



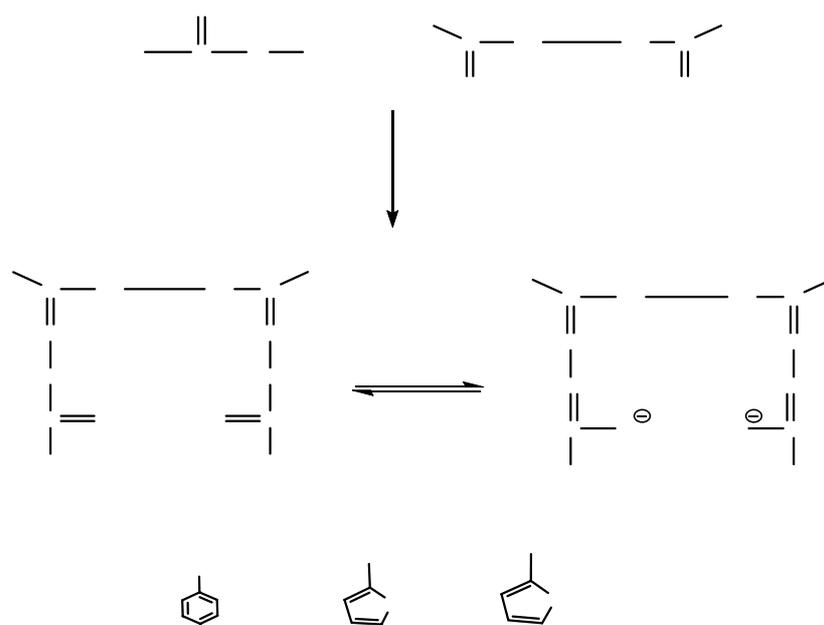
## INTRODUCTION

Hydrazones and their metal complexes play an important role in the coordination chemistry of transition metal ions. Considerable attention has been paid in last decade to hydrazones and their complexes, since they are capable of generating varied molecular architectures and coordination (Alageson *et al.*, 2013; Ibrahim *et al.*, 2009; Jang *et al.*, 2005).

Hydrazones are considered an important class of ligands also because the great variety of their biological activities ranging from antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular, and antitumoral agents (Rollas and Küçüküzgel, 2007). Biological activities of hydrazone metal complexes are also reported for several transition metals (Alageson *et al.*, 2013; Sathyadevi *et al.*, 2012). Moreover, it has recently been shown that hydrazones such as pyradoxal isonicotinoyl hydrazones analogues are effective iron chelators *in vivo* and *in vitro* and may be of value for the treatment of iron overload (Bernharat *et al.*, 2008).

The coordination behavior of aroyl hydrazones is known to depend on the pH of the medium, due to their ability of tautomerism, the deprotonation of the NH group which is readily achieved in complexation, results in the formation of tautomeric anionic species having new coordination properties (Al-Daher and Mustafa, 2013; Galic *et al.*, 2012). Hydrazones have also been proven to show potential application as catalysts (Hosseini-Monfared *et al.*, 2013). Many hydrazone complexes show an excellent catalytic activity in various reactions (Sadhukhan *et al.*, 2011). They are also used as analytical reagents for the determination of several metal ions (Bale and Sawant, 2001).

The desire for understanding versatility in coordination moods together with their pharmacological activity as well as their expected interesting electrical and magnetic properties, makes research on the coordination chemistry of bishydrazone ligands even more attractive (Ibrahim *et al.*, 2009; Stadler and Harrowfield, 2009). In view of the above mentioned significant importance of hydrazone metal complexes in various fields and on continuation of our studies of hydrazone metal complexes (Al-Daher and Mustafa, 2013; Al-Daher and Hadi, 2013; Al-Daher and Al-Qassar, 2011), we were motivated to synthesis Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2,5-hexanedione bis(4-methylbenzoyl hydrazone)(HDMBH), 2,5-hexanedione bis(2-theonyl hydrazone)(HDTH) and 2,5-hexanedione bis(2-furoyl hydrazone)(HDFH), (Scheme1):



