

## Synthesis of Metal Complexes Derived from Salicylidene p-Aminoacetophenone

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### ABSTRACT

The Schiff base ligand (HL) has been prepared by the reaction of p-aminoacetophenone with salicylaldehyde. This ligand was used to prepare complexes of the type  $[ML_2(H_2O)_2]$ , (where  $M^{2+} = Mn, Fe, Co, Ni$  and  $Cu$ ). The resulting product was found to be solid which have been characterized using FTIR and UV-VIS spectroscopy. Elemental analyses have been performed using atomic absorption technique; the magnetic susceptibility and the conductivity have also been measured.

**Keywords:** P-aminoacetophenone, salicylaldehyde, Schiff base Complexes.

تحضير معقدات فلزية مشتقة من السلسليدين بارا - امينو اسيتوفينون

### الخلاصة

تم تحضير ليكند (HL) لقاعدة شف من تفاعل من بارا- امينو اسيتوفينون مع السلسليديهايد . استخدم هذا الليكند لتحضير معقدات نوع  $[ML_2(H_2O)_2]$  حيث  $(M^{2+} = Ni, Co, Fe, Mn)$  . كانت المعقدات المحضرة صلبة وتم تشخيصها باستعمال مطيافية الاشعة تحت الحمراء و (Cu). والاشعة فوق البنفسجية/ المرئية . تم تحليل العناصر باستخدام تقنية الامتصاص الذري ، وتم كذلك قياس الحساسية المغناطيسية والتوصيلية الكهربائية.

## INTRODUCTION

Schiff bases derived from the salicylaldehydes are well known as polydentate ligands [1,2]. These ligands have been playing an important part in the development of coordination chemistry as they easily form stable complexes with most transition metal ions [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 play an essential role in agricultural, pharmaceutical, industrial chemistry [5]. antifungal, antibacterial, anticancer and catalytic activities [6-8].

The metal complexes of Schiff bases have also received much attention. These complexes play an important role not only in the development of coordination chemistry, but also in catalysis, enzymatic reactions, magnetism, and molecular architectures [9], and they exhibit interesting biological activities [10].

## EXPERIMENTAL

### Chemical and Instrumentals

Metal salts ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) were obtained from Fluka Company without further purity. Salicylaldehyde, ethanol, and methanol were from B.D.H. Company.

### Physical Measurements and Analysis

Melting points were recorded by using of 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 by using of UV/-VIS-1650 PC Shimadzu spectrophotometer at wavelength (200-1100) nm at  $25^\circ\text{C}$  in  $10^{-3}\text{ M}$  in DMSO. Conductivity was measured by capacitor analyzer in DMSO solution  $10^{-3}\text{ M}$  at  $25^\circ\text{C}$ . Magnetic susceptibility measurements were obtained at  $25^\circ\text{C}$  by using of Balance magnetic susceptibility of Bruke Magnet B.M.6, England. The metal percent in the complexes were determined by using of Shimadzu 680cc-flame/Japan atomic absorption.

### Preparation of the Schiff Base (L)

The Schiff base ligand was prepared by the condensation of the p-aminoacetophenone (1 mmol) with (0.9381ml) (1 mmol) salicylaldehyde in absolute ethanol (10 ml). The resulting mixture was then refluxed for 90 mins. The yellow precipitate formed was filtered and recrystallized from ethanol to give yellow needles [11].

### Preparation of the Complexes.

Ethanolic solution of ligand L (1 mmole) was added to an aqueous solution of each the metal salts (1 mmole) ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). 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), recrystallization from ethanol and dried at  $70^\circ\text{C}$ .

**RESULTS AND DISCUSSION**

The physical properties and data of the ligand (L) with their metal complexes are given in Table (1). The values of molar conductivity ( $\Lambda$ ) in DMSO[12].

**Table (1): Physical Characteristics and analytical data for (L) and their metal complexes.**

Compound	Colour	Melting Point °C	Yield %	Conductivity ( $\mu\text{s.cm}^{-1}$ )	Elemental analysis M%	
					Calc.	Found
Ligand (L)	Yellow	120-123	86	-	-	-
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Green-brown	110-112	81	58	10.11	10.38
[FeL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Black	143-145	85	47	10.26	11.25
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Deep-red	118-120	81	45	10.76	10.86
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	brown	123-125	87	55	10.74	10.75
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Black-red	115-117	80	60	11.51	12.31

