

Synthesis and Characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with Aroylhydrazonemonoximes

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ABSTRACT

Two novel aroylhydrazonemonoxime ligands and their metal (II) complexes of $[Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}]$ were synthesized. These ligands are Diacetylmonoxime-4-nitrobenzoylhydrazone (L_1H_2), Diacetylmonoxime-4-hydroxybenzoylhydrazone (L_2H_2). The synthesized 4-hydroxybenzoyl hydrazide and 4-nitrobenzoylhydrazide were reacted with diacetyl monoxime to obtain the (L_1H_2 , L_2H_2) ligands. Mononuclear complexes of these ligands of the type $[M(L_nH)_2]$ where ($M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}$; $n = 1, 2$) with metal:ligand molar ratio of (1:2) were prepared in the presence of Et_3N . The metal ions complexes $[M(L_nH)_2]$ are proposed to be six-coordinated with a N_4O_2 donor environment. Each ligand is coordinated through the oxime nitrogen, the imine nitrogen and the enolic oxygen atoms while the phenolic hydroxyl and oxime hydroxyl groups of aroylhydrazonemonoxime moiety do not participate in coordination. The structures of the complexes were suggested on the basis of 1H -NMR, ^{13}C -NMR, FT-IR, elemental analysis (CHN), magnetic susceptibility measurements and U.V.–visible spectroscopy.

Keywords: Aroylhydrazonemonoxime, Schiff base, diacetyl monoxime, hydrazide compounds, metal complexes.

(II) (II) (II) (II)
 - (II)

aroylhydrazonemonoxime

Diacetylmonoxime-4-hydroxybenzoyl : $[Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}]$

.Diacetylmonoxime-4-nitrobenzoylhydrazone(L_2H_2) hydrazone(L_1H_2)

4-hydroxybenzoylhydrazide 4-nitrobenzoylhydrazide diacetyl monoxime

(metal: L_nH_2 : Et_3N)

(1:2:2)

Et_3N

$[M(L_nH)_2]$

(Mononuclear)

			[M= Ni ^{II} , Co ^{II} , Cu ^{II} , Zn ^{II} , Cd ^{II} ; n=1,2]
	(C=N)	(N-OH)	
			(C-O)
(OH)			(N ₄ O ₂)
			.
		(¹³ C-NMR, ¹ H-NMR)	
(Magnetic	(U.V-visible)	-	(FT-IR)
	(CHN)		Susceptibility)
		.	
		-	:
		.	

INTRODUCTION

The coordination chemistry of aroyl hydrazones are quite interesting as it presents a combination of donor sites such as protonated / deprotonated amide oxygen, an imine nitrogen of hydrazone moiety and additional donor site (usually N or O) provided from the aldehyde or ketone forming the Schiff base. (Uppadine *et al.*, 2004 ; Uppadine and Lehn, 2004 ; Ruben and Vaughan, 2003).

The vast literature on structural studies of oxime complexes reveals some interesting features of its coordination behavior (Angelusiua *et al.*, 2010; Iskander *et al.*, 2004; Armstrong *et al.*, 2003). It may coordinate to one metal ion through the nitrogen atom and another metal ion through the oxygen atom. Thus it can form oximate-bridged extended network (Ross *et al.*, 2004 ; Sreerama and Pal, 2002). The hydrogen atom of the oxime -OH group can form potentially strong intra or intermolecular hydrogen bonds (Singha and Kumar, 2006; Kukulkin *et al.*, 1997) with other donor atoms or groups. Thus metal complexes bearing nondeprotonated oximes may be considered as supramolecular synthons, capable of forming extended supramolecular networks via intermolecular hydrogen bonds (Bendre *et al.*, 2005). The orientation of the oxime group in these molecules plays a major role in determining the dimensionality of the extended network.

Due to biological activities, the coordination chemistry of tridentate aroylhydrazones derived from orthohydroxy aromatic aldehydes (Ainscough *et al.*, 1999 ; Ainscough *et al.*, 1998 ; Koh *et al.*, 1998) and 2-N-heterocyclic aldehydes (Chaston and Richardson, 2003) have been extensively studied (Bernhardt *et al.*, 2001 ; Sangeetha and Pal, 2000).

In the present work, we have synthesized two Schiff bases of diacetyl monoxime with 4-hydroxy benzoylhydrazide, and 4-nitro benzoylhydrazide, to study the supramolecule forming abilities of these Schiff bases. Keeping this in mind, we report the synthesis, characterization and spectroscopic studies of some metal(II) complexes of the type

[M(L_nH)₂] when [M= Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}; n= 1, 2] obtained from the reaction of substituted aroylhydrazone oximes with metal(II) ions.

EXPERIMENTAL

Materials and Physical measurements

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich-Sigma Chemical Co. (Milwaukee, WI, USA), and used without further purification. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400MHz spectrometer in DMSO-d₆ with TMS as the internal standard. FT-IR spectra were recorded using Bruker-ALPHA Infrared Spectrophotometer Fourier Transform FTIR-4100. CHN analyzer were measured on Eurovetor-CA-3000(Italy). Magnetic susceptibility measurements were performed at room temperature (25C^o) by Faraday method (Bruker B.M6). UV-visible spectra were measured on Jasco Japanese companies V-350 Spectrophotometer in the regions (50000-9090cm⁻¹).

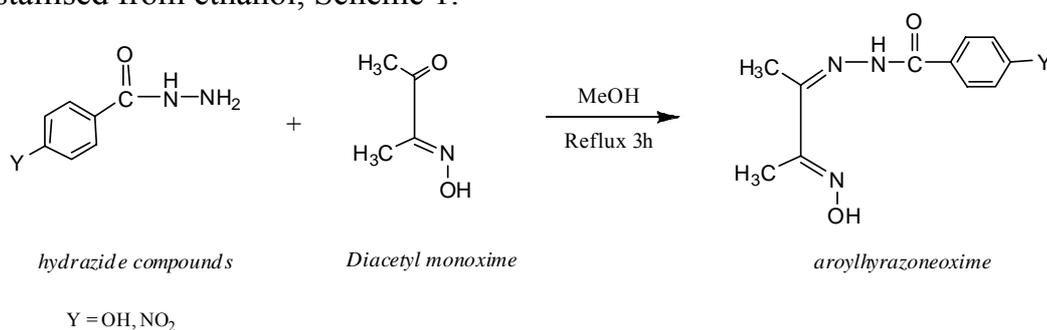
Synthesis of acid hydrazides

4-hydroxy benzoylhydrazide, and 4-nitro benzoylhydrazide were prepared by refluxing (1.66gm, 10mmol) of Ethyl-4-hydroxybenzoate or Ethyl-4-nitrobenzoate (1.95gm, 10mmol) in 50ml methanol with an excess of hydrazine hydrate NH₂NH₂.H₂O (1.5 ml, 25 mmol) (80%, d=1.03) for 4 h (Salem *et al.*, 2005 ; Bagrov and Vasil'eva, 2002). The compounds precipitated on standing over night, filtered and washed with distilled water. The pure hydrazides were obtained by recrystallization from ethanol.

Synthesis of Schiff base ligands

The two aroylhydrazoneoxime were prepared by known method (Salem *et al.*, 2005; Rodd, 1954). The two Schiff base ligands used in this study were prepared by refluxing an equimolar amounts of diacetyl monooxime and the respective substituted benzoyl hydrazide in methanolic medium. A typical synthesis is described below:

To a 30 ml methanol solution of diacetyl monooxime (1.01 g, 10 mmol), 4-hydroxy benzoylhydrazide (1.52g, 10 mmole) or 4-nitro benzoylhydrazide (1.81g, 10 mmole) in 50 ml methanol was added and the reaction mixture was stirred with refluxing for 3 h. On reducing the volume to ~30 ml. The resultant solid was filtered and thoroughly washed with ethanol (2 × 5 ml) followed by diethyl ether (2 × 5 ml). The solid was recrystallised from ethanol, Scheme 1.

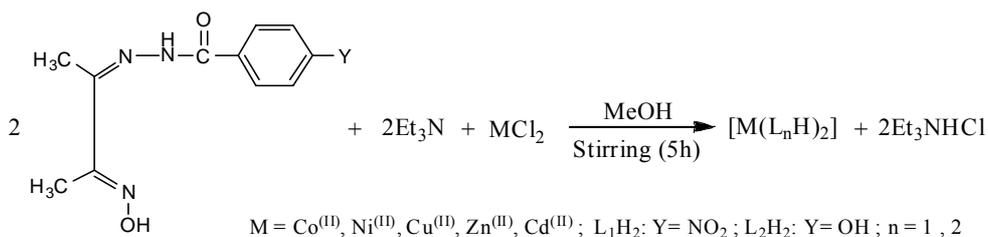


Scheme 1

Syntheses of the complexes

All the complexes were prepared following the same method by reacting a methanolic solution of the metal salt, ligand and Et₃N in a 1:2:2 molar ratio. Preparation of one of the complexes is described below: (Ozcan *et al.*, 2002).

