

Synthesis and Characterization of New Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Benzil Bis-hydrazone ligands

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Abstract: A number of new Co(II), Ni(II), Cu(II) and Zn(II) complexes with benzil bis(acetoyl hydrazone) (BNAH), benzil bis(picolinoyl hydrazone) (BNPH) and benzil bis(2-theonyl hydrazone) (BNTH) have been prepared. The bis-hydrazone ligands were synthesized by the condensation of benzil with (acetyl hydrazide, picolinic acid hydrazide or 2-thiophene carbohydrazide) in 1:2 molar ratio. The reaction of metal(II) acetate with the ligands in (1:1) molar ratio in ethanol in presence of triethylamine lead to isolation of complexes having the general formula $[M(L-2H)(H_2O)_2]$ $[Ni(L-2H)]$ where (M= Co(II), Ni(II), Cu(II) and Zn(II)), and (L-2H=doubly deprotonated ligands BNAH, BNTH and BNPH). The ligands and complexes have been characterized by spectral (IR, UV-Vis), elemental analysis, (1H -NMR), magnetic and molar conductance measurements, which revealed that the ligands BNAH, BNTH and BNPH acts as dinegative charge tetradentate ($NNOO^{2-}$) donor ligands in the metal complexes, coordinated through the two azomethine group nitrogen atoms and the two enolic oxygen atoms. All complexes provide an octahedral geometry except $[Ni(L-2H)]$ is provide an square planer geometry.

Keywords: Benzil, Bis-hydrazones, Complexes, Transition metals.

تحضير و تشخيص معقدات جديدة لـ Co(II) و Ni(II) و Cu(II) و Zn(II) مع ليكاندات ثنائية الهيدرازون

للبنزل

الملخص: حضرت عدد من المعقدات الجديدة للكوبلت (II) و النيكل (II) و النحاس (II) و الزنك (II) مع بينزل بس (أسيثيل هيدرازون) (BNAH) ، بينزل بس (2-بيكولينويل هيدرازون)، بينزل بس (2-ثايونيل هيدرازون)، (BNTH). حضرت الليكاندات بس-هيدرازون من تكاثف بينزل مع (أسيثيل هيدرازيد) او (بيكولينك اسيد هيدرازيد) او (2-ثايوفين كاربوهيدرازيد) و بنسب موليه (2:1). تفاعلت خلاات الفلزات مع الليكاندات بنسبة موليه (1:1) في الايثانول بوجود ثلاثي أميل أمين واعطت المعقدات ذات الصيغة العامة: $[M(L-2H)(H_2O)_2]$ و $[Ni(L-2H)]$ حيث (M= Co(II), Ni(II), Cu(II) و Zn(II)) (L-2H = ليكاندات منزوعة البروتونين، BNAH, BNTH BNPH شخصت الليكاندات والمعقدات من خلال تحليل الدقيق للعناصر وطيف الرنين النووي المغناطيسي (1H -NMR) وقياسات الاطياف (IR, UV-Vis) والعزوم المغناطيسية والتوصيلية المولارية. اوضحت النتائج ان الليكاندات (BNTH, BNAH BNPH) تسلك سلوك رباعية السن ثنائية الشحنة السالبة ($NNOO^{2-}$) , وقد تناسقت الليكاندات مع الايونات الفلزية من خلال ذرتي نيتروجين مجموعتي الايزوميثان وذرتي الاوكسجين الاينويليتين . وان جميع المعقدات المحضرة لها تركيب ثنائي السطوح ماعدا المعقد $[Ni(L-2H)]$ له تركيب مربع مستوي.

