ℙ periodica polytechnica

Chemical Engineering
56/2 (2012) 83–90
doi: 10.3311/pp.ch.2012-2.06
web: http://www.pp.bme.hu/ch

RESEARCH ARTICLE

Synthesis and characterization of bis-acylhydrazone derivatives as tetradentate ligands and their dinuclear metal(II) complexes

M. Al-Ne'aimi Mohammed

Received 2012-03-20, revised 2012-06-20

Abstract

Two novel bis-acylhydrazone where as 1,4-diacetylbenzene bis(4-hydroxy benzoyl hydrazone) H_2L^1 and 1,4-diacetylbenzene bis(4-nitrobenzoyl hydrazone) H_2L^2 ligands bearing two hydrazone side groups and their metal(II) complexes have been synthesized and characterized by ^{1}H-NMR^{13} C-NMR, elemental analysis, FT-IR infrared spectra, magnetic susceptibility measurements and UV-vis electronic absorption spectra. The L_1H_2, L_2H_2) ligands were synthesized by reacting 4-hydroxybenzohydrazide and 4-nitrobenzohydrazide with 1,4-diacetylbenzene, respectively. The ligands H_2L^1, L_2H_2) react with metal(II) chlorides anhydrous to form polymeric dinuclear metal(II) complexes with general formula $[(M_2(L_x)_2\}_n]$ with a metal to ligand ratio of 1:1 when [x = 1, 2; M = Ni(II), Co(II), Cu(II), Zn(II) and Cd(II)]. In the complexes, the ligands act as dianionic tetradentate and coordination takes place in the enol tautomeric form with the enolic oxygen and azomethine nitrogen atoms while the phenolic hydroxyl and nitro groups of dihyrazone moiety do not participate in coordination.

Keywords

bis-acylhydrazone · Schiff base · dinuclear metal (II) complexes · azomethine · keto-enol tautomeric

Acknowledgement

The authors would like to express their thanks and appreciation to Albaath University for its help and encouragement to carry out this research. We are very grateful to EMISA Company for Drugs manufacture for measuring samples on FTIR spectrophotometer.

M. Al-Ne'aimi Mohammed
Department of Environment Science, Mosul University, Mosul 41002, Iraq
e-mail: tohe68@yahoo.com

1 Introduction

Hydrazones are the condensation products of hydrazine derivatives with carbonyl compounds, they contain an acyclic group >C=N-N< . It is long since hydrazones and their derivatives, due to their high complexing ability, have attracted the attention of scientists. Depending on various factors (the nature of the hydrazone and the metal atom, reaction conditions, the ratio of reactants etc.) hydrazones form either mono- or polynuclear coordination compounds with metal atoms [1].

Aroyl hydrazones and their metal derivatives often possess biological activity and can inhibit enzymatic reactions in the cell [2]-[4]. Edward et al. have shown that replacement of the aromatic group by other moieties in some antibiotics improves their antibiotic activity [5, 6]. Apart from biological applications owing to the presence of the toxicologically important N–C=O moiety, hydrazones act as potential donors for different metal ions. These ligands contain an amide bond and are capable of undergoing keto-enol tautomerism: they can coordinate to central metal ions through nitrogen and/or oxygen [7]. Their coordination behaviour also depends upon the pH of the medium, the nature of the substituents and the metal [8].

Intensive investigations of the coordination chemistry of dinuclear metal complexes with chelating ligands continue to be stimulated by interest for metallobiomolecules [9], the search for appropriate systems for binding and activating simple molecules, catalysis and magnetic interactions [10, 11]. In spite of the greatest effort and success in the study of dinuclear copper(II) complexes, such complexes have still attracted much attention due to their interesting properties and the relative simplicity of their synthesis.

Many studies of polyfunctional Schiff bases and monohydrazones as well as their complexes have been carried out [12, 13]. Relatively few reports are available on the coordination behaviour of bis-acylhydrazone. These ligands might have interesting ligational features since they contain additional donor sites, i.e. C=O, N–H, azomethine nitrogen atom, etc. Herein, we report the synthesis and spectroscopic studies of dinuclear metal(II) polymeric complexes containing 1,4-diacetylbenzene bis(4-hydroxy benzoylhydrazone) (H_2L^1) and

1,4-diacetylbenzene bis(4-nitrobenzoylhydrazone) (H_2L^2) are described.

2 Experimental

2.1 Materials

All the chemicals used were purchased from Fluka Chemical Co. (Switzerland), Aldrich-Sigma Chemical Co. (Milwaukee, WI, USA), and used without further purification.

2.2 Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 400MHz spectrometer in DMSO-d_6 with TMS as the internal standard. FT-IR spectra were recorded using Bruker-ALPHA 4100. CHN analyzer were measured on Euro-Vetor-AC-3000 (Italy). Magnetic susceptibility measurements were performed (Brucker B.M6) at room temperature by Faraday method. UV-visible spectra were measured on Jasco V-350 Spectrophotometer (Japan) in the regions (50000-9090cm^{-1}). AAS used to determine metal ion concentration in the aqueous phase was Phoenix-986 (UK).

2.3 Synthesis of hydrazide compound

Hydrazide compounds were prepared by refluxing (10 mmol, 1.66 g) of ethyl-4-hydroxybenzoate or ethyl-4-nitrobenzoate (10 mmol, 1.95 g) in 50ml methanol with hydrazine hydrate $NH_2NH_2.H_2O$ (25 mmol,1.5 ml) (80%, d=1.03) for 4 hours[14]. The compounds precipitated on standing over night, filtered and washed with distilled water. The pure hydrazides were obtained by recrystallization from hot ethanol, Scheme 1.

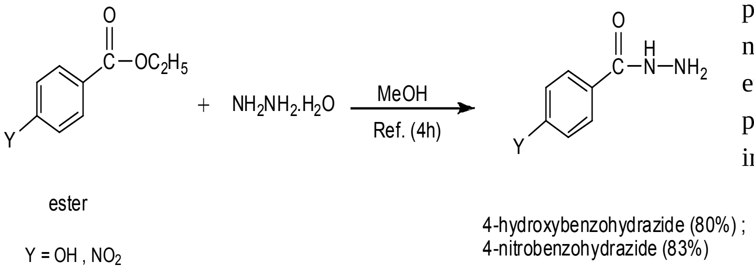

Fig. 1. Scheme 1

2.4 Synthesis of H_2L^1 and H_2L^2 ligands

The ligands synthesized are described [16] as follows:

4-hydroxybenzohydrazide (10 mmol, 1.52 g) and 4-nitrobenzohydrazide (10 mmol, 1.81 g) dissolved in hot ethanol 30 ml was added to solution 1,4-diacetylbenzene (5 mmol, 0.81 g) respectively, with 3-5 drops of glacial acetic acid in ethanol 20 ml. The reaction mixture was stirred and gently heated under reflux on a water bath for 5h., while the mixture reaction was refluxing the precipitation was formed gradually. After cooling at room temperature the precipitated solid was filtered off by Buchner Fennel, washed with water and hot ethanol, followed by dry diethyl ether (2×5 ml), then dried in a vacuum oven, Scheme 2.

