Synthesis and Characterization of Bis-acylhydrazone Derivatives as Tetradentate Ligands and Their Dinuclear Metal(II) Complexes

Mohammed M. Al-Ne'aimi

College of Environmental Mosul University, Iraq

(NJC)

(Recevied on 26/2 /2012) **(Accepted for publication 1/7/2012)**

Abstract

Two new bis-acylhydrazone where as 1,4-diacetylbenzene bis(4-hydroxy benzoyl-hydrazone) (L_1H_2) and 1,4-diacetylbenzene bis(4-nitrobenzoylhydrazone) (L_2H_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 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 (L_1H_2, L_2H_2) react with anhydrous metal(II) chlorides 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= Co(II), Ni(II), Cu(II), Zn(II), 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.

الخلاصة

تم تحضير وتوصيف مرتبطتين جديدتين لـ4,1-داي استيل بنزين بس(4-هيدروكسي بنزويل هيدرازون) (L_1H_2) و 4,1-داي استيل بنزين بس(4-نترو بنزويل هيدرازون) (L_2H_2) تضم مجموعتي هيدرازون جانبية ومعقداتهما البوليمرية ثنائية النوى لبعض ايونات العناصر الفلزية [Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}] بوساطة تقنيات مطيافية الرنين النووي المغناطيسي (^{13}C-NMR, ^{1}H-NMR) ومطيافية الأشعة ما تحت الحمراء (FT-IR) ومطيافية الأشعة فوق البنفسجية-المرئية (U.V-visible) والحساسية المغناطيسية (Magnetic Susceptibility) إضافة إلى التحليل العنصري (CHN)، وبينت نتائجهذه الدراسة أنها كانت متفقة مع الصيغ التركيبية المتقرحة لهذه المعقدات البوليمرية. وقد حضرت المرتبطتين (L_1H_2) و (L_2H_2) من تفاعل 4-هيدروكسي بنزوهيدرازيد و4-نتروبنزوهيدرازيد (المحضرة مخبريا) مع 4.1-ثنائي استيل بنزن وعلى التوالي. وإن تكاثف المرتبطات المحضرة مع كلوريدات المعادن اللامائية بنسبة مولية (1:1) على التوالي، أدى إلى تشكل معقدات بوليمرية معدنية ثنائية النوى (dinuclear) تحمل الصيغة العامة $[\{M_2(L_x)_2\}_n]$ حيث أن [x = 1,2 ; M= Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}]، وتتفاعل المرتبطات المحضرة على شكل رباعية السن (ثنائية الشحنة السالبة)، إذ يحدث التساند مع أيونات المعادن عندما تكون المرتبطة بهيئة الشد الاينولي من خلال ذرات

نتروجين الآزوميثين من جهة وأوكسجين الاينول. كما تبين أن مجموعتي الهيدروكسيل الفينولية والنترو العائدة لثنائي الهيدرازون لا تشارك في التساند لتكوين المعقد البوليمري.

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(1). 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 ions(2).

Aroyl hydrazones and their metal derivatives often possess biological activity and can inhibit enzymatic reactions in the cell(3-5). Edward et al. have shown that replacement of the aromatic group by other moieties in some antibiotics improves their antibiotic activity(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 type of the metal(8).

Intensive investigations of the coordination chemistry of dinuclear metal complexes with chelating ligands continue to be stimulated by interest for metallo-biomolecules(9), the search for appropriate systems for binding and activating simple molecules, catalysis and magnetic inter-actions(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.

In our previous work, we reported the synthesis and spectroscopic studies of poly-functional Schiff bases and mono-hydrazones as well as their complexes(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 containing1,4-diacetyl-benzene bis(4-hydroxy benzoylhydrazone) (L_1H_2) and 1,4-diacetyl benzenebis(4-nitro-benzoylhydrazone) (L_2H_2) are described.

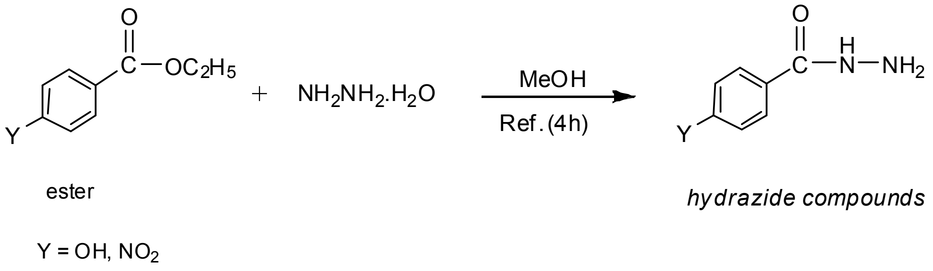
Experimental

Materials

All the chemicals used were purchased from Fluka Chemical Co. (Switzerland), Aldrich-Sigma Chemical Co. (USA), and used without further purification. ^{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 FTIR-4100. CHN analyzer were measured on Euro-vetor-AC-3000 (Italy). Magnetic sus-ceptibility measurements were performed at room temperature by Faraday method (Brucker B.M6). UV-visible spectra were measured Jasco V-350 Spectrophotometer (Japan) in the regions (50000-9090cm^{-1}). AAS used to determine metal ions concentration in the aqueous phase was Phoenix-986 (UK).

Synthesis of hydrazide Compound (14)

Hydrazide compounds were prepared by refluxing (10 mmol, 1.66gm) of Ethyl-4-hydroxybenzoate or Ethyl-4-nitrobenzoate (10 mmol, 1.95gm) in 50ml methanol with hydrazine hydrate $NH_2NH_2.H_2O$ (25mmol, 1.5ml) (80%, d=1.03) for (4) hours. 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.