INTRODUCTION

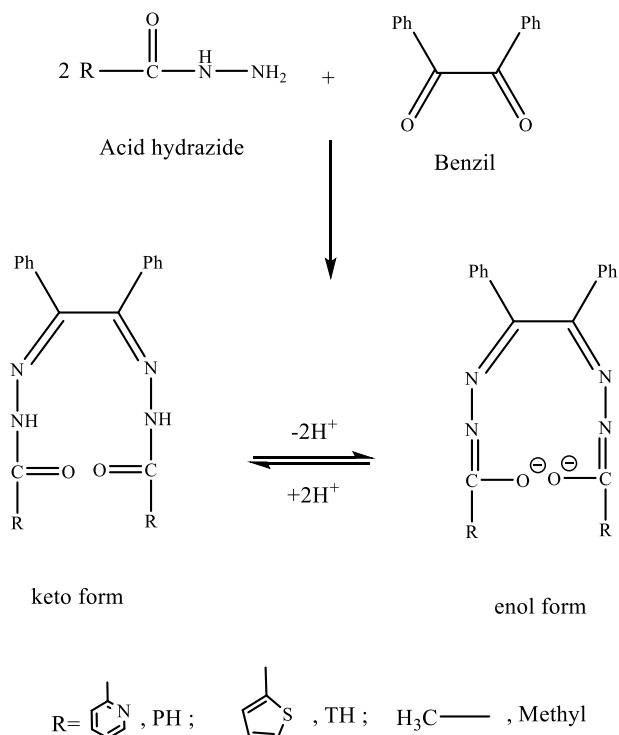
The ligating properties of hydrazones have attracted considerable research interest due to their versatility in binding to metal ions in different ways generating varied molecular architectures and coordination (Alageson *et al.*, 2013, Ibrahim *et al.*, 2009 and Jang *et al.*, 2005).

Aroyl hydrazones and their metal complexes often possess great variety of biological activity ranging from antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular, and antitumoral agents (Rollas and Küçükgül, 2007; Alageson *et al.*, 2013; Sathyadevi *et al.*, 2012). Moreover, it has recently been shown that some hydrazones 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 reaction medium, due to their ability of enolisation, the deprotonation of the NH group which is readily achieved in complex formation, results in the formation of tautomeric anionic species having new coordination properties (Al-Daher and

Mustafa, 2013 and Galic *et al.*, 2012). Hydrazones have also been proven to show probable application as catalysts (Hosseini-Monfared *et al.*, 2013). Many hydrazone complexes show a good catalytic activity in various reactions (Sadhukhan *et al.*, 2011). They are also used as analytical reagents for spectrophotometric determination of several metal ions (Bale and Sawant, 2001).

The desire for understanding versatility in coordination modes 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 and Al-Daher and Al-Qassar, 2011), we were motivated to synthesize Co(II), Ni(II), Cu(II) and Zn(II) complexes with benzil bis(2-acetyl hydrazone) (BNAH), benzil bis(picolinoyl hydrazone) (BNPH) and benzil bis(2-theonyl hydrazone) (BNTH) (Scheme 1):



Scheme 1

Tatumeric forms of ligands (BNAH),(BNPH),(BNTH)

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 (400-4000) cm^{-1} of the ligands and complexes were recorded on Tensor Shimadzu and 27 Bruker FT-IR spectrophotometer as KBr discs. The C.H.N.S. elemental analyses were performed on Elemental Combustion System (ECS 4010) Costech Instrument. ^1H -NMR spectra were recorded in DMSO solution using TMS as internal standard on AVANCE (III) 400MHz Bruker spectrophotometer. 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(200-1100 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 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:

Acetyl hydrazide, 2-thiophene carbohydrazide and picolinoyl hydrazide 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 and Al-Daher and Hadi, 2013).

Preparation of Bis hydrazones:

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

To a solution of acid hydrazide (0.02 mol) [1.48 g, acetyl hydrazide or 2.74g picolinoyl hydrazide or 2.84 g, 2-thiophene carbohydrazide] in absolute ethanol (25 mL) was added to the (2.1 g, 0.01 mol) benzil 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 reaction and partial removal of solvent, the white yellow 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 °C).

Preparation of the Metal Complexes

The complexes were prepared by reacting the corresponding metal acetate with each ligand (1:1) molar ratio in absolute ethanol in presence of triethyl amine, according to the following procedures:

a: The complexes $[M(L-2H)(H_2O)_2]$, $[Ni(BNAH-2H)]$, $M = Co(II), Ni(II), Cu(II)$,

$Zn(II)$, A solution containing metal acetate (0.001 mol) (0.249 g $Co(CH_3COO)_2 \cdot 4H_2O$; 0.249g, $Ni(CH_3COO)_2 \cdot 4H_2O$; 0.199g, $Cu(CH_3COO)_2 \cdot H_2O$; 0.21 g $Zn(CH_3COO)_2 \cdot 2H_2O$] in (10 mL) absolute ethanol was added with continuous stirring to (15) mL ethanolic solution of (0.322g, 0.001 mole) of the ligand (BNAH), (0.448g, 0.001 mole) of the ligand (BNPH) or (0.458g, 0.001 mole) of the ligand (BNTH) and triethyl amine (0.200 g, 0.002 mol) in absolute ethanol (10 mL) with continuous stirring. The mixture was further stirred for 12 h at room temperature, upon which precipitate formed. The solid complex was separated by filtration, washed with absolute ethanol (5 mL) then with ether (5 mL) and dried in an oven at (70-80) °C.

