Journal of Al-Nahrain University Vol.15 (4), December, 2012, pp.68-73 Science

Synthesis of new metal complexes derived from 5-nitroso 8-hydroxy quinoline and Salicylidene P-imino acetophenone with Fe(II), Co(II), Ni(II) and Cu(II) ions

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Abstract

Bidentate Schiff-bases have been among those that are extensively used in preparing metal complexes. These ligands are described according to their donor set N, N-donor and N, O- donor Schiff-bases. Bidentate schiff base having nitrogen and oxygen atom was prepared by condensation of the P-amino-acetophenone with salicylaldehyde in absolute ethanol. An ethanol solution of Schiff base and an ethanol solution of 5- nitroso 8-hydroxy- quinoline were reacted with aqueous solution of metal salts to give complexes with the general formula [M(L)(Q)], where Q = 5- nitroso 8-hydroxyquinoline, L = (salicylaldehyde + p-amino-actophenone) and M^{II} = Fe, Co, Ni and Cu ions. The resulting products were found to be solids which were characterized using FTIR and UV-Vis spectroscopy. An elemental analysis was performed using atomic absorption technique; magnetic susceptibility and the conductivity were also measured.

Keywords: 5-nitroso 8- hydroxyquinoline, salicylaldehyde, P-amino acetophenone, salicylaldehyde mixed ligand complexes, Schiff base.

1. Introduction

Schiff bases derived from aromatic amines and aldehydes have a wide variety and an important class of ligands in coordination chemistry and find extensive applications in different fields, *e.g.*, biological, inorganic and analytical chemistry [1, 2]. Many biologically important Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, antitumor and anti HIV activities [3,4]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [5].

The interaction of these donors ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active [6]. Several research papers reported the synthesis and characterization of transition metal complexes of Schiff bases derived from salicylaldehyde [7,8]. A search through literature revealed that there is no work reported done on the transition metal complexes of the Schiff base and 5-nitroso 8-hydroxyquinoline.

2. Experimental

2.1. Chemicals and Instrumentals

Metal salts; ($FeCl_2.2H_2O$, $CoCl_2$. $6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$) were obtained from Fluka Company in high purity. Salicylaldehyde, p-amino acetophenone, 5-nitroso 8-hydrox-yquino-line, ethanol, and methanol were from B.D.H. Company.

2.2. Physical Measurements and Analysis

Melting points were 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 4000-200 cm^{-1}. Electronic spectra were obtained using UV-Vis-1650 PC Shimadzu spectrophotometer using 1 cm quartz cell in the range 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 25ºC 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.

2.3. Preparation of the Schiff Base (L)

The Schiff base ligand was prepared by the condensation of the p-amino-acetophenone 1.6278 g (10 mmol) with 1 ml (9.381 mmol) salicylaldehyde in absolute ethanol 10 ml. The resulting mixture was then refluxed for 90 mints. The yellow precipitate formed was filtered and recrystalized from ethanol to give yellow needles [9].

2.4. Preparation of the Complexes, General Method.

An ethanol solution of ligand L 0.2390 g (1 mmole) and an ethanol solution of ligand Q 0.1740 g (1 mmole) were added respectively to an aqueous solution of each the metal salts (1 mmole). The reaction mixture was continuously stirred for 90 mints. The required product was shortly precipitated at room temperature, filtered off and washed with 1 : 1 (ethanol : water), crystallized from ethanol and dried at 50°C.

3. Results and Discussion

The physical properties and data of the ligands L and Q with their metal complexes are given in Table (1). The values of molar conductivity (Λ) in DMSO indicated that all complexes were electrolyte, except the complex [Co(L)(Q)] was unknown [10]

Table (1)

Physical Characteristics and analytical data for (L), (Q) and their for metal complexes.

Compound	***Color***	***Melting Point C***	***Yield %***	***Conductivity ($\mu s.cm^{-1}$)***	***Conductivity*****	***Elemental analysis M%***	
						Calc.	***Found***
L	Yellow	120-123	86	-	-	-	-
Q	Pale yellow	> 236 d*	-	-	-	-	-
[Fe(L)(Q)]	Black	190-192	94	50.3	Conductive	12.017	11.231
[Co(L)(Q)]	Brown	82-84	96	36.3	Unknown	12.635	13.576
[Ni(L)(Q)]	Dark brown	> 300 d*	64	44.3	Conductive	12.560	11.788
[Cu(L)(Q)]	Black	> 300 d*	83	40.8	Conductive	13.486	12.930

(d*) = Decomposition, Q= 5-nitroso 8-hydroxyquinoline, L= salicylidene P-imino-actophenone.