Tatumeric forms of ligands (HDMBH),(HDTH),(HDFH)

## EXPERIMENTAL

### Material and Measurements

All chemicals used were reagent grade from B.D.H., Fluka or Merck chemical companies, used as supplied. The infrared spectra (4000-400)  $\text{cm}^{-1}$  of the ligands and complexes were recorded on Tensor Shimadzu and 27 Bruker FT-IR spectrophotometer as KBr discs. Molar conductance's of the complexes were determined in DMF ( $10^{-3}$  M solutions) at room temperature using PMC3 Jenway conductivity meter. The UV-Vis spectra (1100-200 nm) were recorded at room temperature on Labo Med, inc 1650Pc spectrophotometer using DMF as solvent in 1cm quartz cures. Magnetic susceptibilities were measured with balance Sherwood scientific Cambridge at ambient temperature. The necessary diamagnetic corrections for ligands were done using Pascal's tables. The metal content of the complexes was determined spectrophotometrically using SENSAA, GBC scientific equipment atomic absorption spectrometer (Co, Ni, Cu and Zn). Melting points were obtained on 9300 Electrothermal melting point apparatus in open capillaries.

### Preparation of the Ligands

#### Preparation of Acid Hydrazides

4-methylbenzoic acid hydrazide, 2-thiophene carbohydrazide and 2-furic acid carbohydrazide were prepared by the reaction of the corresponding ethyl esters with excess hydrazine hydrate as described previously (Furniss *et al.*, 1989; Al-Saady and Al-Daher, 2000; Al-Daher and Hadi, 2013).

#### Preparation of Bis hydrazones

These were prepared according to the literature method (El-Asmy *et al.*, 2013), by the reacting of 2,5-hexanedion and the corresponding acid hydrazide in (1:2) molar ratio in absolute ethanol as shown in (Scheme 1).

For a solution of acid hydrazide (0.02 mol) [3.00 g, 4-methylbenzoic acid hydrazide or 2.84 g, 2-thiophene carbohydrazide or 2.52g 2-furic acid carbohdrazide] in absolute ethanol (25 mL) was added to the solution of (1.14 g, 0.01 mol) 2,5-hexanedion in absolute ethanol (25 mL) and few drops of glacial acetic acid as catalyst. The reaction mixture was stirred and boiled under reflux for 3hrs. After completion of the reaction and partial removal of solvent, the white brown crystalline solids that precipitated on cooling were separated by filtration, washed with cold ethanol (5 mL) then with ether (5 mL) and dried in an oven at (80 - 90  $^{\circ}\text{C}$ ).

#### Preparation of the Metal Complexes

A stirred hot ethanolic solution (20 mL) of the appropriate metal chloride (0.001 mole) [0.238g,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.238g,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.170g,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; 0.136g,  $\text{ZnCl}_2$ ] was added to (0.378g, 0.001 mole) of the ligand (HDMBH), (0.362g, 0.001 mole) of the ligand (HDTH) or (0.330g, 0.001 mole) of the ligand (HDFH) in absolute ethanol (10 mL) and (0.200g, 0.001 mole) of triethylamine. The reaction mixture was then heated under reflux with constant stirring for 3hrs upon which the solid complexes were separated, filtered off and washed with ethanol (5 mL) and dried as above.

## RESULTS AND DISCUSSION

The bis hydrazones of 2,5-hexanedion (HDMBH, HDTH and HDFH) were synthesized in good yields by condensation with acid hydrazides in 1:2 molar ratio in absolute ethanol (Scheme 1). The reaction of these hydrazones with metal(II) chlorides in the presence of triethyl amine yield 1:1 complexes in which the ligands enolize and doubly deprotonated during complexation as indicated by analytical data (Table 1). All the complexes are coloured non-hygroscopic solids, stable to air and moisture at room temperature. They are generally insoluble in water and non-polar organic solvents, slightly soluble in ethanol, methanol, chloroform, but are more soluble in highly polar organic solvents, like DMF and DMSO. Most complexes melt in temperature range (205-295)  $^{\circ}\text{C}$  which may indicate the non-polymeric nature of the complexes. The low molar conductance values of the DMF solutions of the complexes (4.53-9.8  $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$ ) indicated that they are non-electrolyte (Geary, 1971).

