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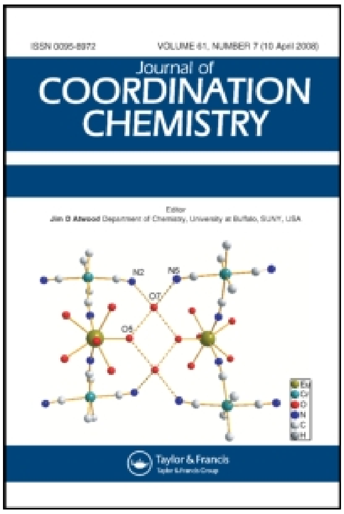

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Spectroscopic, crystal structure and thermal studies of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 5-amino-4-arylazo-3-methyl-1-phenylpyrazole (aryl=C_6H_5,o-C_6H_4COOH,o-C_6H_4OH)

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Spectroscopic, crystal structure and thermal studies of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 5-amino-4-arylazo-3-methyl-1-phenylpyrazole (aryl = C_6H_5,o-C_6H_4COOH,o-C_6H_4OH)

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5-Amino-4-arylazo-3-methyl-1-phenylpyrazole (aryl = C_6H_5,o-C_6H_4COOH,o-C_6H_4OH) and its complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions were synthesized. The complexes are in the ratio 1 : 1 and 1 : 2 (metal : ligand). Ligands and complexes were subjected to elemental analysis, IR, Raman, UV-Vis and ^{1}H-NMR spectroscopy. The mass spectra of the ligands were discussed. Thermal analysis and magnetic measurements were carried out for the prepared complexes. The X-ray single crystal structure of [Ni(**L1**)$_2$] was performed. The investigated pyrazole compounds coordinate as bidentate ligands through amino and azo nitrogens or tridentate through NNO. The molar conductance of the chelates is measured and reflected the non-electrolytic nature of the prepared complexes.

Keywords: Arylazo-pyrazoles; Azo-complexes; Spectroscopy; X-ray; Thermal; Magnetic moment

1. Introduction

Azo compounds are involved in a number of biological reactions with high activity against bacteria and fungi [1–4]. They have also been used in applications such as the coloring of fibres [5, 6], photoelectronic applications [7] and optical storage technology [8, 9]. The 5-aminopyrazoles that contain azo group, particularly, were found to be useful in industrial applications, as ink jets [10], in dyeing papers [11], fibres, wool and leather [12, 13] due to their strong dyeing powers. Another important industrial process is their utilization as a brightener and fluorescent in subtractive photographic processes [14]. Metal chelates of pyrazoles that contain azo groups have wide applications in dye industry [15], as analytical reagents in the microdetermination of metals and in biological uses [16]. When the amino group is chelating it shows high ligating behavior with transition metal ions [17]. In this work we prepare new arylazo derivatives of 5-amino-3-methyl-1-phenylpyrazole and confirm their structures by elemental analyses, Mass, IR, Raman, ^{1}H-NMR and UV-Vis spectra. Due to the complexing ability of

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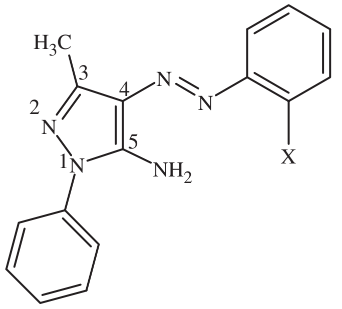
azo-metal chelates we investigate reactions of these ligands with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). The complexes are studied by elemental analyses, molar conductance, IR, Raman, ^{1}H-NMR, UV-Vis spectroscopy, TGA, magnetic susceptibility and an X-ray crystal structure.



5-amino-4-arylazo-3-methyl-1-phenylpyrazole derivatives
X = H (**L1**), COOH (**L2**), OH (**L3**)