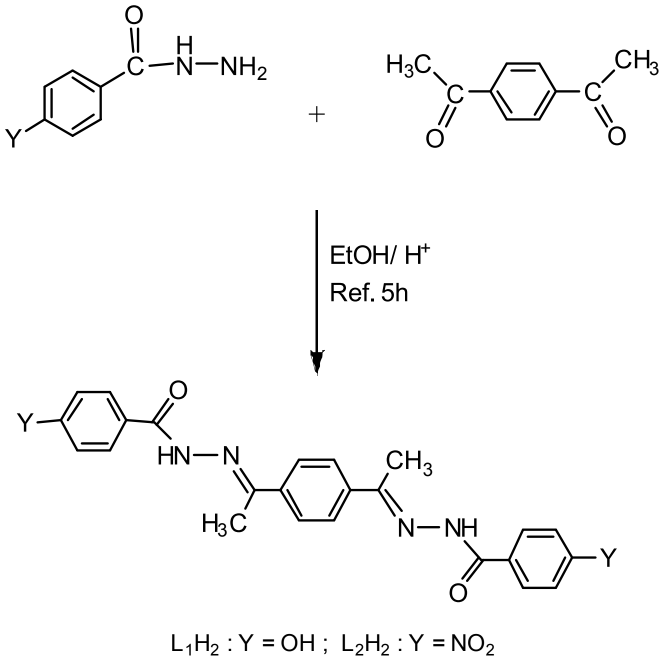

Fig. 2. Schema 2

2.5 General synthesis of metal complexes

A hot solution of potassium hydroxide KOH (20 mmol, 1.12 g) in ethanol 15 ml was added to a suspension of the ligands (H_2L^1, H_2L^2) (10 mmol) in ethanol 50 ml respectively. To the resulting yellow solution, a hot solution of metal(II) chloride anhydrous (10 mmol) when [M = Ni(II),Co(II), Cu(II), Zn(II) and Cd(II)]in ethanol 25 ml was added. The mixture was then refluxed, with constant stirring, for 4 hours to complete the precipitation. The resultant cooling at room temperature, then the precipitated complex compounds were filtered by Buchner Fennel, washed with hot water and ethanol, followed by dry diethyl ether (2×3 ml), then dried in a vacuum oven (Scheme 3). Some properties of the synthesized of ligands and complexes are given in Table1.

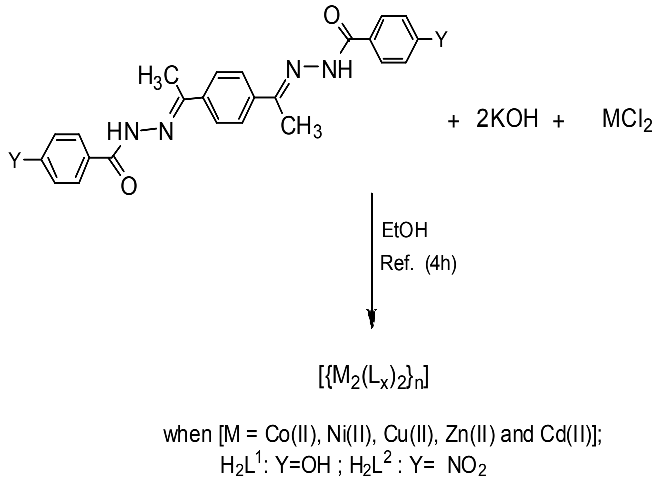

Fig. 3. Schema 3

Tab. 1. Color, melting points, yields, and elemental analytical results of the ligands and their metal complexes

Comp.	Formulas (MW)	Color	M.p^a (^{o}C)	μ_{eff} (B.M)	Yield (%)	Calculated / (Found) %			
						C	H	N	M
H_2L^1	$C_{24}H_{22}N_4O_4$ (430.46 g.mol^{-1})	white	289	—-	86	66.97 (66.71)	5.15 (5.73)	13.02 (13.11)	—
H_2L^2	$C_{24}H_{20}N_6O_6$ (488.45 g.mol^{-1})	Pale yellow	257	—-	72	59.01 (58.12)	4.13 (4.01)	17.21 (16.73)	—
$[\{Co_2(L^1)_2\}_n]$	$C_{48}H_{40}N_8O_8Co_2$ (974.74 g.mol^{-1})	Green	310 ^{a}	6.18	94	59.14 (58.63)	4.14 (3.92)	11.50 (11.61)	12.09 (11.95)
$[\{Ni_2(L^1)_2\}_n]$	$C_{48}H_{40}N_8O_8$ Ni_2 (974.27 g.mol^{-1})	Green yellowish	321 ^{a}	3.68	90	59.17 (60.03)	4.14 (3.92)	11.50 (11.14)	12.04 (12.11)
$[\{Cu_2(L^1)_2\}_n]$	$C_{48}H_{40}N_8O_8Cu_2$ (983.98 g.mol^{-1})	Dark Brown	293	2.53	97	58.59 (58.19)	4.10 (3.83)	11.39 (11.52)	12.91 (12.83)
$[\{Zn_2(L^1)_2\}_n]$	$C_{48}H_{40}N_8O_8Zn_2$ (987.7 g.mol^{-1})	Pale Yellow	329	^{b}	92	58.37 (58.08)	4.08 (3.79)	11.34 (10.84)	13.24 (13.11)
$[\{Cd_2(L^1)_2\}_n]$	$C_{48}H_{40}N_8O_8Cd_2$ (1081.7 g.mol^{-1})	Pale Yellow	344 ^{a}	^{b}	78	53.30 (52.56)	3.73 (3.81)	10.36 (9.98)	20.78 (21.02)
$[\{Co_2(L^2)_2\}_n]$	$C_{48}H_{36}N_{12}O_{12}Co_2$ (1090.74 g.mol^{-1})	Brown reddish	258	6.01	67	52.86 (51.87)	3.33 (3.05)	15.41 (15.08)	10.80 (10.62)
$[\{Ni_2(L^2)_2\}_n]$	$C_{48}H_{36}N_{12}O_{12}$ Ni_2 (1090.26 g.mol^{-1})	Brown yellowish	248 ^{a}	3.4	83	52.88 (51.99)	3.33 (3.17)	15.42 (15.11)	10.76 (10.58)
$[\{Cu_2(L^2)_2\}_n]$	$C_{48}H_{36}N_{12}O_{12}Cu_2$ (1099.96 g.mol^{-1})	Green	257	2.33	64	52.41 (51.84)	3.30 (3.02)	15.28 (14.99)	11.55 (11.31)
$[\{Zn_2(L^2)_2\}_n]$	$C_{48}H_{36}N_{12}O_{12}Zn_2$ (1103.7 g.mol^{-1})	Yellow	271	^{b}	79	52.23 (52.54)	3.29 (3.03)	15.23 (14.95)	11.85 (11.79)
$[\{Cd_2(L^2)_2\}_n]$	$C_{48}H_{36}N_{12}O_{12}Cd_2$ (1197.7 g.mol^{-1})	Orange	188	^{b}	71	48.14 (47.99)	3.03 (2.93)	14.03 (14.12)	18.77 (18.26)

