Journal of Kirkuk University –Scientific Studies , vol.4, No.2,2009

Synthesis and Characterization of Some Schiff Bases(derived from thiazole)and Their Complexes With Co(II),Ni(II) and Cu(II)

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Abstract

The synthesis of some new coordination compounds for cobalt (II), nickel(II)and copper(II)with Schiff bases derived from(2-aminobenzothiazole,6-nitro-2-aminobenzothiazole,4,6-dibromo-2-aminobenzothiazole) and 4-N-dimethylbezaldehyde to give ligands (La,Lan and Ladb) were prepared and then reacted with metal salts in ethanol as a solvent in 1:2 ratio (metal : ligand). The complexes which have the general formula $[ML_2Cl_2]$ Where M=Co (II) , Ni (II) and Cu (II),(L=La,Lan,or Ladb) all ligands and it's metal complexes were characterized using metal analysis by Atomic absorption, Infrared spectra ,Electronic spectra, Molar conductance and Magnetic moment measurements ; These measurements indicated that the ligands coordinate with metal (II) ion in a bidentate manner through the nitrogen atoms in ligands, Octahedral structures were suggested for metal complexes.

Introduction

Schiff bases derived from an amine and aldehyde are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively(Arora & Sharma,2003;Vigato & Tamburini,2004 and Katsuki,1995). These complexes are play an important role in the development of coordination chemistry(Sousa et al.,2003;Kou et al.,2004).

Thiazole derivatives have been found a number uses in medicinal and pharmaceutical fields(Malik & Rajeev,1982). Some of them have been showed to have antitumer activity(Bradshaw ,2002;Ioaizaperez,2002 and Racane,2006)anticandidous(Sidoova et.al,1997)Parkinson's disease (Alain et.al,1997) antihistaminic and antiflammatory (Abignente et.al,1983).Benzothiazole have also shown significant effect against cancer (Swarnkar et.al, 2007)and antibacterial agent (Lednicar & Matcher,1997; Karia & Parsania,1999) .Another area of application of these Schiff bases is analytical chemistry where some of compounds were used as ligand in complexometry topic (Rodriguez et.al,2004) and catalysts as a corrosion

inhibitor in chemical industry (Ramesh & Sivagamasundari,2003) .Thus the aim of this work to prepared some new transition metal complexes of Schiff bases derived from substituted benzothiazoles prepare and characterized of these complexes.

Experimental Part

Materials:

All the chemicals were supplied by BDH and Fluka and used without further purification.

Instruments:

The following Instruments have been used for spectroscopic measurements and physical properties for ligands and their complexes :-

1-Infrared spectra were record by a SHIMADZU infrared spectrophotometer FT-IR model 8400S in the 4000-400cm^{-1} Range using KBr disc.

2-Electronic spectra were recorded on HITACHI model 2000U spectrophotometer using DMSO as a solvent.

3-Melting point or decomposition temper. were determined by an Electro thermal melting point model 9300.

4-Magnetic susceptibility measurement were measured on by Faraday method at 25C^{o} using Bruker BM 6 instrument .

5-The molar conductivity of complexes (0.001M) in DMSO was measured using HANNA model 214EC conductivity meter.

6-Determination of metals percentage by atomic absorption spectrophotometer on Perkin-Elmer model 2280.

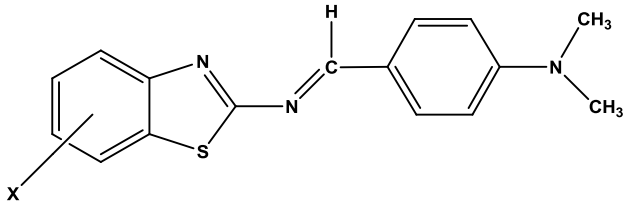
Preparation of the ligands :

2-aminobenzothiazole,6-nitro-2-aminobenzothiazole,4,6-dibromo-2-aminobenzothiazole were prepared according to the general procedure ,literature(Misa,1958)(Mebra et.al, 1980). The ligands(La),(Lan) and (Ladb) were prepared by the same method; A mixture of 4-N-dimethylbezaldehyde (1.49g,0.01mol)in 30 ml absolute ethanol and 2-aminobenzothiazole(1.50g, 0.01 mol) , 6-nitro-2aminobenzothiazole(1.95g, 0.01 mol) or 4,6-dibromo-2-aminobenzothiazole(2.29g, 0.01 mol) 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 off, dried and recrystallized from ethanol(Jassim & Abdullah, 2002) (Fig.1).

• Preparation of the complexes :

The complexes were prepared by dissolving (2mmole) of (La) or (Lan)

or(Ladb) in 40 ml absolute ethanol which then added drop wise with stirring to (1mmole) of MCl_2 metal salts M=Co(II), Ni(II) and Cu(II) which were dissolved in 10 ml of hot distilled water. The mixture was heated to 50C° for 30 min. , then left overnight. The precipitated complex was filtered off, washed with 10 ml cold ethanol and dried.



