# Some New Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff Base derived from 4,4<sup>-</sup> diaminodiphenyl methane with benzoyl acetone

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#### **Abstract :**

The synthesis of some new complexes was performed by the reaction of Co(II), Ni(II), Cu(II) and Zn(II) metal ions with Schiff base (molar ratio 1:1). The ligand bis ( $\alpha$ - acetonyl benzylidine) - 4,4<sup>-</sup> - diaminodi phenyl methane (AB)<sub>2</sub> – APM was obtained by the condensation of 4, 4<sup>-</sup> diaminodiphenyl methane with benzoyl acetone .The complexes of the general formula [M<sub>2</sub>LH<sub>2</sub>Cl<sub>4</sub>] and [M<sub>2</sub>LCl<sub>2</sub>] (where LH<sub>2</sub> and L are neutral and dibasic form of the ligand , M=Co(II), Ni(II), Cu(II) or Zn(II). For those formed by the reaction of metal salts and the ligand in neutral and basic medium, respectively. The resulting complexes were characterized by using elemental analysis, molar conductances , infrared , electronic spectra and magnetic measurements. These studies revealed that {(AB)<sub>2</sub> – APM} ligand formed tetradentate dinuclear and high stability complexes with most expected tetrahedral or square planar for complexes formed in neutral and alkaline medium.

#### Introduction:

Schiff bases have received agreat attention in recent years because of their proven antitumor and careinostatic activities **[1,2]** besides, they found some application in the field of analytical chemistry, industrial, antifungal, antibacterial and herbicidal **[3-5]**.

The design and synthesis of transition metal complexes containing Schiff base ligands have been studied widely because of the variety of way in which these species could be bonded to the metal ions[6-8]. These N-N and N-O donor Schiff bases act as multidentate ligands to yield plenty of mono, bi, tri and poly-nuclear complexes [9-10].

The present paper aims to prepare and characterize the chemical structure of some divalent metal complexes of  $bis(\alpha$ - acetonyl benzylidine) -4,4<sup>-</sup> - diamino diphenyl methane.

#### **Experimental**:

#### **Materials and Methods**

All chemicals were of analytical grade as supplied without further purification . The ligand and complexes were analysed microanalytical for CHN using Costech instrument Model:4010,The molar conductances were measured for  $10^{-3}$ M solution of the complexes in dimethyl formamide (DMF) with conductivity meter type PCM3-Jenway. The magnetic susceptibility measurements were made by the Farady method at 25C° using Bruker BM6 instrument .

Infrared absorption spectra of the Ligand and its complexes were recorded in 200-4000cm<sup>-1</sup> rang using KBr and CsI discs on a Bruker Tensor 27Co. FT- IR spectrophotometer .Electronic spectra of the complexes were studied by using Shimadzo 1601 spectrophotometer in DMF at  $25^{\circ}$  for  $10^{-3}$  M solution of the compounds using 1cm quartz cell .

#### a. Preparation of the ligand:

The Schiff base bis ( $\alpha$ - acetonyl benzylidine) -4, 4<sup>-</sup> - diamino dipenyl methane (AB)<sub>2</sub> – APM was prepared by using the following procedure : 4,4<sup>-</sup> - diamine diphenyl methane (0.01 mol, 1.98 g) in ethanol 15cm<sup>3</sup> was mixed with benzoyl acetone (0.02mol, 3.24g) in 15cm<sup>3</sup> ethanol in 100cm<sup>3</sup> round bottomed flask and the mixture was boiled under reflux for 6h. It was

allowed to cool at room temperature and on further cooling in ice bath, the resulting precipitate was removed by filteration, washed with cold ethanol and then dried in air and finally in vacuum.

#### **b.** Preparation of the complexes :

Two general procedures were used for the preparation of the complexes :

i- Neutral medium complexes :( 0.01mol) of the metal salt dissolved in 15cm<sup>3</sup> ethanol was added to a hot solution of the ligand 0.01mol in 15cm<sup>3</sup> ethanol (1:1 metal to ligand ratio). The reaction mixture was heated to the boiling point of ethanol under reflux for 2h with occasional shaking and on cooling coloured crystals were separated out , then the product was washed with cold( ethanol ,diethyl ether) and dried in vacuum .

ii- Basic medium complexes : Amixture of 1:1 metal to ligand molar ratio was prepared by adding an ethanolic solution containing (0.01 mol) of the ligand to an ethanolic solution of (0.01 mol) of the metal salt

. To this mixture 1N ethanolic KOH solution was added until complete precipitation of the complexes which occurred at pH 8-9.

The mixture was then digested on a water bath for about 30 minutes and cooled . The colour precipitated complexes were filtered off washed with cold ethanol , diethyl ether and dried in vacuum.