^{a} decomposition ; ^{b} diamagnetic

3 Results and discussion

3.1 Stereo electronic nature of the ligands

The bis-acylhydrazone ligands can undergo deprotonation from enolised amide oxygen. When these synthesized ligands reacted with metal (II) ions, the ligands get deprotonated from the two hydrazone amide moiety and the metal (II) complex is formed. Suggestion, the bis-acylhydrazone ligands are tetradented di-negative [16], (Fig. 4).

3.2 Syntheses

The Schiff base ligands (H_2L^1) and (H_2L^2) were prepared according to the method described above. The ligands confirmed by the spectroscopic data (^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Visible spectra and CHN analysis). All the complexes were obtained by refluxing the reactants with constant stirring in ethanol. Use of two equivalent of base KOH for each one equivalent of ligand and metal ion. The elemental analyses suggest that the complexes possess 1:1 stoichiometry.

3.3 ^{1}C-NMR and ^{13}C-NMR spectra of the Schiff base ligands

Bis-acylhydrazone such as synthesized in this study may exist in the keto or in the enol tautomeric form in the solid state (Fig. 4). The tautomeric keto forms of ligands were also indicated by ^{1}H-NMR spectroscopy since the enolic OH signals of enol forms of ligands were not observed but amide NH signal of keto forms appeared around 10.14–11.19 ppm [17, 18]. Furthermore, the observation of strong ν(C=O) absorption bands around 1649–1664 cm^{-1} in the infrared spectra of the ligands

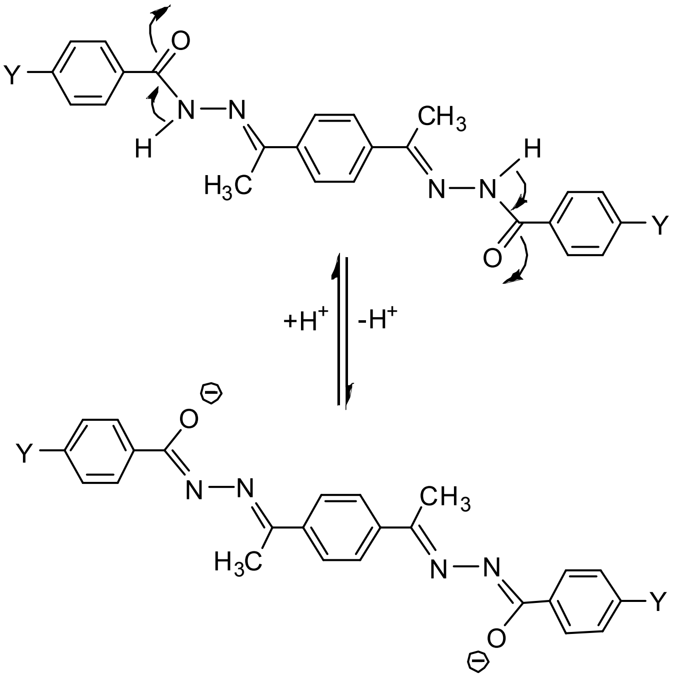

Fig. 4. Tautomeric forms of the ligands. When H_2L^1: Y=OH; H_2L^2 Y=NO_2

suggest that the ligands are in the keto form in the solid state [19, 20].

In the ^{1}H-NMR spectra of (H_2L^1) the phenolic (OH) and amide (NH) resonances appear as singlets at δ 10.58 (s, 2H) and δ10.14 (s, 2H) ppm, respectively. Furthermore, the phenolic moiety appears as 2 different doublets peaks at δ 7.81 (d, 4H)-7.99 (d, 4H) ppm. While in the ^{1}H-NMR spectra of (H_2L^2), the proton of amide group (NH) appears as singlets at

δ 11.19 (s, 2H) ppm [19, 20]. The other obtained values for ^{1}H-NMR chemical shifts of these compounds (*the ring protons and methyl resonances*) are given Table 2. These data are in agreement with that previously reported for similar compounds [?21-25].

In the ^{13}C-NMR spectrum of ligands different signals is appeared at δ 146.9 and 146.46 ppm for H_2L^1 and H_2L^2 due to (-$\underline{C}$=N-NH). The signals of the carbon ring (Ar-$\underline{C}$) of (H_2L^1) ligand appears at δ 115.33, 124.9, 126.94, 128.75, 139.28, 161.01 ppm, while that of (H_2L^2) ligand observes at δ 123.9, 128.76, 130, 137.9, 139.99, 149.73 ppm, Table 2. Furthermore, spectra of (-$\underline{C}$=O) appears at δ 169.21 and 163.46 ppm for (H_2L^1 and H_2L^2) ligands, as expected [24]. However, the signal of primary carbon of methyl groups appear at 27.28 ppm for (H_2L^1 and H_2L^2), respectively. Table 2. These data are in agreement with that previously reported for similar compounds [19, 20, 26, 27].