RESULTS AND DISCUSSION

The bis hydrazones of benzil (BNAH, BNTH and BNPH) were synthesized in good yields by condensation with acid hydrazides in 1:2 molar ratio in absolute ethanol (Scheme1). The reaction of these hydrazones with metal(II) acetate in 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 they are more soluble in highly polar organic solvents, like DMF and DMSO. The low molar conductance values of the DMF solutions of the complexes ($4.7-15.9 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$) indicating 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 ⁰)	Yield %	Conductivity ohm ⁻¹ mol ⁻¹ cm ² (DMF)	Metal %	
						Calc.	Found
L ₁	BNAH (C ₁₈ H ₁₈ N ₄ O ₂) M.wt=322	White	218-219	92			
1	[Co(BNAH-2H)(H ₂ O) ₂]	brown	>300d	78	5.6	14.20	13.85
2	[Ni(BNAH-2H)]	Brown	260-261	59	4.7	15.49	14.96
3	[Cu(BNAH-2H)(H ₂ O) ₂]	Green	248-249	63	6.5	15.14	14 .66
4	[Zn(BNAH-2H)(H ₂ O) ₂]	Yellow	130-131	67	5.9	15.51	14.47
L ₂	BNPH(C ₂₆ H ₂₀ N ₆ O ₂) M.wt=448	White yellow	160-161	85			
5	[Co(BNPH -2H)(H ₂ O) ₂]	Brown	141-142	86	5.4	10.89	10.06
6	[Ni(BNPH-2H)(H ₂ O) ₂]	Gray	198-199	71	10.7	10.85	9.96
7	[Cu(BNPH-2H)(H ₂ O) ₂]	Brown	178-179	65	12.9	11.64	11.16
8	[Zn(BNPH-2H)(H ₂ O) ₂]	Yellow	>300d	70	6.8	11.94	10.99
L ₃	BNTH(C ₂₄ H ₁₈ N ₄ O ₂ S ₂)	White	112-	87			

	M.wt=458	yellow	113				
9	[Co(BNTH-2H)(H ₂ O) ₂]	Brown	231-232	63	5.4	10.54	10.21
10	[Ni(BNTH-2H)(H ₂ O) ₂]	Brown	271-272	76	10.7	10.65	10.18
11	[Cu(BNTH-2H)(H ₂ O) ₂]	Black	235-236	79	10.1	11.43	10.09
12	[Zn(BNTH-2H)(H ₂ O) ₂]	Orange	215-216	61	15.9	11.72	10.83

d= decomposition temperature

Table 2: Elemental analysis of compounds (L1,L2,L3,12) (C.H.N.S)

Com. No.	Formula	Elemental analysis, Calculated / (Found)			
		C%	H%	N%	S%
L1	BNAH (C ₁₈ H ₁₈ N ₄ O ₂)	67.08 / (66.68)	5.59 / (6.23)	17.39 / (16.86)	
L2	BNPH (C ₂₆ H ₂₀ N ₆ O ₂)	69.64 / (70.18)	4.46 / (5.03)	18.75 / (18.88)	
L3	BNTH (C ₂₄ H ₁₈ N ₄ O ₂ S ₂)	62.88 / (63.79)	3.93 / (4.44)	12.22 / (11.49)	13.97 / (13.30)
12	[Zn(BNTH-2H).2H ₂ O]	50.05/ (49.45)	2.87/ (2.79)	9.73 / (9.13)	11.12/ (10.88)