To a 50 ml methanolic solution of the L_1H_2 (0.246g, 1mmol) or L_2H_2 (0.235g, 1mmol), Et_3N (0.101 g, 1 mmol) was added with stirring. When the initially colorless solution turned yellow. Addition (0.5 mmol) of $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ and $CdCl_2$ (0.65g, 0.64g, 0.67g(anhydrous), 0.68g and 0.93g) respectively, to the yellow solution, the color of the solution was changed immediately. After 5 h of stirring the volume of the solution was reduced to ~20 ml and filtered. The resultant solid obtained was washed with methanol (3×3 ml), followed by diethyl ether (2×5 ml), Scheme 2. Results of the compositional and spectroscopic data are shown in Tables 1-5.



Scheme 2

Table 1: Characterization of the Schiff base Ligands and metal (II) Complexes.

Compound s	Formula M.Wt (calculated)	Color	M.p ^a (°C)	μ_{eff} B.M	Yield (%)	Calculated / (Found) %		
						C	H	N
L_1H_2	$C_{11}H_{12}N_4O_4$ (264.24 g.mol ⁻¹)	Pale yellow	158	----	80	50.00 (49.32)	4.58 (4.02)	21.20 (20.36)
L_2H_2	$C_{11}H_{13}N_3O_3$ (235.24 g.mol ⁻¹)	White	273	----	90	56.16 (56.02)	5.57 (5.78)	17.86 (17.71)
$[Co(L_1H)_2]$	$C_{22}H_{22}N_8O_8Co$ (585.39 g.mol ⁻¹)	Brown reddish Crystals	136	5.04	83	45.14 (44.61)	3.79 (3.09)	19.14 (18.50)
$[Ni(L_1H)_2]$	$C_{22}H_{22}N_8O_8Ni$ (585.15 g.mol ⁻¹)	Dark Brown	214 ^a	2.89	70	45.16 (44.65)	3.79 (3.03)	19.15 (18.92)
$[Cu(L_1H)_2]$	$C_{22}H_{22}N_8O_8Cu$ (590 g.mol ⁻¹)	Bright-Light Olive	272 ^a	2.08	76	44.79 (44.36)	3.76 (3.27)	18.99 (19.03)
$[Zn(L_1H)_2]$	$C_{22}H_{22}N_8O_8Zn$ (591.87 g.mol ⁻¹)	Bright Yellow	342 ^a	dia.	64	44.64 (44.81)	3.75 (3.33)	18.93 (18.47)
$[Cd(L_1H)_2]$	$C_{22}H_{22}N_8O_8Cd$ (638.87 g.mol ⁻¹)	Orange	310 ^a	dia.	77	41.36 (40.54)	3.47 (3.14)	17.54 (16.74)
$[Co(L_2H)_2]$	$C_{22}H_{24}N_6O_6Co$ (527.40 g.mol ⁻¹)	Brown reddish	281 ^a	4.78	84	50.10 (49.88)	4.59 (4.22)	15.93 (15.68)
$[Ni(L_2H)_2]$	$C_{22}H_{24}N_6O_6Ni$ (527.16 g.mol ⁻¹)	Brown	289 ^a	2.83	90	50.12 (49.88)	4.59 (4.15)	15.94 (15.35)
$[Cu(L_2H)_2]$	$C_{22}H_{24}N_6O_6Cu$ (532.11 g.mol ⁻¹)	Bright-Olive	280 ^a	2.25	61	49.67 (49.55)	4.55 (4.08)	15.80 (15.33)
$[Zn(L_2H)_2]$	$C_{22}H_{24}N_6O_6Zn$ (533.87 g.mol ⁻¹)	Yellow	273 ^a	dia.	72	49.49 (48.91)	4.53 (4.15)	15.74 (15.51)
$[Cd(L_2H)_2]$	$C_{22}H_{24}N_6O_6Cd$ (580.87 g.mol ⁻¹)	Dark-Yellow	264 ^a	dia.	86	45.49 (45.59)	4.16 (4.19)	14.47 (14.02)

^a = decomposition

RESULTS AND DISCUSSION

Stereo electronic nature of the ligands

The aroylhydrazonemonoxime ligands may undergo deprotonation of the enolised amide carbonyl oxygen as well as the oxime oxygen and may be the phenolic oxygen for (L_2H_2). When these ligands are reacted with metal (II) ions in the presence of Et_3N in (2:1:2) molar ratio, the ligands deprotonated from the hydrazone amide moiety and the metal (II) neutral complexes were formed, Figure I. (Uppadine *et al.*, 2004; Uppadine and Lehn, 2004)

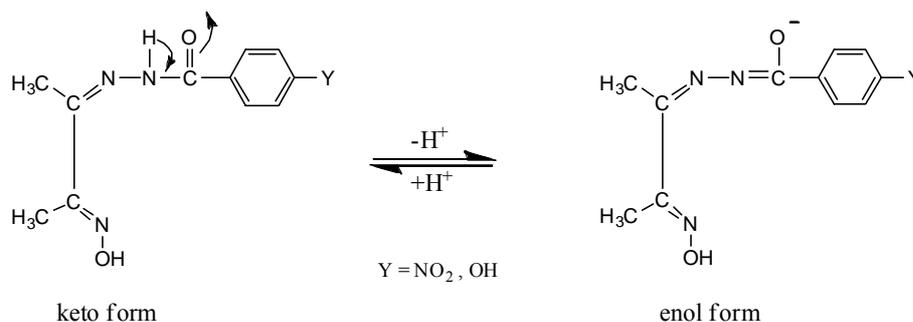


Fig. I: Tautomeric forms of the ligands

Syntheses

The Schiff base ligands (L_1H_2 and L_2H_2) ligands were prepared according to the method described above. The ligands were obtained in good yield and high purity, as confirmed by the elemental analyses (CHN) and spectroscopic data (1H -NMR, ^{13}C -NMR, IR and UV-visible spectra). All the complexes were obtained easily by stirring the metal salt, ligand and Et_3N in a 1:2:2 molar ratio at room temperature in methanol.

The elemental analyses (CHN) suggest that the complexes possess 1:2 stoichiometry with compositions of $[M(L_nH)_2]$; $n = 1,2$ as shown in Fig. IV.

1H -NMR and ^{13}C -NMR spectra in $DMSO-d_6$ in δ (ppm)

The 1H -NMR spectrum of the ligands (Fig. 1 and 2) showed peaks corresponding to (NH) proton appear as a singlet at δ 10.20 (s, 1H) ppm for L_1H_2 and δ 10.13 (s, 1H) ppm for L_2H_2 . The characteristic oxime OH proton is observed at δ 11.04 ppm (s, 1H) for L_1H_2 and δ 11.52 ppm (s, 1H) for L_2H_2 . These chemical shifts are characteristic value for hydrazones and oximes (Gup and Kirkan, 2005 ; Gup, 2006).

The other obtained values for 1H -NMR chemical shifts of hydrazone compound: As expected, the aromatic protons of compounds appear at δ 8.43 (d, 2H)-7.93 (d, 2H) ppm for L_1H_2 and δ 7.76 (d, 2H)-6.79 (d, 2H) ppm for L_2H_2 , as 2 different doublets (Gup and Beduk, 2002). In the 1H -NMR spectrum, 2 peaks are present for the CH_3 protons neighboring on oxime group ($CH_3-C=NOH$) and imine group ($CH_3-C=N-NH$) appears as a singlet at δ 2.04, 2.19 (s, 3H) ppm for L_1H_2 and δ 2.00, 2.16 (s, 3H) ppm for L_2H_2 respectively (Abraham *et al.*, 1985). Additionally, OH (phenolic) for L_2H_2 ligand appear at δ 10.46 (s, 1H) ppm. These data are in agreement with previously reported for similar compounds (Gup and Kirkan, 2005 ; Koh *et al.*, 1998), (Table 2).