#### **Result and Discussion**

The reaction of the metal salts with the Schiff base was carried out in neutral and basic media may be depicted as follows :

 $2\dot{M}Cl_2$ .  $nH_2O + LH_2 \longrightarrow [M_2LH_2Cl_4] + (n+2)H_2O$ 

$$2MCl_2. nH_2O + LH_2 + 2KOH \longrightarrow [M_2 L Cl_2]$$
$$+ 2KCl + (n+4)H_2O$$

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

 $LH_2$  represents the ligand  $(AB)_2 - APM$ , L = dibasic form of the ligand , and n=(0,2 or 6).

2:1 metal to ligand molar ratio was confirmed by elemental analysis (Table 1).

All complexes are stable to air at room temperature. Their analytical data (Table 1) are in a good agreement with the given formulations as shown in above equations.They are insoluble in water, but



moderately soluble in dimethyl formamide . The molar conductivities in DMF for  $10^{-3}$  M solutions at room temperature (Table 1) suggested non electrolytic nature for the complexes .

The coordination of the ligand through their different active sites was studied by the carful comparison of the infrared absorption spectra of the ligand and their complexes . The main characteristic bands of the ligand were located at 1614 and 1672cm<sup>-1</sup> which are due to vC = N and vC = O (Table 2). For complexes formed in neutral medium , these absorption bands were shifted lower frequency region by about  $\Delta v$  39-43 and 56-78cm<sup>-1</sup> respectively. These negative shifts suggest coordination through both nitrogen atom of azomethine and oxygen atom of carbonyl. [12-15]. On the other hand, for complexes formed in basic medium the band due to carbonyl group was absent. This is due to coordination in basic medium through deprotonation of this group [12], and new band is observed at 1282-1284 cm<sup>-1</sup> due to C – O group, thereby establishing coordination of the ligand through the enolic oxygen atom [16, 17]. In addition vC = N stretching was also shifted to lower frequency by 16-39cm<sup>-1</sup>, suggesting involvement of the azomethine nitrogen in coordination .For both types of complexes new bands were noticed around 415-555 and 554-629cm<sup>-1</sup> are tentatively assigned to the M-N and M-O stretching modes , respectively [18-19].

Furthermore, the IR spectra of the complexes formed in neutral medium showed another band was observed at about 290-354cm<sup>-1</sup>which may be assigned to

v(M-Cl) vibrations [20, 21] and in basic medium the vM-Cl stretching band around  $(233-269 \text{cm}^{-1})$ . These observation suggested that the chloride ion joined to the metal ion as bridging monodentate ligand [18, 28]. The electronic spectra of complexes in DMF as a solvent are recorded (Table 3).

The spectra of Co(II) complexes (1,5) exhibited absorption bands in the region 14925 and 16722cm<sup>-1</sup> respectively corresponding to v<sub>3</sub>which are attributed to the transitions  ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(P)$  in tetrahedral environment for Co(II) while v<sub>1</sub> and v<sub>2</sub> was not observed due to instrument limit. The observed magnetic moments (4.14 – 4.36)BM are in agreement with this structure [22].

Table 1: Analytical, Conductance and some physical properties for ligand and its co	omplexes.
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No.	Compounds	Melting point	Color	Analy found (calc.) %			)	$\Box_{M}$ (DMF)	Yield%
		(°C)		С	Н	Ν	М	oh m <sup>-1</sup> -cm <sup>2</sup> -mole <sup>-1</sup>	
	(AB) <sub>2</sub> -APM	124-126	Pale yellow	81.77	6.02	5.52	-	-	74
			-	81.37	6.13	5.64			
1	[Co <sub>2</sub> LH <sub>2</sub> Cl <sub>4</sub> ]	210 d*	Dark green	53.01	3.91	3.62	15.63	17	66
				53.04	4.02	3.75	15.79		
2	[Ni <sub>2</sub> LH <sub>2</sub> Cl <sub>4</sub> ]	178 d	Beige	52.12	4.01	3.46	15.42	26	61
			_	53.08	4.11	3.75	15.73		
3	$[Cu_2LH_2Cl_4]$	200d	Black	52.20	3.52	3.45	16.43	12	87
				52.41	3.96	3.71	16.82		
4	$[Zn_2LH_2Cl_4]$	220d	Yellow	52.08	3.84	3.55	17.03	8	68
				52.19	3.95	3.69	17.24		
5	$[Co_2L Cl_2]$	234 d	Olive	58.46	4.08	4.14	17.28	28	71
				58.79	4.15	4.16	17.49		
6	[Ni <sub>2</sub> L Cl <sub>2</sub> ]	260d	Pale brown	58.56	4.04	4.07	16.86	8	64
				58.84	4.13	4.16	17.24		
7	$[Cu_2L Cl_2]$	172 d	pale olive	58.26	4.10	4.03	18.25	15	77
				58.01	4.53	4.10	18.60		
8	$[Zn_2L Cl_2]$	192d	pale yellow	57.28	3.94	4.05	19.04	10	55
				57.76	4.08	4.08	19.08		