3.4 IR spectra of the H_2L^1, H_2L^2 ligands and their complexes

In the IR spectra of ligands, the bands appearing at 1649 and 1664 cm^{-1} for (H_2L^1 and H_2L^2), respectively, are attributed to the characteristic amide I ν(C=O) band. The absorption band of the $\nu(C{=}N_{imine})$ group is observed at 1607 and 1596 cm^{-1} for (H_2L^1 and H_2L^2), respectively. Also the amide ν(NH) stretching band of these compounds is observed in the IR spectra at 3139 and 3184 cm^{-1} for (H_2L^1 and H_2L^2), respectively. Table 3.

In the case of (H_2L^1) ligand a broad peak is observed in the 3322 cm^{-1} region which is assigned to phenolic (OH) absorption, while in the case of IR spectra of (H_2L^2) ligand, the peaks observed at 1521 and 1353 cm^{-1} are attributed to symmetric and asymmetric stretching vibrations of nitro group [17, 20], [28]-[31]. The characteristic IR peaks of hydrazone compounds synthesized in this work are given in Table 3.

The characteristic IR frequency values of the complexes are given in Table 3. The bands due to amide I, ν(C=O), $\nu(C{=}N_{imine})$ and amide ν(NH) are absent in the IR spectra of the complexes, but two new bands appear at 1581, 1592 cm^{-1} and ~1160 cm^{-1} probably due to (C=N-N=C) and (C-O) stretching, respectively, suggesting that the NH proton is likely lost via deprotonation induced by the metal and the resulting enolic oxygen and the azomethine nitrogen take place in coordination [19-21]. The shift of ν(N-N) stretch of the complexes to higher energy by ~15–31 cm^{-1} comparing to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination [28, 31, 32]. The IR spectra of complexes derived from H_2L^1 ligand shows a broad band between 3354-3213 cm^{-1}, which can be attributed to the free OH stretching mode indicating non-participation of phenolic (OH) group in coordination. The symmetric and asymmetric stretching vibrations of nitro group $\nu(NO_2)$ of H_2L^2 ligand are observed almost at the same frequencies as that of the free ligand indicating their non-involvement on coordination.

3.5 Magnetic studies of metal(II) complexes

The magnetic susceptibility measurements of the complexes (Table 1) shows cobalt(II), nickel(II) and copper(II) complexes are paramagnetic, while zinc(II) and cadmium(II) complexes are diamagnetic. However, the magnetic moment values of the cobalt(II) complexes are in the region of 6.01-6.18 B.M while those of the nickel(II) and copper(II) complexes are in the region of 3.40-3.68B.M and 2.33–2.53 B.M at 298 K, respectively. These results can be observed that these magnetic moment values of these complexes are higher than the theoretical value of 3.87 B.M for d^7 cobalt ion, 2.82 B.M for d^8 nickel ion and 1.73 B.M for d^9 copper ion. Furthermore, these magnetic moment values are lower than that expected for dinuclear cobalt(II), nickel(II) and copper(II) complexes. All these data (Table 1) are in agreement with previously reported for similar (four coordination, Tetrahedral) complexes [23, 33]-[35]. These subnormal magnetic moment values of the dinuclear complexes may be explained by weak antiferromagnetic intramolecular interaction since this situation can occur when two equivalent metal ions are coupled via on exchange interaction in a polynuclear complex [36]-[38].

3.6 Electronic absorption spectra

The spectrum of the ligands (Table 4) exhibit bands with shoulders in the range of 36764-31645 cm^{-1} region, probably due to $\pi \rightarrow \pi^*$ transition of the benzenoid moiety of these compounds and intraligand $\pi \rightarrow \pi^*$ transitions, and also at 29498 and 27777 cm^{-1} due to $n \rightarrow \pi^*$ transitions of the imine (C=N) and carbonyl (C=O) groups [22, 39, 40]. In the complexes, the bands due to $n \rightarrow \pi^*$ transitions are shifted to higher or lower values and also the charge transfer bands (LMCT) were observed in the range of 27397–25906 cm^{-1}.

The electronic spectrum of the Co(II) complexes (Fig. 2) show one band at 13966 and 13495 cm^{-1}, may be assigned to $^4A_2(F)\rightarrow{}^4T_1(P)(\nu_3)$ transition [34, 41, 42], further support the presence of tetrahedral geometry around the metal ion. In the electronic spectrum of Ni(II) complexes (Fig. 2), the band at 11507 and 11415 cm^{-1} is attributed to the $^3T_1(F)\rightarrow{}^3T_1(P)(\nu_3)$ transition, This band are characteristic for tetrahedral symmetry. As expected, in the tetrahedral compounds (four coordinate) the $^4A_2(F)\rightarrow{}^4T_2(F)(\nu_1)$, $^4A_2(F)\rightarrow{}^4T_1(F)(\nu_2)$ and $^3T_1(F)\rightarrow{}^3T_2(F)(\nu_1)$, $^3T_1(F)\rightarrow{}^3A_2(F)(\nu_2)$ transitions for Co(II) and Ni(II) complexes, respectively, are probably located above 1000 nm, which is beyond the detection range of our instrument.

In addition to the ligand bands, the Cu(II) complexes (Fig. 6)

Tab. 2. ^{1}H-NMR and ^{13}C-NMR spectra of the ligands in DMSO-d_6 in δ (ppm).

Comp.	Chemical Shift ppm , δ		Chemical Shift ppm , δ	
	Groups	^{1}H-NMR	Groups	^{13}C-NMR
L_1H_2	2(C$\underline{H}_3$C=N)	2.39 (s, 6H)	2($\underline{C}$H$_3$C=N) (8, 8')	27.28
	Ar-$\underline{H}$ (2, 3, 5, 6)	6.88 (s, 4H)	Ar-$\underline{C}$ (14-15 ,14'-15')	115.33
	Ar-$\underline{H}$ (14-15, 14'-15')	7.81-7.89 (d, 4H)	Ar-$\underline{C}$ (12, 12')	124.9
	Ar-$\underline{H}$ (13, 16, 13', 16')	7.96-7.99 (d, 4H)	Ar-$\underline{C}$ (2,3,5,6)	126.94
	2(-N$\underline{H}$)	10.14 (s, 2H)	Ar-$\underline{C}$ (13, 16, 13', 16')	128.75
	2(-O$\underline{H}$)	10.58 (s, 2H)	Ar-$\underline{C}$ (1, 4)	139.28
			2(CH$_3\underline{C}$=N) (7, 7')	146.90
			Ar-$\underline{C}$ (17, 17')	161.01
			2(-$\underline{C}$=O) (11,11')	169.21
L_2H_2	2(C$\underline{H}_3$C=N)	2.37 (s, 6H)	2($\underline{C}$H$_3$C=N) (8, 8')	27.28
	Ar-$\underline{H}$ (2, 3, 5, 6)	7.75 (s, 4H)	Ar-$\underline{C}$ (14-15 ,14'-15')	123.90
	Ar-$\underline{H}$ (13, 16, 13', 16')	8.01-8.13 (d, 4H)	Ar-$\underline{C}$ (2,3,5,6)	128.76
	Ar-$\underline{H}$ (14, 15, 14', 15')	8.13-8.35 (d, 4H)	Ar-$\underline{C}$ (13, 16, 13', 16')	130.00
	2(-N$\underline{H}$)	11.19 (s, 2H)	Ar-$\underline{C}$ (12, 12')	137.90
			Ar-$\underline{C}$ (1, 4)	139.99
			2(CH$_3\underline{C}$=N) (7, 7')	146.46
			Ar-$\underline{C}$ (17, 17')	149.73
			2(-$\underline{C}$=O) (11,11')	163.46