(**) =The conductivity measured in DMSO solvent at 25 ° C. Where (0-20) are non-conductive; (20-40) are unknown; (40-60) are conductive [10].

3.1. Magnetic Properties

The magnetic moment μ_{eff} for the complexes of Fe^{+2}(d^6) and Co^{+2} (d^7) were found to be 4.9 B.M and 3.9 B.M respectively, which within the expected spin-only values [8,11]. The higher value of μ_{eff} of the Ni^{+2}(d^8) complexes 3.0 B. M may be due to the orbital contribution [12]. Finally, the μ_{eff} of the Cu^{+2} (d^9) complexes was found to be 1.8 B.M which lies within the expected value for one electron [8]. All the data and remarks are found in Table (2).

Table (2)

The magnetic properties of the complexes at 25°C.

Complexes	***No.of Ele.***	***No.of Unpaird Electron***	***Electron Configuration***	***Term Symbol***	***Term Symbol Ground State in Td***	***Orbital Configuration***	***μ_{eff}***	
							Found	***Calculate***
Fe(L)(Q)	d^6	4	$E^3t_2g^3$	^5D	^5E	NO	4.930	4.898
Co(L)(Q)	d^7	3	$e^4t_2g^3$	^4F	$^4A_2$	NO	3.994	3.872
Ni(L)(Q)	d^8	2	$e^4t_2g^4$	^3F	$^3T_1$	Yes	3.021	2.828
Cu(L)(Q)	d^9	1	$e^4t_2g^5$	^2D	$^2T_2$	Yes	1.833	1.732

3.2. The Electronic Spectra

3.2.1. Electronic Spectra of Free Ligands

The spectrum of free ligand L shows a strong band at 269 nm which may be attributed to $\pi \rightarrow \pi^*$ and anothers at 307, 327, 339 nm due to $n \rightarrow \pi^*$ [8,13]. The 5-nitroso 8-hydroxyquinoline spectrum shows absorption bands at 297, 313 nm respectively due to $\pi \rightarrow \pi^*$ and another bands at 322, 353, 372 nm belong to $n \rightarrow \pi^*$.

3.2.2. Electronic Spectra of the Complexes

1. [Fe (L) (Q)] complex.

The electronic spectrum of black complex shows a band at 355 nm which belongs to charge transfer and another band at 450 nm which caused by the electronic transition $^5E_{(D)} \rightarrow {}^5T_{2(D)}$ [8,14].

2. [Co (L) (Q)] complex.

The electronic spectrum of brown complex shows a band at 225 nm may be due to charge transfer charge transfer. The other band at 360 nm may be attributed to $^4A_{2\,(F)} \rightarrow {}^4T_{1\,(P)}\,(\nu_3)$, and the electronic transition of $^4A_{2\,(F)} \rightarrow {}^4T_{1\,(F)}(\nu_2)$, was found at 628 nm. Finally, the absorption band at 688 nm is due to $^4A_{2\,(F)} \rightarrow {}^4T_{2\,(F)}\,(\nu_1)$, transitions.

Accordingly, the ligand field splitting energy, 10Dq was taken as equal to the electronic transition (ν_1) 14534.88 cm^{-1} and the Racah inter electronic repulsion parameter B^- was found to be 96.694 cm^{-1} from the relation.

$$\beta = \left(\frac{B^-}{B^o}\right)$$

β was found to be equal 0.099 .These parameters are accepted for Co (II) tetrahedral complexes.

3. [Ni (L) (Q)] complex.

The electronic spectrum of dark brown complex of Ni (II) shows band at 354 nm due to charge transfer. The other bands at 381, 510 nm may be attributed to $^3T_{1\,(F)} \rightarrow {}^3A_{2\,(F)}\,(\nu_3)$ and $^3T_{1\,(F)} \rightarrow {}^3T_{1\,(P)}\,(\nu_2)$ respectively and the electronic transition at 830 nm, is due to $^3T_{1\,(F)} \rightarrow {}^3T_{2\,(F)}\,(\nu_1)$ transition.

The 10Dq value for the complex was equal to 7559.651 cm^{-1} and B^- value found to be 647.332 cm^{-1} while β was equal to 0.628 .These are the characteristics for tetrahedral complexes of Ni (II).

4. [Cu (L) (Q)] complex.

The spectrum of the dark-green complex of Cu (II) shows very strong band at 279 nm which belongs to the charge transfer. The shoulder found in the visible region at 421 nm attributed to the electronic transition $^2T_{2\,(D)} \rightarrow {}^2E_{\,(D)}$ [15]. All transitions with their assignments are summarized in Table (3).

Table (3)

U.V-Visible spectra of free ligand and their complexes in 10^{-3} M in DMSO.

