## Synthesis and Characterization of a new Schiff Base {N-(2-{[(4bromophenyl)imino]methyl}phenyl)acetamide} and its complexes with some transition metal

Sajda .S. Afatt Prof. Haider.A.Mahdi Chemistry Dept. College of Science – Thi-Qar University

### <u>Abstract</u>

A new ligand {N-(2-{[(4-bromophenyl)imino]methyl}phenyl)acetamide} (L) and it complexes with Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) were synthesized . These compounds were identified by elemental analysis , Molar conductivity, as well as spectroscopic methods (IR, <sup>1</sup>HNMR ,Mass) . It may be concluded that the ligand coordinate through Nitrogen atoms for all the complexes and act as a bidentate ligand which bond through -C=N and -NH groups ,This view is further supported by the appearance of a band corresponding to the metal – nitrogen stretching vibration at (524-550) Cm<sup>-1</sup> in the complexes . On the bases of these studies we suggest formation octahedral geometry for all preparded complexes .

### Introduction

Schiff bases named after Hugo Schiff described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde [1,2]. A Schiff's base is a functional group with the general formula of  $R_1R_2C=N-R_3[3]$ . Schiff bases have played and continue to play an important role in the development of coordination chemistry [4-6] . Schiff base ligands containing various donor atoms (like N, O, S etc.) show broad biological activity and are

of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities[7]. А considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds [8,9]. Transition metals are known to form Schiff base complexes and Schiff bases have often been used as chelating ligands in the field of coordination chemistry. Transition

metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical,analytical,industrial in addition to their important roles in catalysis and organic synthesis[10]. Some of Schiff base complexes are used as model molecules for biological oxygen carrier systems [11].

### Procedures

### **Preparation of the ligand**

The ligand of {N-(2-{[(4bromophenyl)imino]methyl}phenyl)ac etamide} was synthesized by mixing (0.02mole, 3.26 g) of 2acetmidobenzaldehyde dissolved in methanol (15ml) and (0.02 mole, 3.34 g) of 4-bromoaniline dissolved in (15ml) from the same solvent and add catalytic amount of glacial acetic acid (2drops). The reaction mixture was refluxed for four hours (Scheme 1), then the formed precipitate was filtered and washed several times with ethanol and dried in air. The purity of the compound was followed by TLC on precoated silica gel. Yield: 75.7%. m. p. 181-183<sup>o</sup>C.



Scheme 1. Synthesis of the Schiff base ligand

### **Preparation of complexes**

The Cr(III), Co(III), Fe(III), Ni(II) and Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (1 mmol) in 10 ml methanol with 20 ml of an methanoic solution of the ligand (2mmol, 0.634

### Apparatuses

C. H . N analysis were carried out on a Thermofinigan flash analyzer, the FTIR spectra in the range (200-4000)  $\text{cm}^{-1}$  were recorded as CsI discs using a gm) for 3 hrs. The producted solids were separated, filtered, washed with ethanol and dried in air.

Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720,.The <sup>1</sup>H nuclear

magnetic	reso	nance	spectra	a were			
recorded	on a	Bruker	DRX	System			
AL500	(500	MHZ)	spect	rometer,			
relative	to th	ne inte	ernal	standard			
tetramethylsilane (TMS) , CDCL3							
used as	solvent	. Meltin	ng poir	ts were			

**Results & Discussion** 

The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent, elemental analysis was tabulated in Table (1), Melting point, physical properties and molar conductance of all the determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. Mass spectra were recorded in the range (0-800) m/e on a 5973 network mass selective detector.

compounds studied are tabulated in Table (2). The calculated values were in a good agreement with the experimental values .