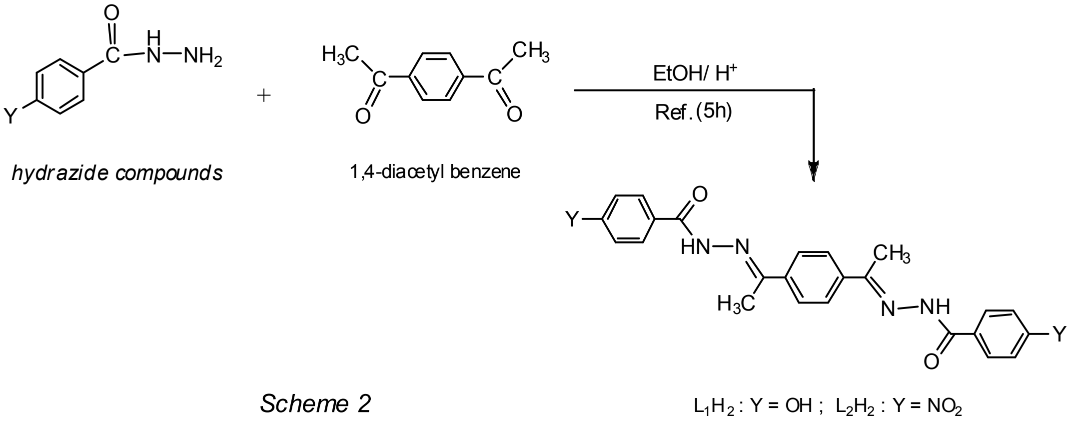


Scheme 1

Synthesis of L_1H_2 and L_2H_2 ligands

The ligands synthesized according to the method described in the in literature(15).

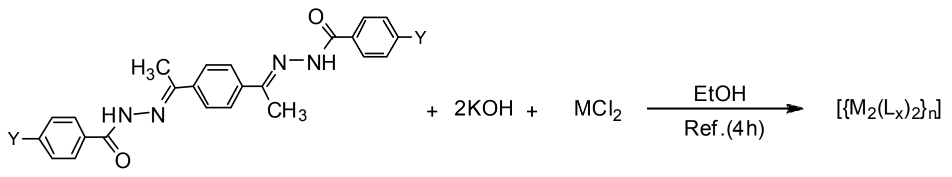
4-hydroxybenzohydrazide (10 mmol, 1.52 gm) and 4-nitrobenzohydrazide (10 mmol, 1.81 gm) dissolved in hot ethanol (30 ml) was added to solution 1,4-diacetylbenzene (5 mmol, 0.81 gm) respectively, with (3-5) drops of glacial acetic acid in ethanol (20 ml). The reaction mixture was stirred while refluxing for (5) hours. The resultant precipitated were filtered off and washed with water and hot ethanol, and dried in air at room temperature. Scheme 2.



Scheme 2

General Synthesis of metal Complexes

A hot solution of potassium hydroxide KOH (20mmol, 1.12 g) in ethanol 15 ml was added to a suspension of the ligands (L_1H_2, L_2H_2) (10 mmol, 0.43, 0.48g) in ethanol 50ml respectively. To the resulting yellow solution, a hot solution of anhydrous metal(II) chloride (10 mmol, 0.129, 0.130, 0.134, 0.136, 0.186g) each of Ni(II), Co(II), Cu(II), Zn(II) and Cd(II) salts in ethanol 25 ml was added. The mixture was refluxed, with constant stirring, for 4 hours. The isolated complex was filtered off and washed with water and ethanol, followed by dry diethyl ether, then dried in air at room temperature (Scheme 3). Some properties of the synthesized ligands and complexes are given in Table1.



L_1H_2 , Y=OH and L_2H_2 , Y= NO_2

[M = Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}];
L_x = L_1 or L_2

Scheme 3

Results and Discussion

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 Suggested tetradented di-negative bis-acylhydrazone ligands(16) (Fig. 1), and the metal (II) complexes are formed.

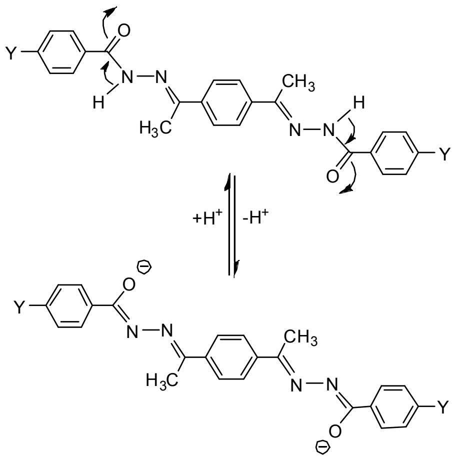


Figure 1. Tautomeric forms of the ligands. When L_1H_2 : Y = OH ; L_2H_2 : Y = NO_2

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.

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

Bis-acylhydrazone usually exist in the keto-enol tautomeric form in the solid state (Fig. 1). The presence of keto form of ligands were indicated by ^{1}H-NMR spectro-scopy 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 suggest that the ligands are in the keto form in the solid state(19,20).

In the ^{1}H-NMR spectra of (L_1H_2) ligand (Fig. 2) the phenolic (OH) and amide (NH) resonances appear as singlets at δ 10.58 (s, 2H) and δ10.14 (s, 2H) ppm, respectively. The ring proton resonance of the 1,4-diacetylbenzene moiety of this ligand is observed as a singlet at δ 6.88 ppm (s, 4H) while that of the phenolic moiety appears as 2 different doublets peaks at δ 7.81 (d, 4H)-7.99 (d, 4H) ppm, and then the protons of methyl groups (CH_3) is observed as a singlet at δ 2.39 ppm (s, 6H). In the ^{1}H-NMR spectra of (L_2H_2) ligand (Fig. 3), 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 proton and methyl resonances*) are given in Table 2. These data are in agreement with that previously reported for similar compounds(21-25).

In the ^{13}C-NMR spectrum of the ligands (Fig. 4, 5) different signals were appeared at δ 146.9 and 146.46 ppm for L_1H_2 and L_2H_2 due to (-$\underline{C}$=N-NH). The signals of the carbon ring (Ar-$\underline{C}$) of (L_1H_2) ligand appears at δ 115.33, 124.9, 126.94, 128.75, 139.28, 161.01 ppm, while that of (L_2H_2) ligand observe at δ 123.9, 128.76, 130, 137.9, 139.99, 149.73 ppm, Table 2. Furthermore, signals of (-$\underline{C}$=O) appears at δ 169.21 and 163.46 ppm for L_1H_2 and L_2H_2 respectively, as expected(25). However, the signal of primary carbon of methyl groups appear at 27.28 ppm for (L_1H_2 and L_2H_2), respectively, Table 2. These data are in agreement with that previously reported for similar compounds (19,20, 26,27).

