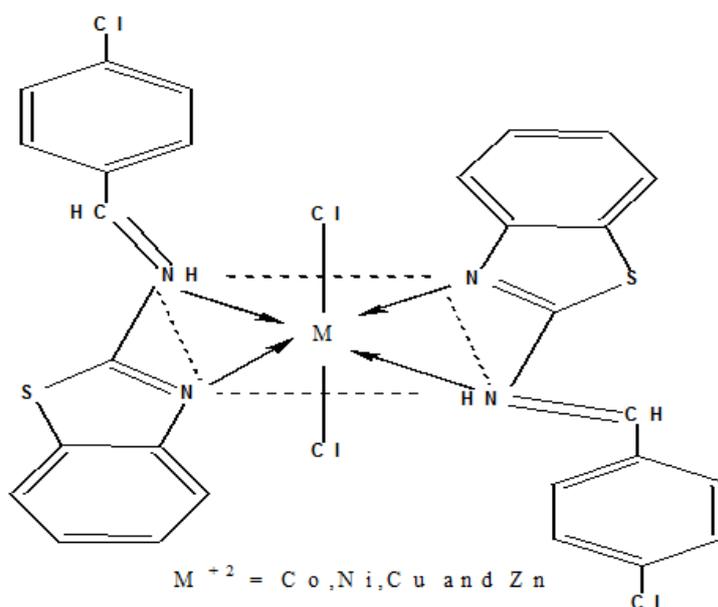
The molar conductance of the complexes as (10^{-3}M) in ethanol indicating their non-electrolytic nature⁽¹²⁾, the data were recorded in (Table 2). The UV-Vis spectra data for the free ligand and all metal complexes are listed in (Table-2). The effective magnetic moments (Table-2) of the complexes lie in the range (1.72-4.76) B.M. This value refers to a paramagnetic (high spin) which has been reported for most octahedral geometry.⁽¹³⁾

The UV-Vis spectrum of the ligand (L) (Fig-1) shows three peaks at 223, 262 nm and 343 nm assigned to ($\pi-\pi^*$) and ($n-\pi^*$) electronic transitions^(13,15). The spectrum of Co(II) complex (Fig-2) showed peaks at 270 nm and 320 nm due to ligand field. The peak at 382 nm was assigned to charge transfer. Other three peaks at 648 nm, 730 nm and 780 nm were found to be caused by (d-d) electronic transition type ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{P})}$, ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{A}_{2g(\text{F})}$ and ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{2g(\text{F})}$ respectively⁽¹⁶⁾. The spectrum of Ni(II) complex appeared absorption peak at 233 nm was related to ligand field, then other three peaks at 360 nm, 540 nm and 772 nm were assigned to electronic transition type ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{P})}$ with charge transfer, ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{2g(\text{F})}$ and ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{F})}$ respectively⁽¹⁷⁾. The spectrum of Cu(II) complex gave absorption peak at 279 nm due to charge transfer. The peak at 808 nm was caused by electronic transition⁽¹⁸⁾ ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$. The spectrum of Zn(II) complex showed absorption peaks at 332

nm and 380 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 octahedral complex⁽¹⁹⁾.

In order to study the binding mode of the ligand with the metal ions, a comparison was made for the FT-IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-3). The IR spectrum of the ligand (L) (Fig-3) exhibited bands at 3066 cm⁻¹ and 29366 cm⁻¹ refers to $\nu(\text{C-H})$ aromatic and aliphatic⁽²⁰⁾. The band at 1693 cm⁻¹ due to $\nu(\text{C=N})$ of thiazole and imine group, shifted to lower frequency with change in shape in spectra of the complexes (Fig-4), which is an indication of the engagement of this group in the coordination with the metal ion^(21,22). The bands in the ligand spectrum at 1639 cm⁻¹ and 1589 cm⁻¹ were assigned to $\nu(\text{C=C})$ ⁽²³⁾. The new bands observed at (435-474) cm⁻¹ are tentatively assigned to $\nu(\text{M-N})$ (Metal-Ligand) stretching bands^(24,25).

According to the results obtained and spectral analysis an octahedral structure has been suggested to these complexes, the molecular structure represented in Scheme-2 .



(Schem-2): Preparation of Metal Complexes.

