



## CHARACTERIZATION AND IDENTIFICATION OF NEWLY SYNTHESIZED HETEROCYCLIC SCHIFF BASE AND ITS METAL COMPLEXES

\*Eman Turkey Shamkhy

College of Dentistry, University of Baghdad, Baghdad, Iraq

\*Corresponding authors email: dr.alkarkhi@gmail.com

### ABSTRACT

New ligand was prepared by reacting ethyl hydrazinecarbodithioate (EHC) and 1H-indole-2,3-dione (HID) to form a novel Schiff base ethyl (2Z)-2-(2-oxo-1,2-dihydro-3H-indol-3-ylidene) hydrazinecarbodithioate ( $L_h$ ), new ligand was identified using different instrumentation techniques, metal complexes were also synthesized by reacting the novel ligand with the salts of Cd(II), Cu(II), Ni(II) and Zn(II). All the calculated measurements values match with the theoretical one, the complexations of metals coordinated with the ligand as one negative charged ligand which can coordinated with the metal through nitrogen, Sulphur and oxygen, the expected structures of the complexes are tetrahedral for Cd, Cu and Zn while it is expected to be octahedral for Ni complexes.

**KEY WORDS:** Heterocyclic, Hydrazine, Characterization.

### INTRODUCTION

Inorganic-organic heterocyclic compounds were expected huge attention over the previous years because of their wide possible applications in optical properties, catalysis and electro-conductivity<sup>[1]</sup>, high productive preparation approaches which lead to additional uses<sup>[2]</sup>. Supra molecular buildings shaped via organo-metal molecules have rising attention for structural variety and possible use in moieties devices, in green chemistry, new medicinal treatments and also in the design of electronics (semi-conductors)<sup>[3]</sup>. Though a lot of interest has been focused to study of the ligands derived from 1H-indole-2,3-dione (HID), no research work have seemed achieved to describe the ligands derived from methylhydrazine carbodithioate. Besides, only limited researches have been done on ligands that have ONS donor orders. Thus and as a part of our current study on ligands derivative of carbodithioate we report here the preparation, identification of new NSO donor ligands<sup>[4]</sup>.

### MATERIALS & METHODS

#### Physical measurements

The Infra redR spectra were verified by a Perkin–Elmer FT IR 1750 X spectrophotometer ( $4000\text{--}400\text{cm}^{-1}$ ). Hydrogen, Sulphur, Nitrogen and Carbon (CHNS) were achieved via the instrument (LECO CHNS- 932). Mass spectra were verified via Shimadzu Gas Chromatography- Mass Spectrometer (GCMS-QP5050 A) via through injection (DI-MS) technique.

#### Preparation of methylhydrazinecarbodithioate

This inorganic-organic was prepared as formerly reported<sup>[7]</sup>. Potassium hydroxide (KOH) was liquefied totally in alcohol (normally ethanol), the blend chilled using ice bath. Hydrazine hydrate was poured

gradually using continuous stirring. Carbon disulfide drowsily added with strong stirring. The reaction temperature of the mixture must be kept lower than  $5^\circ\text{C}$  (during the addition of carbon disulphide). The oily yellow product isolated and dissolved in alcoholic (ethanol). The addition of methyl iodide was gradually achieved by dynamic stirring. White precipitate eventually formed which isolated using filter paper. Melting point determined and it was  $81^\circ\text{C}$  and the yield were: 72%.

#### Preparation of ligand ( $L_h$ )

The ligand was prepared by reacting ethyl hydrazine carbodithioate (EHC) and 1H-indole-2, 3-dione (HID), each one of the reactant was dissolved in hot 95% ethanol and were added in an equimolar quantity. The mixture was heated for 20 minutes to guaranteed the full conversion of the reactant to product. The product cooled using ice bath, filtered, washed with cold alcohol and recrystallized and dried. The melting point was determined and found  $225^\circ\text{C}$  while the yield was 78%.