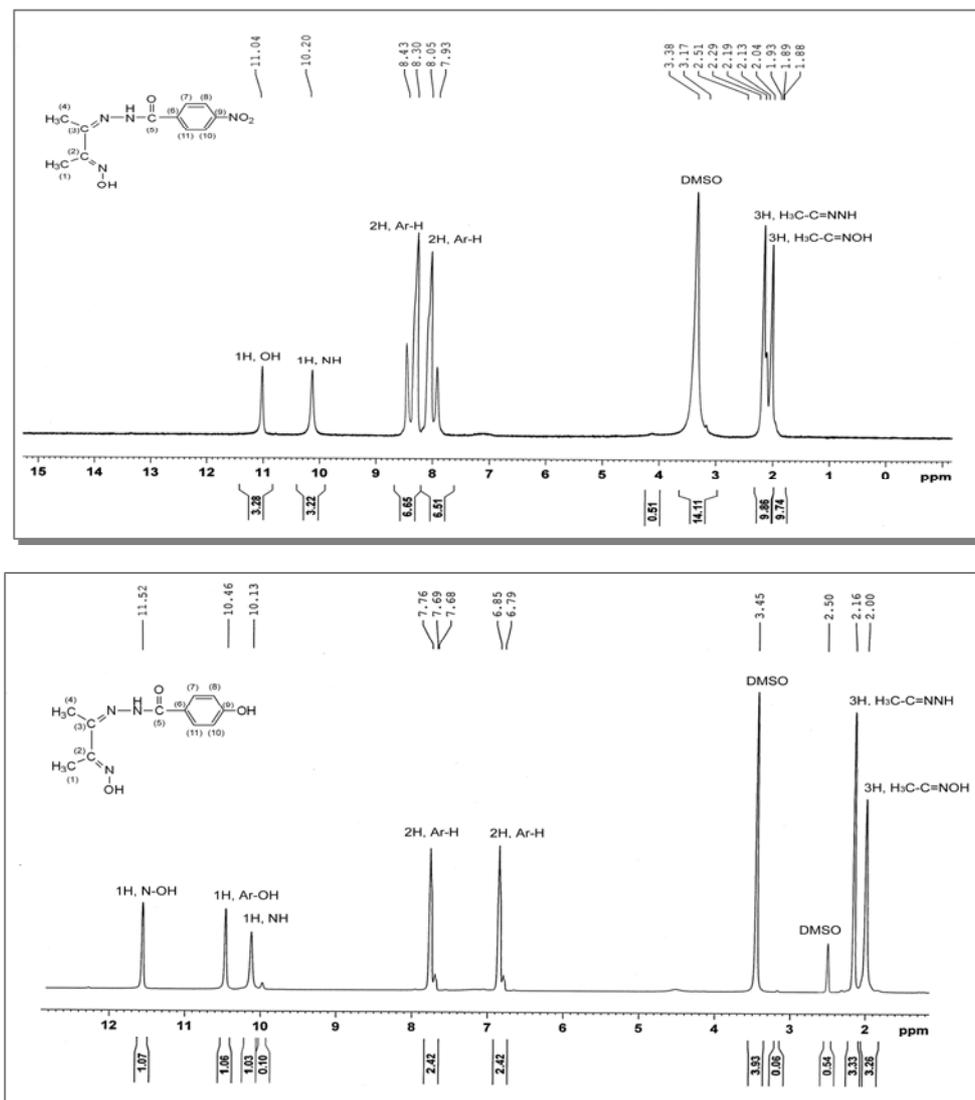


Fig. 2: ¹H-NMR spectrum of L₂H₂

In the ¹³C-NMR spectrum of ligands (Fig. 3 and 4) different signals, which were observed at δ 149.38 ppm for L₁H₂, δ 150.30 ppm for L₂H₂ ($-\underline{\text{C}}=\text{N}-\text{NH}$), δ 155.27 ppm for L₁H₂, and δ 155.34 ppm for L₂H₂ ($-\underline{\text{C}}=\text{N}-\text{NOH}$), show asymmetrically substituted for hydrazones and oximes (Kaminsky *et al.*, 2002). The signals of the C_{aromatic} carbon were observed at δ 124.02, 129.99 ppm for L₁H₂ and δ 115.28, 130.29 ppm for L₂H₂, corresponding to C-(8,10); C-(7,11) respectively, and δ 139.47, 151.51 for L₁H₂ and δ 124.72, 161.04 for L₂H₂ corresponding to C-(6,9) respectively. Spectra of ($-\underline{\text{C}}=\text{O}$) appear at δ 164.37 ppm for L₁H₂ and δ 166.45 ppm for L₂H₂, as expected (Ram *et al.*, 2007). The signals of CH₃ were shown at δ 9.78, 12.67 ppm for L₁H₂ and δ 9.78, 12.12 ppm for L₂H₂. ¹³C-NMR spectra at 2 different frequencies in each case indicates that corresponding to C-(1,4) respectively show asymmetrically substituted for hydrazones and oximes (Gup and Kirkan, 2005; Kaminsky *et al.*, 2002). The detailed ¹³C-NMR spectral data are given in Table 2.

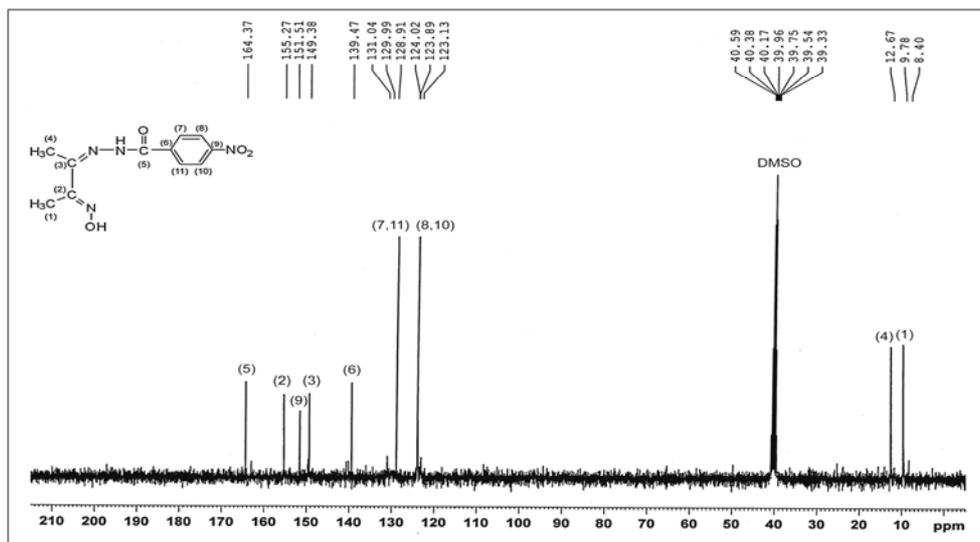


Fig. 3: ^{13}C -NMR spectrum of L_1H_2

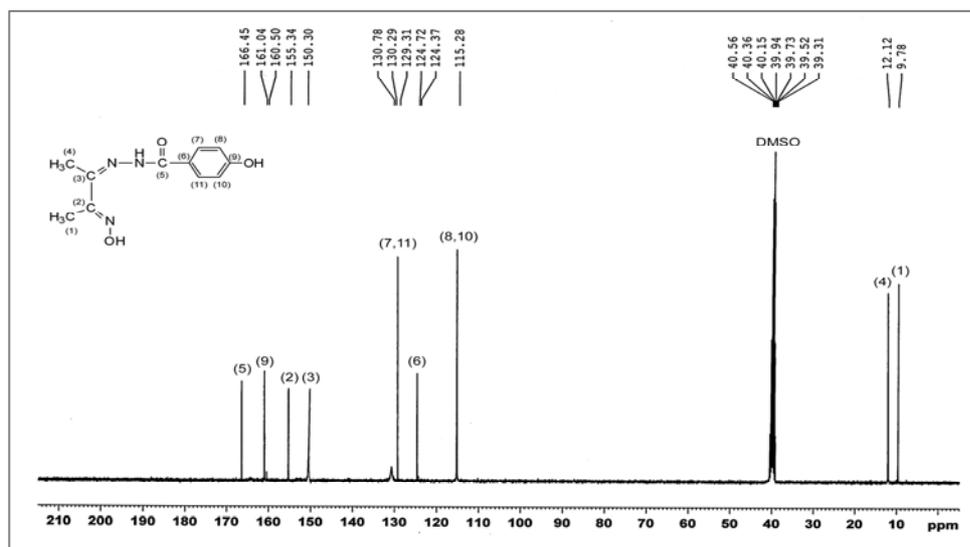


Fig. 4: ^{13}C -NMR spectrum of L_2H_2

Table 2: $^1\text{H-NMR}$ / $^{13}\text{C-NMR}$ spectra of the ligands in DMSO-d_6 in $\delta(\text{ppm})$

Compound	Chemical Shift ppm, δ		Chemical Shift ppm, δ	
	Groups	$^1\text{H-NMR}$	Groups	$^{13}\text{C-NMR}$
L_1H_2	$\text{CH}_3\text{-C=NOH}$	2.04 (s, 3H)	$\text{CH}_3\text{-C=NOH}$	9.78
	$\text{CH}_3\text{-C=N-NH}$	2.19 (s, 3H)	$\text{CH}_3\text{-C=N-NH}$	12.67
	Ar-H (7-11)	7.93-8.05 (d, 2H)	Ar-C (8, 10)	124.02
	Ar-H (8,10)	8.30-8.43 (d, 2H)	Ar-C (7, 11)	129.99
	-NH	10.20 (s, 1H)	Ar-C (6)	139.47
	-NOH (oxime)	11.04 (s, 1H)	-C=N-NH	149.38
			Ar-C-NO ₂ (9)	151.51
			-C=N-NOH	155.27
			C=O	164.37
Compound	Chemical Shift ppm, δ		Chemical Shift ppm, δ	
	Groups	$^1\text{H-NMR}$	Groups	$^{13}\text{C-NMR}$
L_2H_2	$\text{CH}_3\text{-C=NOH}$	2.00 (s, 3H)	$\text{CH}_3\text{-C=NOH}$	9.78
	$\text{CH}_3\text{-C=N-NH}$	2.16 (s, 3H)	$\text{CH}_3\text{-C=N-NH}$	12.12
	Ar-H (8-10)	6.79-6.85 (d, 2H)	Ar-C (8, 10)	115.28
	Ar-H (7,11)	7.69-7.76 (d, 2H)	Ar-C (6)	124.72
	-NH	10.13 (s, 1H)	Ar-C (7, 11)	130.29
	Ar-OH (phenolic)	10.46 (s, 1H)	-C=N-NH	150.30
	-NOH (oxime)	11.52 (s, 1H)	-C=N-NOH	155.34
			Ar-C-OH (9)	161.04
			C=O	166.45