IR spectra of the L_1H_2 , L_2H_2 ligands and their complexes

In the IR spectra of ligands (Fig. 6 and 7), the bands appeared at 1649 and 1664 cm^{-1} for (L_1H_2 and L_2H_2), respectively, are attributed to the characteristic amide I *ν*(C=O) band. The absorption band of the *ν*(C=N_{imine}) group is observed at 1607 and 1596 cm^{-1} for (L_1H_2 and L_2H_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 (L_1H_2 and L_2H_2), respectively, Table 3.

In the case of (L_1H_2) (Fig. 6) a broad peak is observed in the 3322 cm^{-1} region which is assigned to phenolic (OH) absorption, while in the case of (L_2H_2) (Fig. 7), the peaks observed at 1521 and 1353 cm^{-1} are attributed to symmetric and asymmetric stretching vibrations of nitro group. These values are in accord with that previously reported for hydrazone derivatives(17,20,28-31). The other characteristic IR peaks of hydrazone compounds synthesized in this work are given in Table 3.

The characteristic IR frequency values of the complexes (Fig. 8-11) are given in Table 3. The IR spectra of the complexes show significant differences from the free ligand. The bands due to amide I, *ν*(C=O), *ν*(C=N_{imine}) and amide *ν*(NH) are absent in the IR spectra of the complexes, but two new bands appeared at 1581, 1592 cm^{-1} and ~1163 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 the complexes spectra to higher frequency 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 L_1H_2 ligand (Fig. 8-9) shows a broad band between 3354-3222 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 L_2H_2 ligand (Fig. 10-11) are observed almost at the same frequencies as that of the free ligand indicating their non-involvement on coordination.

Magnetic studies of metal(II) complexes

The magnetic susceptibility measurements (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 2.33–2.53B.M at 298 K, respectively. These results can be concluded 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(33). 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 an exchange interaction in a polynuclear complex(36-38).

Electronic absorption spectra

The spectrum of the ligands (Table 4) exhibit bands with shoulders at 36764, 35211, 32051 and 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(23,40,41). In the complexes (Table 4), the bands due to $n\rightarrow\pi^*$ transitions are shifted to higher or lower values it may refer to interaction with metal cations and also the charge transfer bands (LMCT) were observed in the range of 27397–25906 cm^{-1}.

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.

The electronic spectrum of the Co(II) complexes (Fig. 12) 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. 12), 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. 13) show a distinct d-d band at 11876 and 11695 cm^{-1}, may be assigned to $^2T_2\rightarrow{}^2E$ transition(43), suggesting a 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 show no bands in the visible region as expected for d^{10} systems(44,45).

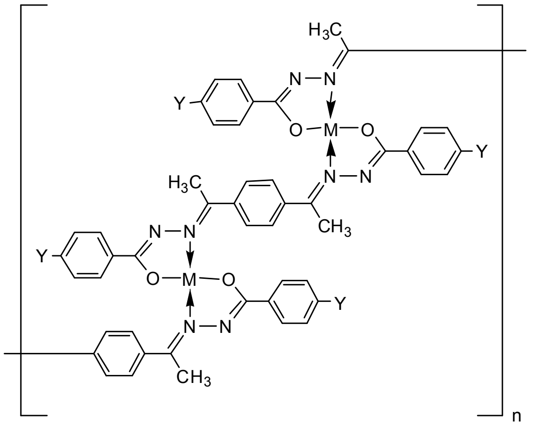
Conclusion

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) (L_1H_2) or 1,4-diacetylbenzene bis(4-nitro benzoyl hydrazone) (L_2H_2) and two equivalent molar of KOH with anhydrous metal chlorides yields the complex $[\{M_2(L_x)_2\}_n]$; x =1,2 where the ligands suggested to act as dinegative, tetradentate and the coordination takes place in the enol tautomeric form, seem 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.

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 proposed the polymeric dinuclear metal(II) complexes $[\{M_2(L_x)_2\}_n]$ (x= 1,2) an tetrahedral geometry around the metal(II) ions.(Fig. 14).

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 = Co(II) , Ni(II), Cu(II), Zn(II) ; L_1H_2 : Y = OH ; L_2H_2 : Y = NO_2

Figure 14: Suggested structure for the polymeric dinuclear complexes $[\{M_2(L_x)_2\}_n]$

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

Compounds	Formulas (MW)	Color	m.p^{a} (°C)	μ_{eff} (B.M)	Yield (%)	Calculated / (Found) %			
						C	H	N	M
L_1H_2	$C_{24}H_{22}N_4O_4$ (430.46 g.mol^{-1})	white	289	----	86	66.97 (66.71)	5.15 (5.73)	13.02 (13.11)	---
L_2H_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)	---
$[\{Co_2(L_1)_2\}_n]$	$C_{24}H_{20}N_4O_4Co_2$ (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)
$[\{Cu_2(L_1)_2\}_n]$	$C_{24}H_{20}N_4O_4Cu_2$ (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)
$[\{Zn_2(L_1)_2\}_n]$	$C_{24}H_{20}N_4O_4Zn_2$ (987.7 g.mol^{-1})	Pale Yellow	329	Dia	92	58.37 (58.08)	4.08 (3.79)	11.34 (10.84)	13.24 (13.11)
$[\{Cd_2(L_1)_2\}_n]$	$C_{24}H_{20}N_4O_4Cd_2$ (1081.7 g.mol^{-1})	Pale Yellow	344 ^{a}	Dia	78	53.30 (52.56)	3.73 (3.81)	10.36 (9.98)	20.78 (21.02)
$[\{Co_2(L_2)_2\}_n]$	$C_{24}H_{18}N_6O_6Co_2$ (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)
$[\{Cu_2(L_2)_2\}_n]$	$C_{24}H_{18}N_6O_6Cu_2$ (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)
$[\{Zn_2(L_2)_2\}_n]$	$C_{24}H_{18}N_6O_6Zn_2$ (1103.7 g.mol^{-1})	Yellow	271	Dia	79	52.23 (52.54)	3.29 (3.03)	15.23 (14.95)	11.85 (11.79)
$[\{Cd_2(L_2)_2\}_n]$	$C_{24}H_{18}N_6O_6Cd_2$ (1197.7 g.mol^{-1})	Pale Orange	188	Dia	71	48.14 (47.99)	3.03 (2.93)	14.03 (14.12)	18.77 (18.26)

a = decomposition

Table 2: ^{1}H-NMR and ^{13}C-NMR spectral 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') 2(-$\underline{C}$=O) (11,11')	161.01 169.21
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