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تحضير و تشخيص لمعدّات الكوبلت (II)، النيكل (II)، النحاس (II) والخارصين (II) مع بنزو ثيازول 2- يل- (4- كلورو- بنزلدلين)- امين. حميد منلول الكبيسي، حوراء كاظم سلوم، ونام حسن كاظم، شيما حميد شاكر قسم الكيمياء- كلية العلوم للنبات- جامعة بغداد

الخلاصة

حضرت الليكاند بنزو ثيازول 2- يل- (4- كلورو- بنزلدلين)- امين من تفاعل 2-امينو بنزو ثيازول مع 4-كلورو بنزلدليهايد. شخص الليكاند المحضر بواسطة اطيفاف الأشعة تحت الحمراء وفوق البنفسجية - المرئية والتحليل الدقيق للعناصر (C.H.N). تمت مفاعلة الليكاند مع ايونات الكوبلت (II)، النيكل (II)، النحاس (II) والخارصين (II) وبنسبة مولية (2:1) فلز: ليكاند. شخصت المعدّات المحضرة بواسطة التحليل الدقيق للعناصر (C.H.N)؛ تقنية الإمتصاص الذري اللهيبي واطيفاف الأشعة تحت الحمراء وفوق البنفسجية - المرئية، فضلا عن قياسات التوصيلية الكهربائية والحساسية المغناطيسية، ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعدّات المحضرة.

الكلمات المفتاحية: الدراسات الطيفية، المعدّات، العناصر الإنتقالية.

Table(1):- Physical properties and elemental analysis of the complexes.

Compounds	Color	M.P ^o C	Yield%	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	yellow	185	85	-	61.65 (60.78)	3.30 (2.93)	10.27 (9.68)
[Co(L) ₂ Cl ₂]	orange	211	73	9.76 (8.79)	55.63 (54.77)	2.98 (1.96)	9.27 (8.76)
[Ni(L) ₂ Cl ₂]	green	218	77	9.72 (8.65)	55.65 (54.94)	2.98 (2.10)	9.27 (8.85)
[Cu(L) ₂ Cl ₂]	blue	220	78	10.50 (9.85)	55.17 (54.78)	2.95 (2.32)	9.19 (8.67)
[Zn(L) ₂ Cl ₂]	Pal yellow	232	73	10.65 (9.83)	55.08 (54.92)	2.95 (2.88)	9.18 (8.98)

Table(2):- UV-Vis and conductance measurements data.

Compounds	(λ nm)	ABS	ϵ_{\max} (L.mol ⁻¹ .cm ⁻¹)	ϵ_m (S.cm ² .mol ⁻¹) In Absolute ethanol	ϵ_{eff}
Ligand(L)	223	1.4150.8	1415	-	-
	262	12	812		
	343	0.018	18		
[Co(L) ₂ Cl ₂]	270	0.4241.4	424	11.56	4.76
	320	20	1420		
	382	0.683	683		
	648	0.095	95		
	730	0.195	195		
	780	0.205	205		

[Ni(L) ₂ Cl ₂]	233 360 540 772	2.3500.8 14 0.012 0.008	2350 814 12 8	9.36	3.03
[Cu(L) ₂ Cl ₂]	279 808	2.001 0.071	2001 71	12.43	1.72
[Zn(L) ₂ Cl ₂]	332 380	1.578 0.698	358 837 1357	9.72	Dia

Table(3):- The Main Frequencies of the Ligands and It's Complexes(cm⁻¹).

Compounds	□ (CH) aromatic+ □ (CH) alphatic	□ (C=N) thiazole + □ (C=N) imine	□ (C=C)	□ (M-N) thiazole and imine
Ligand(L)	3066 w. 2966 w.	1693 sh.	1589 s. 1570 sho.	-
[Co(L) ₂ Cl ₂]	33062 w. 2958 w.	1639 s.	1589 sho. 1569 sho.	470 w. 459 w.
[Ni(L) ₂ Cl ₂]	33062 w. 2960 w.	1635 s.	1585 s. 1570 s.	474 w. 455 w.
[Cu(L) ₂ Cl ₂]	33074 w. 2970 w.	1639 sh.	1585 s. 1570 sho.	474 w. 435 w.
[Zn(L) ₂ Cl ₂]	3093 w. 29862 w.	1630 sh.	1587 sho. 1570 sho.	455 w. 439 w.