**Table 1: Physical properties and analysis data of the ligands and their complexes**

Com. No.	Formula	Color	M.P (C <sup>0</sup> )	Yield %	Conductivity ohm <sup>-1</sup> mol <sup>-1</sup> cm <sup>2</sup> (DMF)	Metal %	
						Calc.	Found
L <sub>1</sub>	HDMBH(C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> ) M.wt=378	White brown	171-173	78	.....	.....	.....
1	[Co(HDMBH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Dark brown	260-262	65	5.46	12.52	12.14
2	[Ni(HDMBH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Black	250-252	57	6.37	12.47	11.43
3	[Cu(HDMBH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Dark green	>300d	72	4.53	13.36	13.50
4	[Zn(HDMBH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Light brown	205-207	59	7.3	13.69	13.33
L <sub>2</sub>	HDTH(C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> ) M.wt=362	White	150-151	92	.....	.....	.....
5	[Co(HDTH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Light purple	293-295	73	9.8	12.95	11.38
6	[Ni(HDTH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Blue green	210-212	69	7.4	12.91	12.09
7	[Cu(HDTH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Black red	277d	63	8.8	13.81	12.96
8	[Zn(HDTH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Light orange	>300d	57	6.5	14.17	13.3
L <sub>3</sub>	HDFH(C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> ) M.wt=330	White	188-190	85	.....	.....	.....
9	[Co(HDFH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Black	257-259	54	6.5	13.39	13.42
10	[Ni(HDFH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Brown	270-272	61	7.37	13.88	14.07
11	[Cu(HDFH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Black	288-290	62	8.34	14.85	13.96
12	[Zn(HDFH-2H)(H <sub>2</sub> O) <sub>2</sub> ]	Yellow	>300d	66	5.32	15.23	14.29

d= decomposition temperature

### Infrared spectra

IR spectra usually provide a lot of valuable information on coordination behavior of the ligands with metals. The IR spectra of the free ligands and their corresponding metal complexes were compared (Table 2). Remarkable differences between the IR spectra of the ligands and those of the corresponding complexes were observed. The IR spectral bands observed at the ranges (3286 – 3215), (1666– 1654), (1630– 1629) and (1012 – 990)cm<sup>-1</sup>, in the spectra of the free ligands are assigned to  $\nu$ (N-H),  $\nu$ (C=O),  $\nu$ (C=N) and  $\nu$ (N-N) respectively (El-Asmy *et al.*, 2010; Sathyadevi *et al.*, 2012). The bands of  $\nu$ (N-H) and  $\nu$ (C=O) were absent in the spectra of the deprotonated complexes (1-12) suggesting coordination via enol- form, by deprotonation of the N-H proton, during the complication process. The appearance of a new  $\nu$ (C-O) band in these complexes at the region (1276-1191cm<sup>-1</sup>) suggests bonding of the ligands to the metal ions through deprotonated (C-O) group (Singh *et al.*, 2013; Sathyadevi *et al.*, 2012).