Table 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	ν(OH): 3322
$[\{Co_2(L_1)_2\}_n]$	----	----	----	1583	1272	1167	1036	ν(OH): 3354br
$[\{Ni_2(L_1)_2\}_n]$	----	----	----	1581	1270	1170	1035	ν(OH): 3213br
$[\{Cu_2(L_1)_2\}_n]$	----	----	----	1592	1237	1163	1032	ν(OH): 3284br
$[\{Zn_2(L_1)_2\}_n]$	----	----	----	1590	1272	1166	1033	ν(OH): 3222
$[\{Cd_2(L_1)_2\}_n]$	----	----		1589	1270	1168	1031	ν(OH): 3244
L_2H_2	3184	1664	1596	----	----	----	958	$\nu(NO_2)$: sy:1353; asy:1521
$[\{Co_2(L_2)_2\}_n]$	----	----	----	1586	1267	1167	978	$\nu(NO_2)$: sy:1337; asy:1524
$[\{Ni_2(L_2)_2\}_n]$	----	----	----	1585	1265	1167	977	$\nu(NO_2)$: sy:1337 ; asy:1533
$[\{Cu_2(L_2)_2\}_n]$	----	----	----	1592	1263	1165	984	$\nu(NO_2)$: sy:1338 ; asy:1530
$[\{Zn_2(L_2)_2\}_n]$	----	----	----	1589	1265	1167	989	$\nu(NO_2)$: sy:1338 ; asy:1523
$[\{Cd_2(L_2)_2\}_n]$	----	----	----	1587	1265	1168	980	$\nu(NO_2)$: sy:1337 ; asy:1521

Table 4: Electronic spectral data λ_{max} nm, $\nu(cm^{-1})$ of the ligands and their metal complexes.

Compounds	Electronic spectral data $\lambda_{max}(cm^{-1})$
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)