s-singlet; d-doublet; t-triplet; m-multiplet

Zinc and cadmium complexes (1-3) have been characterized by $^1\text{H-NMR}$ spectroscopy due to their diamagnetic character. The essential features of the $^1\text{H-NMR}$ spectra of the metal complexes (Fig. 5 and 6) are observed at chemical shift values very near to those of the ligands, but the disappearance of the (NH) band in all spectra of the complexes confirms that complexation of the (L_1H_2 , L_2H_2) ligands with zinc(II) and cadmium(II) ions has indeed taken place with the enol form through deprotonation of the hydrazone amide moiety. Furthermore, The characteristic oxime OH proton and phenolic OH proton were observed almost at the same frequencies as that of the free ligands (Tables 2,3) indicating their non-involvement on coordination. The other obtained values for $^1\text{H-NMR}$ chemical shifts of the complexes are given in Table 3. These data are in agreement with previously reported for similar compounds (Koh *et al.*, 1998).

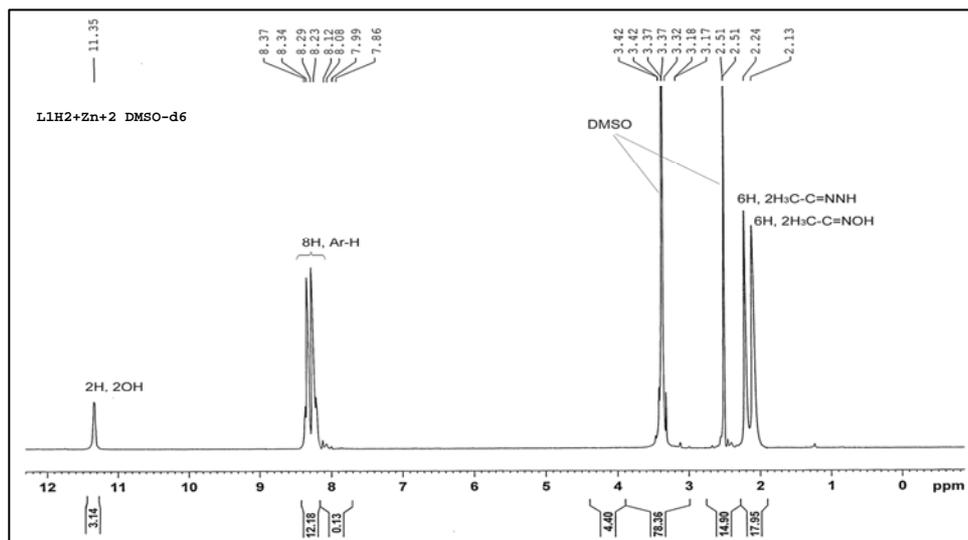


Fig. 5: ¹H-NMR spectrum of [Zn(L₁H)₂] complex in DMSO-d₆

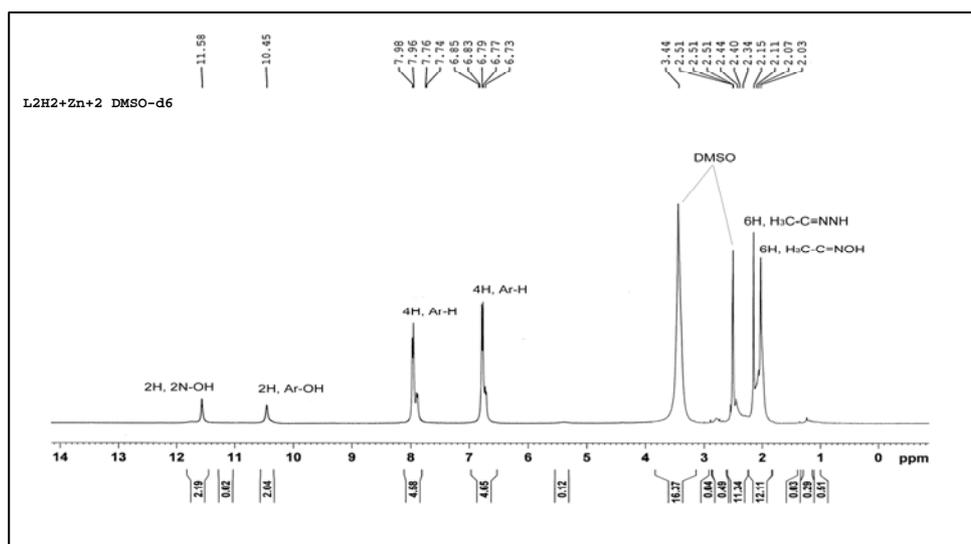


Fig. 6: ¹H-NMR spectrum of [Zn(L₂H)₂] complex in DMSO-d₆

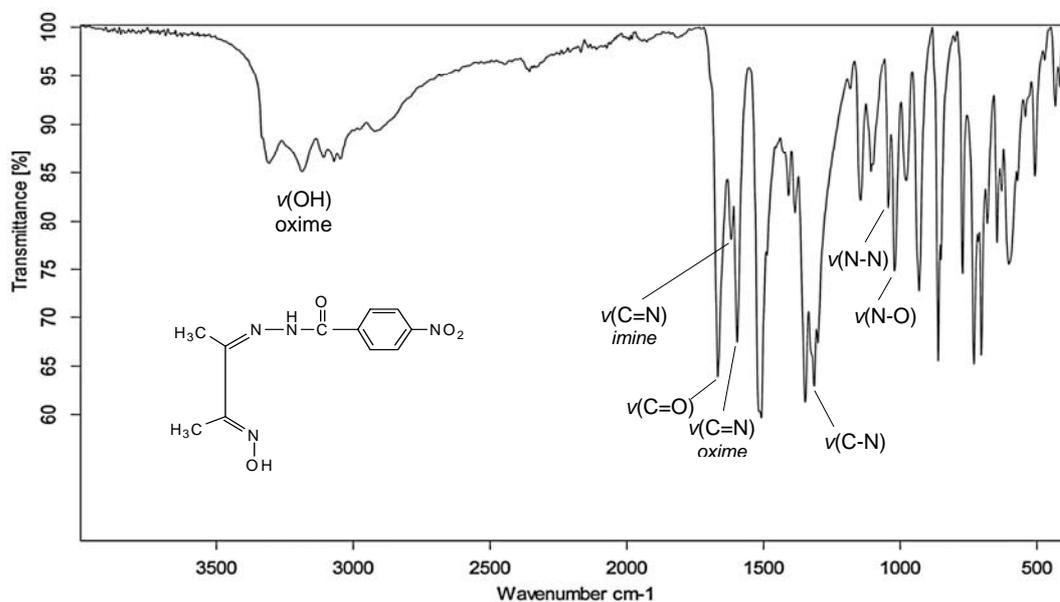
Table 3: $^1\text{H-NMR}$ spectra of the Zn(II) and Cd(II) complexes in DMSO- d_6 in δ (ppm).

No.	Compound	Chemical Shift ppm, δ	
		Groups	$^1\text{H-NMR}$
1	[Zn(L ₁ H) ₂]	CH ₃ -C=NOH	2.13 (s, 6H)
		CH ₃ -C=N-NH	2.24 (s, 6H)
		Ar-H	8.12-8.23 (d, 4H)
			8.29-8.37 (d, 4H)
		-NH	----
	-OH (oxime)	11.35 (s, 2H)	
2	[Cd(L ₁ H) ₂]	CH ₃ -C=NOH	1.87 (s, 6H)
		CH ₃ -C=N-NH	2.12 (s, 6H)
		Ar-H	8.26-8.28 (d, 4H)
			8.37-8.45 (d, 4H)
		-NH	----
	-OH (oxime)	11.12 (s, 2H)	
3	[Zn(L ₂ H) ₂]	CH ₃ -C=NOH	2.07 (s, 6H)
		CH ₃ -C=N-NH	2.15 (s, 6H)
		Ar-H	6.79 (d, 4H)
			7.98 (d, 4H)
		-NH	----
		Ar-OH (phenolic)	10.45 (s, 2H)
	-OH (oxime)	11.58 (s, 2H)	

s-singlet; d-doublet; t-triplet; m-multiplet

IR spectra of the L₁H₂, L₂H₂ ligands and their complexes

In the IR spectra of the ligands (Fig. 7 and 8), the characteristic amide I [$\nu\text{C=O}$] band appears at 1658-1666 cm^{-1} . The stretching vibration of the C=N_{imine} and C=N_{oxime} are observed at 1616, 1596 cm^{-1} for L₁H₂ and 1606, 1582 cm^{-1} for L₂H₂, respectively. The broad medium intensity band appearing at 3100-3400 cm^{-1} is assigned to the characteristic (oxime, phenolic) OH absorptions. The other bands observed in the IR spectra of the ligand are given in Table 4. These values are in accord with the previously reported hydrazone and oxime derivatives (Gup and Kirkan, 2005; Kaminsky *et al.*, 2002; Maekawa *et al.*, 1999; Abraham *et al.*, 1985; Butcher *et al.*, 1979).