The stretching vibrations of azomethine group  $\nu$ (C=N) are shifted to lower frequencies in all the complexes spectra by(16-55cm<sup>-1</sup>), which prove that nitrogen atoms of azomethine groups are involved in complexation. Coordination of nitrogen to the metal atom reduces the electron density in the azomethine group causing a shift in the  $\nu$ (C=N) band to lower frequencies (El-Asmy *et al.*, 2013; Shit *et al.*, 2009). The  $\nu$ (N-N) observed at (1012-990) cm<sup>-1</sup> in the spectra of the ligands, shifts to higher frequencies by (8-51) in their complexes, and indicates the coordination of nitrogen atom of (N-N) group with metal ions (Singh *et al.*, 2013; Sathyadevi *et al.*, 2012). This phenomenon is owing to the diminution of the lone pair electrons repulsion which come from the two adjacent nitrogen atoms, by sharing the electrons out to the metal ion (Shit *et al.*, 2009). These observations were further substantiated by the appearance of non-ligand bands at the ranges (525-444cm<sup>-1</sup>) and (479-401cm<sup>-1</sup>) which are tentatively assigned to  $\nu$ (M-O),  $\nu$ (M-N) respectively (El-Boraey and Aly, 2013). Hence, it may be concluded that in all complexes, (1-12) are deprotonated and the ligands (HDMBH,HDTH and HDFH) act as dianionic tetradentate (NNOO<sup>-2</sup>) donor, chelating through the two enolate oxygens and two azomethane nitrogen atoms.

The band observed at (850cm<sup>-1</sup>) due to  $\nu$ (C-S-C) of thiophene ring spectrum of the free ligand (HDTH) remains almost at the same position in the spectra of its complexes which indicate non-

involvement of thiophene sulfur atom in bonding, (Singh *et al.*, 2011). The band observed in the spectrum of the free ligand (HDFH) at  $1078\text{ cm}^{-1}$  assigned for  $\nu(\text{C-O-C})$  stretching vibration of furan ring is almost unaltered in the spectra of the metal complexes indicating non-participation of the furan ring oxygen atom in bonding with metal (Shivakumar *et al.*, 2008 ; Bikas *et al.*, 2013; Al-Daher and Mustafa, 2013).

The spectra of complexes exhibit a broad band centered around  $3400\text{ cm}^{-1}$  due to the symmetric and asymmetric stretching mode of coordinated water molecule. Furthermore weak bands in the  $877\text{-}889$ ,  $669$  and  $679\text{ cm}^{-1}$  ranges may represent the wagging and rocking modes of coordinated water respectively (Singh, 2008).

**Table 2: Selected infrared frequencies of the ligands and their complexes**

Comp. No.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{O-H})$ $\text{H}_2\text{O}$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L <sub>1</sub>	3282 <sub>(m)</sub>	1666 <sub>(vs)</sub>	1630 <sub>(s)</sub>	.....	1012 <sub>(m)</sub>	.....	.....	.....
1	.....	.....	1611 <sub>(m)</sub>	1273 <sub>(s)</sub>	1027 <sub>(m)</sub>	3396 <sub>(m)</sub>	525 <sub>(w)</sub>	479 <sub>(m)</sub>
2	.....	.....	1612 <sub>(m)</sub>	1276 <sub>(s)</sub>	1037 <sub>(m)</sub>	3409 <sub>(m)</sub>	502 <sub>(m)</sub>	449 <sub>(m)</sub>
3	.....	.....	1612 <sub>(s)</sub>	1265 <sub>(s)</sub>	1028 <sub>(m)</sub>	3434 <sub>(w)</sub>	482 <sub>(m)</sub>	435 <sub>(m)</sub>
4	.....	.....	1614 <sub>(m)</sub>	1271 <sub>(s)</sub>	1025 <sub>(s)</sub>	3389 <sub>(w)</sub>	472 <sub>(w)</sub>	448 <sub>(m)</sub>
L <sub>2</sub>	3215 <sub>(m)</sub>	1654 <sub>(s)</sub>	1630 <sub>(s)</sub>	.....	990 <sub>(m)</sub>	.....	.....	.....
5	.....	.....	1602 <sub>(m)</sub>	1256 <sub>(s)</sub>	1032 <sub>(m)</sub>	3395 <sub>(m)</sub>	501 <sub>(m)</sub>	431 <sub>(w)</sub>
6	.....	.....	1598 <sub>(m)</sub>	1236 <sub>(s)</sub>	1041 <sub>(m)</sub>	3410 <sub>(w)</sub>	509 <sub>(m)</sub>	478 <sub>(w)</sub>
7	.....	.....	1595 <sub>(m)</sub>	1272 <sub>(s)</sub>	1027 <sub>(m)</sub>	3351 <sub>(w)</sub>	451 <sub>(m)</sub>	401 <sub>(w)</sub>
8	.....	.....	1598 <sub>(m)</sub>	1270 <sub>(s)</sub>	1027 <sub>(m)</sub>	3426 <sub>(m)</sub>	444 <sub>(m)</sub>	410 <sub>(w)</sub>
L <sub>3</sub>	3286 <sub>(s)</sub>	1660 <sub>(vs)</sub>	1629 <sub>(m)</sub>	.....	1008 <sub>(s)</sub>	.....	.....	.....
9	.....	.....	1598 <sub>(m)</sub>	1228 <sub>(s)</sub>	1017 <sub>(m)</sub>	3380 <sub>(w)</sub>	485 <sub>(w)</sub>	428 <sub>(m)</sub>
10	.....	.....	1574 <sub>(m)</sub>	1224 <sub>(s)</sub>	1028 <sub>(s)</sub>	3414 <sub>(m)</sub>	460 <sub>(m)</sub>	433 <sub>(w)</sub>
11	.....	.....	1592 <sub>(s)</sub>	1226 <sub>(s)</sub>	1015 <sub>(m)</sub>	3390 <sub>(w)</sub>	447 <sub>(m)</sub>	402 <sub>(m)</sub>
12	.....	.....	1593 <sub>(m)</sub>	1191 <sub>(s)</sub>	1015 <sub>(m)</sub>	3488 <sub>(m)</sub>	475 <sub>(m)</sub>	415 <sub>(w)</sub>