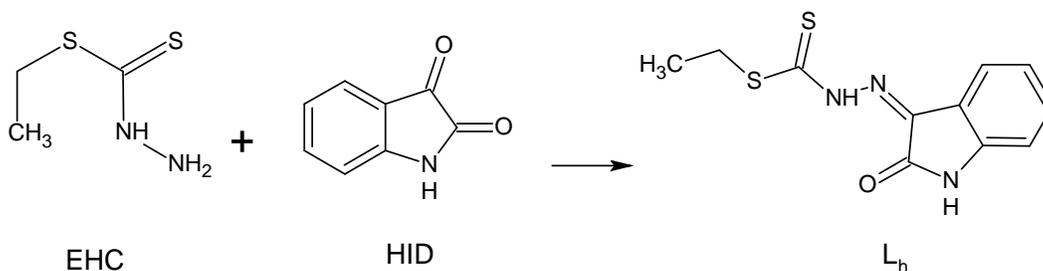
#### Preparation of Metal Complexes

Metals were used in form of acetate salts was added to (0.2 mole) of the ligand both of them were dissolved in ethanol before addition to each other. The mixture was stirred and heated for a while (around 20 minutes). The product was gained by chilling then isolated by filtration and dried up. The metals that were used were cadmium (II) acetate, copper (II) acetate, nickel (II) acetate tetrahydrate and zinc (II) acetate. (Yield: 60-70%).

### RESULTS & DISCUSSION

The synthesis equation of new L4 Schiff base is shown in scheme 1. The percent of carbon, hydrogen, nitrogen and sulfur of the compound and the physical data were listed in Table 1.

## Heterocyclic schiff base and its metal complexes


**Scheme 1:** Synthesis of  $L_h$  ligand

The analytical outcomes were found closely to the calculated value. The formula of the Schiff base in addition to all the metal complexes is presented in Table 1.

**TABLE 1:** Physical Properties of the Synthesized Compounds

Compounds	Color	Yield%	Melting point ( $^{\circ}\text{C}$ )	% Found and calculated				
				%C	%H	%N	%S	%M
$L_h$	Orange	78%	225	47.59	3.55	16.48	25.35	--
$\text{C}_{11}\text{H}_{11}\text{N}_3\text{OS}_2$				(47.79)	(3.61)	(16.72)	(25.52)	
$\text{Cd}(L_h)_2$	Dark Yellow	65%	> 300	38.91	2.73	13.43	19.66	18.14
$\text{C}_{22}\text{H}_{20}\text{CuN}_6\text{O}_2\text{S}_4$				(39.18)	(2.63)	(13.71)	(20.92)	(18.34)
$\text{Cu}(L_h)_2$	Deep Grey	61%	> 300	42.36	2.95	14.80	22.61	11.17
$\text{C}_{22}\text{H}_{20}\text{CuN}_6\text{O}_2\text{S}_4$				(42.58)	(2.86)	(14.90)	(22.73)	(11.26)
$\text{Ni}(L_h)_2$	Brown	62%	298	42.68	2.97	14.98	22.88	10.42
$\text{C}_{22}\text{H}_{20}\text{NiN}_6\text{O}_2\text{S}_4$				(42.95)	(2.88)	(15.03)	(22.93)	(10.49)
$\text{Zn}(L_h)_2$	Orange	68%	> 300	42.32	2.90	14.78	22.58	11.47
$\text{C}_{22}\text{H}_{20}\text{NiN}_6\text{O}_2\text{S}_4$				(42.44)	(2.85)	(14.85)	(22.66)	(11.55)

**FTIR Spectroscopy**

The information of the organometallic compounds and the Schiff base are presented in Table 2. The functional groups are the (C=N), (C=O) and (N-N) bands were

chosen to afford a sensible investigation, those groups were shifted to greater or lesser wave numbers due to new coordination with the metal ions.

**TABLE 2:** Infrared Measurements for the Synthesized Complexes

Compound	hBands ( $\text{cm}^{-1}$ )			
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}-\text{SS})$
$L_h$	1622	1692	1132	1053
$\text{Cd}(L_h)_2$	1615	1698	1048	981
$\text{Cu}(L_h)_2$	1617	1699	1069	995
$\text{Ni}(L_h)_2$	1612	1675	1055	991
$\text{Zn}(L_h)_2$	1605	1711	1083	993

The existence of  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{N}-\text{N})$  and  $\nu(\text{C}-\text{SS})$  bands at ca.  $1622-1605\text{ cm}^{-1}$ ,  $1132-1048\text{ cm}^{-1}$  and  $1053-981\text{ cm}^{-1}$  correspondingly shows that the harmonization of the ligand to the central ion is through azomethine nitrogen, the thiolate sulphur atom, and bands generally undergo shift from their position in the spectrum of  $L_h$  to whichever

lesser or greater frequency upon coordination through the metal ions.<sup>[8,9]</sup>

**Molar Conductivity, Magnetic Susceptibility and Ultra Visible Analysis**

Molar conductivities of all the metal complexes are below 30, as shown in Table 3 which indicates non-electrolytes complexes<sup>[10]</sup>.