**Magnetic Properties**

The magnetic moment  $\mu_{eff}$  for the complexes of Mn<sup>+2</sup>(d<sup>5</sup>), Fe<sup>+2</sup>(d<sup>6</sup>) and Co<sup>+2</sup> (d<sup>7</sup>) were found to be 6.0 B.M , 5.2 B.M , 4.1 B.M. respectively, which within the expected spin-only values [13, 14]. The higher value of  $\mu_{eff}$  of the Ni<sup>+2</sup>(d<sup>8</sup>) complexes 3.1 B. M may be due to the orbital contribution [15]. Finally, the  $\mu_{eff}$  of the Cu<sup>+2</sup> (d<sup>9</sup>) complexes was found to be 1.8 B.M which lies within the expected value for one electron [13]. All the data are found in Table (2).

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

Complexes	No.of Elec.	No.of Unpaired Electron	Electron Configuration	Term Symbol	$\mu_{eff}$	
					Calc.	Found
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	d <sup>5</sup>	5	T <sub>2g</sub> <sup>3</sup> Eg <sup>2</sup>	<sup>6</sup> S	5.92	6.05
[FeL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	d <sup>6</sup>	4	T <sub>2g</sub> <sup>4</sup> Eg <sup>2</sup>	<sup>5</sup> D	4.90	5.21
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	d <sup>7</sup>	3	T <sub>2g</sub> <sup>5</sup> Eg <sup>2</sup>	<sup>4</sup> F	3.87	4.16
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	d <sup>8</sup>	2	T <sub>2g</sub> <sup>6</sup> Eg <sup>2</sup>	<sup>3</sup> F	2.83	3.12
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	d <sup>9</sup>	1	T <sub>2g</sub> <sup>6</sup> Eg <sup>3</sup>	<sup>2</sup> D	1.73	1.85

### The Electronic Spectra

The spectrum of free ligand L shows a strong band at 288 nm which may be attributed to  $\pi \rightarrow \pi^*$  and another at 30864, 28409, 26315 cm<sup>-1</sup> due to  $n \rightarrow \pi^*$  [16].

The electronic spectra of Mn (II) complex shows a single band at 520 cm<sup>-1</sup>, assigned to  $\nu$ M-O vibration. For a high spin d<sup>5</sup> ion, there is no d-d transitions and all such bands in the spectra of Mn (II) complex is of low intensity.

Most of bands are fairly broad, but those which resulted from charge transfer transitions are sharp. Such phenomenon was seen in the complex. A band of 38910 cm<sup>-1</sup> (257nm) is attributed to a charge transfer transition for p<sub>π</sub> of the phenolate oxygen to the partially filled d<sub>π</sub> orbital on Mn(II) ion and the band at 28571cm<sup>-1</sup> (350nm) is due to <sup>6</sup>A<sub>1g</sub> → <sup>6</sup>T<sub>1g</sub>(p) transition. The observed data confirmed the presence of an octahedral geometry [17]. The magnetic moment value of the complex displays the presence of a high spin complex; this means that Mn (II) ion has five unpaired electrons.

The electronic spectrum of Fe (II) complex shows a band at 19569 cm<sup>-1</sup> which belongs to <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub> transfer.

The electronic spectrum Co (II) complex shows two bands 14836 cm<sup>-1</sup> and 22222 cm<sup>-1</sup>, assigned as  $\nu_2$  and  $\nu_3$  absorption bands respectively, which clearly indicate that the complex has coordination octahedral geometry.

The electronic spectrum Ni (II) complex shows two bands, 18018 cm<sup>-1</sup> and 25000 cm<sup>-1</sup>, assigned as  $\nu_2$  and  $\nu_3$  absorption bands respectively, which clearly indicate that the complex has six coordination octahedral geometry.

The electronic spectrum Cu(II) complex shows only one broad band is observed at 20618 cm<sup>-1</sup> assigned to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> transition which is in conformity with octahedral geometry [18].

**Infrared Spectral Studies****Infrared Spectrum of Free Ligand**

The characteristic vibrations and assignments of ligand L and their complexes as CsI disc are described in Table 3.

The spectrum of ligand L exhibited weak bands at  $3360\text{ cm}^{-1}$  and  $3050\text{ cm}^{-1}$ , this could be attributed to  $\nu(\text{O-H})$  and  $\nu(\text{C-H})$  aromatic respectively [19]. While the strong band at  $1678\text{ cm}^{-1}$  which belongs to  $\nu(\text{C=O})$  and the other strong bands belong to the  $\nu(\text{C=N})$  and  $\nu(\text{C=C})$  aromatic were found at  $1620\text{ cm}^{-1}$  and  $1460\text{ cm}^{-1}$  respectively [20, 21], Figure 1.