(vs)= very strong , (s)= strong , (m)= medium , (w)= weak

### Electronic Spectra and Magnetic Properties :

The electronic spectra of ligands and their metal complexes in the range 200-1100nm, were carried out in DMF. Table (3) shows the electronic spectral bands and magnetic moments of the prepared complexes.

The spectra of the ligands in DMF solution exhibit two main absorption bands at  $36363\text{-}35587\text{ cm}^{-1}$  and  $32362\text{-}28490\text{ cm}^{-1}$ . The first band probably due to  $\pi \rightarrow \pi^*$  transition of the chromophore ( $-\text{C}=\text{N}-\text{NH}-\text{CO}-$ ), and the second band might be attributed to the  $n \rightarrow \pi^*$  transitions resulting from nitrogen and oxygen atoms. In the spectra of the complexes, the shift of the ligand transitions to a lower wavelength (red shift) is ascribed to the ligand complexation with metal ions (Abd El-Motaleb *et al.*, 2005). The new intense band observed in the spectra of all complexes at the region  $27777\text{-}20964\text{ cm}^{-1}$  may be associated with the charge transfer transitions (LMCT).

The magnetic moment values of Co(II) complexes (1,5 ,9) are in the range 4.62-5.19 B.M, which are fairly close to the values reported for three unpaired electrons in an octahedral environment (Singh *et al.*, 2013). These complexes exhibit three bands in their spectra at the regions  $25316\text{-}16447\text{ cm}^{-1}$ ,  $14880\text{-}14836\text{ cm}^{-1}$  and  $10940\text{-}9803\text{ cm}^{-1}$  indicating an octahedral geometry around the metal ion. These transitions are assigned as  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$ ,  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$  respectively. (Cotton *et al.*, 1999; Singh *et al.*, 2013).

The magnetic moment values of Ni(II) complexes (2,6,10) are in the range 2.91-3.13 BM which are very close to the spin only value of two unpaired electrons, indicating octahedral environment around Ni(II) ion. It is further confirmed by their electronic spectral bands observed at the regions  $23809\text{-}17825\text{ cm}^{-1}$ ,  $15384\text{-}13422\text{ cm}^{-1}$  and  $10940\text{-}9661\text{ cm}^{-1}$  assignable to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{p})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  transitions respectively (Cotton *et al.*, 1999; Singh *et al.*, 2014).

