Preparation and Study of Some New Schiff Base Complexes of Co(II), Ni(II) and Cu(II)

A. M. Al-Dabagh
Department of Chemistry / College of girls Education
University of Mosul

Received 24 / 10 / 2011 **Accepted** 08 / 01 / 2012

الخلاصة :

يتضمن هذا البحث تحضير الليكاند (بارا – هيدروكسي فنيل بنزيليدين) من نوع قاعدة شيف من تفاعل التكثيف بين بارا–أمينو فينول والبنزلديهايد، وحضرت منه معقدات بعد مفاعلته مع كلوريدات الكوبلت والنيكل والنحاس الثنائية بنسبة (١:١) في الوسط المتعادل والقاعدي.

وقد شخصت المعقدات المحضرة بالطرق الفيزيائية والكيميائية المختلفة منها قياس محتوى الفلز، التوصيل الكهربائي، الخواص المغناطيسية، قياسات الأشعة تحت الحمراء والأطياف الالكترونية.

وتم الحصول على المعقدات ذات الصيغة $[M_2(LH)_2(H_2O)_4Cl_4]$ في الوسط المتعادل، في حين تم الحصول على المعقدات ذات الصيغة $[M_2(L)_2(H_2O)_6Cl_2]$ في الوسط القاعدي حيث أن:

M =Cu(II), Ni(II), Co(II), LH =$C_{13}H_{11}NO$, L =$C_{13}H_{10}NO$

ولقد وجد من دراسات الأشعة تحت الحمراء بأن الليكاند يعمل بشكل ثنائي السن في الوسط المتعادل وأحادي القاعدة في الوسط القاعدي، حيث يرتبط من خلال ذرة النتروجين في الأزوميثاين وذرة الأوكسجين الفينولية. وقد اتضح من خلال قيم الأطياف الالكترونية والحساسية المغناطيسية بأن المعقدات ثنائية النوى المتجانسة سدساية التناسق ذات بنية ثماني السطوح الأكثر احتمالاً.

Abstract:

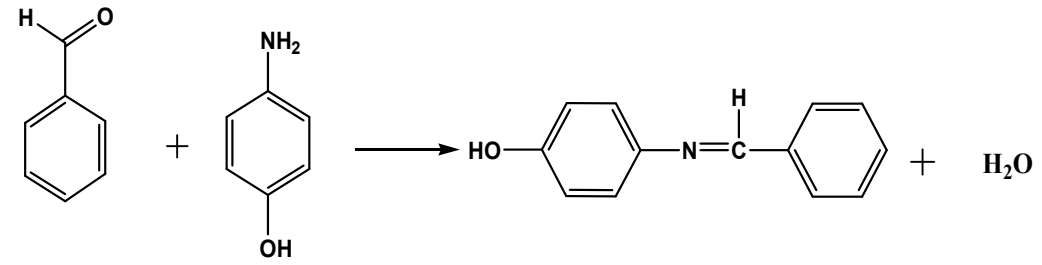
The ligand (LH) [P-hydroxy phenyl benzilidene] derived from a condensation product of p-hydroxy aniline and benzaldehyde and its complexes with Cobalt(II), Nickel(II) and Copper(II) has been synthesized and characterized by metal analysis molar conductance, magnetic moments, Infrared Spectra. The complexes were observed to

have an octahedral geometry around central metal ion in both neutral and basic media. The stoichiometry reaction between the metal (II) ion and synthesized ligand in molar ration of M: L (1:1) in both neutral and basic media. In neutral media forms the metal complexes of type of $[M_2(LH)_2(H_2O)_4Cl_4]$ while in basic media forms type $[M_2(L)_2(H_2O)_6 Cl_2]$ (where M= Co(II), Ni(II), or Cu(II), LH=$C_{13}H_{11}NO$, L= $C_{13}H_{10}NO$) respectively. The infrared spectra of free ligand and all complexes reveal that the ligand has been coordinated to metal ion through the nitrogen of azomethine group and oxygen atom of phenol group in neutral media but in alkaline medium acts as mono basic. In all these complexes the metal ions are hexacoordinate with most probable octahedral structure.

Introduction:

Schiff bases are considered as a very important class of organic compounds, which have wide applications in many biological aspects [1]. Transition metal complexes of Schiff base are one of the most adaptable and thoroughly studied systems. These complexes have also application in clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [2]. Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists [3,4]. Earlier work reported that some drugs showed increased activity when administered as metal Complexes rather than as organic compounds [5,6].