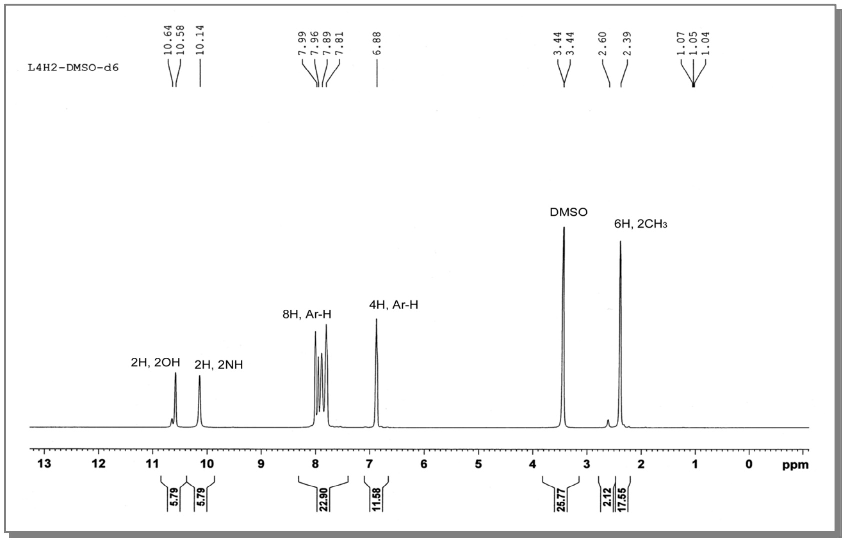


Figure 2: ^{1}H-NMR spectrum of L_1H_2 in DMSO-d6

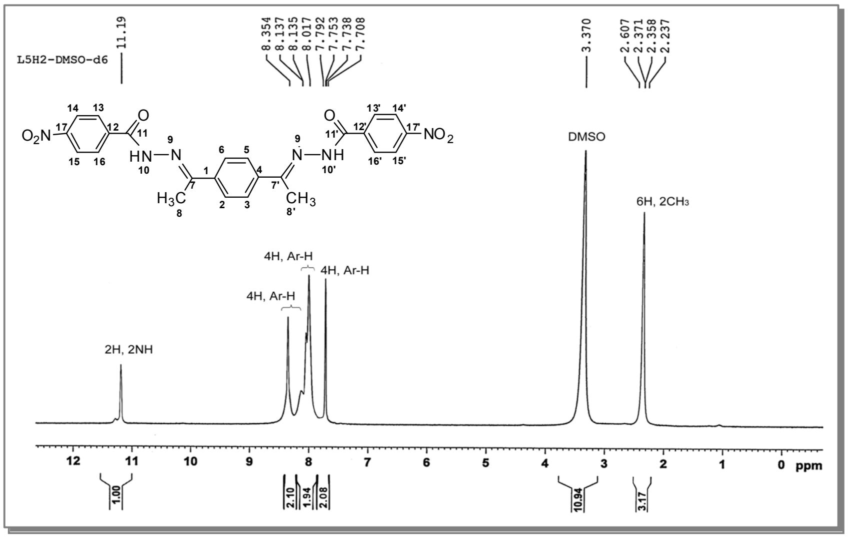


Figure 3: ^{1}H-NMR spectrum of L_2H_2 in DMSO-d6

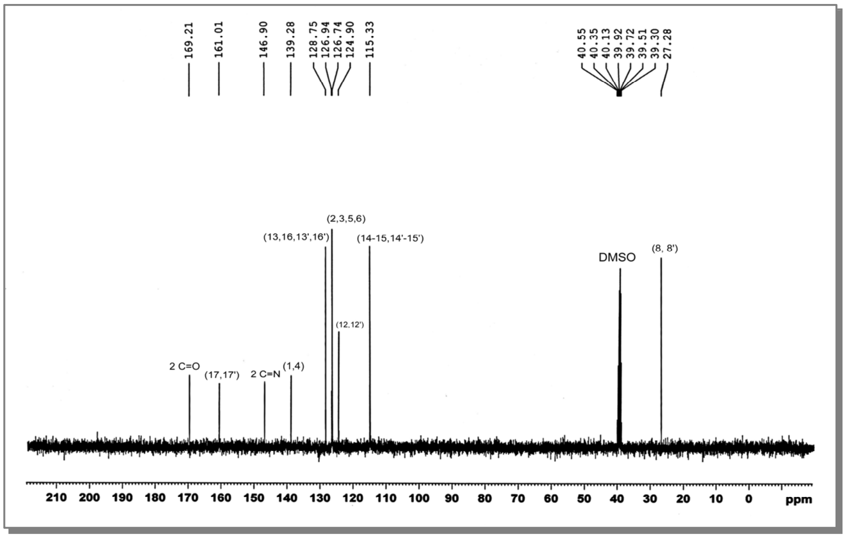


Figure 4: ^{13}C-NMR spectrum of L_1H_2 in DMSO-d6

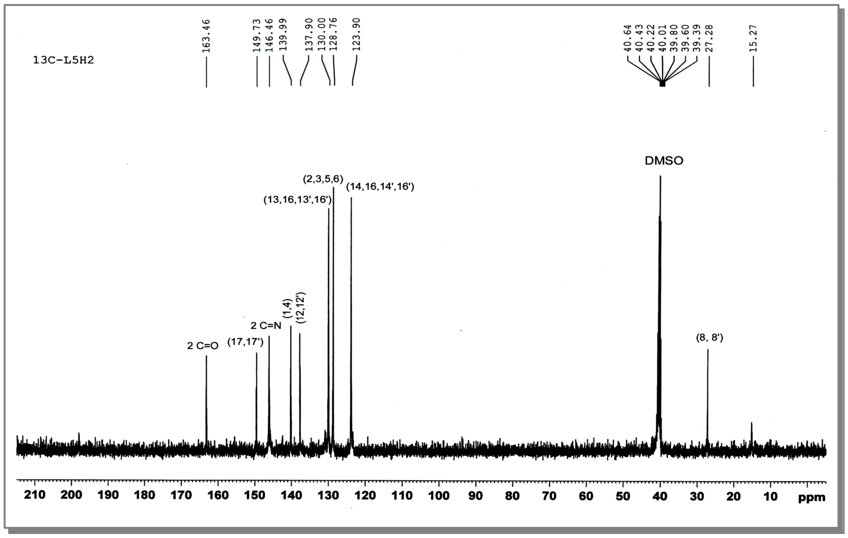


Figure 5: ^{13}C-NMR spectrum of L_2H_2 in DMSO-d6

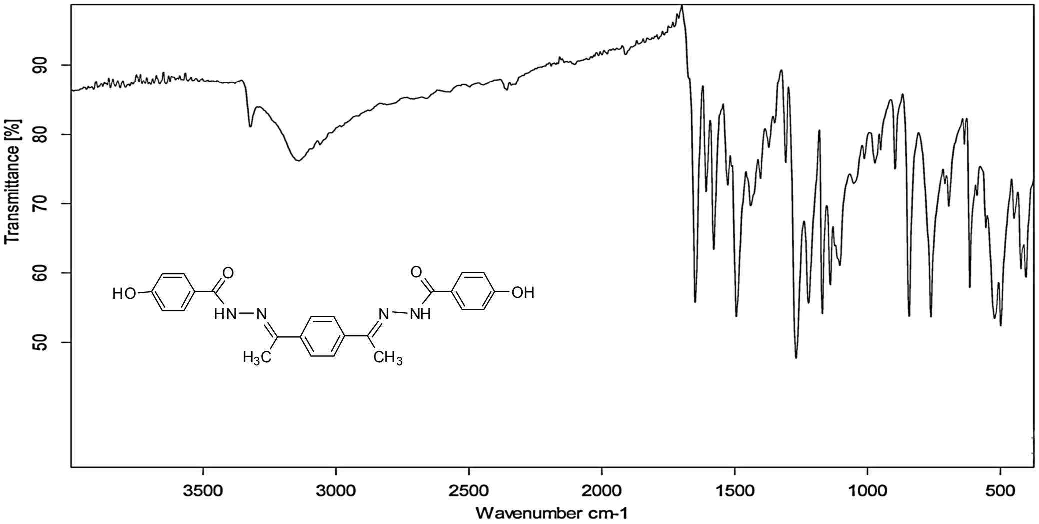


