

Preparation and Characterization of Mixed Ligands Metal Complexes Derived from Acetylacetyl P-Imino Acetophenone and 5-Nitroso8-Hydroxyquinoline With Fe (II), Co (II), Ni (II) and Cu (II) Ions

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Received on: 14/12/2011 & Accepted 3/5/2012

ABSTRACT

The Schiff base ligand (HL) has been prepared by the reaction of P-aminoacetophenone with acetylacetyl. This ligand reacted with 5-nitroso8-hydroxyquinoline (HQ) and salts of first transition series (M) where M= (Fe(II), Co(II), Ni(II) and Cu(II) ions) to get mononuclear metal (II) complexes of the type [MLQ(H₂O)₂] have also been synthesized. The formation of the Schiff base ligand and its complexes have been envisaged from FTIR, UV-VIS, magnetic susceptibility, conductivity and atomic absorption technique studies. These studies confirm an octahedral environment around the metal ion in all our complexes.

Keywords: acetylacetyl, 5-nitroso8-hydroxyquinoline, p-aminoacetophenone, Schiff base.

تحضير وتشخيص معقدات فلزية مشتقة من 5-نايروزو 8- هايدروكسيديكونيولين واستيل استينونيل بارا-امينو استيونيون مع ايونات Cu(II), Ni(II), Co(II), Fe(II)

الخلاصة

ليكند قاعدة شف (HL) المحضر من تفاعل بارا امينواسيتوفينون مع الاستيل اسيتون . هذا الليكند تم تفاعلة مع 8-هيدروكسي 5- نايتروزوكوينولين [HQ] وبعض املاح فلزات السلسلة الانتقالية الاولى (M) حيث ان M = الفلزات (Fe (II) , Co (II) , Ni (II) و Cu (II)) للحصول على معقدات فلزية لايونات ثنائية التكافؤ احادية النواة ذات نوع [MLQ(H₂O)₂]. قاعدة شف والمعقدات المحضرة تم تشخيصها بواسطة مطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية / المرئية، الحساسية المغناطيسية، التوصيلية الكهربائية والامتصاص الذري وهذه النتائج اظهرت ان الشكل الهندسي هو ثماني السطوح في جميع المعقدات المحضرة.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields [1-3]. The interaction of these donor ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active [4]. Schiff base complexes of transition metals containing ligands with N,O donors are known to exhibit interesting significant antifungal, antibacterial, anticancer and catalytic activities [5]. Thus, in recent years metal complexes of Schiff bases have attracted considerable attention due to their biologically active [6-7]. It has been reported that transition metal complexes of Schiff base derived from acetylacetylonyl are synthesized and characterized [8]. A search through literature reveals that there is no work done on the transition metal complexes of the Schiff base and 5-nitroso8-hydroxyquinoline [9].

EXPERIMENTAL

Chemicals

Metal salts ($\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), acetylacetylonyl, p-aminoacetophenone, 5-nitroso8-hydroxyquinoline, ethanol and methanol. All chemicals were from Fluka and B.D.H company without further purification.

Physical Measurements and Analysis

Melting point was recorded by using Gallenkamp M.F.B- 600 F melting point apparatus. FTIR spectra were recorded as CsI discs using FTIR-8400S, Shimadzu in the range of $4000\text{-}200\text{ cm}^{-1}$. Electronic spectra were obtained using UV-VIS-1650 PC Shimadzu spectrophotometer, at wavelength (200-1100) nm at 25°C in 10^{-3} M in DMSO. Conductivity was measured by capacitor analyzer in DMSO solution 10^{-3} M at 25°C . Magnetic susceptibility measurements were obtained at 25°C by balance magnetic susceptibility of Bruke Magnet B.M.6, England. The metal percent in the complexes were determined using the atomic absorption Shimadzu 680cc-flame/Japan.