The aim of this work is to synthesize a Schiff base derived from p-hydroxy aniline and benzaldehyde with some transition metal and characterize them. The structures of the ligand are shown in figure 1.



benzaldehyde p-hydroxy aniline p-hydroxy phenyl benzanilide

Figure 1: The structures of the ligand (LH)

Experimental:

All chemical used in this study have been supplied from (Fluka, BDH or Aldrich).

1. **Synthesis of the ligand (LH) :**
   It has been prepared by refluxing (0.02:0.02) molar ratio of p-hydroxy aniline (2.18 g) and benzaldehyde (2.12 g) for about (5) hr. The product has been filtered recrystallized from ethanol.
2. **Synthesis of the complexes :**

In neutral medium: In an ethanolic solution of (0.01) mole of metal chlorides $CoCl_2.6H_2O$ (2.38 g), $NiCl_2.6H_2O$ (2.38 g) and $CuCl_2.2H_2O$ (2.42 g) with ligand was refluxed for (1) hr. The resulted solution has been reduced to half its volume and cooled. The product is isolated by filtration washed with ethanol and dried in vacuo. In basic medium complexes have prepared by applying the same amounts used in neutral medium and after mixing the metal chlorides with the ligand, the pH of the solution has been adjusted (8-9) by potassium hydroxide solution (1M KOH).The mixture has been heated on a water bath for half an hour then allowed to stand, cooled off washed with ethanol and dried in vacuo.

3. Analysis and physical measurements :

Metal contents have been determind by applying gravimetric method after the decomposition of the complexes with concentrated nitric acid (7). Conductivity measurement have been carried out with an electrolytic conductivity measuring set LF – 42 using 10^{-3}M dimethyl formamide solution at room temperature. Magnetic susceptibility of the complexes have been measured by Brucker B.M6. The infrared spectra has been recorder on Ft-IR spectrophotometer in the 400-4000 cm^{-1} range using KBr disk. Electronic spectra has recorder on Shimadzu UV – 1601 spectrophotometer for 10^{-3}M solutions of the complexes in DMF at 25 Ċ using a 1 cm cell.

Results and Discussion :

The formation of complexes of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ with Schiff base in ethanol in neutral medium is presented in the following reaction:

$$2MCl_2.6H_2O + 2LH \longrightarrow [M_2(LH)_2(H_2O)_4Cl_4] + 8H_2O$$

M= Co, Ni LH= $C_{13}H_{11}NO$

$$2CuCl_2.2H_2O + 2LH \longrightarrow [Cu_2(LH)_2(H_2O)_4Cl_4]$$

LH= $C_{13}H_{11}NO$

While in basic medium is presented in the flowing reaction:

$$2MCl_2.6H_2O + 2LH + 2KOH \longrightarrow [M_2(L)_2(H_2O)_6Cl_2] + 2KCl + 8H_2O$$

M= Co, Ni L= $C_{13}H_{10}NO$

$$2CuCl_2.2H_2O + 2LH + 2KOH \longrightarrow [Cu_2(L)_2(H_2O)_6Cl_2] + 2KCl$$

L= $C_{13}H_{10}NO$

All metal (II) complexes were prepared by using the respective metal chloride with the ligand in molar ratios of metal: ligand (1:1), in both the neutral and basic media. All the complexes are colored and moisture stable solids. They are in soluble in common organic solvents and only

soluble in DMF. Molar conductance values (Table 1) indicate that all complexes are non electrolytic in nature and consistant with elemental analysis (8).

Table 1 : Analytical and some physical properties of the compounds.

No.	Compounds	Color	M.P.C° or decomp.	μeff B.M	%yield	Λ_M in DMF	% M analysis Calc(obser) Co, Ni and Cu
—	LH	grey	103	—	٧٥	—	—
1.	$[Co_2(LH)_2(H_2O)_4Cl_4]$	Black	23١	4.7	73	7.3	16.25 (16.57)
2.	$[Ni_2(LH)_2(H_2O)_4Cl_4]$	Brown	145	2.50	68	17.5	16.12 (15.90)
3.	$[Cu_2(LH)_2(H_2O)_4Cl_4]$	Deep brown	350 d*	174	70	5.5	17.27 (17.47)
4.	$[Co_2(L)_2(H_2O)_6Cl_2]$	Black	137	5.2	65	7	17.12 (16.96)
5.	$[Ni_2(L)_2(H_2O)_6Cl_2]$	Deep grey	350 d	3.41	61	14.9	17.05 (16.85)
6.	$[Cu_2(L)_2(H_2O)_6Cl_2]$	Brown	350 d	1.76	71	40	18.19 (18.37)

* d= decomp.Temp.