d =decomposed

Table 2: IR absorption (cm<sup>-1</sup>) for ligand and its complexes

No.	compound	v(C=N)	v(C=O)	v(C-O) enol	v(M-N)	v(M-O)	v(M-Cl)
	(AB) <sub>2</sub> -APM	1614	1672	-	-	-	-
1	$[Co_2LH_2Cl_4]$	1571	1596	-	479	626	297
2	[Ni <sub>2</sub> LH <sub>2</sub> Cl <sub>4</sub> ]	1574	1597	-	504	555	306
3	$[Cu_2LH_2Cl_4]$	1572	1594	-	555	619	354
4	$[Zn_2LH_2Cl_4]$	1575	1616	-	489	554	290
5	$[Co_2L Cl_2]$	1595	-	1282	415	555	233
6	[Ni <sub>2</sub> L Cl <sub>2</sub> ]	1575	-	1282	477	554	239
7	$[Cu_2L Cl_2]$	1590	-	1284	517	583	269
8	$[Zn_2L Cl_2]$	1598	-	1283	555	629	240



No.	complexes	Absorption	possible assignments	µeff
		region(cm <sup>-1</sup> )		(B.M.)
1	$[Co_2LH_2Cl_4]$	14925	${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$	4.36
2	[Ni <sub>2</sub> LH <sub>2</sub> Cl <sub>4</sub> ]	13123	$^{3}T_{1}(F) \rightarrow ^{3}T_{1}(P)$	3.75
3	$[Cu_2LH_2Cl_4]$	17152	$^{2}B_{1}g \rightarrow ^{2}Eg$	1.85
4	$[Zn_2LH_2Cl_4]$	27322	Charge transfer	Diamagnetic
5	$[Co_2LCl_2]$	16722	${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$	4.14
6	[Ni <sub>2</sub> LCl <sub>2</sub> ]	12269	$^{3}T_{1}(F) \rightarrow ^{3}T_{1}(P)$	3.41
7	$[Cu_2LCl_2]$	15337	$^{2}B_{1}g \rightarrow \ ^{2}Eg$	1.84
8	$[Zn_2LCl_2]$	27932	Charge transfer	Diamagnetic

 Table (3) : Electronic spectra and Magnetic moment of new complexes

The electronic spectra of Ni(II) complexes exhibited absorption bands in the region (12269 and 13123)cm<sup>-1</sup> which are attributed to the  ${}^{3}T_{1}$  (F)  $\longrightarrow {}^{3}T_{1}$ (P) (v<sub>3</sub>) transition[23]while the other two transitions v<sub>1</sub> and v<sub>2</sub> could not be observed since they are located below the limits of our instrument . The complexes of Ni(II) showed the magnetic moment value of (3.41 -3.75) BM which are in the range expected for tetrahedral structure [22, 24].

In the electronic spectra of Cu(II) complexes were noticed the presence of bands  $(15337-17152 \text{ cm}^{-1})$ assigned to the  ${}^{2}B_{1}g \longrightarrow {}^{2}Eg$  transition [24]. These transitions, as well as the measured values of the magnetic moment( 1.83-1.85)BM suggest a square planers stoichemistry of the complexes [25]. The Zn(II) complexes due to their diamagnetic properties and no d-d transitions and based on elemental analysis and stoichiometry of these complexes, we assumed a tetrahedral geometry [20,26,27].

From the above consideration and the various physicochemical, spectral and analytical studies, it was concluded that the ligand, which gave very stable complexes with the various metal ions in this study, acts in two ways. As neutral tetra dentate in neutral medium and as dibasic tetradentate in basic medium. In all complexes the ligand forming tetracoordinate binuclear complexes with most probable tetrahedral or square planar structure (Figure 1).









Fig. 1: The Suggested Structure of (AB)<sub>2</sub> APM Complexes















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## بعض المعقدات الجديدة لـ(Ni(II), Co(II), الا(II) و Zn(II) مع قاعدة شيف المشتقة من 4,<sup>-</sup>4 -ثنائي أمينو ثنائي فنيل ميثان مع بنزويل أسيتون

### هبة عزيز محمد النعيمي

قسم الكيمياء ، كلية التربية للبنات ، جامعة الموصل ، الموصل ، العراق ( تاريخ الاستلام: 27 / 2 / 2012 ---- تاريخ القبول: 5 / 9 / 2012 )

#### الملخص

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