X =H(La);=6-nitro(Lan)
X =2H= 4,6-dibromo(Ladb)

Fig. (1): The structure of ligands.

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 solvents such as DMSO,DMF and Ethanol ,low conductivity values(8.15-13.20 cm^2ohm^{-1} mol^{-1})indicated that the complexes are non-electrolytes(Shallary et.al, 1979; Geary,1971). The metal percentage in complexes analytical and some of physical data of ligands and complexes are given in Table (1).

Table (1): Analytical and some of the physical data of ligands and it's complexes

Compounds	Formula	Color	M.P c°	Yield %	% Metal calc.(found)	Conductivity ohm^{-1}cm^{2}mol^{-1} In DMSO
La	$C_{16}H_{15}N_3S$	orange	186-188	73	---	---
Lan	$C_{15}H_{14}N_4SO_2$	Red	162-164	70	---	---
Ladb	$C_{16}H_{13}N_3SBr_2$	yellow	175-177	75	---	---
$[Co(L_a)_2Cl_2]$	$C_{32}H_{30}N_6S_2Cl_2Co$	green	223-225	68	8.52(8.50)	8.15
$[Ni(L_a)_2Cl_2]$	$C_{32}H_{30}N_6S_2Cl_2Ni$	Red	214-216	66	8.49(8.46)	9.25
$[Cu(L_a)_2Cl_2]$	$C_{32}H_{30}N_6S_2Cl_2Cu$	brown	241-243d	65	9.12(9.08)	11.64
$[Co(L_{an})_2Cl_2]$	$C_{30}H_{28}N_8S_2O_4Cl_2Co$	Red	210-212	70	7.53(7.51)	8.65
$[Ni(L_{an})_2Cl_2]$	$C_{30}H_{28}N_8S_2O_4Cl_2Ni$	Red	195-197d	69	7.50(7.48)	10.26
$[Cu(L_{an})_2Cl_2]$	$C_{30}H_{28}N_8S_2O_4Cl_2Cu$	black	218-220	71	8.08(8.06)	13.20
$[Co(L_{adb})_2Cl_2]$	$C_{32}H_{26}N_6S_2Br_4Cl_2Co$	yellow	219-221	62	5.84(5.80)	9.43
$[Ni(L_{adb})_2Cl_2]$	$C_{32}H_{26}N_6S_2Br_4Cl_2Ni$	brown	205-207d	66	5.82(5.79)	12.30
$[Cu(L_{adb})_2Cl_2]$	$C_{32}H_{26}N_6S_2Br_4Cl_2Cu$	brown	216-218	69	6.27(6.23)	13.12

 # d=decomposition temper.

Infrared spectra:

The important infrared spectra data of ligands and their complexes are given in Table (2),The bands in the region 1625-1633 cm^{-1} and 1600-1615 cm^{-1} due to ν(C═ N) vibration of thiazole ring and azomethine group in the ligands respectively. These values are increased(thiazole ring) and shifted to lower frequencies(azomethine group) after copmlexation(EL-Bindary & EL-Sonbati, 1999).The bands ν(C-S-C) in region 750-755 cm^{-1} which remains in the same region in free ligands and after copmlexation that mean's the sulfur atom in thiazole group doesn't coordinate with metal in complexes (Chattopadhyay & Sinha, 1996). New weak bands in the region 415-450 cm^{-1} were observed in the spectra of metal complexes , which were not appeared in the spectra of ligands due to ν(M –N) (Nakamoto,1986; Arpalahti & Lehikoinen, 1990) .

Table (2): IR absorption bands of ligands and their complexes in cm^{-1}

Compounds	ν(C═N) thiazole ring	ν(C–S-C)	ν(C═N) azomithine group	ν(M–N)
La	1625	755	1600	---
Lan	1628	751	1608	---
Ladb	1633	753	1615	---
$[Co(L_a)_2Cl_2]$	1647	753	1582	422
$[Ni(L_a)_2Cl_2]$	1644	754	1586	415
$[Cu(L_a)_2Cl_2]$	1642	752	1583	448
$[Co(L_{an})_2Cl_2]$	1646	751	1589	428
$[Ni(L_{an})_2Cl_2]$	1645	750	1592	425
$[Cu(L_{an})_2Cl_2]$	1653	753	1590	450
$[Co(L_{adb})_2Cl_2]$	1650	750	1600	429
$[Ni(L_{adb})_2Cl_2]$	1648	753	1598	424
$[Cu(L_{adb})_2Cl_2]$	1652	754	1597	446