The electronic spectra of Cu(II) complexes (3,7,11) contain a broad band at the region 13513–13071 $\text{cm}^{-1}$ . These bands are typical of d-d band of Jahn-Teller distorted Cu(II) complexes in distorted octahedral geometry, and can be assigned to two or three of the transitions  ${}^2B_{1g} \rightarrow {}^2E_g$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  (Singh, 2008). Magnetic moment of these complexes are in range 1.79–2.2 BM corresponding to one unpaired electron and suggesting a monomeric octahedral geometry (Cotton *et al.*, 1999).

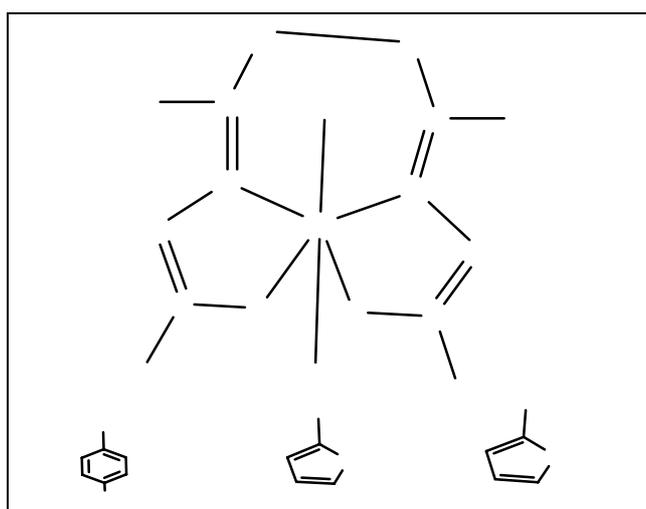
The diamagnetic Zn(II) complexes (4,8,12) show no prominent absorption in the visible region because of  $d^{10}$  configuration of Zn(II).

**Table 3: Electronic spectra and magnetic moments data of the ligands and their complexes**

Complex No.	$M_{eff}$ B.M	Electronic spectrum $\text{cm}^{-1}$
L <sub>1</sub>	.....	36363,30303
1	4.68	34843,27027,23809,16447,14858,10940
2	3.12	32363,29575,23255,20618,15384,9794
3	2.01	34843,29762,20964,13513
4	dia	34965,31250,27397
L <sub>2</sub>	.....	35587,32362
5	4.62	33670,28571,26315,16447,14836,9940
6	3.13	31645,28985,25974,17825,14992,9661
7	1.79	34965,29411,25000,13071
8	dia	34482,31250,27027
L <sub>3</sub>	.....	35971,28490
9	5.19	34965,30303,27777,25316,14880,9803
10	2.91	34364,27397,25316,23809,13422,10940
11	2.2	34246,29411,25974,13245
12	dia	32573,28571,25380

### CONCLUSION

Based on stoichiometries and spectro-chemical studies, the bis hydrazone ligands, act as a dibasic tetradentate ligands ( $\text{NNOO}^{-2}$ ) in all prepared deprotonated complexes (1-12) coordinating through the two enolate oxygens and two azomethine groups nitrogen atoms. Octahedral geometry is proposed for all complexes Fig.(1).