**TABLE 3:** Molar Conductivity, Magnetic Susceptibility and UV-Visible Analysis

Compound	$\Lambda^{-1}\text{ cm}^2\text{ mol}^{-1}$	(B.M) at 298 $^{\circ}\text{K}$	$\lambda_{\text{max}}(\text{nm})$
$L_h$	-	--	264(4.61), 380(4.85)
$\text{Cd}(L_h)_2$	3.44	Diamagnetic	258(4.07), 390(4.54), 445(4.43)
$\text{Cu}(L_h)_2$	2.23	1.52	265(4.31), 351(4.27), 389(4.26)
$\text{Ni}(L_h)_2$	2.12	3.18	264(4.13), 381(4.28), 486(4.35), 923(1.98)
$\text{Zn}(L_h)_2$	1.27	Diamagnetic	263(4.22), 389(4.39), 448(4.38)

The compounds does not have electrolyte nature and all the complexes indicate that the ligand harmonized with metal ion as a uni-negatively charged tridentate moiety via Sulphur, nitrogen and amide oxygen in nickel complex. For cadmium, copper and zinc complexes the ligand coordinated as bidentate via nitrogen and sulphur atom,

while it is coordinated as tridentate to Ni metal ion via nitrogen, oxygen and sulphur atom.<sup>[10, 11, 12]</sup>

The nickel (II) complex shows a magnetic moment value 3.38 B.M, it shows the normal range (2.80-3.50 B.M) for octahedral structure<sup>[10]</sup>.

The value of 1.52 B.M for Cu ( $L_C$ )<sub>2</sub> which indicates geometry of distorted square-planar<sup>[10]</sup>. The metal complexes of Zn (II) and Cd (II) exhibit diamagnetism due to  $d^{10}$  configuration which causes them to exist in tetrahedral structures<sup>[14]</sup>.

The Ultra-Violet data of the synthesized complexes are shown in Table 3. The ligand show groups at 264 nm plus 380 nm endorsed to the ( $n \rightarrow \pi^*$ ) and ( $\pi \rightarrow \pi^*$ ) shifts correspondingly, these bands were shifted to upper or lower wavelengths which point to the harmonization of the Schiff base with ions.<sup>[11]</sup>

The appearance of LMCT band at 486 nm in the electric bands of nickel (II) complex stands as a solid sign shows that nickel (II) central ion is harmonized to the ligand through the sulfur atom. The octahedral structure of nickel (II) complex expected to exhibit three bands in their electronic spectra corresponding to the  ${}^3A_{2g}$ ,  ${}^3T_{2g}$  and  ${}^3A_{2g}$ ,  ${}^3T_{1g}$  (F) shifts. The copper (II) compound demonstrate groups at 265 nm 351 nm and 389 nm respectively, the position of the bands of this complex is similar to other square-planar copper (II) complexes determined by X-ray diffraction.<sup>[13]</sup>

In UV spectra the cadmium and zinc complexes show only the intra-ligand band at 258 nm to 390nm and S  $M^{II}$  LMCT transitions at 445 nm and 448 nm respectively.<sup>[14]</sup>

## CONCLUSION

1. New Schiff base and four metal compounds were successfully prepared.
2. The infra-red data shows that the ligand exist in thione form due to  $-NH(C=S)$  SR- functional group, while the metal complexes contain two ligands.
3. Based on the UV-Vis data, the ligand shows absorption on  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  while the metal complexes absorbed on d-d transition.
4. From the result of all physio-chemical measurement the expected structure is octahedral for Ni( $L_h$ )<sub>2</sub> and square planner Cu( $L_h$ )<sub>2</sub> complex while Cd( $L_h$ )<sub>2</sub> and Zn( $L_h$ )<sub>2</sub> tends to be tetrahedral geometry.