Fig. 6: IR spectrum of L_1H_2 ligand

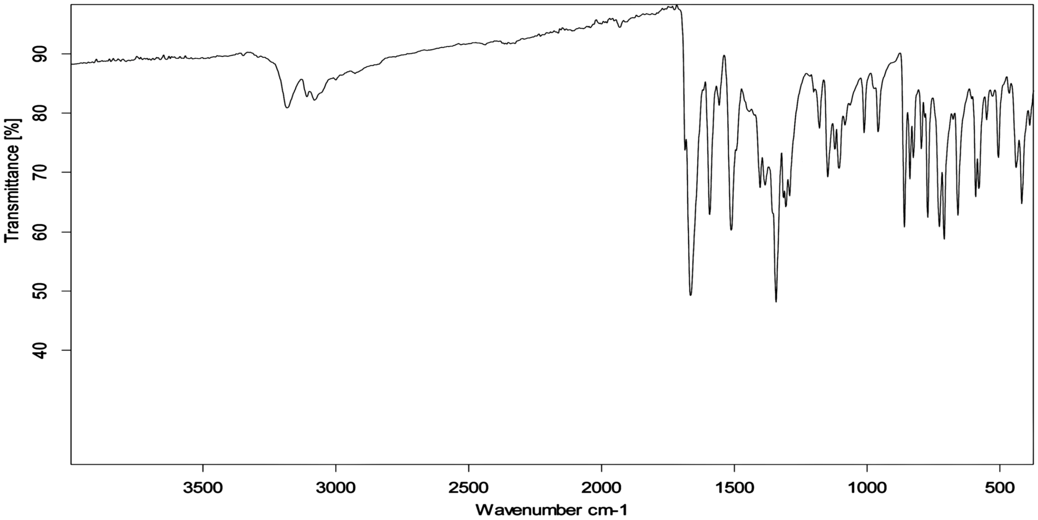


Fig. 7: IR spectrum of L_2H_2 ligand

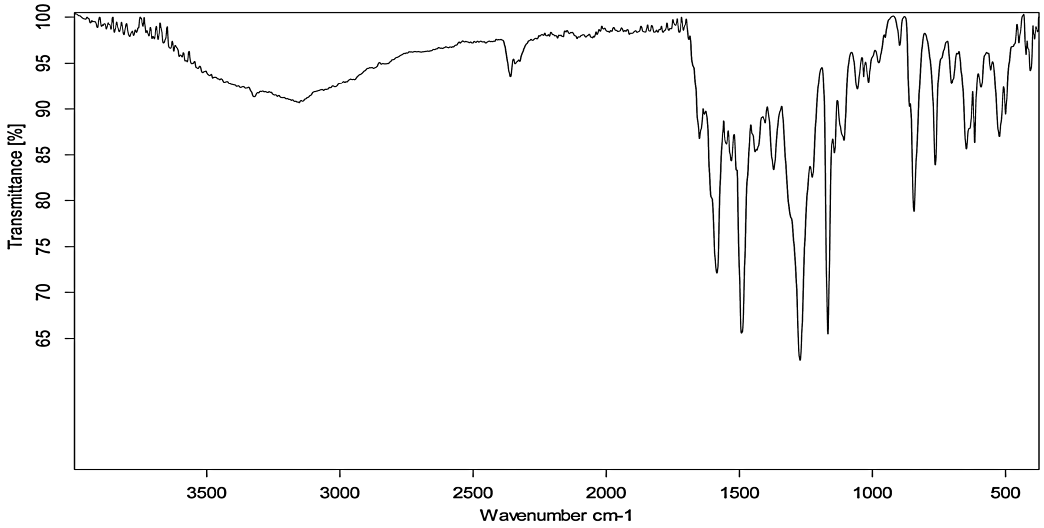


Fig. 8: IR spectrum of [{$Co_2(L_1)_2\}_n$] complex

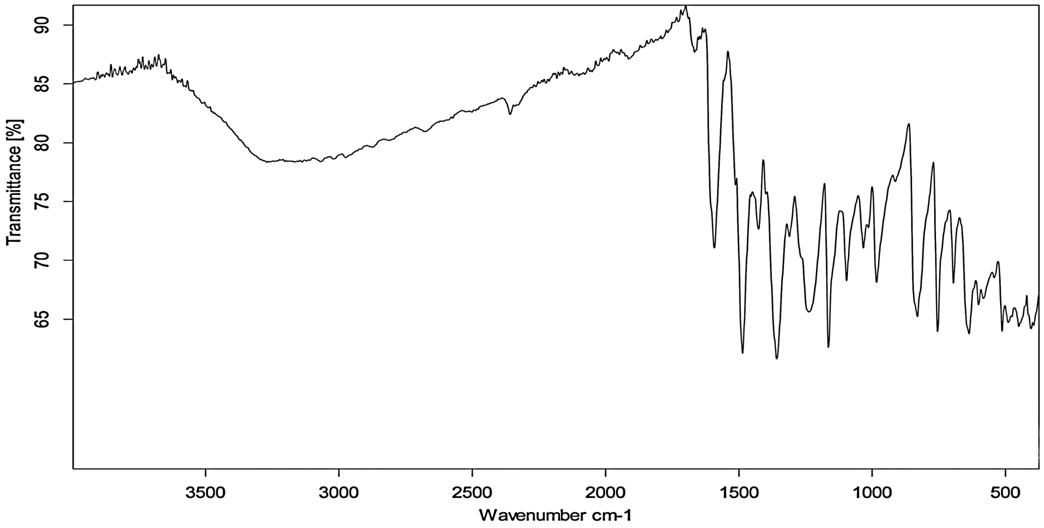


Fig. 9: IR spectrum of [{$Cu_2(L_1)_2\}_n$] complex

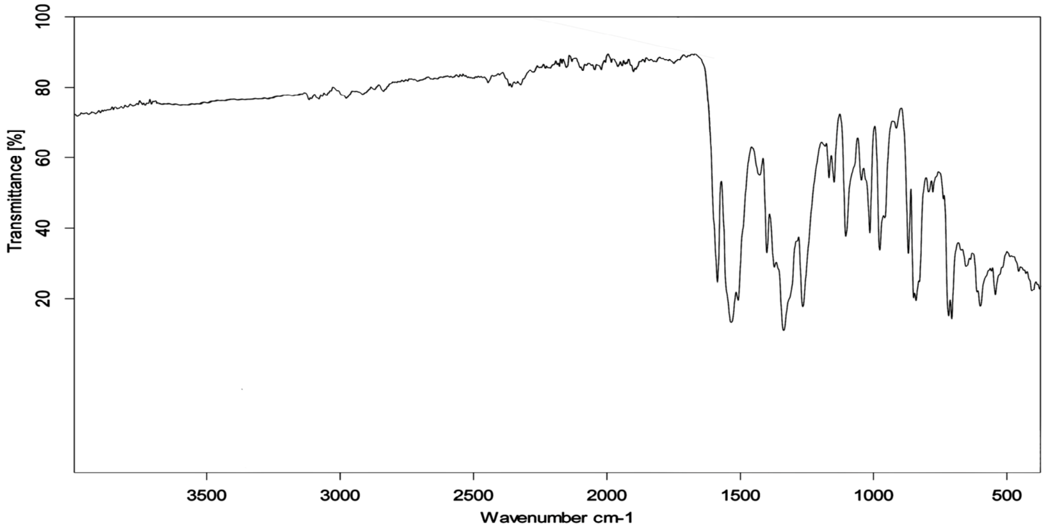


Fig. 10: IR spectrum of [{$Ni_2(L_2)_2\}_n$] complex

