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Synthesis and Characterization of Some Schiff Base Complexes Containing Heterocyclic Compounds With Cobalt(II) , Nickel(II), Copper(II) and Zinc(II)

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A B S T R A C T

The Synthesis of Complexes for Cobalt(II) , Nickel(II), Copper(II) and Zinc(II) with New ligands Schiff base ; N-[5-(phenyl)2-(amino)1,3,4-thiadiazolebenzylidene] (L1) and N-[5-(phenyl)2-(amino)1,3,4-thiadiazole-4-N-dimethylbenzylidene] (L2) have been prepared and Characterized by, Atomic absorption spectrophotometer (AAS),Infrared spectra , Electronic spectra, Molar conductivity measurements and Magnetic moment measurements ; It has been found that the ligands behaves as a neutral bidentate , Ligands forming chalets with 1:2 (metal : ligand), Octahedral structure is suggested for metal Complexes according to the analytical results.

Introduction:

Schiff base ligands and their transition metal complexes have been extensively studied for many years (1-4). These complexes have been widely used as bidentate ligands in the field of coordination chemistry (5-10).Thiadiazole synthesized and tested for their antifungal (11). Nematocidal (12). Antibacterial (13). Anti-inflammatory activities(14).Besides industrial applications(15). and agricultural used (16). Thus it will be interesting to prepare and study of complexes containing Schiff base derived from 1,3,4 –thiadiazole and benzaldehyde or 4- [N-]dimethyl benzaldehyde, The aim of this work is prepared transition metal complexes of N-5-phenyl 2-amino 1,3,4 –thiadiazolbenzylidene(L1) and N-5-phenyl 2-amino 1,3,4 – thiadiazole 4-N-dimethylbenzylidene(L2).

Experimental Part

All the chemical substances were supplied by BDH and Fluka and of purity more than 99%, Infrared spectra were record by a SHIMADZU infrared spectrophotometer FT - IR model 8400S in the 4000-200 cm-1.

Range using KBr disc, Ultraviolet spectra were recorded on HITACHI model 2000U spectrophotometer using DMF as a solvent, melting point were determined by an Electrothermal melting point model 9300,Magnetic susceptibilities were measured on instrument type Bruker BM 6 were carried at room temperature by Faraday method , the molar conductivity of complexes (0.001 M) in DMF was measured using HANNA model 214EC conductivity meter, determination of metals percentage by atomic absorption spectrophotometer on Perkin-Elmer model 2280.

● Synthesis of the ligands and complexes

2-amino-5-phenyl-1,3,4-thaidiazole was prepared according to following general procedure (17,18). The ligands (L1) and (L2) are prepared by a same method ; A mixture of benzaldehyde (1.06 g, 0.01 mole) or 4-N-dimethylbezaldehyde (1.49 g, 0.01 mole) in 30 ml absolute ethanol and 2-amino-5-phenyl-1,3,4-thaidiazole (1.77 g, 0.01 mole) with 2-3 drops of glacial acetic acid was refluxed for 2 hours with continues stirring, after cooling at room temperature, the precipitate was filtered, dried and recrystallized from ethanol (19) scheme(1). The complexes were prepared by dissolving (0.265 g, 1mmole) of (L1) or (0.308 g, 1mmole) of (L2) in 40 ml absolute ethanol which then added drop wise with vigorous stirring to (0.5 mmole) of MCl2 metal salts [M=Co(II), Ni(II), Cu(II) and Zn(II)] dissolved in 10 ml hot distilled water the mixture was heated to 50oC for 30 min. , then left overnight, the solid complex formed was filtered, washed with 10 ml ethanol and dried.

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X = H, or -N(CH$_3$)$_2$.
    (L$_1$) , (L$_2$)
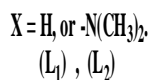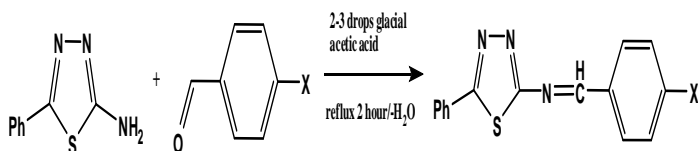
Scheme (1); show the structure of ligands L1 and L2.

Results and Discussion

● Characterization of ligands and it's metal complexes

The ligands and it's metal complexes were insoluble in water but soluble in organic solvent such as DMSO,DMF the metal percentage in complexes and physical data of ligands and complexes are given in table (1).

Table (1): metal percentage and physical data of ligands and it's complexes.

