Preparation, Charaterization and Study of Cobalt (II), Nickel (II), Copper (II) and Zinc (II) Complexes of Some Schiff Bases

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الخلاصة

أجرينا في هذا البحث تحضير ودراسة بعض معقدات الكوبلت والنيكل والنحاس والزنك في حالة الأكسدة الثنائية الموجبة ذوات الصيغة العامة $[ML]X_2$ و $[MLX_2]$ التي تم الحصول عليها من مفاعلة ليكاندات من نوع قواعد شيف (مشتقة من اورثو هيدروكسي استيوفينون مع اورثو امينو فينول، اثيل امين و 1،3-بروبان ثنائي الأمين مع أملاح هذه الفلزات في الايثانول. شخصت المعقدات الناتجة بدراستها بوساطة تحليل العناصر والتوصيل الكهربائي والقياسات الطيفية وقد وجد ان المعقدات تتكون بنسبة 2:1 و 1:1 من الملح الفلزي إلى الليكاند، واقترحت بنيات ثماني ورباعي السطوح لجميع المعقدات.

ABSTRACT

Some complexes having the general formula $[ML]X_2$, $[MLX_2]$, where (M= Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2}, L= the ligand) obtained by the condensation of o-hydroxy acetophenone with o-amino phenol, ethyl amine and 1,3-propane diamine and X= chloride ion) where prepared by the reaction of the metal salt with the ligand in ethanolic solution. The complexes have the molar ratio 1:2, 1:1. The complexes were characterized by elemental analysis, molar conductance, infrared and UV. spectral measurements. The studies revealed that the neutral ligands and giving the most expected octahedral and tetrahedral structures for all complexes.

INTRODUCTION

Schiff bases have been widely used in the field of coordination chemistry[1-5]. The Schiff base complexes have been catalytic reaction

[6] and as models for biological system [7,8]. The biological activity of Schiff base is attributed to the formation of stable complex with the transition metal present in the cell [9,10] and they are found to exhibt awide variety of pharmacological properties, clinical and analytical [11].

Earlier work was showed that some drugs increased activity when administered as metal chelates rather than as organic compounds and that the coordination possibility of amine has been improved by condensing with variety of carbonyl compounds. In recent years many complexes of Schiff bases were prepared [12,13]. This may be attributed to their stability, biological activity[14] and potential applications in many fields such as oxidation catalysis [15], electrochemistry [16], etc. It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complexes [17]. Schiff bases with nitrogen and oxygen donor atoms set are well known to coordinate with various metal ions, and this has attracted many authers [18]. This is because of their potential as catalysts for the insertion of oxygen into an organic substrate [19].

In this paper we report the synthesis of a new Schiff base type ligands formed by the condensation of o-hydroxy acetophenone with o-amino phenol, ethyl amine and 1,3-propyl diamine. The ligands system have both nitrogen and oxygen donor sites.

EXPERIMENTAL

Preparation of the ligands

The Schiff base ligand HAOP was prepared by reacting equimolar amounts of *o*-hydroxy acetophnone (0.01 mol; 1.36 g) and *o*-amino phenol (0.01 mol; 1.09 g) in 40 cm^3 ethanol. The reaction mixture was refluxed for about 3 h. The excess solvent was partially evaporated and the resulting product was precipitated by cooling and filtered off, washed with ethanol and dried.

HAEA was prepared from *o*-hydroxy acetophenone (0.01 mol; 0.45g) and ethyl amine (0.01 mol, 0.45 g) whereas HAPA was prepared from *o*-hydroxy acetophenone (0.02 mol; 2.72 g) and 1,3-propane diamine (0.01 mol; 0.74 g) using the above mentioned procedure.

Preparation of complexes

An ethanolic solution of Schiff bases HAOP, HAEA (0.01 mol) and HAPA (0.02 mol) was refluxed with $MCl_2.6H_2O$ where M=Ni or Co, $CuCl_2$. $2H_2O$, $ZnCl_2$ (0.01 mol) in ethanol for about 3h. After refluxing the volume of the solution was reduced and the concentrate cooled at room temperature. The solid complex formed was filtered, washed with ethanol and dried.

Analysis and physical measurements

The complexes were characterized by elemental analysis and molar conductance in DMF solvent with Lf-42 conductivity bridge. The IR spectra were recorded using the KBr disc technique (400-4000) cm^{-1} on a Bruker-Tension 27 spectrophotometer. The electronic spectra in the range 200-1100 nm range were obtained in DMF on a shmadzu UV- 1650 pc spectrophotometer. Magnetic measurements were carried out by faraday method.