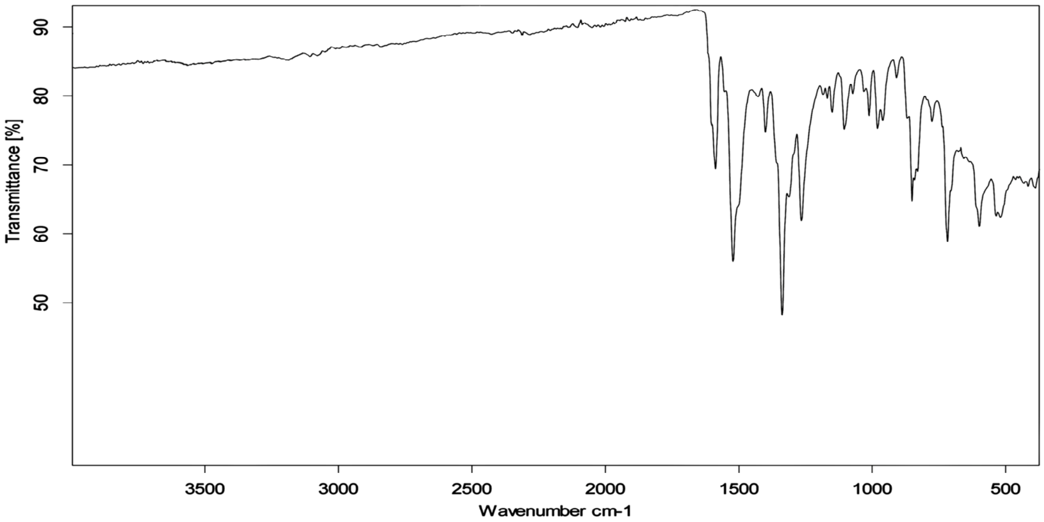


Fig. 11: IR spectrum of $[\{Cd_2(L_2)_2\}_n]$ complex

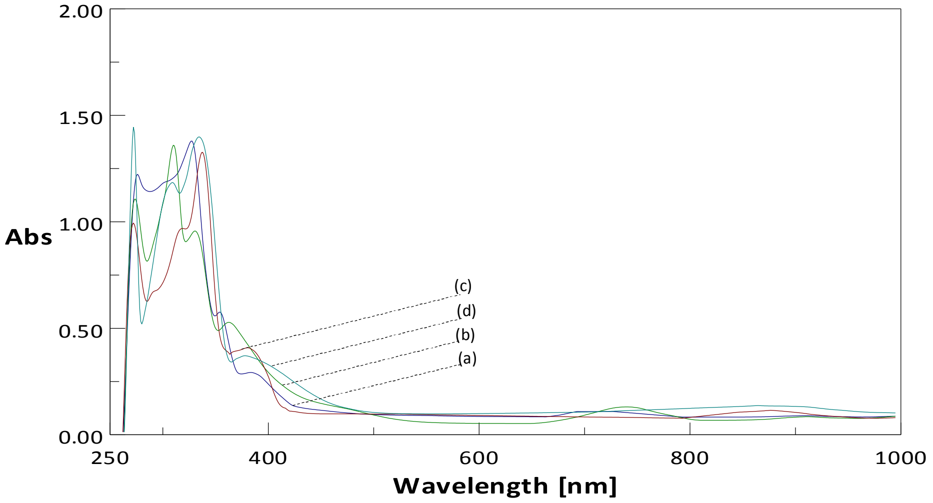


Figure 12: Electronic absorption spectra of Co^{+2} and Ni^{+2} complexes in DMF (10^{-2})M:

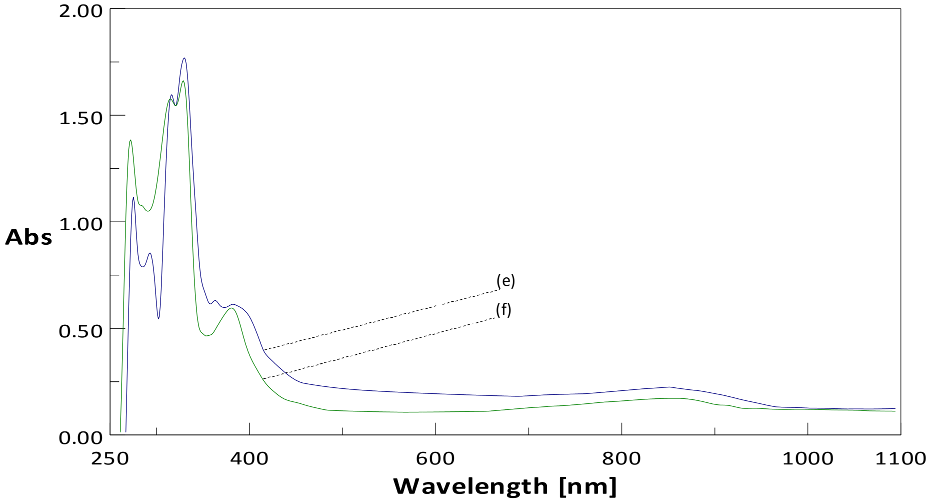


Figure 13: Electronic absorption spectra of Cu^{+2} complexes in DMF (10^{-2})M: (e) $[\{Cu_2(L_1)_2\}_n]$; (f)