Compound	Formula	Color	M.p c°	Yield %	% Metal calc.(found)
L$_1$	C$_{15}$H$_{11}$N$_3$S	yellow	238-236	72	---
L$_2$	C$_{17}$H$_{16}$N$_4$S	yellow	217-215	75	---
[Co(L$_1$)$_2$Cl$_2$]	C$_{30}$H$_{22}$N$_6$S$_2$Cl$_2$Co	Deep yellow	268-266	69	8.93 (8.90)
[Ni(L$_1$)$_2$Cl$_2$]	C$_{30}$H$_{22}$N$_6$S$_2$Cl$_2$Ni	orange	275-273	65	8.90 (8.86)
[Cu(L$_1$)$_2$Cl$_2$]	C$_{30}$H$_{22}$N$_6$S$_2$Cl$_2$Cu	Brown	256-254	70	9.55 (9.58)
[Zn(L$_1$)$_2$Cl$_2$]	C$_{30}$H$_{22}$N$_6$S$_2$Cl$_2$Zn	white	251-249	68	9.51 (9.47)
[Co(L$_2$)$_2$Cl$_2$]	C$_{34}$H$_{32}$N$_8$S$_2$Cl$_2$Co	Deep yellow	245-243	68	7.90 (7.85)
[Ni(L$_2$)$_2$Cl$_2$]	C$_{34}$H$_{32}$N$_8$S$_2$Cl$_2$Ni	orange	258-256	62	7.87 (7.82)
[Cu(L$_2$)$_2$Cl$_2$]	C$_{34}$H$_{32}$N$_8$S$_2$Cl$_2$Cu	Brown	239-237	71	8.46 (8.50)
[Zn(L$_2$)$_2$Cl$_2$]	C$_{34}$H$_{32}$N$_8$S$_2$Cl$_2$Zn	white	232-230	66	9.17 (9.14)

● Infrared **spectra**

The important infrared spectra data of ligands and it's complexes are given in table (2),The bands in region 1637-1626 cm-1 attributed ν(C═ N) vibration thiazole ring ,This value was increased after Copmlexation (20).The bands ν(C –S-C) in region 755-750 cm-1 ,This band remains in the same region in free ligands and after Copmlexation that mean is the sulfur atom in thiazole group doesn't coordinate with metal in complexes (21) .The bands in the range 1618-1600 cm-1due to azomethine group in the ligands and then was shifted to lower frequencies after Copmlexation which are 1595-1574 cm-1, New weak bands in the region 456-415 cm-1 were observed in the spectra of metal complexes ,These bands were not present in the spectrum of ligands ,and they due to ν(M –N) (22-23).

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Table (2): IR absorption bands of ligands and it's complexes in cm-1 units.

Compound	ν(C=N) thiazole ring	ν(C –S-C)	ν(C = N) azomithine	ν(M–N)
L$_1$	1637	755	1618	---
L$_2$	1626	750	1600	---
[Co(L$_1$)$_2$Cl$_2$]	1658	754	1592	422
[Ni(L$_1$)$_2$Cl$_2$]	1657	753	1587	415
[Cu(L$_1$)$_2$Cl$_2$]	1655	754	1586	448
[Zn(L$_1$)$_2$Cl$_2$]	1649	752	1590	456
[Co(L$_2$)$_2$Cl$_2$]	1652	751	1573	424
[Ni(L$_2$)$_2$Cl$_2$]	1651	750	1581	416
[Cu(L$_2$)$_2$Cl$_2$]	1654	749	1575	450
[Zn(L$_2$)$_2$Cl$_2$]	1650	752	1578	455