**Fig. 1: The proposed octahedral structure for the complexes  $[\text{M}(\text{L}-2\text{H})(\text{H}_2\text{O})_2]$   
M= Co(II), Ni(II), Cu(II), Zn(II) L= HDMBH, HDTH, HDFH**

## REFERENCES

- Abd El-Motaleb, A.; Ramadan, M.; Issa, R.M. (2005). Synthesis, characterization and ascorbic acid oxidize mimetic catalytic activity of copper(II) picolyl hydrazone complexes. *Trans. Met. Chem.*, **30**, 471-480.
- Alagesan, M.; Bhuvanesh, N.S.P.; Dharmaraj, N. (2013). Potentially cytotoxic new Copper(II) hydrazone complexes: synthesis, crystal structure and biological properties. *J. Chem. Soc., Dalton Trans.*, **42**,7210-7223.
- Al-Daher, A.G.M.; Al-Qassar, I.A. (2011). Synthesis and characterization of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 2-furaldehyde 2-theonyl hydrazone. *Raf. J. Sci.*, **22**(4),109-120.
- Al-Daher, A.G.M.; Mustafa, S.M.(2013). Synthesis and characterization and antibacterial activity of 2-acetylpyridine-2-furoylhdrazone complexes with UO<sub>2</sub>(VI), Th(IV), Co(II), Ni(II), Cu(II), and Zn(II). *Raf. J. Sci.*, **24**(5),72-86.
- Al-Daher, A.G.M.; Hadi, A.A. (2013). Synthesis characterization and antibacterial activity of thorium(IV), dioxouranium(VI), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) complexes with picolinoyl hydrazone. *Raf. J. Sci.*, accepted for publication.
- Al\_Saady, S.K.; Al\_Daher, A.G.M. (2000). Preparation and study of uranyl chloride complexes with some acid hydrazides. *Iraqi J. Chem.*, **26** (2), 462-470.
- Bale, M.N.; Sawant, A.D. (2001). Solvent extraction and spectrophotometric determination of uranium(IV) with pyridine-2-carbaldehyde 2-hydroxy benzoyl hydrazone. *J. Radio. Anal. Nucl. Chem.*, **247**, 531-534.
- Bernhardt, P.V.; Wilson, G.J.; Sharpe, P.C.; Kalinowski, D.S.; Richardson, D.R. (2008). Tuning the antiproliferative activity of biologically active iron chelators: characterization of the coordination chemistry of 2-acetylpyridine and 2-benzoylpyridine hydrozone ligands. *J. Biol. Inorg. Chem.*, **13**, 107-119.
- Bikas, R.; Monfared, H.H.; Jeanneau, E.; Shaabani, (2013). Synthesis, structural characterization and electrochemical studies of new oxovanadium(V)complexes derived from 2-furanoylhydrazone derivatives. *J. Chem.*, **2013**, 546287.
- Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. (1999). "Advanced Inorganic Chemistry". 6<sup>th</sup> ed., John Wiley and Sons, New York, pp. 810-842.
- El-Asmy, A.A.; Al-Abdeen, A.Z.; Abo El-Maaty, W.M.; Mostafa, M.M. (2010). Synthesis and spectroscopic studies of 2,5-hexanedione bis(isonicotinylhydrazone) and its first row transition metal complexes. *Spectrochim. Acta A.*, **75**, 1516-1522.
- El-Asmy, A.A.; Shabana, A.; El-Maaty, W.; Mostafa, M.M. (2013). Synthesis spectroscopic characterization molecular modeling and eukaryotic DNA degradation of new hydrazone complexes. *Arabian J. Chem.*, **232**, 92-110.
- El-Boraey, H.A.; Aly, S.A. (2013). Synthesis, spectroscopic characterization, and thermal behavior studies of 2-anilino-N-[(1E)-(2 hydroxyphenyl)methylene]acetohydrazide metal complexes. *Synth. React. Inorg., M-Org.*, **43**, 1130-1138.
- Furniss, B.S.; Rogers, V.; Smith, P.W.G.; Tatchll, A.R. (1989). "Vogel, s Textbook of Practical Organic Chemistry". 5<sup>th</sup> ed. Longman Scientific and Technical, England, 1269 p.
- Galic, N.; Dijaanosic, A.; Kontrec, D.; Miljanic, S. (2012). Structural investigation of aroyl hydrazone in dimethyl sulphoxide, water mixture. *Spectrochim. Acta., A.*, **95**, 347-353.
- Geary, W.J. (1971). The use of conductivity measurement in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.*, **7**, 81-122.
- Hosseini-Monfared, H.; Asghari-Lalami, N.; Pazio, A.; Wozniak, K.; Janiak, C. (2013). Dinuclear vanadium, copper, manganese and titanium complexes containing O,O,N-dichelating ligands: synthesis, crystal structure and catalytic activity. *Inorg. Chim. Acta.*, **406**, 241-250.
- Ibrahim, K.M.; Gaber, I.M; Zaky, R.R. (2009). Synthesis and magnetic, spectral and thermal eukaryotic DNA studies of some 2-acetyl pyridine [N-(3-hydroxy-2-naphthoyl)] hydrazone complexes. *J. Coord. Chem.*, **62**(7),1100-1111.