**Fig. 7:** IR spectrum of L₁H₂ ligand

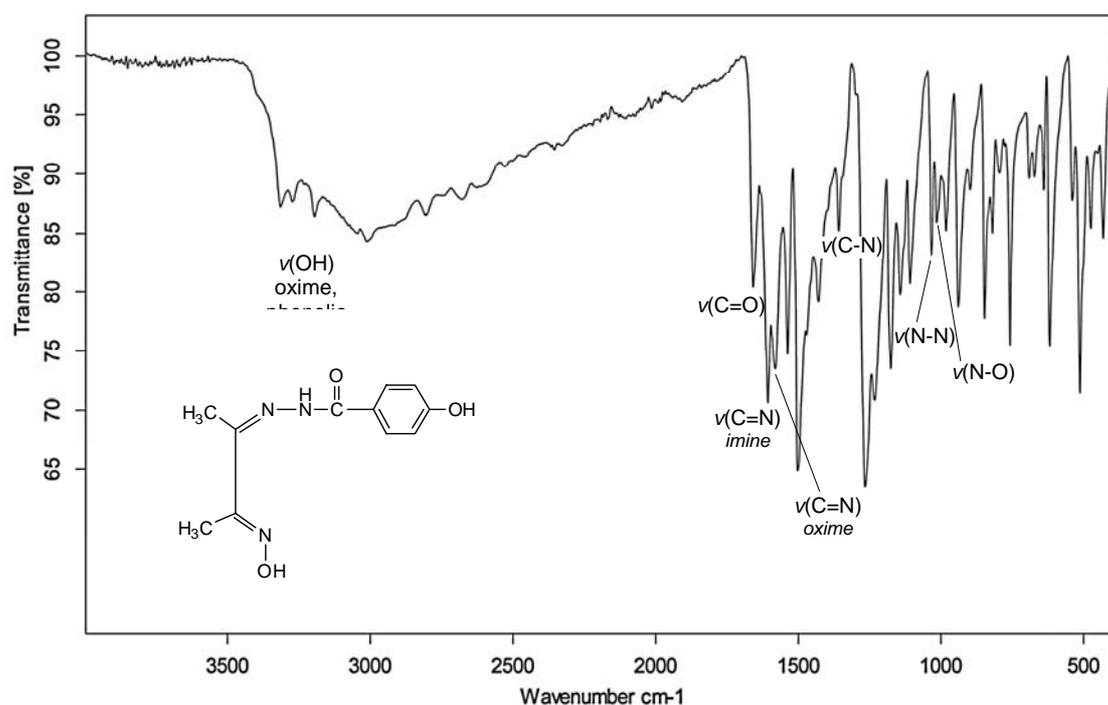


Fig. 8: IR spectrum of L_2H_2 ligand

The IR spectra of L_1H_2 and L_2H_2 exhibits a very broad medium intensity peak 3400-2600 cm^{-1} region, which are assigned to the intramolecular H-bonding vibration (O-H...N) (Gup and Kirkan, 2005; Bagrov and Vasil'eva, 2002). Also the amide NH stretching band of ligands was not observed in the IR spectra probably due to overlapping with the intermolecular hydrogen-bonded OH stretching frequency, or may be buried under the broad band of -OH.

Table 4: IR spectral data of the ligands and their metal complexes (cm^{-1})

Comp.	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$ <i>imine, oxime</i>	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{N}-\text{O})$
L_1H_2	3187,3306 br	1666	1616, 1596	1315	----	1039	1020
$[\text{Ni}(L_1H_2)_2]$	3472 br	----	1606, 1521	1338	1225	1056	1009
$[\text{Co}(L_1H_2)_2]$	3197 br	----	1586, 1519	1339	1243	1057	1012
$[\text{Cu}(L_1H_2)_2]$	3351 br	----	1607, 1521	1340	1209	1068	1010
$[\text{Zn}(L_1H_2)_2]$	3339 br	----	1604, 1520	1339	1192	1059	1010
$[\text{Cd}(L_1H_2)_2]$	3234 br	----	1596, 1523	1339	1178	1047	994
L_2H_2	3314,3195 br	1658	1606, 1582	1348	----	1027	1015
$[\text{Ni}(L_2H_2)_2]$	3251 br	----	1594, 1556	1350	1272	1057	1004
$[\text{Co}(L_2H_2)_2]$	3365 br	----	1602, 1587	1361	1265	1059	991
$[\text{Cu}(L_2H_2)_2]$	3123 br	----	1596, 1588	1356	1276	1032	1009
$[\text{Zn}(L_2H_2)_2]$	3400 br	----	1593	1370	1278	1058	1004
$[\text{Cd}(L_2H_2)_2]$	3188 br	----	1577, 1538	1357	1264	1052	1003

In the $^1\text{H-NMR}$ spectra of ligands, two and three absorption bands, which are assigned the OH groups, and amide NH protons, appear at lower field (Table 2); according to IR and $^1\text{H-NMR}$ data, isomer (Fig. II) are more suitable owing to the position of strong intramolecular hydrogen bonding (O–H \cdots N); therefore, we attributed the peaks appearing at δ 11.04, 10.20 ppm for L_1H_2 ligand due to oxime OH proton and amide NH proton, respectively, and δ 11.52, 10.46, 10.13 ppm for L_2H_2 ligand due to phenolic OH proton, oxime OH proton and amide NH proton, respectively. However, the shift of the amide NH proton absorption to relatively lower field cannot be explained by the intramolecular hydrogen bonding but may be explained by the intermolecular hydrogen bonding since the amide and carbonyl groups of ligands can bond by intermolecular hydrogen bonding to produce dimer with an *s-cis* conformation (Fig. III), (Bagrov and Vasil'eva, 2002 ; Shetti *et al.*, 1993).

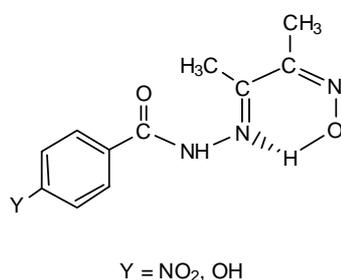


Figure II. Intramolecular hydrogen bonding of ligands

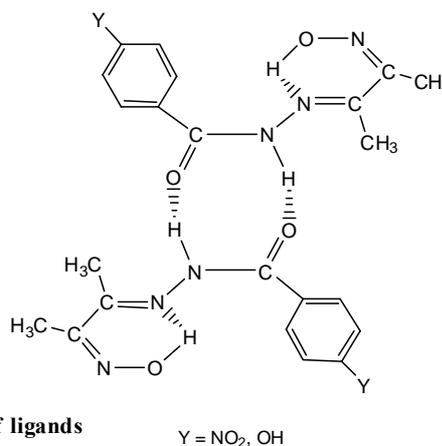


Figure III. Intramolecular hydrogen bonding *s-cis* Conformation of ligands

The infrared absorption bands of the complexes (Fig. 9 and 10) are given and assigned in Table 4. The IR spectra of the complexes show significant differences from the free ligand. The bands due to amide I, $\nu(\text{C}=\text{O})$ and amide $\nu(\text{NH})$ are absent in the IR spectra of the complexes (Gup and Kirkan, 2005), but new band appear at $1278\text{--}1178\text{ cm}^{-1}$ probably due to C–O stretching, suggesting that the NH proton is likely lost via deprotonation and the resulting enolic oxygen and the azomethine nitrogen take place in coordination (Sreekanth *et al.*, 2004 ; Sreeja *et al.*, 2004 ; Dinda *et al.*, 2002). Comparing these data with those of the free ligands it is obviously seen that $\nu(\text{C}=\text{N})_{\text{imine}}$, $\nu(\text{C}=\text{N})_{\text{oxime}}$ and $\nu(\text{N}-\text{O})$ bands shifted to lower frequencies, whereas $\nu(\text{C}-\text{N})$ absorptions are moved to higher frequencies (Issa *et al.*, 2001). The shift of $\nu(\text{N}-\text{N})$ stretch of the complexes to higher energy by $\sim 10\text{--}30\text{ cm}^{-1}$ comparing to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination (Iskander *et al.*, 2003).