References

1. P. A. Vigato, S. Tamburini, ***Coord. Chem. Rev.***, 2008, **252**, 1871.
2. L. Labib, L.A. Mohamed, M.F. Iskander, K. Griesar, W. Haase, ***Transition Met. Chem.***, 2000, **25**, 700-705.
3. A.O. Bulaov, B.S. Lukyanov, V.A. Kogan, V.V. Lukov, ***Russ J. Coord. Chem.***, 2002, **29**, 658.
4. F. Al-Assar, K. N. Zelenin, E. E. Lesiovskaya, I. P. Bezhan, B. A. Chakchir, ***Pharm Chem J.***, 2002, **36**, 11, 598.
5. V. K. Sharma, and S. Srivastava, ***Synt. React. Inorg. Met. Org. Nano. Met. Chem.***, 2005, **35**, 311, (*and references therein*).
6. E. I. Edward, R. Epton, G. Marr, ***J. Organomet. Chem.***, 1975, **85**, C23-C25.
7. J. K. Pandey, O. P. Pandey, S. K. Sengupta, ***Indian J. Chem.***, 2004, **43A**, 1906, (*and references therein*).
8. B. G. Vatsa, O. P. Pandey, S. K. Sengupta, ***Bioinorg. Chem. Appl.***, 2005, **3**, 151.
9. K. D. Karlin, and J. Zubieta, "***Copper Coordination Chemistry***", *Biochemical and Inorganic Perspectives*, Adenine Press, New York, **1983**.
10. R. Eisenberg and D. E. Hendrikson, ***Adv. Catal.***, 1979, **28**, 79.
11. D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio, (Eds.), ***NATO ASI Series***, E198, Kluwer, Dordrecht, **1991**.
12. A. A. Soliman, and W. Linert, ***Monatsh. Chem.***, 2007, **138**, 175.
13. W. Radecka-Paryzek, V. Patroniak, J. Lisowski, ***Coord. Chem. Rev.***, 2005, **249**, 2156.
14. R.S. Baligar, and V.K. Revankor, ***J. Serb. Chem. Soc.***, 2006, **71**, 12; pp.1301–1310.
15. B.A. Khairallah, ***M.Sc. Thesis***, Department of Chemistry, College of Education, Tikrit University, Iraq, **2008**.
16. L.H. Uppadine and J.-M. Lehn, ***Angew Chem. Int. Ed.***, 2004, **43**, 240.
17. P.E. Lee, C.T. Yong, D. Fon, J.J. Vittal, J.D. Ranford, ***Polyhedron***, 2003, **22**, 2781.
18. E.W. Ainscough, A.M. Brodie, W.A. Denny, G.J. Finlay, S.A. Gothe, J.D. Ranford, ***J. Inorg. Biochem.***, 1999, **77 (3-4)**, 125.
19. R. Dinda, P. Sengupta, S. Ghosh, T. C. W. Mak, ***Inorg. Chem.***, 2002, **41**, 1684.
20. R. Dinda, P. Sengupta, S. Ghash, W. S. Sheldrick, ***Eur. Inorg. Chem.***, 2003, 363.
21. R. Gup, and B. Kirkan, ***Spectrochim. Acta***, 2005, **A62 (4–5)**, 1188-1195.
22. S. Naskar, S. Biswas, D. Mishra, B. Adhikary, L.R. Falvello, T. Soler, C.H. Schwalbe, S.K. Chattopadhyay, ***Inorg. Chem. Acta***, 2004, **357**, 4264.
23. L.L. Koh, O.L. Kon, K.W. Loh, Y.C. Long, J.D. Ranford, A.L.C. Tan, Y.Y. Tjan, ***J. Inorg. Biochem.***, 1998, **72**, 155.
24. A.M. Khambekar, and A.D. Sawant, ***Indian J. Chem.***, 1997, **36**, 459.
25. J.J. Norman, R.M. Heggie, J.B. Larose, ***Can. J. Chem.***, 1962, **40**, 1547.
26. S. Sinha, A.K. Srivastava, S.K. Sengupta, O.P. Pandey, ***Transition Met. Chem.***, 2008, **33**:563–567.
27. A.L. Ram, B. Debajani, K. Arjun, De. A. Kumar, ***Trans. Met. Chem.***, 2007, **32**, 481–493.
28. A. Sreekanth, U.L. Kala, C.R. Nayar, M.R.P. Kurup, ***Polyhedron***, 2004, **23**, 41.
29. T. R. Rao, S. Shrestha, A. Prasad, K. K. Narang, ***Synt. React. Inorg. Met. Org. Chem.***, 2002, **32**, 419.

30. Bagrov, F. V. and Vasil’eva, T. V., ***Russ. J. Org. Chem.***, 38, 1309, (2002).
31. R.M. Issa, S.A. Abdel-Latif, H.A. Abdel-Salam, ***Synth. React. Inorg. Met.-Org. Chem.***, 2001, **31**, 95.
32. P.B. Sreeja, M.R.P. Kurup, A. Kishore, C. Jasmin, ***Polyhedron***, 2004, **23**, 575.
33. S.J. Gruber, G.M. Harris, E. Sinn, ***J. Inorg. Nucl. Chem***., 1968, **30**, 1805.
34. T.A. Kabanos, and J.M. Tsangaris, ***J. Coord. Chem***., 1984, **13**, 89.
35. D. Nicholls, "***The Chemistry of Iron, Cobalt and Nickel***" Pergamon Press, Oxford, 1st ed., 1090, **1973**.
36. R. Gup, and E. Giziroglu, ***Spectrochimica Acta***., 2006, **A 65**, 719–726.
37. B. Moubaraki, K.S. Murray, J.D. Ranford, J.J. Vittal, X. Wang, Y. Xu, ***J. Chem. Soc., Dalton Trans.***, 1999, 3573.
38. J.D. Ranford, J.J. Vittal, Y.M. Wang, ***Inorg. Chem.***, 1998, **37**, 1226.
39. D. Maiti, H. Paul, N. Chanda, S. Chakrabort, B. Mondal, V.G. Puranik, G.K. Lahiri, ***Polyhedron,*** 2004**, 23**, 831.
40. N.M. Rageh, ***Spectrochim. Acta***, 2004,
A 60, 103-109.
41. N.V. Huggi, M.B. Halli, A.C. Hiremath, ***J. Indian. Chem. Soc.***, 1982, 1017.
42. M.V. Haghes and K. J. Rutt, ***J. Chem. Soc***., 1970, **18**, 3015.
43. S.P. Perlepes, T. Kabanos, V. Lazaridou, J.M. Tsangaris, ***Inorg. Chim. Acta***, 1986, **117**, 27.
44. L. M. M. Al-Mahrouqi, ***M. Sc. Thesis***, Faculty of Science University of Kualalumpur, **2009**.
45. R.C. Aggarwal, N. Sing, S. Singh, ***Polyhedron***, 1985, **4**, 343.