Compounds	λ_{max} nm	*Wav number cm^{-1}*	*Transitions*
L	214	46728.971	$\pi \rightarrow \pi^*$
	269	37174.721	$\pi \rightarrow \pi^*$
	307	32573.289	$n \rightarrow \pi^*$
	327	30581.039	$n \rightarrow \pi^*$
	339	29498.525	$n \rightarrow \pi^*$
Q	297	33670.033	$\pi \rightarrow \pi^*$
	313	31948.881	$\pi \rightarrow \pi^*$
	322	31055.900	$n \rightarrow \pi^*$
	353	28328.611	$n \rightarrow \pi^*$
	372	26881.720	$n \rightarrow \pi^*$
[Fe(L)(Q)]	355	28169.014	C.T
	450	22222.222	$^5E_{(D)} \rightarrow {}^5T_{2(D)}$
[Co(L)(Q)]	225	44444.444	C.T
	360	27777.777	$^4A_{2(F)} \rightarrow {}^4T_{1\,(P)}\,(\nu_3)$
	628	15923.566	$^4A_{2(F)} \rightarrow {}^4T_{1\,(F)}\,(\nu_2)$
	688	14534.883	$^4A_{2(F)} \rightarrow {}^4T_{2\,(F)}\,(\nu_1)$
[Ni(L)(Q)]	354	28248.547	C.T
	381	26246.719	$^3T_{1(F)} \rightarrow {}^3A_{2\,(F)}\,(\nu_3)$
	510	19607.843	3T$_{1(F)} \rightarrow {}^3T_{1\,(P)}\,(\nu_2)$
	830	12048.192	$^3T_{1(F)} \rightarrow {}^3T_{2\,(F)}\,(\nu_1)$
[Cu(L)(Q)}	279	35842.29	C.T
	421	23752.96	$^2T_{2\,(D)} \rightarrow {}^2E_{\,(D)}$

3.3. Infrared Spectral Studies

3.3.1. Infrared Spectra of the Free Ligands

The characteristic vibrations and assignments of ligand L and Q and their complexes as CsI discs are listed in Table (4).The spectrum of ligand L exhibited a weak band at 3360 cm^{-1} due to hydroxyl groups ν(O-H) (ligand showed weak broad band due to formation of hydrogen bonds between hydroxyl groups and the lone pairs of the nitrogen atoms of the Schiff-base) and 3050 cm^{-1}, this could be attributed to ν(C-H) aromatic [16] , while the other strong bands were found at 1678, 1620, 1460, 1360 and 1260 cm^{-1} belong to the ν(C=O), ν(C=N), ν(C=C), δ(C-H) for -CH_3 and ν(C-O) respectively [17,18]. Fig.(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 [19].

3.3.2. Infrared Spectra of Complexes

The infrared spectra of the prepared complexes exhibited ν(C=N) in the range of 1570-1600 cm^{-1} which shows a shifting to the lower frequencies by 50-20 cm^{-1} compared with ligand L, also appeared shifting to the higher frequencies between 40-10 cm^{-1} compared with ligand Q, indicated the coordination of ligands with metal ions through the nitrogen atoms in their structures. Other bands appeared in the range of 1155-1170 cm^{-1} belongs to the ν(C-O), shifted to the lower frequencies by 105-90 cm^{-1} and 80-55 cm^{-1} compared with ligands L and Q respectively. The disappearing of band for ν(OH) vibration in the spectra of complexes indicating the coordination of phenolic oxygen with metal ions [8,20]. The spectra bands of complexes at about 1680 and 1380 cm^{-1} were characterized for the carbonyl and nitroso groups which did not suffer a shift. Thus, it is suggested that the oxygen atom of the carbonyl and nitroso groups are not coordinated to the metal ion.

3.3.3. Metal - Ligand Bond

The infrared of the prepared complexes showed weak bands in the range of 500-520 and 419- 460 cm^{-1} which may be attributed to the 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(N=O)*	*ν(C-O)*	*ν(M-O)*	*ν(M-N)*
Q	3200 b	3070 sh	-	1610s	1485 v.s	1380	1225 s	-	-
L	3360 w	3050 w	1678 v.s	1620 v.s	1460 s	-	1260 s	-	-
[Fe(L)(Q)]	-	3060 w	1680 s	1600 v.s	1460 s	1374 s	1170 s	520 w	460 w
[Co(L)(Q)]	-	3000 w	1679 v.s	1598 v.s	1450 s	1375v.s	1183 s	540 w	420 w
[Ni(L)(Q)]	-	3020v.w	1685 s	1580 s	1464 s	1378 s	1151 s	552 w	422 w
[Cu(L)(Q)]	-	3030 w	1675 v.s	1570 s	1461 s	1385 s	1155 s	500 w	419 w

b= broad, sh= shoulder, w= weak, v= very, s= strong.