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 (3166–3288), (1639–1685), (1577–1593) and (937–990) cm^{-1} , in the spectra of the free ligands are assigned to $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C=N})$ and $\nu(\text{N-N})$ respectively (El-Asmy, *et al.*, 2010; Sathyadevi, *et al.*, 2012). The bands of $\nu(\text{N-H})$ and $\nu(\text{C=O})$ 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 complexation process. The appearance of a new $\nu(\text{C-O})$ band in these complexes at the region (1180-1127 cm^{-1}) suggest 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 $\nu(\text{C=N})$ are shifted to lower frequencies in all the complexes spectra by (8-54 cm^{-1}), which proves 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 $\nu(\text{C=N})$ band to lower frequencies (El-Asmy, *et al.* 2013; Shit, *et al.*, 2009). The $\nu(\text{N-N})$ observed at (990-1000)

cm^{-1} in the spectra of the ligands, shifts to higher frequencies by (16-44) in their complexes, 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 (510-448 cm^{-1}) and (403-475 cm^{-1}) which are tentatively assigned to $\nu(\text{M-O})$, $\nu(\text{M-N})$ respectively (El-Boraey and Aly, 2013). Hence, it may be concluded that in all complexes (1-12) are deprotonated and the ligands (BNAH, BNTH and BNPH) acts as dianionic tetradentate (NNOO^{2-}) donor, chelating through the two enolate oxygens and two azomethane nitrogen atoms.

The band observed at (852 cm^{-1}) due to $\nu(\text{C-S-C})$ of thiophene ring spectrum of the free ligand (BNTH) remain 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). COC, (Shivakumar *et al.*, 2008 ; Bikas *et al.*, 2013; Al-Daher and Mustafa, 2013).

The spectra of complexes exhibit a broad band centered around 3400 cm^{-1} due to the symmetric and asymmetric stretching mode of coordinated water molecule. Furthermore weak bands in the 843-965 and 646-757 cm^{-1} ranges may represent the wagging and rocking modes of coordinated water respectively (Singh, 2008).

Table 3: Selected infrared frequencies of the ligands and their complexes.

Comp. No.	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{O-H})$ H_2O	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L ₁	3234 _(m)	1685 _(vs)	1582 _(s)		990 _(m)			
1			1556 _(m)	1146 _(s)	1022 _(m)	3311 (b)	453 _(w)	420 _(m)
2			1560 _(m)	1134 _(m)	1020 _(m)		493 _(m)	425 _(m)
3			1565 _(s)	1155 _(s)	1021 _(m)	3342 (b)	448 _(m)	430 _(m)
4			1574 _(s)	1142 _(s)	1012 _(m)	3344 (b)	490 _(w)	448 _(m)
L ₂	3288 _(s)	1662 _(vs)	1593 _(m)		1000 _(s)			
9			1555 _(m)	1147 _(s)	1017 _(m)	3315 (b)	486 _(w)	446 _(m)
10			1546 _(m)	1150 _(m)	1024 _(s)	3409 (b)	449 _(m)	426 _(w)
11			1570 _(s)	1180 _(s)	1016 _(m)	3373 (b)	459 _(m)	412 _(m)
12			1539 _(m)	1127 _(m)	1030 _(m)	3322 (b)	470 _(w)	423 _(w)
L ₃	3166 _(m)	1639 _(s)	1577 _(s)		997 _(m)			
5			1564 _(m)	1163 _(m)	1024 _(m)	3409 (b)	475 _(w)	403 _(m)
6			1546 _(m)	1176 _(m)	1047 _(m)	3378 (b)	480 _(m)	425 _(w)
7			1554 _(m)	1167 _(m)	1032 _(m)	3316 (b)	467 _(m)	421 _(w)
8			1560 _(m)	1172 _(m)	1020 _(m)	3375 (b)	510 _(m)	432 _(w)

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

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) show 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 36231-35211 cm^{-1} and 33670-31847 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 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 27777-24390 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 4.81-5.27 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 24096-20491 cm^{-1} , 15151-14388 cm^{-1} and 10940-9784 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 (6,10) are in the range 3.01-3.24 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 22723-22675 cm^{-1} , 18656-16482 cm^{-1} and 10940-9794 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). Complex number (2) show diamagnetic moment, It is further confirmed by their electronic spectral bands observed at the 27777 cm^{-1} and 20491 cm^{-1} assignable to $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transitions respectively (L'opez-Torres and Mendiola, 2009).