Tab. 3. IR spectral data of the ligands and their metal complexes as KBr pellets cm^{-1}.

Comp.	(NH)	(C=O)	(C=N)	C=N-N=C	(C-N)	(C-O)	(N-N)	*Other*
L_1H_2	3139	1649	1607	—-	—-	—-	1016	v(OH): 3322
$[\{Co_2(L_1)_2\}_n]$	—-	—-	—-	1583	1272	1167	1036	v(OH): 3354br
$[\{Ni_2(L_1)_2\}_n]$	—-	—-	—-	1581	1270	1170	1035	v(OH): 3213br
$[\{Cu_2(L_1)_2\}_n]$	—-	—-	—-	1592	1237	1163	1032	v(OH): 3284br
$[\{Zn_2(L_1)_2\}_n]$	—-	—-	—-	1590	1272	1166	1033	v(OH): 3222
$[\{Cd_2(L_1)_2\}_n]$	—-	—-		1589	1270	1168	1031	v(OH): 3244
L_2H_2	3184	1664	1596	—-	—-	—-	958	v(NO$_2$): sy:1353; asy:1521
$[\{Co_2(L_2)_2\}_n]$	—-	—-	—-	1586	1267	1167	978	v(NO$_2$): sy:1337; asy:1524
$[\{Ni_2(L_2)_2\}_n]$	—-	—-	—-	1585	1265	1167	977	v(NO$_2$): sy:1337 ; asy:1533
$[\{Cu_2(L_2)_2\}_n]$	—-	—-	—-	1592	1263	1165	984	v(NO$_2$): sy:1338 ; asy:1530
$[\{Zn_2(L_2)_2\}_n]$	—-	—-	—-	1589	1265	1167	989	v(NO$_2$): sy:1338 ; asy:1523
$[\{Cd_2(L_2)_2\}_n]$	—-	—-	—-	1587	1265	1168	980	v(NO$_2$): sy:1337 ; asy:1521

Tab. 4. Electronic spectral data λ_{max} nm, v(cm^{-1}) of the ligands and their metal complexes.

Compounds	Electronic spectra data λ_{max}(cm^{-1})
L_1H_2	339 (29498), 312 (32051), 272 (36764)
L_2H_2	360 (27777), 316 (31645), 284 (35211)
$[\{Co_2(L_1)_2\}_n]$	716 (13966), 386 (25906), 355 (28169), 328 (30487), 277 (36101)
$[\{Co_2(L_2)_2\}_n]$	741 (13495), 365 (27397), 332 (30120), 311 (32154), 275 (36363)
$[\{Ni_2(L_1)_2\}_n]$	876 (11415), 379 (26385), 339 (29498), 318 (31446), 273 (36630)
$[\{Ni_2(L_2)_2\}_n]$	869 (11507), 380 (26315), 336 (29761), 310 (32258), 273 (36630)
$[\{Cu_2(L_1)_2\}_n]$	842 (11876), 382 (26178), 330 (30303), 316 (31645), 273 (36630)
$[\{Cu_2(L_2)_2\}_n]$	855 (11695), 384 (26041), 331 (30211), 317 (31545), 294 (34013)
$[\{Zn_2(L_1)_2\}_n]$	371 (26954), 340 (29411), 278 (35971)
$[\{Zn_2(L_2)_2\}_n]$	385 (25974), 350 (28571), 293 (24129)
$[\{Cd_2(L_1)_2\}_n]$	374 (26737), 336 (29761), 271 (36900)
$[\{Cd_2(L_2)_2\}_n]$	389 (25706), 361 (27700), 291 (34364)

show a distinct d-d band at 11876 and 11695 cm^{-1}, may be assigned to $^2T_2 \rightarrow {}^2E$ transition [43], suggested an tetrahedral environment around the Cu^{2+} ion. The spectrum of the Zn(II) and Cd(II) complexes exhibits a strong intense band at 26954-25706 cm^{-1}, which are assigned to a ligand→metal (LMTC) charge transfer excitation. Both of Zn(II) and Cd(II) complexes

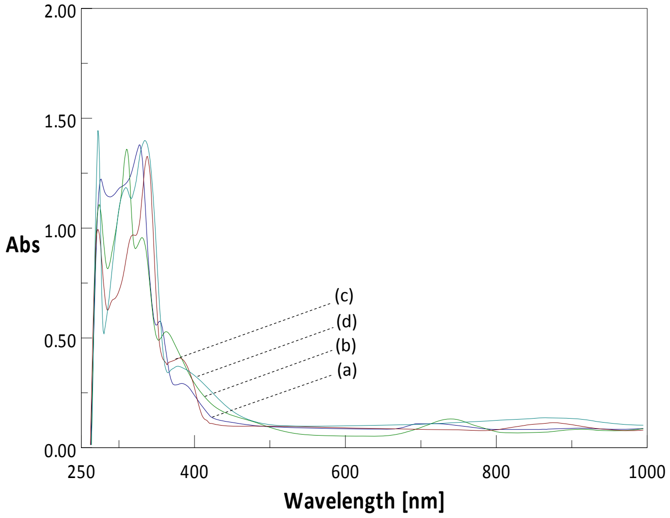

Fig. 5. Electronic absorption spectra of Co^{+2} and Ni^{+2} complexes in DMF (10^{-2})M: (a)$[Co_2(L^1)_{2n}]$; (b) $[Co_2(L^2)_{2n}]$; (c)$[Ni_2(L^1)_{2n}]$; (d) $[Ni_2(L^2)_{2n}]$