Table 1. Elemental analysis data of the ligand

Ligand	Molecular weight	Experimental			Theoretical		
L	317	C%	Н%	N%	C%	Н%	N%
		56.8992	4.2089	8.9074	56.8329	4.1335	8.8367

	Compound	Molecular formula	Color	Λ	Melting
1	Ligand	$C_{15}H_{13}N_2OBr$	Dark Yellow		181-183
2	[Fe(L) <sub>2</sub> Cl <sub>2</sub> ]Cl	$Fe (C_{15}H_{12}N_2OBr)_2 Cl_3$	Pale Brown	37	218-220
3	$[Co(L)_2Cl_2]$	$Co(C_{15}H_{12}N_2OBr)_2 Cl_2$	green Yellow	16	227-228
4	$[Cr(L)_2Cl_2]Cl$	Cr(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> OBr) <sub>2</sub> Cl <sub>3</sub>	green	40	258 d*
5	$[Cu(L)_2Cl_2]$	$Cu(C_{15}H_{12}N_2OBr)_2 Cl_2$	Pale Yellow	20	239-241
6	$[Ni(L)_2Cl_2]$	$Ni(C_{15}H_{12}N_2OBr)_2 Cl_2$	Dark green	18	`220-234

Table 2. conductance, physical properties data of the ligand and its complexes

#### d\*=decomposition

### **Infra-Red Spectroscopy**

The FTIR spectrum for L shows a characteristic stretching absorption bands at 3300 cm<sup>-1</sup>, 3051 cm<sup>-1</sup>, 1624 cm<sup>-1</sup>, 1672cm<sup>-1</sup> and 1597cm<sup>-1</sup> assigned to v(N-H)[14,15], v(C-H)[14,16]Aromtic, v(C=N)[17,18], v(C=O)[19] and v(C=C)[14,20] stretching respectively. The C=N and N-H stretching vibrations are important to predict the bonding mode of the ligand , The C=N bands shift more or lower wavenumber ( $\dot{v}$ ) in the spectra of complexes compare with ligand and the absent band N-H groups in the complexes indicate coordination through Nitrogen atoms for the (C=N and N-H) groups, observed changes are the evidences of complexion had happened .The IR data of the complexes are shown in Table (3) and figures (2-4). The Table lists the stretching wavenumber ( $\dot{\upsilon}$ ) for some of the characteristics groups exhibited for the ligand and complexes .

L	$C_{15}H_{13}N_2OBr$	3300	3051	1624	1597	1672	-	-
1	$[Fe(L)_2Cl_2]Cl$	-	3035	1649	1583	1670	538	250
2	$[Co(L)_2Cl_2]$	-	3070	1620	1585	1674	540	243
3	$[Cr(L)_2Cl_2]Cl$	-	3088	1654	1593	1677	524	248
4	$[Ni(L)_2 Cl_2]$	-	3075	1662	1599	1675	542	257
5	$[Cu(L)_2 Cl_2]$	-	3060	1623	1583	1674	550	265

Table 3: Characteristic absorption bands of ligand and its complexes

# Nuclear Magnetic Resonance (<sup>1</sup>H-NMR Spectra )

The data of proton NMR of the ligand {N-(2-{[(4-bromophenyl)imino] methyl}phenyl)acetamide} displayed good solubility in CDCL<sub>3</sub>. The obtained data give additional support for the composition of the ligand. The spectra also exhibit a singlet –CH<sub>3</sub>

peaks at 2.189 ppm due to methyl group[21,22], another peaks exhibit at 4.641 ppm due to singlet -NH [23]. the aromatic ring exhibit peaks at (7.277-7.879) ppm [24,25]. <sup>1</sup>H-NMR of the ligand shown in figure(5).

### Mass spectra

The mass spectrum of the ligand exhibits a molecular ion peak  $M^{+}$  at m/z 317, the ligand spectra shows fragment at m/z 77 due to phenyl ring , the spectra shows another peaks at m/z (91,103,156,194, 237 and 274) due to (C<sub>6</sub>H<sub>5</sub>N) ,(C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>),(C<sub>6</sub>H<sub>4</sub>Br) , (C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>), (C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O) and (C<sub>13</sub>H<sub>10</sub>Br N<sub>2</sub>) respectively as shown in Figure (6) .