## REFERENCES

- [1]. Qian, C., Kong, F. and Mao, J. (2016) Syntheses, structures and characterizations of three novel vanadium selenites with organically bonded copper/nickel complex. *Journal of Solid State Chemistry* 238, 1–8.
- [2]. Sahaia, A., Goswamia, N., Kaushikb, S.D. and Tripathic, S. (2016) Cu/Cu<sub>2</sub>O/CuO nanoparticles: Novel synthesis by exploding wire technique and extensive characterization. *Applied Surface Science*, 39, 974–983.
- [3]. Mandal, S., Saha, R., Saha, M., Pradhan, R., Butcher, R.J and Saha, N.C. (2016) Synthesis, crystal structure, spectral characterization and photoluminescence property of three Cd (II) complexes with a pyrazole based Schiff-base ligand, *Journal of Molecular Structure* 1110, 11e18.
- [4]. Beloso Inmaculada Jesus Castro, Jose AGracia-Vazquez Paulo Perez-Lourido, Jaime Romero and Antonio Sousa (2006) Electrochemical synthesis and structural characterization of heteroleptic cobalt (II) complexes of N-2-pyridyl sulfonamide ligands. *Polyhedron* 25, 2673-2682.
- [5]. Cakir, S., Bulut Naumov, I., P., Bicer, E. and Cakir, O. (2001) Synthesis and spectroscopic studies of novel Cu (II) Co(II), Ni(II) and Zn(II) mixed ligand complexes with saccharin and nicotinamide, *J. Mol Struct*, 560, 1-7.
- [6]. Lobana, T.S., Rekha, A.P.S. Pannu, G.H., Ray, J.B. and Castineiras, A. (2006) Synthesis and structures of monomeric [Chloro(isatin-3- thiosemicarbazone) bis (triphenylphosphine)] copper (I) Dimeric [dichlorobis (thiophene-2-carbaldehyde thiosemicarbazone) bis (triphenylphosphine)dicopper(I) complexes. T.S. Lobana *et al.*, *polyhedron*, doi: 10.1016/j.poly. 12.044.
- [7]. Abeer Khalid Yaseen and Isam Hussain T Al-Karkhi. (2013) Preparation, Characterization and Spectroscopic Study of New Tridentate Schiff Base and its Cu (II), Ni (II) and Zn (II) Metal Complexes. *J. Baghdad for Sci. Vol.* 10(1).
- [8]. Kalaivanan, R. and Srinivasan, K. (2107) Synthesis, growth and characterization of organic nonlinear optical material: N-benzyl-2-methyl-4-nitroaniline (BNA). *Optics & Laser Technology*, 90, 27–32.
- [9]. Ali Mohammad Akbar, Aminul H. Mirza, Malai Haniti S.A. Hamid, Fatriaah Hj Bujang, and Paul V. Bernhardt. (2004) the preparation and characterization of tin (IV) complexes of the 2-quinolonecarboxaldehydes and the X-ray crystal and molecular structures of the 2-quinolinecarb oxaldehyde Schiff bases of S-benzylidithiocarbamate (Hernandez-Ortega, and its tin (IV) complexes Sn (qaldsbz) I<sub>3</sub>) *polyhedron* 23, 2405-2412.
- [10]. Subhankar Kundu, Ajoy Kumar Pramanik, Apurba Sau Mondal, Tapan Kumar Mondal. (2016). Ni (II) and Pd (II) complexes with new N, O donor thiophene appended Schiff base ligand: Synthesis, electro chemistry, X-ray structure and DFT calculation. *Journal of Molecular Structure* 1116 1e8.
- [11]. Nanjan Nanjundan, Ramaswamy Narayanasamy, Steven Geib, Krishnaswamy Velmurugan, Raju Nandhakumar, Manickam Dakshinamoorthi Balakumaran, Pudupalayam Thangavelu Kalaichelvan (2016) Distorted tetrahedral bis-(N,S) bidentate Schiff base complexes of Ni(II), Cu (II) and Zn (II): Synthesis, characterization and biological studies. *Polyhedron* 110, 203–220.
- [12]. Meriem Drissi, Asmae Nakkabi, Mireille Ninon Mbonzi Ombenga, Noureddine EL Moulaj and Mohammed Fahim. (2015) Synthesis and Characterization of Ligand Diimines N-(1-(Propionyloxy) propylidene) benzene amine, N-(2-methyl-1, 4-diphenyl -4-(Phenylimino) Butylidene) Benzenamine and their complexes of Copper and Zinc. *International Journal of Recent Advances in Multidisciplinary Research*. Vol. 02, Issue 12, pp.1063-1065.
- [13]. Laila H., Ahmed M., Rafat M. and Shima M. (2016) some new nano-sized Fe (II), Cd (II) and Zn (II) Schiff base complexes as precursor for metal oxides: Sonochemical synthesis, characterization, DNA interaction, in vitro antimicrobial and anticancer activities. *Bioorganic Chemistry*, 69, 140–152.
- [14]. Taracad, K., Paul, V., Chris J., Nicholas, F., Gregory, K., Kris, J. and David, C. (2016) Synthesis, characterization and biological activities of semicarbazones and their copper complexes. *Journal of Inorganic Biochemistry* 162, 295–308.