The electronic spectra of Cu(II) complexes (3,7,11) contains a broad band at the region 14880-13171 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 $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$, $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ and $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ (Singh, 2008). Magnetic moment of these complexes are in range 1.87-1.76 BM correspond 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 4 : Electronic spectra and magnetic moments data of the ligands and their complexes

Complex No.	M_{eff} B.M	Electronic spectrum cm^{-1}
L ₁		36231, 33258
1	4.81	36303, 32679, 27701, 20491, 14925, 10940
2	dia	33363, 30303, 27777, 20491
3	1.87	33898, 31250, 25316, 14880
4	dia	34482, 32679, 26660
L ₂		35211, 33670
5	5.27	34843, 31746, 27027, 24096, 14388, 9784
6	3.24	34843, 31746, 28818, 22723, 18656, 9794
7	1.78	33250, 31540, 26315, 13171
8	dia	31746, 28011, 23809
L ₃		35714, 31847
9	5.18	34743, 32759, 27397, 22988, 15151, 9803
10	3.01	33457, 30120, 27027, 22675, 16482, 10940
11	1.76	32453, 31250, 24390, 13605
12	dia	34965, 29585, 24096

¹H-NMR Spectra

¹H-NMR spectra of the ligand BNTH and its Zn(II) complex was recorded in DMSO-d₆ solution. The ¹H-NMR spectra of the free ligands BNTH show a singlet at (12.04) ppm assignable for NH protons and the absence of the signal in the spectrum of Zn(II) complex indicating deprotonation of the –NH–CO– groups confirming that ligand coordinate to Zn(II) in the enolate form after deprotonation (Sonika and Malhotra, 2011).

The multiplet band for benzene rings protons appears at (7.36–7.38) ppm and the thiophene protons at (7.11–8.52) ppm in the spectrum of free ligands. The thiophene protons of BNTH appear as multiplet at (7.31–7.76) ppm in the spectrum of complex, these were almost unaltered in the spectra of Zn(II) complexes, which may suggest non-involvement of thiophene sulfur atom in coordination.