Use of one equivalent of base for each equivalent of ligand left the oxime-OH unaffected, therefore, the oxime OH absorption band in the IR spectra of the complexes derived from L_1H_2 ligand becomes narrow and shifts to higher frequency (Table 4) that indicating non-participation of oxime OH in coordinate with metal(II) ions, also the IR spectra of complexes derived from L_2H_2 ligand shows a broad band around $3400\text{--}2600\text{ cm}^{-1}$, which can be attributed to the free OH stretching mode indicating non-participation of OH groups (phenolic and oxime) in coordination, since the oxime OH was buried under a broad band of phenolic OH (Table 4), suggesting disappearance of intramolecular hydrogen

bonding in the metal complexes and non-involvement of this groups in coordination (Gup and Krikan, 2005; Sreekanth *et al.*, 2004; Dinda *et al.*, 2002). According to IR data and stoichiometry of these complexes, the ligands acts as monoanionic *O,N,N*-tridentate and coordination takes place in the enol form through the oxime nitrogen, the imine nitrogen and the enolate oxygen atoms with a N_4O_2 donor environment forming six-coordination around the metal ion.

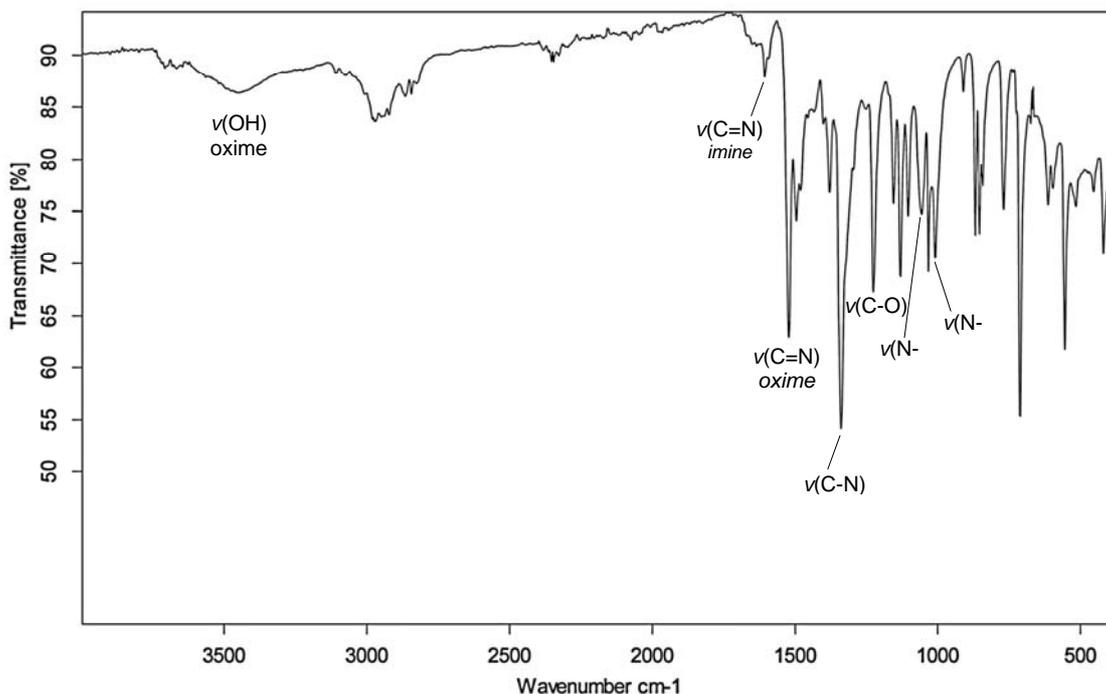


Fig. 9: IR spectrum of $[\text{Ni}(\text{L}_1\text{H})_2]$ complex

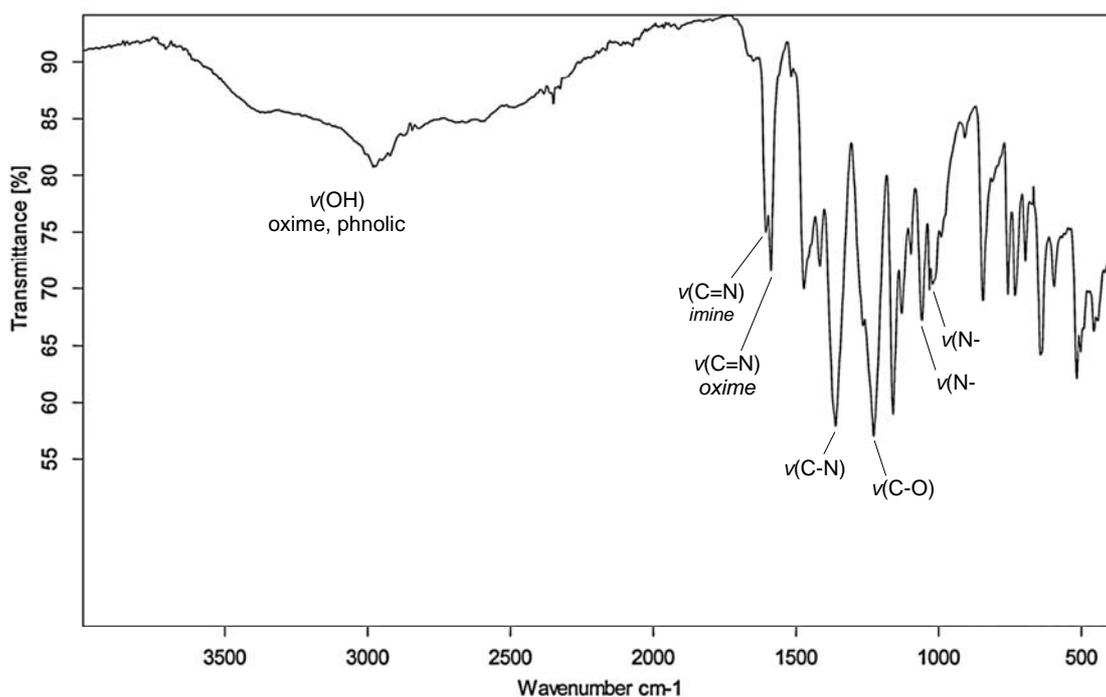


Fig. 10: IR spectrum of $[\text{Co}(\text{L}_2\text{H})_2]$ complex

Magnetic studies

The room temperature magnetic moments of the complexes (Table 1) show that cobalt(II), nickel(II) and copper(II) complexes are paramagnetic while zinc(II) and cadmium(II) complexes are diamagnetic. The measured magnetic moment values for cobalt(II), nickel(II) and copper(II) complexes are found in the range of 4.78-5.04, 2.83-2.89 and 2.08-2.25 B.M respectively, at room temperature, and these higher experimental values than theoretical values of (3.87 B.M for one d^7 cobalt ion and 1.73 B.M for one d^9 copper ion) are evidence for octahedral geometry (Bailar *et al.*, 1973 ; Figgis, 1960). Nickel (II) complexes, however, are mononuclear since their effective magnetic moments correspond to the spin value for two unpaired electron (Singha *et al.*, 2006 ; Ibrahim *et al.*, 1986), while these magnetic moment values of copper(II) and cobalt(II) complexes are higher than that expected for mononuclear copper (II) and cobalt (II) complexes were may be due to orbital contribution for complexes (Angelusiuia *et al.*, 2010 ; Singha *et al.*, 2006). However, all these data (Table 1) are in agreement with previously reported for similar octahedral complexes.

Electronic absorption spectra

Electronic spectra of the metal(II) complexes was achieved in DMF solution (10^{-2})M (Fig. 11,12). The appearance of three bands in the electronic spectra (Table 5) of cobalt(II) complexes in the regions 10905-11737, 13812-15600 and 18726-19685 cm^{-1} may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively (Lever, 1984), arise from an octahedral geometry for Co(II) ions (Gup, 2006; Singha *et al.*, 2006; Martel, 1971). Also the nickel(II) complexes exhibit three electronic spectral bands in the regions 9803-9823, 10976-11001 and 18939-18691 cm^{-1} which may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, suggesting an octahedral geometry around the Ni(II) ions (Gup and Kirkan, 2005 ; Kashyae *et al.*, 1975). The copper(II) complexes show a broad band on the low energy side at 16501-16750 cm^{-1} which may be ascribed to ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, and attributed to a distorted octahedral geometry around the metal ion (Maekawa, 1999; Lever, 1984).

Table 5: Electronic spectral data $\nu(\text{cm}^{-1})$ of the ligands and their metal complexes in DMF (10^{-2})M.

Compounds	Electronic spectra data $\nu(\text{cm}^{-1})$
L_1H_2	30487 , 31645 , 34482
L_2H_2	30674 , 32467 , 34965
$[Co(L_1H)_2]$	11737 , 13812 , 18726 , 29069 , 31250 , 34482
$[Co(L_2H)_2]$	10905 , 15600 , 19685 , 27700 , 34722 , 36496
$[Ni(L_1H)_2]$	9823 , 10976 , 18939 , 25188 , 30581 , 34246
$[Ni(L_2H)_2]$	9803 , 11001 , 18691 , 26737 , 30395 , 34482
$[Cu(L_1H)_2]$	16501 , 23923 , 31847 , 33557
$[Cu(L_2H)_2]$	16750 , 22883 , 25380 , 34843
$[Zn(L_1H)_2]$	23923 , 27472 , 33333
$[Zn(L_2H)_2]$	24630 , 28735 , 34013
$[Cd(L_1H)_2]$	25906 , 32467 , 34482
$[Cd(L_2H)_2]$	26881 , 31847 , 34965

All the spectra of metal(II) complexes show a broad and very strong band in the UV-visible region at $22883\text{-}29069\text{ cm}^{-1}$ which are assigned to a ligand \rightarrow metal (LMTC) charge transfer excitation. Both of zinc(II) and cadmium(II) complexes show no bands in the visible region as expected for d^{10} systems (Al-Mahrouqi, 2009 ; Aggarwal *et al.*, 1985). Additionally, a broad and sharp absorptions exhibit in the range $24000\text{-}35000\text{ cm}^{-1}$ and which may be due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions. (Table 4).