The mass spectrum of the complex  $[Fe(L)_2Cl_2]Cl$  shows a molecular ion peak  $M^+$  at m/z 794 which is equivalent to molecular mass of the

complex. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 759. the ligand spectra shows fragment ion peak with loss two chlorine atom at m/z(723,688) due to  $[Fe(L)_2Cl]$ and respectively. the spectra  $[Cr(L)_2]$ shows fragment ion peak at m/z (372,532 and 602) due to (L-Fe), (FeC<sub>24</sub>H<sub>20</sub>BrN<sub>4</sub>O<sub>2</sub>)and  $(FeC_{26}H_{28}Br_2N_4)$ .

The mass spectrum of the complex  $[Cu(L)_2Cl_2]$  shows a molecular ion peak M<sup>+.</sup> at m/z 766, This complex

shows another a fragment ion peak with loss of chlorine atom at m/z 731and 695, the spectrum shows another peaks at m/z (299 and 379) due to (CuC<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O) and (L-Cu).

The mass spectrum of the complex  $[Ni(L)_2Cl_2]$  shows a molecular ion peak at m/z  $[M^+]$  761, This complex shows another a fragment ion peak

with loss of chlorine atom at m/z 726 and 691, the spectrum shows another peaks at m/z (301, 374) due to ( $C_{14}H_9BrN_2O$ ) and (L-Ni). the mass spectra of the ligand shown in figure (7), (8), (9).

On the basis of the preceding discussion, the structure of the complexes suggested as follows in figure(1)below.



figure (1) : Structural formula of the prepared metal complexes

Analytical and spectra data (<sup>1</sup>H NMR,IR, mass spectra) of all

### Conclution

The ligand {N-(2-{[(4bromophenyl)imino]methyl}phenyl)ac etamide} was successfully synthesized. The ligand was bonded to different transition metal to from the corresponded complexes. It may be concluded that the ligand coordinate through Nitrogen atoms as shown in synthesized compounds were in full agreement with the proposed structure.

figure (1). The ligand acts as a bidentate ligand coordination through –C=N and –NH groups. The elemental analysis, IR, <sup>1</sup>H NMR and mass spectral observations suggest the octahedral geometry for all preparded complexes.

# تحضير وتشخيص قاعدة شف جديدة عمد (4- bromophenyl)imino]methyl}phenyl) ومعقداتها مع بعض [N-(2-{[(4- bromophenyl)imino]methyl} الانتقالية

ساجدة صبار عفات استاذ . حيدر عباس مهدي

الخلاصة:-

تم تحضير بعض معقدات العناصر الانتقالية Cr(III),Fe(III),Co(II),Ni(II) and Cu(II) مع الليكاند -4)]}-N-(2-{[(4- العناصر الانتقالية Cr(III),Fe(III),Co(II),Ni(II) and Cu(II)]} bromophenyl)imino]methyl}

وشخصت الصيغ التركيبية لليكاند ومعقداته باستخدام تقنية تحليل العناصر والتوصيل المولاري بالإضافة إلى استخدام أطياف الأشعة تحت الحمراء وأطياف الرنين النووي المغناطيسي وطيف الكتلة. وتم الاتستنتاج بأن الليكاند هو ثنائي السن ويحصل التناسق من خلال ذرة نيتروجين مجموعة (NH) وذرة النيتروجين لمجموعة (C=N) وهذا الاستنتاج يؤكد من خلال تشخيص حزم امتصاص عند<sup>1</sup>-Cm (524-550) العائدة الى تناسق الذرة المركزية مع ذرة النيتروجين وكانت النتائج مطابقة لما هو متوقع عمليا. وقد أستنتج بأن الهواغ الفراغية لكل المعقدات هي ثماني السطوح.