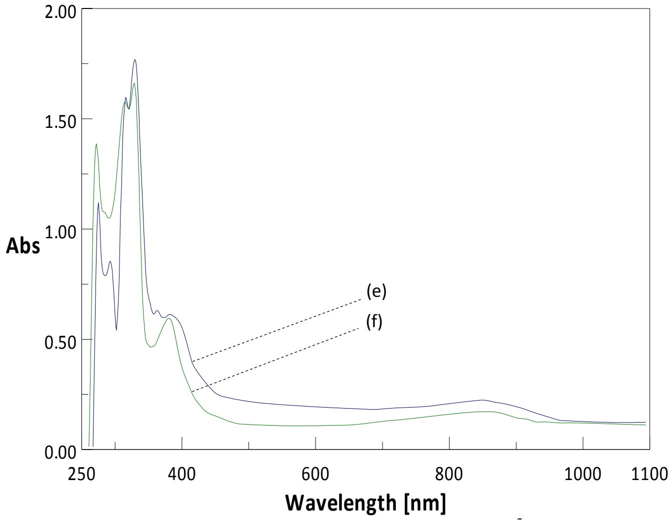

Fig. 6. Electronic absorption spectra of Cu^{+2} complexes in DMF (10-2)M: (e) $[Cu_2(L^1)_{2n}]$; (f)$[Cu_2(L^2)_{2n}]$

show no bands in the visible region as expected for d^{10} systems [44, 45]. The electronic absorption spectra for the bis-acylhydrazone ligands and their metal (II) complexes recorded in DMF solvent $(10^{-2}M)$ are given in Table 4.

4 Conclusion

In this work the synthesis and characterization of the polymeric dinuclear metal(II) complexes derived from the reaction of 1,4-diacetylbenzene bis(4-hydroxy benzoylhydrazone) (H_2L^1) or 1,4-diacetylbenzene bis(4-nitro benzoyl hydrazone) (H_2L^2) and two equivalent molar of base (KOH) with anhydrous metal chlorides yields the complex $[\{M_2(L^x)_2\}_n]$;x =1,2 where the ligands act as dinegative, tetradentate and the coordination takes place in the enol tautomeric form, suggesting, to be four-coordination with a N_2O_2 donor environment. Each ligand is coordinated through the azomethine nitrogen and the enolic oxygen atoms while the phenolic (OH) and nitro (NO_2) groups of bis-acylhydrazone moiety do not participate in coordination.

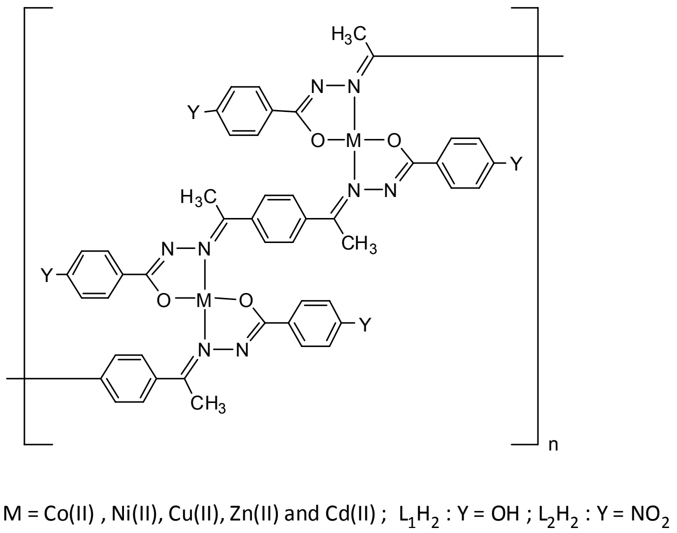

Fig. 7. Suggested structure for the polymetric dinuclear complexes $[\{M_2(L^x)_2\}_n]$

The ^{1}H-NMR, ^{13}C-NMR, elemental analysis(CHN), FT-IR infrared spectra, Magnetic susceptibility measurements and UV–vis. electronic absorption spectra of the (L_1H_2) and (L_2H_2) ligands and their metal(II) complexes were recorded and investigated. Furthermore, the elemental analysis results and spectral data are proposed the polymeric dinuclear metal(II) complexes $[\{M_2(L^x)_2\}_n]$ when [x = 1,2; M = Ni(II), Co(II), Cu(II), Zn(II) and Cd(II)] an tetrahedral geometry around the metal(II) ions.(Fig. 4).

References

1 **Labib L, Mohamed L A, Iskander M F, Griesar K, Haase W**, *Copper(II) and nickel(II) metallopolymers derived from polyacylhydrazones*, Transition Met. Chem. **25** (2000), 700-705, DOI 10.1023/A:1007004103386.

2 **Bulaov A O, Lukyanov B S, Kogan V A, Lukov V V**, *Photo- and thermochromic spirans. New metal chelates based on azomethines and hydrazones containing a spiropyran fragment*, Russ J. Coord. Chem. **28** (2002), 46-49, DOI 10.1023/A:1013715821212.

3 **Al-Assar F, Zelenin K N, Lesiovskaya E E, Bezhan I P, Chakchir B A**, *Synthesis and Pharmacological Activity of 1-Hydroxy-, 1-Amino-, and 1-Hydrazino-Substituted 2,3-Dihydro-1H-pyrazolo[1,2-a]pyridazine-5,8-diones and 2,3-Dihydro-1H-pyrazolo[1,2-b] phtha-lazine-5,10-diones*, Pharm Chem J. **36** (2002), 598-603, DOI 10.1023/A:1022665331722.

4 **Sharma V K, Srivastava S**, *Synthesis, Spectroscopic and Antifungal Studies of Trivalent Chromium, Manganese, Iron and Cobalt Complexes with Hydrazones derived from Benzil α–monoxime and various Aromatic Hydrazides*, Synt. React. Inorg. Met. Org. Nano. Met. Chem. **35** (2005), 311-318, DOI 10.1081/SIM-200055249.

5 **Murukan B, Mohanan K**, *Synthesis, Characterization, Electrochemical Properties and Antibacterial Activity of Some Transiton Metal Complexes with [(2-hydroxy-1-naphthaldehyde)-3-isatin]-bishydrazone*, Transition Met. Chem. **31** (2006), 441-446, DOI 10.1007/s11243-006-0011-7.