Preparation of the Schiff Base ligand (L)

The Schiff base ligand was prepared by the condensation of the p-aminoacetophenone (1.3320 g), (1 mmol) with (1 ml), (1 mmol) acetylacetylonyl in 10 ml absolute ethanol. The resulting mixture was then refluxed for 90 minutes. Yellow precipitate was formed and filtered, recrystallized from ethanol to give pale yellow needles [10].

General Method for Preparation of the Complexes

An ethanol solution of ligand L (0.2030 g), (1 mmole) and an ethanol solution of ligand Q (0.1740 g), (1 mmole) were added respectively to an aqueous solution of the metal salts (1 mmole). The reaction mixture was continuously stirred for 120 minutes. The required product was shortly precipitated at room temperature, filtered off and washed with 1:1 (ethanol : water) and crystallized from ethanol and dried at 50°C .

RESULTS AND DISCUSSION

The physical properties and data of the ligands L and Q with their metal complexes are given in Table 1. The value of molar conductivity (Λ) in DMSO indicates that the all complexes were electrolytes [11].

Table (1) Physical Characteristics and analytical data for (L), (Q) and its metal complexes

Compound	Color	Melting Point C	Yield %	Conductivity ($\mu\text{s.cm}^{-1}$)	Conductivity	Element analysis	
						Calc.	Found
L	Pale yellow	98-99	76	-	-	-	-
Q	Pale yellow	> 236	-	-	-	-	-
[Fe(L)(Q)(H ₂ O) ₂]	Black	53-55	94	100.5	Conductive	12.584	10.638
[Co(L)(Q)(H ₂ O) ₂]	Black	78-79	96	67.7	Conductive	13.169	12.213
[Ni(L)(Q)(H ₂ O) ₂]	Black	> 300 d*	91	272.8	Conductive	13.169	12.045
[Cu(L)(Q)(H ₂ O) ₂]	Black	126- 127	92	45.8	Conductive	14.128	12.823

(d*) = Decomposition., Q= 5-nitroso 8-hydroxyquinoline.

L= (Acetylacetone + P-amino acetophenone).

Magnetic Prop Erties

The magnetic moment μ_{eff} for the complexes of Fe⁺²(d⁶) and Co⁺² (d⁷) were found to be 4.89 B.M and 3.87 B.M respectively, which within the expected spin-only values [12, 13], and that of the Ni⁺²(d⁸) complex was found to be 2.82 B.M. Finally, the μ_{eff} of the Cu⁺² (d⁹) complexes was found to be 1.73 B.M which lies within the expected value for one electron [12]. All the data are found in Table (2).

Table (2) The magnetic properties of the complexes at 25°C.

Complexes	No.of Electron	No.of Unpaired Electron	Electron Configuration	Term Symbol	Term Symbol Ground State in Td	μ_{eff}	
						Calc.	Found
Fe(L)(Q)2H ₂ O	d6	4	$t_{2g}^4 e_g^2$	⁵ D	⁵ T _{2g}	4.89	5.121
	d7	3	$t_{2g}^5 e_g^2$	⁴ F	⁴ T _{1g}	3.87	4.164
Co(L)(Q)2H ₂ O	d8	2	$t_{2g}^6 e_g^2$	³ F	³ A _{2g}	2.82	2.925
	d9	1	$t_{2g}^6 e_g^3$	² D	² E _g	1.73	1.868
Ni(L)(Q)2H ₂ O							
Cu(L)(Q)2H ₂ O							

The Electronic Spectra

Electronic Spectra of Free Ligands

The spectrum of free ligand L show a strong band at 271 nm which is attributed to $\pi \rightarrow \pi^*$ and another at 291 and 342 nm due to $n \rightarrow \pi^*$ [14]. The 5-nitroso8-hydroxyquinoline spectrum show absorption bands at 297, 313 nm respectively due to $\pi \rightarrow \pi^*$ and another bands at 322, 353, 372 nm belongs to $n \rightarrow \pi^*$.