**Infrared Spectra of Complexes**

The infrared spectra of the prepared complexes exhibited  $\nu(\text{C=N})$  in the range of  $1640\text{-}1630\text{ cm}^{-1}$  which shows a shifting to the lower frequencies by  $15\text{-}25\text{ cm}^{-1}$  in compared with ligand L, it is which indicated the coordination of ligand with metal ions through the nitrogen atoms in their structures. The appearing of band for  $\nu(\text{OH})$  vibration in the spectra of complexes is indicating the coordination of water oxygen with metal ions. The spectra bands of complexes at  $1680\text{ cm}^{-1}$  was characterized for the carbonyl group which did not suffer a shift. Thus, it is suggested that the oxygen atom of this group is not coordinated to the metal ion.

**Metal - Ligand Bond**

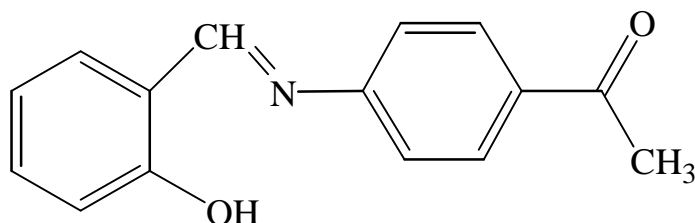
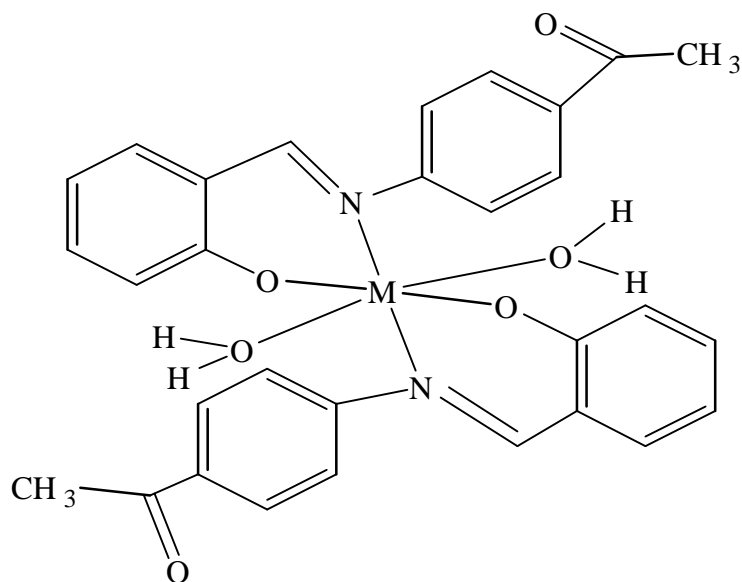
The infrared of prepared complexes have shown weak bands in the range of  $520\text{-}530\text{ cm}^{-1}$  and  $420\text{-}440\text{ cm}^{-1}$  which was attributed to the of  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  respectively.

**Table (3): The characteristic bands of Infrared spectra of the ligands and their complexes.**

Compounds	$\nu(\text{O-H})$	$\nu(\text{C-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L	3360	3050	1678	1615	1460	-	-
$[\text{MnL}_2]2\text{H}_2\text{O}$	3320	3060	1680	1640	1462	520	440
$[\text{FeL}_2]2\text{H}_2\text{O}$	3280	3070	1674	1635	1455	530	420
$[\text{CoL}_2]2\text{H}_2\text{O}$	3300	3080	1675	1630	1460	520	420
$[\text{NiL}_2]2\text{H}_2\text{O}$	3330	3075	1680	1637	1470	520	420
$[\text{CuL}_2]2\text{H}_2\text{O}$	3310	3110	1676	1640	1470	518	440

**CONCLUSIONS**

Schiff base complexes with the general formula  $[ML_2]2H_2O$  where ( $M^{2+} = Mn, Fe, Co, Ni$  and  $Cu$ ), ( $L =$  salicylidene P-amino acetophenone) 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 through the nitrogen and oxygen. From the obtained results, it can be concluded that the bonding of all metal ions ( $M(II)$ ) into the ligand ( $L$ ) leads to form an octahedral structure.. The suggested structure of the prepared complexes as shown in Figure 2:

**Figure (1): Structure of ligand (L).****Figure (2): General structure of the complexes.**

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