RESULTS AND DISCUSSION

The reactions of metal salts and the Schiff base ligands as follows:

$MCl_2.nH_2O + 2HAOP \longrightarrow [M(HAOP)_2]Cl_2 + nH_2O$ ………..I
$MCl_2.nH_2O + 2HAEA \longrightarrow [M(HAEA)_2]Cl_2 + nH_2O$ ………..II
$MCl_2.nH_2O + HAPA \longrightarrow [M(HAPA)Cl_2] + nH_2O$………..…III

Where M= Co^{+2}, Ni^{+2}, Cu^{+2} or Zn^{+2}
n= 2,6

The analytical data of the complexes (Table 1) reasonable and agree well will the given formulation. The complexes are stable in air at room temperature.

Conductance in DMF at room temperature indicates 1:2 electrolytes for type I, II complexes but extremely low conductance value of type III complexes suggest their non-electrolytic nature [20].

Table (I): Molar conductance and analytical data

Compound	M.P. °C	Λ_m (DMF)	M% (found)
HAOP	150		
HAEA	140		
HAPA	135		
$[Co(HAOP)_2]Cl_2$	180	155	(9.56) 10.09
$[Ni(HAOP)_2]Cl_2$	162	160	(9.03) 10.06
$[Cu(HAOP)_2]Cl_2$	176	135	(11.60) 10.80
$[Zn(HAOP)_2]Cl_2$	182	140	(10.32) 11.07
$[Co(HAEA)_2]Cl_2$	170	153	(12.62) 12.93
$[Ni(HAEA)_2]Cl_2$	168	145	(12.71) 12.83
$[Cu(HAEA)_2]Cl_2$	195	138	(12.92) 12.80
$[Zn(HAEA)_2]Cl_2$	185	162	(13.82) 14.14
$[Co(HAPA)Cl_2]$	160	30	(13.10) 13.40
$[Ni(HAPA)Cl_2]$	170	17	(13.13) 13.35
$[Cu(HAPA)Cl_2]$	184	20	(14.21) 14.30
$[Zn(HAPA)Cl_2]$	190	25	(13.85) 14.65

Characterization of the bonding sites of the ligand and the structure of the complexes were carried out by Infrared spectra, electronic spectra and magnetic susceptibility studies.

Infrared spectra

The ligands show characteristic bands around 3450, 1635, 1300, 1210 cm^{-1} which are due to ν_{OH}, $\nu_{C=N}$, δ_{OH} and ν_{C-O} respectively (Table II). For complexes formed, the ν_{OH}, δ_{OH} and $\nu_{C=N}$ band are shifted to lower frequency values by about 100-130, 20-30, and 15-35 cm^{-1} respectively. These negative shifts suggest coordination through hydroxyl oxygen and azomethine nitrogen atoms. Further support to this coordination is the splitting of ν_{C-O} band into two peaks which due to C-O bonding. For all complexes new bands were noticed around (460-470), (425,430) cm^{-1} are attributed to the stretching modes of M-O and M-N respectively [21].

Electronic spectra and magnetic moments

The position of electronic spectral bands and the effective magnetic moments values together are given in (Table III). For type I and III complexes the spectra of cobalt (II) complexes exhibit three bands due to the spin-allowed transitions ${}^4T_1g(F) \longrightarrow {}^4T_2g(F)\nu_1$, ${}^4T_1g(F) \longrightarrow {}^4A_2g(F)\nu_2$, ${}^4T_1g(F) \longrightarrow {}^4T_1g(p)\nu_3$. The three bands in the spectra of nickel (II) complexes are corresponding to ${}^3A_2g(F) \longrightarrow {}^3T_2g(F)\nu_1$, ${}^3A_2g(F) \longrightarrow {}^3T_1g(F)\nu_2$, ${}^3A_2g(F) \longrightarrow {}^3T_1g(P)\nu_3$ transition. The number and positions of these bands corresponding to octahedral structure for both cobalt and nickel complexes [22,23]. The electronic spectra of the copper complexes show only one broad bands, since the location of this band below 15000 cm^{-1} there for octahedral structure is the most probable for this hexacoordination copper (II) complexes, the asymmetric band due to the combined transitions ${}^2B_1g \longrightarrow {}^2A_1g$, ${}^2B_1g \longrightarrow {}^2B_2g$, ${}^2B_1g \longrightarrow {}^2Eg$.