6 **Edward E I, Epton R, Marr G**, *Organometallic derivatives of penicillins and cephalosporins a new class of semi-synthetic antibiotics*, J. Organomet. Chem. **85** (1975), C23-C25, DOI 10.1016/S0022-328X(00)80708-1.

7 **Pandey J K, Pandey O P, Sengupta S K**, *Synthesis and spectroscopic investigations of oxovanadium (IV) derivatives with 1,1'-diacetylferrocenyl-bis(hydrazones)*, Indian J. Chem. **43A** (2004), 1906-1910.

8 **Vatsa B G, Pandey O P, Sengupta S K**, *Synthesis, Spectroscopic and*

Toxicity Studies of Titanocene Chelates of Isatin-3-Thiosemicarbazones, Bioinorg. Chem. Appl. **3** (2005), 151-160, DOI 10.1155/BCA.2005.151.

9 **Karlin K D, Zubieta J**, *Copper Coordination Chemistry, Biochemical and Inorganic Perspectives*, Adenine Press, New York, 1983.

10 **Eisenberg R, Hendrikson D E**, *The Binding and Activation of Carbon Monoxide, Carbon Dioxide, and Nitric Oxide and Their Homogeneously Catalyzed Reactions*, Adv. Catal. **28** (1979), 79-172.

11 **Gatteschi D, Kahn O, Miller J S, Palacio F (eds.)**, *Structural Magnetic Correlation in Magnetic Phase Transition of Molecular Magnetic Materials" in "Magnetic Molecular Materials*, 1991. NATO ASI Series, E198, Kluwer, Dordrecht.

12 **Soliman A A, Linert W**, *Structural Features of ONS-Donor Salicylidene Schiff Base Complexes*, Monatsh. Chem. **138** (2007), 175-189, DOI 10.1007/s00706-007-0585-6.

13 **Radecka-Paryzek W, Patroniak V, Lisowski J**, *Metal complexes of polyaza and polyoxaaza Schiff base macrocycles*, Coord. Chem. Rev. **249** (2005), 2156-2175, DOI 10.1016/j.ccr.2005.02.021.

14 **Baligar R S, Revankor V K**, *Coordination diversity of new mononucleating hydrazone in 3d metal complexes: Synthesis, characterization and structural Studies*, J. Serb. Chem. Soc. **71** (2006), no. 12, 1301–1310, DOI 10.2298/JSC0612301B.

15 **Khairallah B A**, *Synthesis and Study of Bacterial Activity of Some New of Hydrazide-Hydrazone Compounds and Converted to Corresponding 1,3,4-Oxadiazoles*, Department of Chemistry, College of Education, Tikrit University, Iraq, 2008. M.Sc. Thesis.

16 **Uppadine L H, Lehn J-M**, *"Three-Level Synthetic Strategy Towards Mixed-Valence and Heterometallic[2×2] Gridlike Arrays"*, Angew Chem. Int. Ed. **43** (2004), 240-243, DOI 10.1002/anie.200352937.

17 **Lee P E, Yong C T, Fon D, Vittal J J, Ranford J D**, *Synthesis, characterization and physicochemical properties of copper(II) complexes containing salicylaldehyde semicarbazone*, Polyhedron **22** (2003), 2781-2786, DOI 10.1016/S0277-5387(03)00402-9.

18 **Ainscough E W, Brodie A M, Denny W A, Finlay G J, Gothe S A, Ranford J D**, *Cytotoxicity of salicylaldehyde benzoylhydrazone analogs and their transition metal complexes: quantitative structure-activity relationships*, J. Inorg. Biochem. **77** (1999), no. (3-4), 125-133, DOI doi:10.1016/S0162-0134(99)00131-2.

19 **Dinda R, Sengupta P, Ghosh S, Mak T C W**, *Valence Delocalization in a Mixed-Oxidation Divanadium (IV, V) Complex Electrogenerated from Its Structurally Characterized Divanadium (V) Analogue with a Tridentate (ONO) Ligand*, Inorg. Chem. **41** (2002), 1684-1688, DOI 10.1021/ic010865t.

20 **Dinda R, Sengupta P, Ghosh S, Sheldrick W S**, *Synthesis, Structure, and Reactivity of a New Mononuclear Molybdenum(VI) Complex Resembling the Active Center of Molybdenum Oxotransferases*, Eur. Inorg. Chem., posted on 2003, 363-369, DOI 10.1002/ejic.200390049, (to appear in print).

21 **Gup R, Kirkan B**, *Synthesis and spectroscopic studies of copper(II) and nickel(II) complexes containing hydrazonic ligands and heterocyclic coligand*, Spectrochim. Acta **A 62** (2005), 1188-1195, DOI 10.1016/j.saa.2005.04.015.

22 **Naskar S, Biswas S, Mishra D, Adhikary B, Falvello L R, Soler T, Schwalbe C H, Chattopadhyay S K**, *Studies on the relative stabilities of Mn(II) and Mn(III) in Complexes with N_4O_2 Donor Environments: Crystal Structures of [Mn(pybzhz)2] and [Mn(Ophsal)(imzH)$_2$] ClO_4 (pybzhz = N-(benzoyl)-N' - (picolinylidene) hydrazine, Ophsal = N, N' -o-phenylenebis(salicylideneimine), imzH=imidazole)*, Inorg. Chem. Acta **357** (2004), 4257-4264, DOI 10.1016/j.ica.2004.06.018.

23 **Koh L L, Kon O L, Loh K W, Long Y C, Ranford J D, Tan A L C, Tjan Y Y**, *Complexes of salicylaldehyde acylhydrazones: Cytotoxicity, QSAR and crystal structure of the sterically hindered t-butyl dimer*, J. Inorg. Biochem. **72** (1998), 155, DOI 10.1016/S0162-0134(98)10075-2.

24 **Khambekar A M, Sawant A D**, *Extractive And Spectrophotometric Determination Of Co(II) Using P-nitroisonitrosoacetophenone*, Indian J. Chem. **36** (1997), 459.

25 **Norman J J, Heggie R M, Larose J B**, *The Synthesis Of Some Substituted-2-Oximinoacetophenones*, Can. J. Chem. **40** (1962), 1547-1553.

26 **Sinha S, Srivastava A K, Sengupta S K, Pandey O P**, *Microwave assisted synthesis, spectroscopic and antibacterial studies of bis(cyclopentadienyl)hafnium(IV) derivatives with benzil bis(aroyl hydrazones)*, Transition Met. Chem. **33** (2008), 563–567, DOI 10.1007/s11243-008-9080-0.