### **References.**

- 1- H.Schiff, Ann. Chem., 131,118, (1864).
- 2- Y. Shibuya, K. Nabari, M. Kondo, S. Yasue, K. Maeda, F. Uchida and H. Kawaguchi, *Chem. Lett.* 37(1): 78, (2008).
- 3- F. Faridbod, M. R. Ganjali, R. Dinarvand, P. Norouzi, Combinatorial Chemistry & High Throughput Screening, 10,527, (2007).
- 4- A. A. Osowl , *E-Journal of Chemistry*, 5(1) 130-135, (2008).
- 5- C. Spinu, M. Pleniceanu and C. Tigae, *Turk. J. Chem.* 32 – 487, (2008).
- 6- B. Clarke, N. Clarke, D. Cunningham, T. Higgins, P. McArdle, M. Ni Cholchu, M. O'Gara, J. Organometallic Chem. 559, 55, (1998).

G. G . Mohamed and Z. H. Abd El-Wahab, -7 *Spectrochim. Acta A* 61(6) : 1059, **(2005)** .

A .Prakash, B .K. Singh, N. Bhojak and D -8 .Adhikari, *Spectrochim. Acta A* 76(3-4): 356 (2010).

- 9- A.Prakash, B.K. Singh, H.K. Rajour and N. Bhojak, *Main Group Met. Chem.* 33(4-5): 183, (2010).
  - H. Sharghi and M. A. Nasseri, *Bull. Chem.* -10 *Soc. (Jpn.).* 76, 137, **(2003)**.
- 11-K. B. Gudasi, M. S. Patil, R. S. Vadavi,
  R. V. Shenoy, S. A. Patil, and M. Nethaji, *Trans. Met. Chem.* 31, 580, (2006).
- 12-D.H.Williams and I.Fleming ,"Spectroscopic Methods In Organic Chemistry" 5<sup>th</sup> Ed., (2004).
- 13-O. V. Mikhailov, M. R. Kazymova, T. A. Shumilova and S. S. Solovieva , *Transition Met. Chem.*, 20,732, (2004) .
- 14-R.M.Issa, A.M.Khedr and H.Rizk , J. Chin. Chem. Soc. , 55, 4, (2008).

- 15- R.K.Dubey, U.K.Dubey and C.M.Mishra ,*Trans.Met.Chem.*, 31, 849, (2006).
- 16-M.R.Silverstien, F.X.Webster and D.J.Kiemle, Identification of Organic Compouds", 6<sup>th</sup> Ed., (2005).
- 17-N. Hussain, P. Joshi, A. Bhandari, R. Dangi, R. Khanam and G. Talesara, *Int. J. Pham. Sci. & Drug, Res.* 2(4): 272-274, (2010).
- 18-K.H.Reddy and M.R.Reddy , J. Indian Chem. Soc. ,79:219, (2002).
- 19-.H.Ho and W.H.Yao , J. Chin. Chem. Soc., 52, 2, (2005).
- 20-S. Berger, Classics in NMR: understanding spectra of natural products, Wiley-VCH, Washington, ISBN 3-527-32516-6. Page 238-255, (2008).
- 21- D. Belkic, Signal processing in magnetic resonance spectroscopy with biomedical applications, *Wiley, New York.* ISBN 978-1439806449. Page 159-368, (2008)
- 22-R. R. Kamble, B. S. Sudha and D. G. Bhadregowda, J. Serb. Chem. Soc., 73
  (2), 131 138, (2008).

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23-L. H. Cao, C. F. Wang and D. Z.
Wang, J. Chin. Chem. Soc., 53, 1193-1197, (2006).



Figure(2) IR spectra of Ligand ( $C_{15}H_{13}N_2OBr$ )

Figure(3) IR spectra of [Cr(L)<sub>2</sub>Cl<sub>2</sub>] Cl



Figure(5) NMR spectra of the



Figure (8) mass spectra of  $[Cu (L)_2 Cl_2]$ 

 $(L)_2 Cl_2$ ]

Figure (9) mass spectra of [Ni