Electronic Spectra of the Complexes

Only one broad band is observed at (14614 cm^{-1}) in the electronic spectrum of the Fe (II) complex assigned to ${}^5T_{2g} \longrightarrow {}^5E_g$ transition which is in conformity with octahedral geometry [15].

The electronic spectrum of the Co (II) complex showed two spin allowed transition (assigned as ν_2 and ν_3 absorption bands respectively) at (16949 cm^{-1} and 25510 cm^{-1}) assignable to ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(P)$ transition respectively, which clearly indicate that the complex has six coordination octahedral geometry.

The electronic spectrum of the Ni (II) complex display two bands (assigned as ν_2 and ν_3 absorption bands respectively), (18181 cm^{-1} and 25445 cm^{-1}), assignable to ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition respectively which clearly indicate that the complex has six coordination octahedral geometry [16].

Only one broad band is observed at (25974 cm⁻¹) in the electronic spectrum of the Cu (II) complex assigned to ²E_g → ²T_{2g} transition which is in conformity with octahedral geometry [17].

Infrared Spectral Studies

Infrared Spectra of Free Ligands

The characteristic vibrations and assignments of ligand L and Q and their complexes as CsI disc are described in Table 4.

The spectrum of ligand L exhibited weak bands at 3350 cm⁻¹ and 3060 cm⁻¹, this could be attributed to ν(O-H) and ν(C-H) aromatic respectively [18]. While the strong band at 1650 cm⁻¹ which belongs to ν(C=O) and the other strong bands belong to the ν(C=N), ν(C=C) and ν(C-O) were found at 1600 cm⁻¹, 1460 cm⁻¹ and 1280 cm⁻¹ respectively [19,20]. See Figure 1.

In the spectrum of ligand Q, it was noticed that the broad band at 3200 cm⁻¹ which could be attributed to ν(OH) with shoulder at 3070 cm⁻¹ due to ν(C-H) aromatic. The other strong bands are appeared at 1610, 1485, 1225, 1380 and 1350 cm⁻¹ which attributed to ν(C=N), ν(C=C), ν(C-O), ν(N=O), and ν(C-N) respectively [21].

Infrared Spectra of Complexes

The infrared spectra of the prepared complexes exhibited ν(C=N) in the range of 1630-1615 cm⁻¹ which shows a shifting to the lower frequencies by 10-25 cm⁻¹ in compared with ligand L, also appeared shifting to the higher frequencies between 5-30 cm⁻¹ in compared with ligand Q, it is which indicated the coordination of ligands with metal ions through the nitrogen atoms in their structures. The appearing of band for ν(OH) vibration in the spectra of complexes is indicating the coordination of water oxygen with metal ions. The spectra bands of complexes at 1660 and 1285 cm⁻¹ were characterized for the carbonyl and nitrosyl groups which did not suffer a shift. Thus, it is suggested that the oxygen atom of these groups are not coordinated to the metal ion.

Metal - Ligand Bond

The infrared of prepared complexes have shown weak bands in the range of 520-570 cm⁻¹ and 420- 480 cm⁻¹ which was attributed to the of ν(M- O) and ν(M- N) respectively.

Table (4): The characteristic bands of Infrared spectra of the ligands and their complexes.

Compounds	ν(O-H)	ν(C-H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(M-O)	ν(M-N)
Q	3200	3070	-	1610	1500	-	-
L	3350	3060	1660	1640	1460	-	-
[Fe(L)(Q)]2H ₂ O	3360	3010	1630	1623	1456	520	450
[Co(L)(Q)]2H ₂ O	3329	2993	1610	1620	1470	520	440
[Ni(L)(Q)]2H ₂ O	3300	2929	1656	1630	1450	570	480
[Cu(L)(Q)]2H ₂ O	3440	3000	1660	1615	1467	560	420