On the other hands the electronic spectra for HAEA cobalt. Nickel and copper having tetrahedral geometry [22] and the bands are attributed to ${}^4A_2(F) \longrightarrow {}^4T_2(F)$, ${}^4A_2 \longrightarrow {}^4T_1(F)$, ${}^4A_2(F) \longrightarrow {}^4T_1(P)$, ${}^3T_1(F) \longrightarrow {}^3T_2(F)$, ${}^3T_1(F) \longrightarrow {}^3A_2(F)$, ${}^3T_1(F) \longrightarrow {}^3T_1(P)$ and ${}^2T_2(F) \longrightarrow {}^2E$ transition [24].

In the electronic spectra of the zinc (II) complexes, in addition to the broad band observed which due to $\pi \rightarrow \pi^*$ transition of the free ligand, new additional band was observed for complexes 37212-27297 cm^{-1}, this new band may be attributed to charge transfer transition from filled orbitals of the ligand to the orbitals of the metal and thus supporting the formation of complexes some times the ligands are characterized by two observation bands in the UV. region . A high intensity band and second band with lower intensity both bands showed ared shift on coordination with zinc ion. These observation represent of other indication for the coordination of the ligand to zinc ion [25,26].

The magnetic susceptibility of the complexes was measured at room temperature by using the faraday method [27]. Magnetic moment measurements of the complexes correspond to the presence of three, two and one unpaired electrons for Co (II) d^7, Ni (II) d^8 and Cu (II) d^9 species, respectively [28].

On the light of the above studies, its concluded that the ligands (HAOP, HAEA, HAPA) coordinating through hydroxyl and azomethine groups giving the most expected structures as show in fig (I), (II), (III).

Table (II): The most important I.R bands (cm^{-1}) of the ligands and their complexes

Compound	ν_{OH}	$\nu_{C=N}$	δ_{OH}	ν_{C-O}	ν_{M-O}	ν_{M-N}
HAOP	3410	1635	1280	1180	-	-
HAEA	3450	1635	1300	1185	-	-
HAPA	3420	1630	1300	1210	-	-
$[Co(HAOP)_2]Cl_2$	3300	1610	1250	1160	470	425
$[Ni(HAOP)_2]Cl_2$	3290	1610	1250	1160	460	425
$[Cu(HAOP)_2]Cl_2$	3295	1600	1255	1160	460	430
$[Zn(HAOP)_2]Cl_2$	3290	1600	1255	1160	465	420
$[Co(HAEA)_2]Cl_2$	3320	1610	1270	1195	460	430
$[Ni(HAEA)_2]Cl_2$	3290	1615	1270	1190	460	425
$[Cu(HAEA)_2]Cl_2$	3300	1610	1275	1190	470	430
$[Zn(HAEA)_2]Cl_2$	3295	1610	1275	1195	760	420
$[Co(HAPA)Cl_2]$	3330	1615	1280	1165	470	430
$[Ni(HAPA)Cl_2]$	3330	1610	1275	1160	465	420
$[Cu(HAPA)Cl_2]$	3330	1610	1275	1165	465	425
$[Zn(HAPA)Cl_2]$	3300	1615	1270	1165	470	430

Table (III): Electronic spectral data and magnetic of the complexes

Compound	μ_{eff} (B.M.)	Electronic spectra			C.T.
		ν_1	ν_2	ν_3	
$[Co(HAOP)_2]Cl_2$	4.81	10123	14725	21436	28523
$[Ni(HAOP)_2]Cl_2$	3.20	10300	15661	24420	31813
$[Cu(HAOP)_2]Cl_2$	2.14	14401	-	-	24182
$[Zn(HAOP)_2]Cl_2$	-	-	-	-	27297, 37212
$[Co(HAEA)_2]Cl_2$	4.12	-	-	14375	30155
$[Ni(HAEA)_2]Cl_2$	3.64	-	-	13355	30611
$[Cu(HAEA)_2]Cl_2$	1.98	11733	-	-	31011
$[Zn(HAEA)_2]Cl_2$	-	-	-	-	28911, 37236
$[Co(HAPA)Cl_2]$	4.83	10220	15435	121878	30751
$[Ni(HAPA)Cl_2]$	3.17	10712	14175	25211	32815
$[Cu(HAPA)Cl_2]$	2.03	14476	-	-	303211
$[Zn(HAPA)Cl_2]$	-	-	-	-	30864, 36652