- **The Electronic spectra and magnetic measurements**

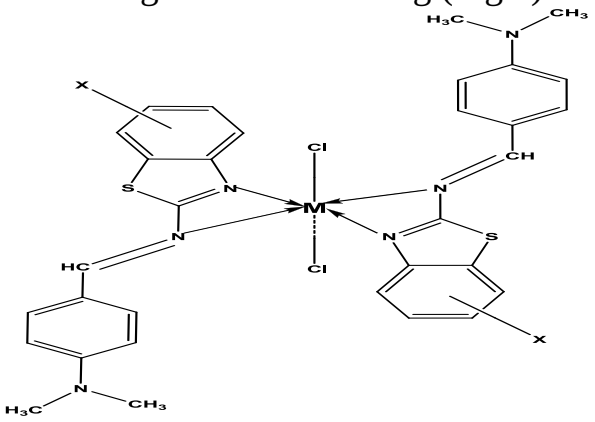
The electronic spectra of ligands (La ,Lan and Ladb) show strong bands in the range 41150-42210cm^{-1} and 33210-33420cm^{-1} which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The electronic spectra of Cobalt (II) complexes showed two absorption bands at 15250-15730cm^{-1} and 23230 - 23470cm^{-1} these were assigned to ^4T_1g (F) → ^4A_2g (F) (ν_2) and ^4T_1g (F) → ^4T_1g (P) (ν_3) transitions respectively, which are characteristic of octahedral stereochemistry. The magnetic moment of cobalt (II) has been found to be (4.79-5.21 B.M) this values of magnetic moment is higher than the spin-only value (3.87 B.M) for there unpaired electrons and may be ascribe to substantial orbital contribution to the moment which is applicable of

high spin octahedral Cobalt (II) complexes(Nicholas1973)(Figgis& Lewis,1960).The magnetic moment for nickel (II) complexes are (2.43-3.60 B.M) and the spectra of this complexes show bands at 15225 -15435 cm^{-1} and 21110 -21290 cm^{-1}which may have existence of ^3A_2g (F) → ^3T_1g (F) (ν_2) and ^3A_2g (F) → ^3T_1g (P) (ν_3) transitions therefore an octahedral configuration suggested . The magnetic moment values of copper (II) complexes (1.86-1.91B.M) which may expressed an octahedral structure. Electronic spectra of these complexes a band show one broad band at 14895-15320 cm^{-1} due to two or three transitions ^2B_1g → ^2A_1g , ^2B_1g →^2B_2g and ^2E_2g → ^2T_2g suggesting a distorted octahedral structure (Nicholas,1973; Figgis & Lewis,1960). The spectral data and magnetic moments of prepared complexes were given in Table (3).

Table(3): Electronic spectra and magnetic moments of the complexes.

Complexes	Electronic spectra cm^{-1}		μ eff.(B.M)
$[Co(L_a)_2Cl_2]$	15250	23230	4.79
$[Ni(L_a)_2Cl_2]$	15328	21193	3.60
$[Cu(L_a)_2Cl_2]$	15320	---	1.89
$[Co(L_{an})_2Cl_2]$	15730	23470	5.21
$[Ni(L_{an})_2Cl_2]$	15225	21110	2.43
$[Cu(L_{an})_2Cl_2]$	14895	---	1.91
$[Co(L_{adb})_2Cl_2]$	15545	23368	4.92
$[Ni(L_{adb})_2Cl_2]$	15435	21290	2.74
$[Cu(L_{adb})_2Cl_2]$	15120	---	1.86

According to these results the octahedral structure suggested for Co(II), Ni (II) and distorted octahedral due to Jahn-Teler effect Cu(II) complexes The Schiff bases coordinate with metal(II) ions through the nitrogen of the azomethine group and nitrogen of thiazole ring (Fig.2).



M = Co(II), Ni(II) and Cu(II) X = H(La); = 6-nitro(Lan) X= 2H = 4,6 diBr(Ladb)

Fig.2: The suggested structure for the complexes

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Journal of Kirkuk University –Scientific Studies , vol.4, No.2,2009

تحضير وتشخيص عدد من قواعد شيف (مشتقة من الثايازول) ومعقداتها لايونات الكوبلت والنيكل والنحاس الثنائية.

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الخلاصة

يتضمن البحث تحضير وتشخيص عدد من معقدات جديدة للكوبلت(II) والنيكل(II) والنحاس(II) مع ليكاندات من نوع قواعد شيف والتي تم الحصول عليها من خلال تكاثف(٢-امينوبنزوثايازول و ٦-نايترو٢-امينوبنزوثايازول و ٤،٦-ثنائي بروموا٢-امينوبنزوثايازول) مع ٤-ن- ثنائي مثيل بنزالديهايد والحصول على اليكاندات (La, Lan, Ladb) ومن ثم مفاعلتها مع املاح الفلزات في مذيب الايثانول بنسبة (٢:١)(فلز:ليكاند) والحصول على معقداتها والتي لها الصيغة $[ML_2Cl_2]$ (ويمثل L=La,Lan,Ladb)وقد شخصت الليكاندات المحضرة ومعقداتها بوساطة تحليل العناصر باستخدام التحليل الطيفي الذري للعناصر و أطياف الأشعة 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 عن طريق ذرات النيتروجين الموجودة في اليكاندات واقتراح الشكل الثماني السطوح لجميع المعقدات الفلزية بالاعتماد على نتائج التحليل التي تم الحصول عليها.