IR Spectra

The infrared spectral data of the ligand and its complexes are listed in Table 2. The ligand shows bands at 3634cm^{-1} as broad due to ν(OH) in the free ligand and this band shifted to lower position in the complexes prepared in neutral medium clearly gave an evidence of involvement in coordination (9). The OH stretching band disappeared due to deprotonation in basic medium and thus coordination through deprotonated hydroxyl oxgen atom. The free ligand exhibited band at 1626 cm^{-1} which is attributed to ν(C=N). On complexation the ν(C=N) band was shifted to lower frequency (1575-1590) cm^{-1} indicated that the ligand was coordinated to the metal ions through the nitrogen atom of the azomethine group (C=N) Table 2. (10). The broad band in the region (3307-3385) cm^{-1} was observed in all the complexes spectra, indicates the presence of coordinated water (11). Different peaks in the region (880-831) cm^{-1} and (744-765) cm^{-1} which could be assigned to rocking and wagging modes of aqua complexes (12,13), respectively. The loss of water molecules at relatively high temperature suggest that these are coordinated and not lattice held (14).In the low frequency region, spectra of metal (II) complexes exhibit new bands which are not present in the spectra of ligand, these bands are located at (484-584) cm^{-1} and (427-504)cm^{-1} which are attributed to ν(M-O) and (M-N) (13,15,16),

respectively. The coordination of chloride could not be inferred from the infrared spectra of the complexes because the band occurred beyond the range of our infrared spectrophotometer but was tested by $AgNO_3$ analysis.

Electronic spectral and the magnetic measurements

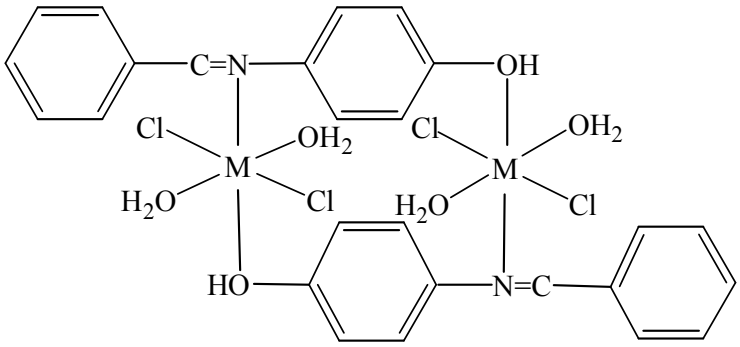
The electronic spectral of complexes (Table 3) in DMF solution have been recorded giving d–d spectra and charge transfer spectra. The Cobalt (II) complexes exhibit three bands due to the spin- allowed transition at (9852-9871) cm^{-1}, (14326-16404) cm^{-1} and (23094-23923) cm^{-1} due to transition $^4T_{1g(F)} \longrightarrow {}^4T_{2g(F)}\ \nu_1$, $^4T_{1g(p)} \longrightarrow {}^4A_{2g(F)}\ \nu_2$ and $^4T_{1g(F)} \longrightarrow {}^4T_{1g(p)}\ \nu_3$, respectively expected for d^7 system in octahedral field (13,17). The magnetic susceptibility measurements (4.5-5.2) for the solid Co (II) complexes is also of three electrons per Co(II) ion suggesting consistenly with their high spin octahedral environment (18). The three bands in the spectra of nickel (II) complexes at (11428-12820) cm^{-1}, (19٦60-20500) cm^{-1}, and (20242-22988) cm^{-1} due to transitions $^3A_{2g(F)} \longrightarrow {}^3T_{2g(F)}\ \nu_1$, $^3A_{2g(F)} \longrightarrow {}^3T_{1g(F)}\ \nu_2$ and $^3A_{2g(F)} \longrightarrow {}^3T_{1g\ (P)}\ \nu_3$, respectively(19). The magnetic moment of Ni- complexes were seen at 2.5- 3.41 B.M for octahedral Ni(II) complexes (10,20).The electronic spectra of Cu (II) complexes showed (Table 3) one broad band centered at (22727- 23041) cm^{-1} due to transition $^2E_g \longrightarrow {}^2T_{2g}$ of ^2D state. This band has been comparable both in position and width with the earlier reported octahedral complexes (21). The magnetic moment of Cu-complexes were seen at 1.74-1.76 B.M for octahedral Cu(II) complexes (22). In viev of the above forgoing discussion m it was concluded that the ligand act as bidentate coordinating through the nitrogen atom of azomethine group and the oxygen atom of phenol group. Thus, hexa-coordinated metal atom with the most probable octahedral structure was suggested for all the complexes (Fig.2).