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2. Experimental

The (C, H, N and Cl) elemental analyses were performed on an Elementer Vario EL III in the microanalytical centre, Cairo University, Giza, Egypt. The metal content of 10–15 mg of the complexes was determined by titration against 0.01 M EDTA after complete decomposition following the recommended procedure [18]. Mass spectra were carried out with the aid of SHIMADZU GCMS-QP 1000 EX mass spectrometer at 70 eV. The molar conductance of the complexes in DMF was measured using a Jenway 4330 conductivity meter with 1.02 cell constant using freshly prepared 0.01 M KCl solution. IR spectra were measured using a SHIMADZU FTIR spectrophotometer from 4000–400 cm^{-1} as KBr plates. Raman spectra were performed on the solid samples using a Bruker model IFS 66/S FT-Raman spectrophotometer in the range 4000–0 cm^{-1}, with a Nd : YAG air-cooled laser beam and liquid nitrogen cooled Ge detector. The output laser power was set to 0–1500 mW. ^{1}H-NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrophotometer using dimethylsulphoxide (DMSO-d_6) with D_2O as solvent and tetramethylsilane as internal standard. A SHIMADZU TGA 50 Hz thermal analyzer was used to record TG thermograms from room temperature to 1000°C with a heating rate of 10°C min^{-1} in a nitrogen atmosphere at a flow rate of 20 mL min^{-1}. The UV-Vis absorption spectra were recorded on a PERKIN-ELMER Lambda 4B spectrophotometer using 1 cm matched quartz cells. Magnetic susceptibility data were obtained by using a SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance calibrated with $Hg[Co(SCN)_4]$.

2.1. *Synthesis of the ligands*

Diazotized aromatic amine (aniline, anthranilic acid or o-aminophenol) was prepared by adding 0.7 g of sodium nitrite in 4 mL water gradually to a cold solution of

Table 1. Elemental analysis and physical properties of the 5-amino-4-arylazo-3-methyl-1-phenylpyrazole derivatives.

Compound	X	Mol. formula M. Wt calcd(found)	Solvent color (M.P. °C) Yield	%Calcd/found C	 H	 N
L1	H	$C_{16}H_{15}N_5$ 277.32 (277)	Ethanol Yellow (138)* 48.70%	69.29 (69.40)	5.45 (5.22)	25.25 (25.79)
L2	o–COOH	$C_{17}H_{15}N_5O_2$ 321.34 (321)	Acetic acid Yellow (216) 77.80%	63.54 (62.83)	4.71 (4.50)	21.79 (21.47)
L3	o–OH	$C_{16}H_{15}N_5O$ 293.3 (293)	Ethanol Yellow (116) 40.90%	65.52 (65.48)	5.11 (5.70)	23.89 (23.45)

*M.P = 140°C [19].

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amine (0.01 mole) in 6 mL 5N HCl within 10 min. This cold diazotized amine was added gradually with constant stirring to a cooled solution of 5-amino-3-methyl-1-phenylpyrazole (0.01 mole, 1.73 g) in 30 ml ethanol containing 3 g sodium acetate; the temperature was kept at 0–5°C and maintained for 2 h at the same temperature. The formed precipitate was filtered, dried and recrystallized from the appropriate solvent. Melting point of **L1** was in accordance with that reported in the literature [19]. Table 1 contains (C, H, N and Cl) analysis and the physical properties of the ligands.

2.2. *Synthesis of complexes*

The complexes were prepared by mixing 30 mL hot ethanolic solution containing 0.001 mole of ligands with [Co(II), Ni(II), Cu(II), Cd(II) and Hg(II)] chlorides and Zn(II) acetate in a proper ratio (1 : 1 or 1 : 2 metal : ligand). The mixture was refluxed for 5 h. When solid chelates did not precipitate on standing, 0.1 M NaOH solution was added dropwise until pH 7–8. The formed precipitates were filtered, washed with ethanol-water mixture and dried at room temperature. The elemental analyses and melting points of the complexes are given in table 2.

2.3. *X-ray crystal structure*

Brown, single crystals of the [Ni(**L1**)$_2$] complex were grown from DMF by slow evaporation of solvent during about 4 weeks and used for X-ray analysis as a representative example. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan) with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 K by the ω scan mode within $2.910 < \theta < 26.022°$. All refinements were performed by full-matrix least-squares on F^2. All hydrogen atoms were placed in idealized positions. The space group, lattice parameters, and other crystal data are listed in table 3.

Table 2. Microanalytical data, physical properties and molar conductance ($\Omega^{-1}\,\mathrm{mol}^{-1}\,\mathrm{cm}^2$).