- Jang, Y.J.; Lee, U.; Koo, B.K. (2005). Synthesis and crystal structures of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) metal complexes with NNO functionalized ligand. *Bull. Korean. Soc.*, **26**(6), 925-929.
- Rollas, L.; Küçükgül, S. G. (2007). Biological activities of hydrazone derivatives. *Molecules*, **12**, 1910-1919.
- Sadhukhan, D.; Ray, A.; Pilet, G.; Rizzoli, C.; Rosair, G.M.; Gomez-Garcia, C.J.; Signorella, S.; Bellu, S.; Mitra, S. (2011). Weak interaction modulating the dimensionality in supermolecular architectures in three new nickel(II) hydrazone complexes, magnetostructural correlation, and catalytic potential for epoxidation of alkenes under phase transfer conditions. *Inorg. Chem.*, **50**, 8326-8339.
- Sathyadevi, P.; Krishnamoorthy, P.; Algesan, M.; Thanigaimani, K.; Muthiah, P.T.; Dharmaraj, N. (2012). Synthesis crystal structure, electrochemistry and studies on protein binding antioxidant and biocidal activities of Ni(II) and Co(II) hydrazone complexes. *Polyhedron*, **31**, 294-306.
- Shit, S.; Samanta, C.B.; Slawin, A.M.Z.; Gramlich, V.; Mitra, S. (2009). Three new coordination complexes of cobalt(III), manganese(II), and copper(II) with N,N,O-donor hydrazine ligands: syntheses and structural characterizations. *Struct. Chem.* **20**, 633-642.
- Singh, P.; Singh, D.P.; Singh, V.P. (2014). Synthesis, spectral and single crystal x-ray diffraction studies on Mn(II), Ni(II), Cu(II) and Zn(II) complexes with 2-hydroxy-benzoic acid (phenyl-pyridin-2-yl-methylene)-hydrazide. *Polyhedron*, **31** 56-65.
- Singh, V.P.; Singh, S.; Singh, D.P.; Singh, P.; Tiwari, K.; Mishra, M.; Butcher, R.J. (2013). "Synthesis, spectral and single crystal X-ray diffraction studies on Co(II), Ni(II), Cu(II) and Zn(II) complexes with o-amino acetophenone benzoyl hydrazine". *Polyhedron.*, **56**, 71-81.
- Singh, V.P.; Singh, P.; Singh, A.K. (2011). Synthesis, structural and corrosion inhibition studies on Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes with 2-acetyl thiophene benzoyl hydrazone. *Inorg. Chim. Acta*, **379**, 56-63.
- Singh, V.P. (2008). Synthesis, electronic and ESR spectral studies on copper (II) nitrate complexes with some acylhydrazines and hydrazones. *Spectrochim. Acta.* **A71**, 17-72.
- Shivakumar, K.; Sashidar, A.; Reddy, P.V.; Halli, M.B. (2008). Synthesis, spectral characterization and activity of benzofuran Schiff bases with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes. *J. Coord. Chem.*, **61**(14), 2274-2287.
- Stadler, A-M.; Harrowfield, J. (2009). Bis-acyl-/aroyl-hydrazones as multidentate ligands *Inorg. Chim. Acta.*, **362**, 4298-4314.