sh = sharp, sho =shoulder, s = strong, w =weak

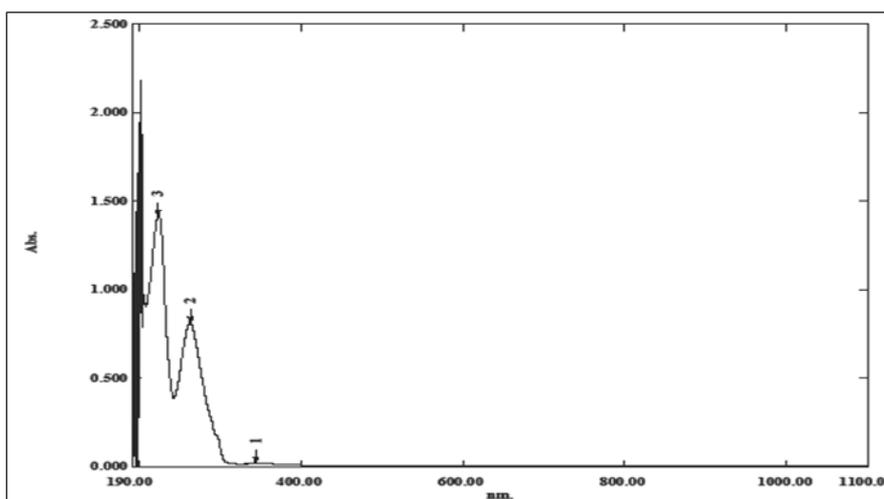


Fig.(1):- UV-Vis spectrum of the ligand.

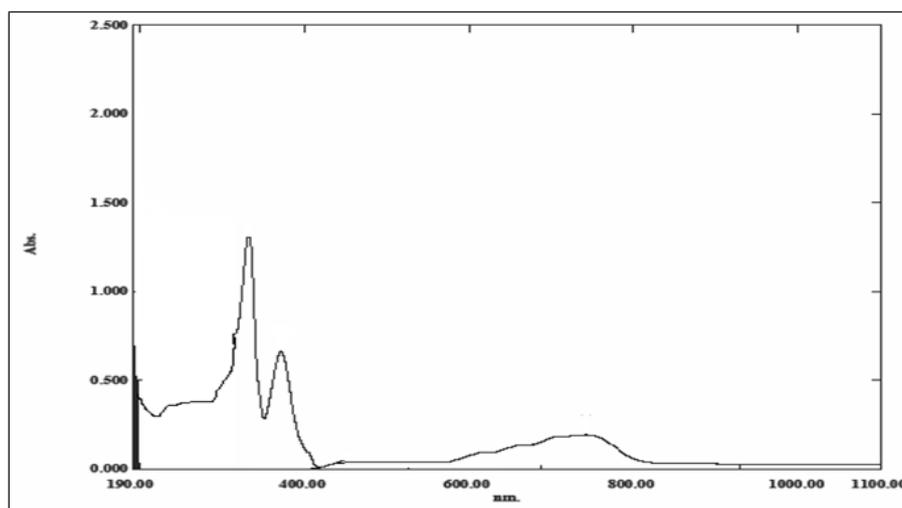


Fig.(2):- UV-Vis spectrum of the [Co(L)₂Cl₂] complex.