		Ratio		M.P. (°C)	% Calcd/found				
Cpd. no.	Compound	M	L	Color yield	C	H	N	M	Molar Cond.
1	$[\mathrm{Co}(\mathbf{L1})_2]$	1	2	310 Black 36.5%	62.85 (62.60)	4.61 (3.97)	22.91 (22.80)	9.64 (8.88)	5.58
2	$[\mathrm{Ni}(\mathbf{L1})_2]$	1	2	242 Brown 68.4%	62.87 (61.06)	4.62 (4.76)	22.91 (22.40)	9.60 (9.05)	5.67
3	$[\mathrm{Cu}(\mathbf{L1})_2]$	1	2	182 Black 61.4%	62.38 (61.63)	4.58 (4.87)	22.73 (22.70)	10.31 (9.74)	3.3
4	$[\mathrm{Zn}(\mathbf{L1})_2]$	1	2	308 Orange 61.3%	62.18 (61.90)	4.57 (4.84)	22.66 (20.28)	10.58 (11.74)	5.8
5	$[\mathrm{Cd}(\mathbf{L1})\cdot 2\mathrm{Cl}]^{*}$	1	1	280 Yellow 36.1%	41.72 (41.12)	3.28 (3.40)	15.20 (14.30)	24.40 (24.59)	5.6
6	$[\mathrm{Hg}(\mathbf{L1})\mathrm{Cl}\cdot \mathrm{H_2O}]^{\triangle}$	1	1	198 Yellow 81.6%	36.23 (36.90)	3.04 (3.14)	13.20 (12.91)	37.78 (37.82)	12.6
7	$[\mathrm{Hg}(\mathbf{L1})_2]$	1	2	206 Orange 43.3%	51.03 (51.07)	3.75 (4.17)	18.60 (18.63)	26.63 (26.25)	15.8
8	$[\mathrm{Co}(\mathbf{L2})\cdot \mathrm{H_2O}]$	1	1	>360 Brown 48.0%	51.53 (51.64)	3.82 (4.29)	17.67 (17.78)	14.87 (14.71)	20.5
9	$[\mathrm{Ni}(\mathbf{L2})\cdot \mathrm{OH}]$	1	1	>360 Brown 83.3%	51.56 (52.42)	3.82 (4.11)	17.68 (17.55)	14.82 (14.28)	15.7
10	$[\mathrm{Cu}(\mathbf{L2})\cdot \mathrm{OH}]$	1	1	262 Brown 74.8%	50.93 (51.04)	3.77 (3.78)	17.47 (17.55)	15.85 (15.21)	11.9
11	$[\mathrm{Zn}(\mathbf{L2})\cdot \mathrm{H_2O}]$	1	1	>360 Orange 91.8%	50.70 (51.79)	3.75 (4.56)	17.39 (17.35)	16.24 (16.72)	22.5
12	$[\mathrm{Cd}(\mathbf{L2})\cdot \mathrm{Cl}]^{\#}$	1	1	310 Yellow 85.4%	43.61 (43.33)	3.01 (3.36)	14.96 (14.52)	24.01 (23.16)	27.5
13	$[\mathrm{Hg}(\mathbf{L2})\cdot 3\mathrm{H_2O}]$	1	1	206 Red 12.1%	35.58 (34.86)	3.34 (3.62)	12.20 (12.25)	34.95 (34.54)	19.5
14	$[\mathrm{Co}(\mathbf{L3})\mathrm{Cl}]\cdot 2\mathrm{H_2O}$	1	1	>360 Violet 54.6%	45.46 (45.64)	4.29 (4.34)	16.56 (16.82)	13.94 (13.16)	54.1
15	$[\mathrm{Co}(\mathbf{L3})_2]\cdot \mathrm{H_2O}$	1	2	>360 Brown 44.3%	58.10 (58.69)	4.57 (4.53)	21.17 (21.05)	8.91 (8.48)	24
16	$[\mathrm{Ni}(\mathbf{L3})\cdot \mathrm{OH}]$	1	1	>360 Brown 54.6%	52.22 (53.01)	4.11 (4.05)	19.08 (19.45)	15.98 (15.14)	42.6
17	$[\mathrm{Cu}(\mathbf{L3})\cdot \mathrm{OH}]$	1	1	>360 Brown 91.3%	51.54 (51.97	4.05 (4.15)	18.78 (19.26)	17.04 (17.46)	44.5
18	$[\mathrm{Zn}(\mathbf{L3})\cdot \mathrm{OH}]$	1	1	304 Orange 69.4%	51.24 (50.74)	4.03 (4.70)	18.68 (17.51)	17.45 (17.79)	21.0
19	$[\mathrm{Cd}(\mathbf{L3})\cdot \mathrm{Cl}]\cdot 2\mathrm{H_2O}^{\mathrm{H}}$	1	1	>360 Brown 25.3%	40.35 (39.84)	3.81 (3.58)	14.71 (14.35)	23.61 (23.23)	8.88

(*Continued*)

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Table 2. Continued.