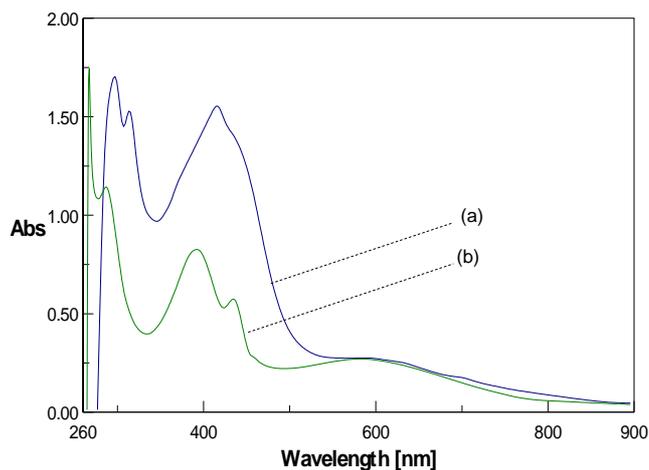


Fig.11: Electronic absorption spectra of Copper complexes in DMF (10^{-2})M: (a) $[\text{Cu}(\text{L}_1\text{H})_2]$; (b) $[\text{Cu}(\text{L}_2\text{H})_2]$.

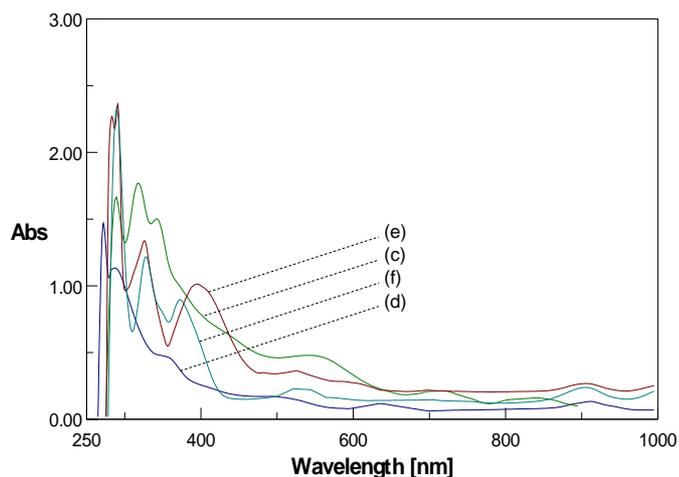


Fig. 12: Electronic absorption spectra of Cobalt and Nickel complexes in DMF (10^{-2})M: (c) $[\text{Co}(\text{L}_1\text{H})_2]$; (d) $[\text{Co}(\text{L}_2\text{H})_2]$; (e) $[\text{Ni}(\text{L}_1\text{H})_2]$; (f) $[\text{Ni}(\text{L}_2\text{H})_2]$

CONCLUSION

This work include the synthesis and characterization of the mononuclear metal(II) complexes using aroylhydrazonemonoxime ligands namely, diacetylmonoxime-4-nitrobenzoylhydrazone (L_1H_2); diacetylmonoxime-4-hydroxybenzoylhydrazone (L_2H_2). The reaction of (L_1H_2), (L_2H_2) and molar equivalent of Et_3N with anhydrous salt MCl_2 [$\text{M} = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, and $\text{Cd}(\text{II})$] yields the complexes $[\text{M}(\text{L}_n\text{H})_2]$; $n = 1,2$ where the (L_1H_2) and (L_2H_2) act as a monobasic O,N,N - tridentate ligands and the coordination takes place in the enol form, suggesting, to be six-coordination with a N_4O_2 donor environment around the metal ions. Each ligands are coordinated through the oxime nitrogen, the imine nitrogen and the enolate oxygen atoms. The phenolic hydroxyl and oxime hydroxyl groups of aroylhydrazonemonoxime moiety are not involved in coordination to the metal ion.

The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, elemental analysis(CHN), FT-IR infrared spectra, Magnetic susceptibility measurements and UV-vis. electronic absorption spectra of the metal(II) complexes were recorded and investigated. The results propose the monomeric complexes $[\text{M}(\text{L}_n\text{H})_2]$; $n = 1,2$ with an octahedral geometry around the metal(II) ions, (Fig. IV).

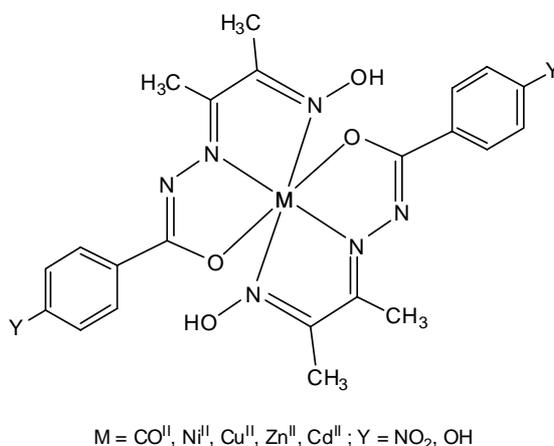


Fig. IV: Suggested structure for the monomeric metal complexes $[M(L_nH)_2]$; $n = 1,2$

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REFERENCES

- Abraham, F.; Capon, J. M.; Nowogrocki, G.; Sueur, S., (1985). Synthesis, X-ray structure and spectroscopy of Cu(II) complexes derived from diacetylazine dioxime. *Polyhedron*, **4**, 1761-1767.
- Aggarwal, R. C.; Sing, N.; Singh, S., (1985). Preparation and characterization of heterobimetallic tetraoxanthes and their complexes with Lewis bases. *Polyhedron*, **4**, 343-348.
- Ainscough, E.W.; Brodie, A.M.; Denny, W.A.; Finlay, G.J.; Gothe, S.A.; Ranford, J.D., (1999). Cytotoxicity of salicylaldehyde benzoylhydrazone analogs and their transition metal complexes: quantitative structure-activity relationships. *J. Inorg. Biochem.*, **77**(3-4), 125-133.
- Ainscough, E.W.; Brodie, A.M.; Dobbs, A. J.; Ranford, J.D.; Waters, J.M., (1998). Antitumour copper(II) salicylaldehyde benzoylhydrazone (H₂sb) complexes: physicochemical properties and the single-crystal x-ray structures of $[\{Cu(H_2sb)(CCl_3CO_2)_2\}_2]$ and $[\{Cu(Hsb)(ClO_4)(C_2H_5OH)\}_2]$ and the related salicylaldehyde acetylhydrazone (H₂sa) complex, $[Cu(Hsa)Cl(H_2O)].H_2O$. *Inorg. Chem. Acta*, **267**, 27-38.
- Al-Mahrouqi, L. M. M., (2009). Synthesis and characterization and biological activities of benzenesulfanohydrazones and their metal complexes. M. Sc. Thesis, Faculty of Science, University of Malaya, Kuala Lumpur.