● *Magnetic measurement and electronic spectra*

The magnetic moment and spectral data of prepared complexes are given in table (3). The magnetic moment of Cobalt (II) has been found to be (4.57, 4.43 B.M) which is with the range of octahedral Cobalt (II) complexes [24]. The electronic spectra of L_1 and L_2 show strong bands in the range 43250-42110 cm^{-1} and 34520-34310 cm^{-1} which are attributed $\pi \to \pi^*$ and $n \to \pi^*$ respectively, the electronic spectra of this complexes show two absorption bands at 16230-16110 cm^{-1} and 22870-22650 cm^{-1} there are assigned to $^4T_{1g}$ (F) $\to$ $^4A_{2g}$ (F) (v_2) and $^4T_{1g}$ (F) $\to$ $^4T_{2g}$ (P) (v_3) transitions respectively, which are characteristic of octahedral stereochemistry. For Nickel (II) complexes its magnetic moment (3.30,3.10 B.M) and spectra of this complexes show bands at 16260-16125 cm^{-1} and 22230-22110 cm^{-1}which suggesting the existence of $^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (F) (v_2) and $^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (P) (v_3) transitions which an octahedral spectral configuration. The magnetic moment value of Copper (II) complexes (1.73,1.61B.M) which may suggest an octahedral structure. Its electronic spectrum show at 15638-15450 cm^{-1} which may assigned to $^2E_{2g} \to ^2T_{2g}$ transition in octahedral structure [24,25]. Zinc (II) complexes are diamagnetic and electronic spectra of these complexes exhibit high intense charge transfer transition [26].
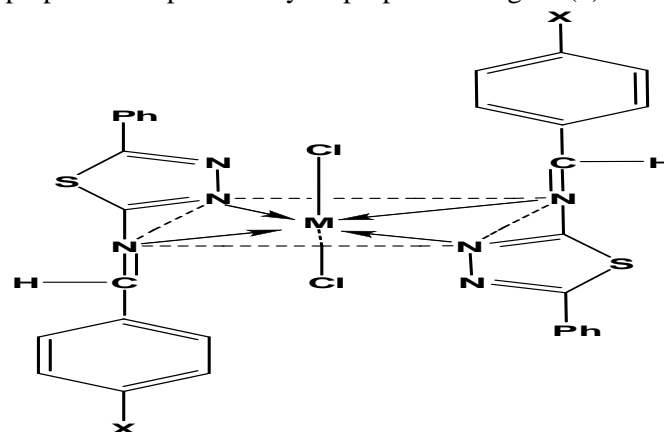
● *Conductivity measurements*:

The molar conductance of the complexes 0.001 M in DMF at room temperature show that all complexes are non-electrolytes [27]. The value in the range 7.32-11.19 $cm^2.ohm^{-1}.mol^{-1}$ table (3). According to these results the structural formula of prepared complexes may be proposed in figure (1).

Table (3): magnetic moment, Electronic spectra, Conductivity of the complexes.

Complexes	Electronic spectra cm⁻¹			transition	Conductivity cm².ohm⁻¹	μ eff. (B.M)
	v_1	v_2	v_3			
[Co(L₁)₂Cl₂]	┆	16238	22872	$^4T_{1g}$ (F) $\to$ $^4A_{2g}$ (F) (v_2); $^4T_{1g}$ (F) $\to$ $^4T_{2g}$ (P) (v_3)	7.32	4.57
[Ni(L₁)₂Cl₂]	┆	16260	22238	$^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (F) (v_2); $^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (P) (v_3)	9.41	3.30
[Cu(L₁)₂Cl₂]	15638	┆	┆	$^2E_{2g} \to ^2T_{2g}$	11.19	1.73
[Zn(L₁)₂Cl₂]	┆	┆	┆	┆	10.47	dia
[Co(L₂)₂Cl₂]	┆	16119	22656	$^4T_{1g}$ (F) $\to$ $^4A_{2g}$ (F) (v_2); $^4T_{1g}$ (F) $\to$ $^4T_{2g}$ (P) (v_3)	8.15	4.43
[Ni(L₂)₂Cl₂]	┆	16125	22110	$^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (F) (v_2); $^3A_{2g}$ (F) $\to$ $^3T_{1g}$ (P) (v_3)	9.63	3.10
[Cu(L₂)₂Cl₂]	15456	┆	┆	$^2E_{2g} \to ^2T_{2g}$	10.88	1.61
[Zn(L₂)₂Cl₂]	┆	┆	┆	┆	9.11	dia

M = Co(II), Ni(II), Cu(II), and Zn(II).
X = H , -N(CH₃)₂.

Fig.1: the proposed structural formula of the complexes.

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تحضير وتشخيص بعض معقدات قواعد شيف والمحتوية على حلقات غير متجانسة لايونات الكوبلت والنيكل والنحاس والخارصين الثنائية

صالح عبد الله احمد.

الخلاصة

يتضمن البحث تحضير معقدات فلزية لايونات الكوبلت(II) ، النيكل(II) ، النحاس(II) والخارصين (II) مع ليكاندات جديدة لقواعد شيف ن [−5−(فنيل) 2−(امينو)−1,3,4− ثايادايازول بنزيلدين](L1) و ن [−5−(فنيل) 2−(امينو) −1,3,4− ثايادايازول−4−ن− ثنائي مثيل بنزيلدين] (L2) . شخصت الليكاندات المحضرة ومعقداتها بوساطة التحليل الطيفي الذري والأشعة تحت الحمراء والأطياف الالكترونية كما درست التوصيلية المولارية والخواص المغناطيسية لهذه المعقدات. ومن خلال نتائج البحث تبين أن الليكاندات تسلك سلوك كليكندات متعادلة ثنائية السن وترتبط مع جميع الايونات الفلزية بنسبة مولية1:2 (فلز : ليكاند) تم اقتراح الشكل الثماني السطوح لجميع المعقدات الفلزية بالاعتماد على نتائج التحليل التي تم الحصول عليها.