27 **Ram A L, Debajani B, Arjun K, Kumar De A**, *Synthesis and spectral characterization of zinc(II), copper(II), nickel(II) and manganese(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde) malonoyl dihydrazone*, Trans. Met. Chem. **32** (2007), 481–493, DOI 10.1007/s11243-007-0189-3.

28 **Sreekanth A, Kala U L, Nayar C R, Kurup M R P**, *Cobalt (III) complexes of 2-hydroxyacetophenone N(4)-phenyl semicarbazone containing heterocyclic coligands: syntheses, structure and spectral studies*, Polyhedron **23** (2004), 41-47, DOI 10.1016/j.poly.2003.09.029.

29 **Rao T R, Shrestha S, Prasad A, Narang K K**, *Synthesis and Structural Studies of Some Lanthanide Complexes of Salicylaldehyde Anthranoyl Hydrazone*, Synt. React. Inorg. Met. Org. Chem. **32** (2002), 419-436, DOI 10.1081/SIM-120003216.

30 **Bagrov F V, Vasil'eva T V**, *2-Diphenylphosphinoyloxybenzaldehyde-4-Nitrophenyl-,4-Phenyl-1-phthalazinyl-, and Aroylhydrazones and Thiosemicarbazone*, Russ. J. Org. Chem. **38** (2002), 1309–1313, DOI 10.1023/A:1021603829630.

31 **Issa R M, Abdel-Latif S A, Abdel-Salam H A**, *Synthesis And Characterization Of New Cu(II) Complexes Derived From Benzilic And Mandelic Hydrazones*, Synth. React. Inorg. Met.-Org. Chem. **31** (2001), 95-105, DOI 10.1081/SIM-100001935.

32 **Sreeja P B, Kurup M R P, Kishore A, Jasmin C**, *Spectral characterization, X-ray strcture and biological investigations of copper (II) ternary complexes of 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazone*, Polyhedron **23** (2004), 575-581, DOI 10.1016/j.poly.2003.11.005.

33 **Gruber S J, Harris G M, Sinn E**, *Metal complexes as ligands-IV [1,2,3]***: Bi- and Tri- nuclear complexes derived from metal complexes of tetradentate salicylaldimines*, J. Inorg. Nucl. Chem. **30** (1968), 1805-1830, DOI 10.1016/0022-1902(68)80357-4.

34 **Kabanos T A, Tsangaris J M**, *Deprotonated And Non-Deprotonated Complexes Of N-(2-Aminophenyl) Pyridine-2-Carboxamide And N-(3-Aminophenyl) Pyridine-2-Carboxamide With Co(II), Ni(II), Cu(II) and Pd(II)*, J. Coord. Chem. **13** (1984), 89-103, DOI 10.1080/00958978408079760.

35 **Nicholls D**, *The Chemistry of Iron, Cobalt and Nickel*, Pergamon Press, Oxford, 1973. 1*st* ed.

36 **Gup R, Giziroglu E**, *Metal complexes and solvent extraction properties of isonitrosoacetophenone 2-aminobenzoylhydrazone*, Spectrochimica Acta. **Part A 65** (2006), 719–726, DOI 10.1016/j.saa.2006.01.004.

37 **Moubaraki B, Murray K S, Ranford J D, Vittal J J, Wang X, Xu Y**, *Preparation, characterisation and structures of copper(II) complexes of an asymmetric anti-cancer drug analogue*, J. Chem. Soc., Dalton Trans. **20** (1999), 3573-3578, DOI 10.1039/a905020e.

38 **Ranford J D, Vittal J J, Wang Y M**, *Dicopper(II) Complexes of the Antitumor Analogues Acylbis(salicylaldehyde hydrazones) and Crystal Structures of Monomeric [Cu_2(1,3-propanedioyl bis(salicylaldehyde hydrazone))($H_2O)_2$]·(ClO_4)2·3H_2O and Polymeric [Cu_2(1,6-hexanedioyl bis(salicylaldehyde hydrazone))(C_2H_5OH)2m]·(ClO_4)2m·m(C_2H_5OH)*, Inorg. Chem. **37** (1998), 1226-1232, DOI 10.1021/ic970805g.

39 **Maiti D, Paul H, Chanda N, Chakrabort S, Mondal B, Puranik V G, Lahiri G K**, *Synthesis, structure, spectral and electron-transfer properties of octahedral-[CoIII(L)2]+/[ZnII(L)2] and square planar-*

[CuII(L)OC(?O)CH3] complexes incorporating anionic form of tridentate bis(8-quinolinyl)amine [N'$C_9H_6N_2C_9H_6N_{3,}$,L^-] Ligand, Polyhedron **23** (2004), 831–840, DOI 10.1016/j.poly.2003.11.053.

40 **Rageh N M**, *Electronic spectra, solvatochromic behavior and acid–base properties of some azo cinnoline compounds*, Spectrochim. Acta **A 60** (2004), 103-109, DOI 10.1016/S1386-1425(03)00210-5.

41 **Huggi N V, Halli M B, Hiremath A C**, *Study of Transition and Non-Transition Metal Complexes with 3-amino-2-benzoylbenzofuran*, J. Indian. Chem. Soc. **59** (1982), 1017.

42 **Hughes M V, Rutt K J**, *Complexes of thiazoles. Part III. Complexes of thiazole with cobalt(II), nickel(II), copper(II), zinc(II), and palladium(II) salts*, J. Chem. Soc. **18** (1970), 3015-3019, DOI 10.1039/j19700003015.

43 **Perlepes S P, Kabanos T, Lazaridou V, Tsangaris J M**, *The coordination chemistry of N-(2-aminophenyl)- and N-(3-aminophenyl)quinoline-2′-carboxamide; two potentially tridentate ligands containing secondary amide and N-donor groups*, Inorg. Chim. Acta **117** (1986), 27-37.

44 **Al-Mahrouqi L M M**, *Synthesis and characterization and biological activities of benzenesulfanohydrazones and their metal complexes*, Faculty of Science University of Malaya Kualalumpur, 2009. M. Sc. Thesis.

45 **Aggarwal R C, Sing N, Singh S**, *Preparation and characterization of heterobimetallic tetraxanthates and their complexes with Lewis bases*, Polyhedron **4** (1985), 343-348, DOI 10.1016/S0277-5387(00)84510-6.