CONCLUSIONS

Mixed ligand complexes containing schiff base ligand HL (acetylacetonyl p-iminoacetophenone) and HQ (5-nitroso-8-hydroxyquinoline) were reacted with (Fe(II), Co(II), Ni(II) and Cu(II) ions) and get general formula $[M(L)(Q)]$ were synthesized. All complexes are paramagnetic in nature. The molar conductivity of all complexes in DMSO solution were electrolyte and the configurations were performed to coordinate the Schiff base (HL) and (HQ) through the nitrogen and oxygen atoms, the absence of any band below 10000 cm^{-1} eliminate the possibility of a tetrahedral environment. According to the above mentioned data (spectra, molar conductance, metal analyses and magnetic properties), the proposed structures of complexes are octahedral and as shown below in Figure 2.

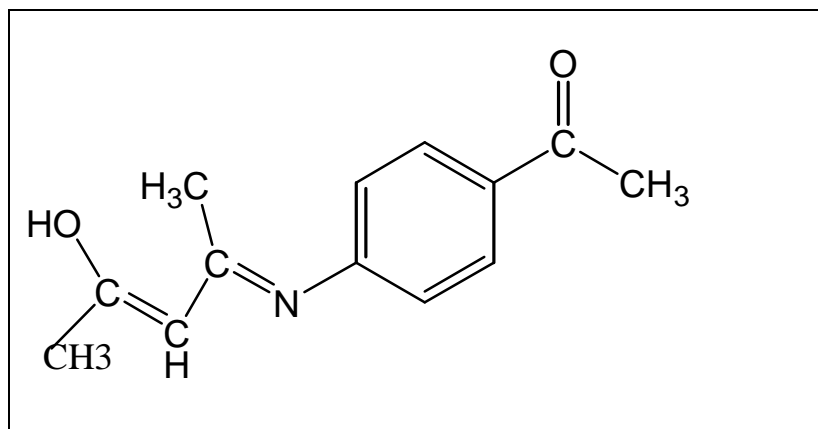


Figure (1): Structure of ligand (L)

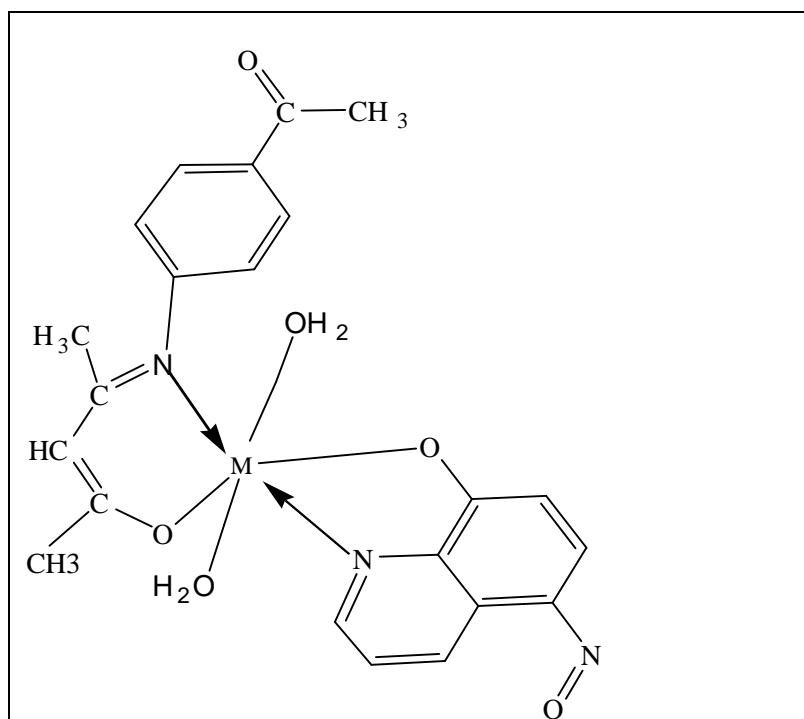


Figure (2): Suggested structure of the complexes

M = Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺

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