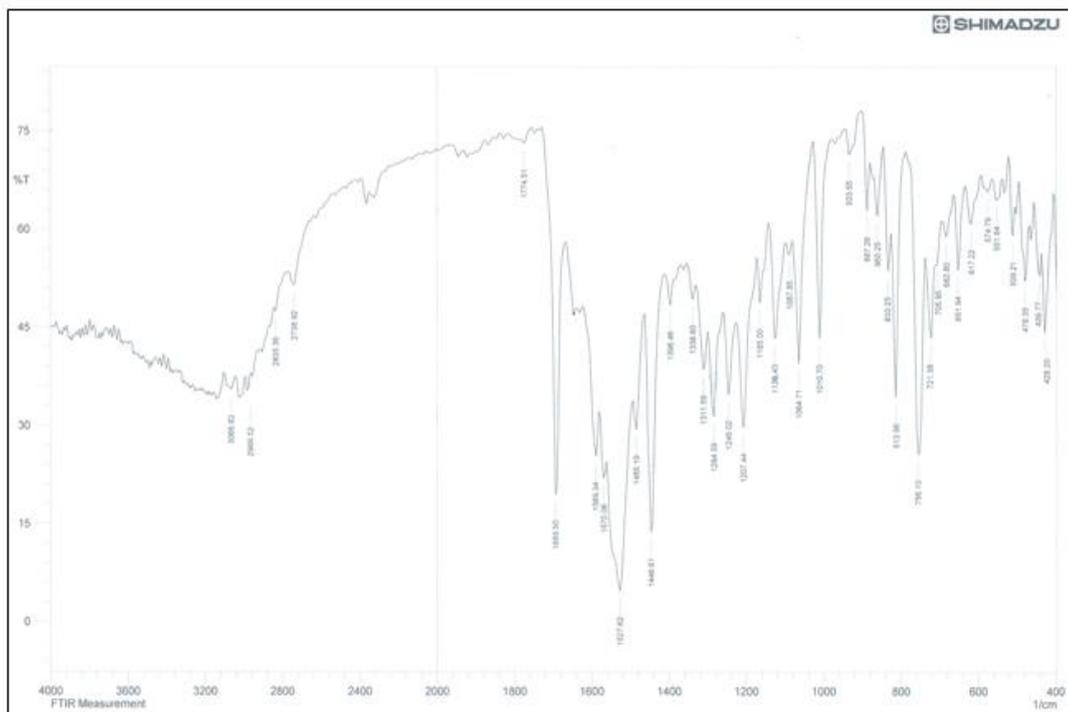


Fig.(3):- FT-IR spectrum of the ligand.

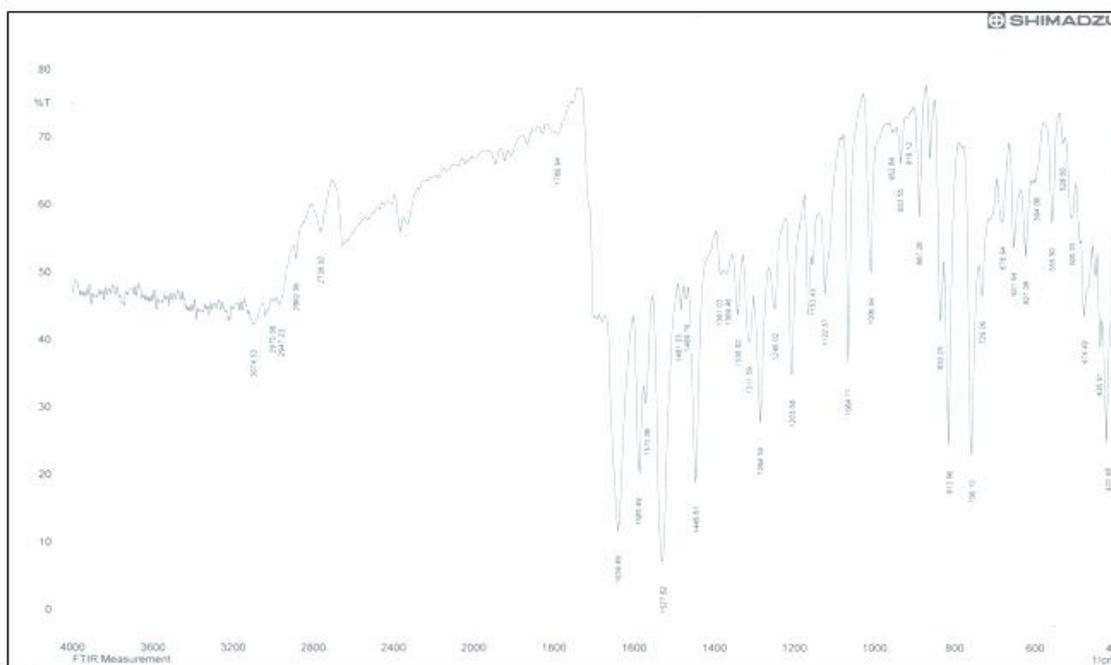


Fig.(4):- FT-IR spectrum of [Er(L)₃] complex.

Fig.(3):- FT-IR spectrum of the ligand.

Fig.(4):- FT-IR spectrum of the [Cu(L)₂Cl₂] complex.