- Angelusiu, M. V.; Barbuceanub, S.-F.; Draghici, C.; Almajanb, G. L., (2010). New Cu(II), Co(II), Ni(II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation. *Eur. J. Med. Chem.*, **45**, **5**, 2055-2062.
- Armstrong, C.M.; Bernhardt, P.V.; Chin, P.; Richardson, D. R. (2003). Structural Variations and Formation Constants of First-Row Transition Metal Complexes of Biologically Active Aroylhydrazones. *Eur. J. Inorg. Chem.*, **6**, 1145-1156.
- Bagrov, F. V.; Vasil'eva, T. V., (2002). 2-Diphenylphosphinoyloxybenzaldehyde 4-Nitrophenyl-, 4-Phenyl-1-phthalazinyl-, and Aroylhydrazones and Thiosemicarbazone. *Russ. J. Org. Chem.*, **38**, 1309-1313.
- Bailar, J. C.; Emeleus, H. J.; Nyholm, S. R.; Dickenson, A. F. T. (1973). "Comprehensive Inorganic Chemistry". 1st edn., Pergmans Press, Oxford, pp. 16, 20, 92, 1087-1089, 1151-1158.
- Bendre, R.S.; Butcher, R.J.; Kuwar, A.S. (2005). 2-Formylthymol oxime. *Acta Cryst.*, **E61**, 3511-3513.
- Bernhardt, P.V.; Chin, P.; Richardson, D. (2001). Unprecedented oxidation of a biologically active aroylhydrazone chelator catalysed by iron(III): serendipitous identification of diacylhydrazine ligands with high iron chelation efficacy. *J. Biol. Inorg. Chem.*, **6**, 801-809.
- Butcher, R. J.; O'Connor, C. J.; Sinn, E. (1979). Synthesis and relation between magnetism and structure of the binuclear copper(II) oxime complex $[\text{Cu}_2\text{L}_2(\text{ClO}_4)_2] \cdot [\text{Cu}_2\text{L}_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$, where HL=1-(N,N-dimethyl-2-aminoethylimino)-1-phenyl-2-oximopropane. *Inorg. Chem.*, **18**, 1913-1918.
- Chaston, T.B.; Richardson, D.R. (2003). Interactions of the pyridine-2-carboxaldehyde isonicotinoyl hydrazone class of chelators with iron and DNA: implications for toxicity in the treatment of iron overload disease. *J. Biol. Inorg. Chem.*, **8**, 427-438.
- Dinda, R.; Sengupta, P.; Ghosh, S.; Mak, T. C. W. (2002). 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**, 1684-1688.
- Figgis, B. N.; Lewis, J. (1960). "Modern Coordination Chemistry". Inter Science, New York, 400 p.
- Gup, R., (2006). A new unsymmetrical vic-dioxime bearing salicylaldehyde 4-aminobenzoylhydrazone and its homo- and heterotrimeric complexes with copper(II) and nickel(II) ions. *Russ. J. Coord. Chem.*, **32**, 99-108.
- Gup, R.; Beduk, A.D. (2002). Synthesis and characterization of complexes of Ni(II), Co(II), and Cu(II) With Four 4-Aminobenzoate Derivatives Of Unsymmetrical Vic-Dioximes. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1043-1057.
- Gup, R.; Kirkan, B. (2005). Synthesis and spectroscopic studies of copper(II) and nickel(II) complexes containing hydrazonic ligands and heterocyclic coligand. *Spectrochim. Acta*, **A 62** (4-5), 1188-1195.
- Ibrahim, K. M.; Bekheit, M. M.; Abu El-Reash, G. M.; Mostafa, M. M. (1986). Spectral, thermal and magnetic studies of biacetylmonoxime isonicotinoylhydrazone complexes. *Polyhedron*, **5**, 1635-1638.

- Iskander, M. F.; El-Sayed, L.; Salem, N.M.H.; Haase, W.; Lindner, H. J.; Foro, S. (2004). Synthesis, characterization and magnetochemical studies of some copper(II) complexes derived from n-salicylidene-n-alkanoylhydrazins: X-ray crystal and molecular structure of bis [monochloro-(μ -n-salicylidene myristoylhydrazine)ono(-1)] dicopper(II). *Polyhedron*, **23**, 23-31.
- Iskander, M.F.; El-Sayed, L.; Salem, N.M.H.; Werner, R.; Haase, W. (2003). Metal Complexes Derived from Hydrazoneoxime Ligands: I. Synthesis, Characterization and Magnetochemical Studies of (Acylhydrazoneoxime) Copper(II) Complexes. *J. Coord. Chem.*, **56**, 1075-1084.
- Issa, R.M.; Abdel-Latif, S.A.; Abdel-Salam, H.A. (2001). Synthesis And Characterization Of New Cu(II) Complexes Derived From Benzilic And Mandelic Hydrazones. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 95-105.
- Kaminsky, W.; Jasonsli, J.P.; Woudenberg, R.; Goldberg, K.I.; West, D.X. (2002). Structural study of two N(4)-substituted thiosemicarbazones prepared from 1-phenyl-1,2-propanedione-2-oxime and their binuclear nickel(II) complexes. *J. Mol. Struct.*, **608**, 135-141.
- Kashyae, B.C.; Janeja, A.D.; Banriji, S.K. (1975). Complexes of Co (II) and Ni (II) with some N-aryl, N'-2-(5-halo-pyridyl) thioureas. *J. Inorg. Nucl. Chem.*, **37**, 612.
- Koh, L.L.; Kon, O.L.; Loh, K.W.; Long, Y.C.; Ranford, J.D.; Tan, A.L.C.; Tjan, Y.Y. (1998). Complexes of salicylaldehyde acylhydrazones: Cytotoxicity, QSAR and crystal structure of the sterically hindered t-butyl dimmer. *J. Inorg. Biochem.*, **72**, 155-162.
- Kukuskin, V.Y.; Nishioka, T.; Tudela, T.; Isobe, K.; Kinoshita, I. (1997). Hydrogen-bonding patterns in oxime/oximate platinum(II) species providing the formation of one-dimensional chains, Two-Dimensional Networks, and Cages. *Inorg. Chem.*, **36**, 6157-6165.
- Lever, A.B.P. (1984). "Inorganic Electronic Spectroscopy". 2nd Elsevier, Amsterdam. 507p.
- Maekawa, M.; Kitagawa, S.; Nakao, Y.; Sakamoto, S.; Yatani, A.; Mori, W.; Kashino, S.; Munakata, M.S. (1999). Syntheses, crystal structures and autoreduction behavior of antiferromagnetically coupled dicopper(II) oximate complexes. *Inorg. Chem. Acta.*, **293**, 20-29.
- Martel, A. E. (1971). "Coordination Chemistry". Vannostrans Reinhold, New York, 1 p.
- Ozcan, E.; Karapinar, E.; Demirta, B. (2002). Synthesis of four new vic-dioximes and their nickel(II), cobalt(II), copper(II) and cadmium(II) complexes. *Trans. Met. Chem.*, **27**, 557-561.
- Ram, A. L.; Debajani, B.; Arjun, K.; Kumar, De. A. (2007). 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**, 481-493.
- Rodd, E. H. (1954). "Chemistry of Carbon Compounds". Vol.3, part A, Elsevier, London, 556 p.
- Ross, S.; Weyhermuller, T.; Bill, E.; Bothe, E.; Florke, U.; Wieghardt, K.; Chaudhuri, P. (2004). Asymmetric Heterodinuclear Fe^{III} M^{II} (M = Zn, Cu, Ni, Fe, Mn), Co^{III} Fe^{II} and Fe^{II} Co^{III} Species: Synthesis, Structure, Redox Behavior, and Magnetism. *Eur. J. Inorg. Chem.*, 984-997.

- Ruben, M.; Lehn, J. M.; Vaughan, G. (2003). Synthesis of ionisable [2 3 2] grid-type metallo-arrays and reversible protonic modulation of the optical properties of the $[\text{Co}^{\text{II}}_4 \text{L}_4]^{8+}$ species. *Chem. Commun.*, **21**, 1338-1339.
- Salem, N. M. H.; El-Sayed, L.; Haase, W.; Iskander, M.F. (2005). Metal complexes derived from hydrazoneoxime ligands: II. Synthesis, electrospray mass spectra and magnetochemical studies of some copper(II) complexes derived from p-substituted aroylhydrazoneoximes. *J. Coord. Chem.*, **58**, 1327-1343.
- Sangeetha, N.R.; Pal, S. (2000). Copper(II)-activated transformation of azomethine to imidate: synthetic and structural studies. *Polyhedron*, **19**, 2713-2717.
- Shetti, S. N.; Murty, A. S. R.; Tembe, G. L. (1993). Synthesis and spectral characterization of Mn (II), Co(II), and Zn (II), complexes of isonitroso acetophenonethiosemicarbazone and isonitroso 4-chloro acetophenone Thiosemicarbazone. *Indian J. Chem.*, **32A**, 511-516.
- Singha, P. K.; Kumar, D. N. (2006). Spectral studies on cobalt(II), nickel(II) and copper(II) complexes of naphthaldehyde substituted aroylhydrazones. *Spectrochim. Acta*, **64**(4), 853-858.
- Sreeja, P.B.; Kurup, M.R.P.; Kishore, A.; Jasmin, C. (2004). Spectral characterization, X-ray structure and biological investigations of copper (II) ternary complexes of 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazone. *Polyhedron*, **23**, 575-581.
- Srekanth, A.; Kala, U.L.; Nayar, C.R.; Kurup, M.R.P. (2004). Cobalt (III) complexes of 2-hydroxyacetophenone N(4)-phenyl semicarbazone containing heterocyclic coligands: syntheses, structure and spectral studies. *Polyhedron*, **23**, 41-47.
- Sreerama, S. G.; Pal, S. (2002). A Novel carboxylate-free ferromagnetic trinuclear μ_3 -oxo-manganese(III) complex with distorted pentagonal-bipyramidal metal centers. *Inorg. Chem.*, **41**, 4843-4845.
- Uppadine, L. H.; Gisselbrecht, J. -P.; Lehn, J. M. (2004). Protonic modulation of redox properties in ionisable [2 × 2] grid-like metalloarrays. *Chem. Commun.*, 718 -719.
- Uppadine, L. H.; Lehn, J. M. (2004). Three-Level synthetic strategy towards mixed-valence and heterometallic [2×2] Gridlike Arrays. *Angew Chem. Int. Ed.*, **43**, 240-243.