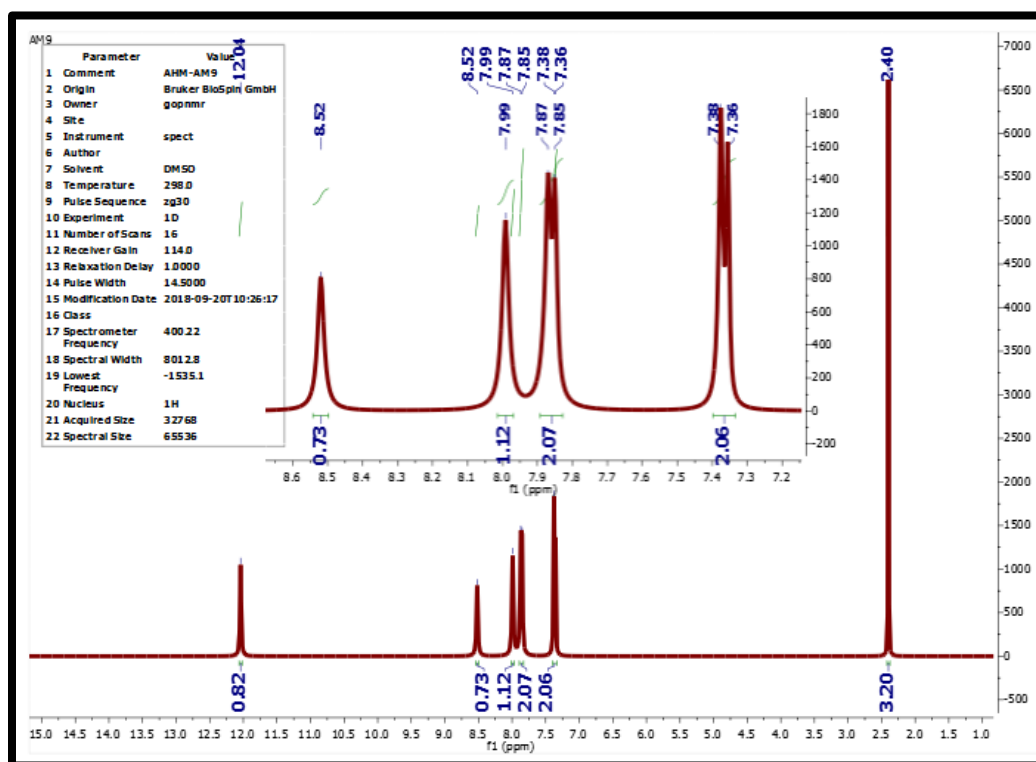


Fig1
¹H.NMR spectrum for BNTH ligand

CONCLUSION

"Based on stoichiometries and spectro-chemical studies, the bis hydrazone ligands , acts as a dibasic tetradentate ligands(NNOO^{-2}) in all prepared deprotenated complexes (1-12)

coordinating through the two enolate oxygens and two azomethine groups nitrogen atoms.Octahedral geometry proposed for all complexes fig.1 exepte complexe number (2) has squer planer geometry" .

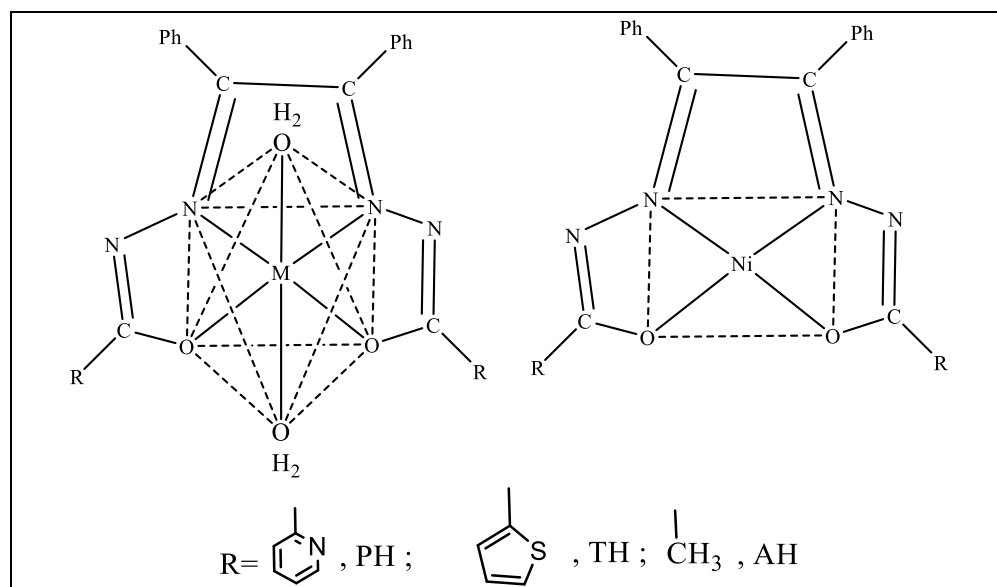


Fig 2

**The proposed structure for the complexes $[\text{M}(\text{L}-2\text{H})(\text{H}_2\text{O})_2]$, $[\text{Ni}(\text{BNAH}-2\text{H})]$
M= Co(II),Cu(II),Zn(II)
L= BNAH, BNTH, BNPH**

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 $\text{UO}_2(\text{VI})$, $\text{Th}(\text{IV})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Zn}(\text{II})$. *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: charactrization 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 ". 6th 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 characerization 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*-[(1*E*)-(2 hydroxyphenyl)methylene]acetohydrazide metal complexes, *Synth.React.Inorg.,M-Org.*,**43**,1130-1138.
- Elena, M L. T. and M. A. Mendiola., Structural diversity of benzil bis(benzoylhydrazone): Mononuclear, binuclear,and trinuclear complexes, *J. Royal Soc. Chem.*, Dalton Trans,7639-7647(2009).
- Furniss,B.S.; Rogers,V.; Smith, P.W.G.; Tatchll, A.R.(1989) " Vogel,s Textbook of practical organic chemistry " , 5th Edn Longman Scientific and Technical , England , p.1269 .
- Galic, N.; Dijaanosic, A.; Kontrec, D.; Miljanic, S. (2012). Structural investigation of aroyl hydrazone in dimethyl sulphoxide , water mixture. *Spectrochim. Acta.*, **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, manganes 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; and 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) hydrazine 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*, **81** 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