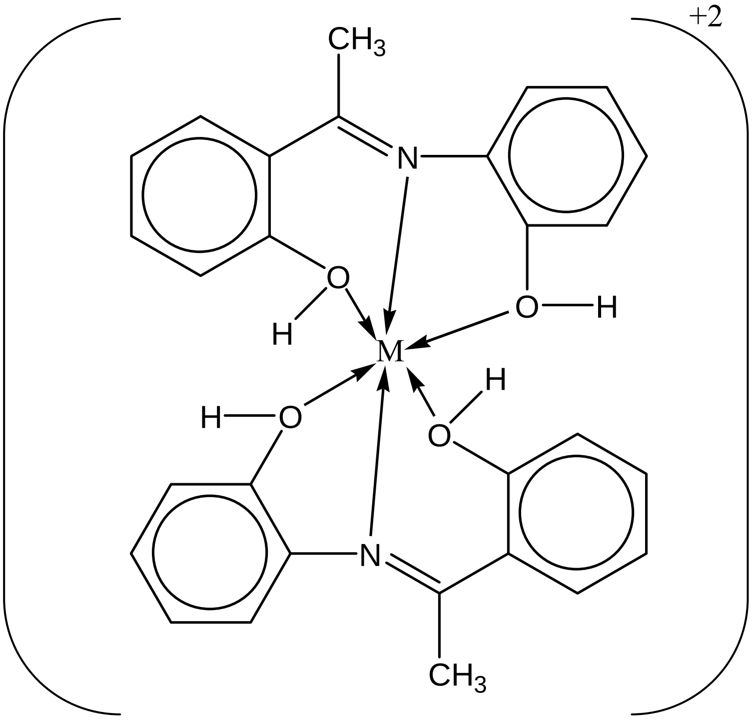

Fig (I)

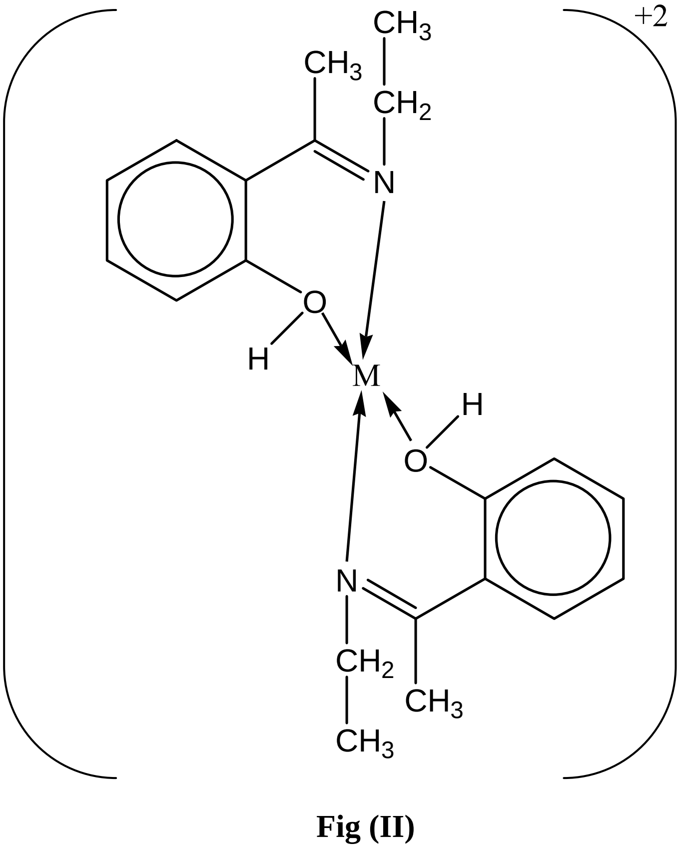

Fig (II)

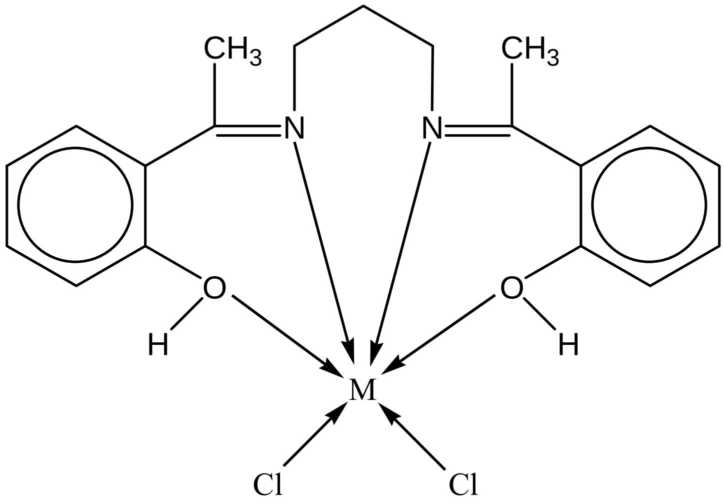

Fig (III)

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

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