Table 2: IR data of the compounds (values in cm^{-1})

No.	ν_{O-H}	ν_{H2O}	$\nu_{C=N}$	$\nu_{(H2O)}$ coordinated (M-O)	$\nu_{(M-O)}$	$\nu_{(M-N)}$
LH	3634	-	1626	-	-	-
1.	3375	3307	1584	850,765	502	427
2.	3444	3222	1585	847,760	484	449
3.	3400	3385	1590	831,746	516	465
4.	-	3375	1575	880,760	584	423
5.	-	3383	1576	878,744	583	504
6.	-	3355	1590	845,745	517	435

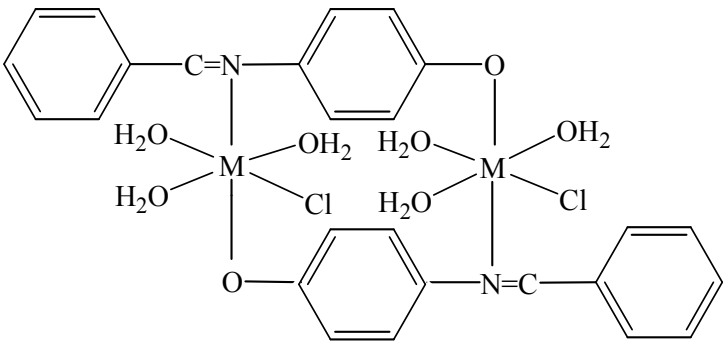
Table 3: Electronic spectral data of the complexes (values in cm^{-1})

No.	ν_1	ν_2	ν_3	C.T
1.	9852	14326	23923	34722
2.	11428	19960	20242	303030
3.	23041	-	-	34482
4.	9871	16404	23094	33222
5.	12820	20500	22988	35460
6.	22727	-	-	34246



M= Co(II), Ni(II), Cu(II)

Neutral medium complexes



M= Co(II), Ni(II), Cu(II)

Basic medium complexes

Figure (2): The suggested structures of the complexes

References:

1) Tovrog.B.S., Kitko. D.J, and Dragom. R.S, J. Am. Chem. Soc. 98, 5144 (1976).

2) Sharghi. H and Nasseri. M.A, Bull. Chem. Soc. (JPn) 76, 137 (2003).

3) Choi. Y.K, Chjo. K.H, Park. S.M, and Doddapaneni. N, J. Electchem. Soc. 142, 4107 (1995).

4) Katia. B, Simon. L, Anne. R, Gerard. C, Francoise. D. and Bernard. M, Inorg. Chem. 35, 387 (1996).

5) Hodnett. E.M and Mooney. P.D, J. Med. Chem. 13, 786 (1970).

6) Hodnett. E.M and Dunn. W.J, J. Med. Chem. 15, 339 (1972).

7) Vogel. A.I, "Textbook of quantitative inorganic analysis",4th, Longman Inc. New York, (1998).

8) Geary. W. J, Coord. Chem. Rev, 7, 81(2001)

9) Nakamato.K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 3rd.Ed. John Wiley and Sons, New York, (1997).

10) Mounika.k., Anupama. B, Pragathi. J, and Gyanakumari. C, J. Sci. Res. 2(3), 513-524 (2010).

11) Sulltan. N, Arayne. M.S and Afzal. M, P.J. Ph. Sci, 36-42 (2005).

12) Gamo. I, Bull. Chem. Soc, 34,760,1430 (1961).

13) Mohamed. G.G, Omar. M.M. and Hindy. A.M., Turk. J.Chem, 361-382, (2006).

14) Kabanos. T. A. and Tsangris. J. M., J. Coord. Chem., 13,89(1984).

15) Shaker. S.A., Mohammed. H. A. and Salih.A. A., Austrralian J.Basic and Applied Sci, 4 (10), 5178- 5183 (2010).

16) Yaul. S.R, Yaul. A.R, Pethe. G.B and Aswar. S, Am-Euras. J. Sci. Res, 229-234 (2009).

17) Lever. A.B.P., J.Chem. Ed, 45,711, (1968).

18) Fetoh. S.H, Eid, A.E,Abo. A.O. El-Kareen. H.S and Wassel. M.A, Synth. React. Inorg. 30,513 (2000).

19) Al-Shaheen.A. j., National J. Chem., 37,111-127, (2010).

20) Prasad. R, Thankachan. P.P, Thomas. M.T and Pathak. R, J. Ind. Chem. Soc. 78, 28-31 (2001).

21) Raman. N, Raja. S.J, Joseph. J, Sakthivel. A and Raja. J.D, J.Chil. Chem. Soc, 1599-1604 (2008).

22) KulKarni. A.D, Patil. S.A and Badami. P.S, Int. J. Electro Chem. Sci, 4,717-729 (2009).