4. Conclusion

In this paper new mixed ligand complexes containing Schiff base and 5-nitroso 8-hydroxyquinoline with the general formula [M(L)(Q)], where L= salicyledene p-imino acetophenone (Fig.(1)) and Q= 5-nitroso 8-hydroxyquinoline were synthesized. The elemental analysis, magnetic susceptibility, molar conductivity, FTIR and UV-Visible electronic spectral observations and the configurations were performed to coordinate the Schiff base and 5-nitroso 8-

hydroxyquinoline through the nitrogen and oxygen atoms suggest the tetrahedral geometry for the Fe(II), Co(II), Ni(II), and Cu(II) complexes and exhibit coordination number four. The general structure of the complexes is shown in Fig.(2).

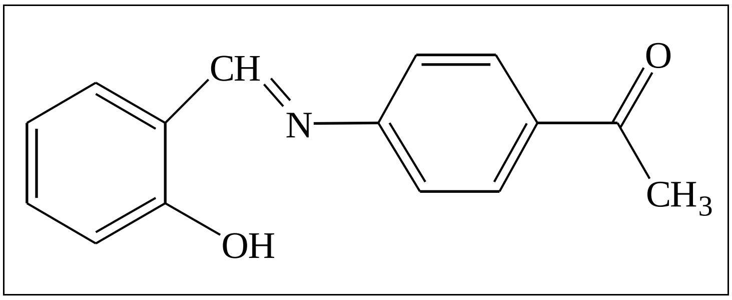
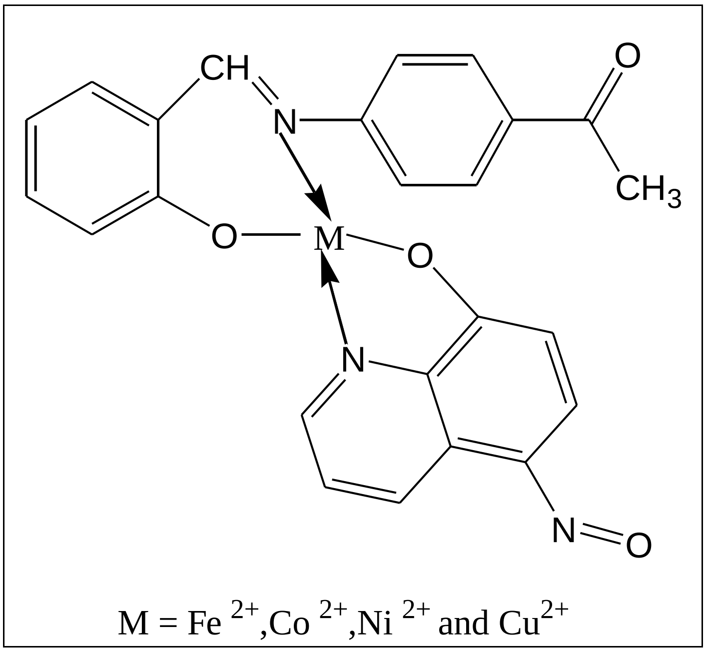


Fig.(1) Structure of ligand (L).



M = Fe $^{2+}$,Co $^{2+}$,Ni $^{2+}$ and Cu^{2+}

Fig.(2) Suggested structure of the complexes.

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الخلاصة

قواعد– شف ثنائية المخلب هي بين تلك الليكندات التي تستخدام بشكل واسع لتحضير المعقدات الايونية. وتصنف هذه الليكندات حسب مجاميعها المانحة لقواعد– شف مثل N,N – مانحة و N,O– مانحة . تم تحضير قواعد شف ثنائية المخالب الحاوية على ذرتي الاوكسجين والنايتروجين من تكثيف بارا–امينو استيوفينون مع السلسلديهايد في الايثانول المطلق ومفاعلة المحلول الايثانولي لقاعة شف المحضرة والمحلول الايثانولي لمركب ٥– نايتروزو ٨– هيدروكسي كوينولين مع المحلول المائي لبعض املاح الفلزات للحصول على معقدات بصيغة عامة [M(L)(Q)] حيث ان Q = ٥– نايتروزو ٨– هيدروكسي كوينولين، L = بارا–ايمينو استيوفينون و M = ايونات Fe(II),Co(II), Ni(II) Cu(II). تم قياس النواتج الصلبة باستخدام مطيافية الاشعة تحت الحمراء والاشعة الفوق البنفسجية المرئية والجساسية المغناطيسية. تم تقدير الفلزات باستخدام تقنية الامتصاص الذري والتوصيلية الكهربائية.