Cpd. no.	Compound	Ratio M	Ratio L	M.P. (°C) Color yield	% Calcd/found C	% Calcd/found H	% Calcd/found N	% Calcd/found M	Molar cond.
20	[Hg(**L3**) · Cl] · $2H_2O^I$	1	1	240 brown 3.5%	34.05 (33.45)	3.21 (2.96)	12.41 (11.39)	35.54 (35.50)	22.0

Cl%: Calcd (found): * = 15.39 (15.93); Δ = 6.68 (6.71); = 7.57 (7.60); H = 7.44 (7.25); I = 6.28 (5.90).

Table 3. Crystallographic data and structure refinement for $[Ni(\mathbf{L1})_2]$.

Empirical formula	$C_{32}H_{28}N_{10}Ni$
Formula weight	611.356
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	15.9503 (6)
b	7.4588 (2)
c	24.9803 (11)
α	90.00
β	102.4747 (14)
γ	90.00
V (Å^3)	2901.7 (2)
Z	4
Dx (mg m^{-3})	1.399
θ Range (°)	2.910–26.022°
Absorption coefficient μ (mm^{-1})	0.71
Absorption correction	None
Measured reflections	9535
Independent reflections	6402
Observed reflections	2141
Criterion	$I > 3.00\ \sigma(I)$
R(int)	0.043
θ Max	26.04
Index range	$h = -19 \rightarrow 19$, $k = -7 \rightarrow 7$, $l = -30 \rightarrow 30$
Reflections collected	2138
Restraints/parameters	0/388
R(all)	0.167
R(gt)	0.044
wR(ref)	0.076
wR(all)	0.118
wR(gt)	0.077
S(ref)	2.292
S(all)	2.485
S(gt)	2.29
Δ/σ_{max}	0.006
Δ/ρ_{max} (e Å^3)	0.87
Δ/ρ_{min} (e Å^3)	−0.93

3. Results and discussion

3.1. *Mass spectrometry*

The mass spectra showed base peaks at $m/z = 277$, 321 and 293 for **L1**, **L2** and **L3**, respectively, corresponding to molecular weights that confirm the suggested molecular

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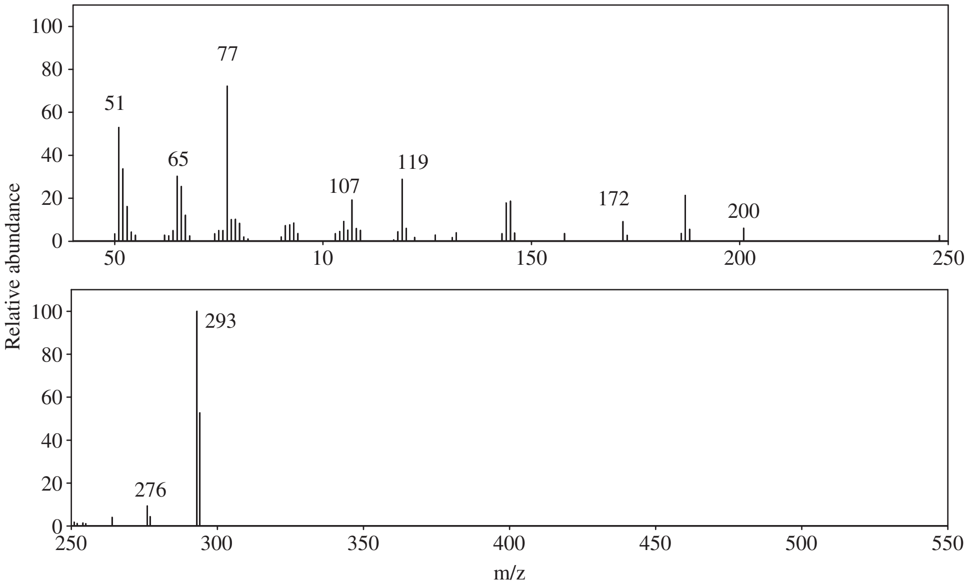

Figure 1. Mass spectrum of **L3**.

formula as represented in figure 1. The fragmentation, scheme 1, proceeds through four pathways. Pathway A shows the loss of the substituent, leading to $m/z = 276$. Fragment at $m/z = 172$ corresponding to the pyrazole moiety can be achieved from pathway B. Pathway C shows a peak at $m/z = 200$ as a result of the pyrazolyl azo fragment. Pathway D, due to cleavage of heterocyclic skeletal, gives $m/z = 119$. **L3** shows $m/z = 107$ through an additional pathway E corresponding to ($C_6H_6NO^+$) that may be attributed to the hydrogen bond between azo and hydroxyl group. This fragment undergoes further cleavage to produce ($C_6H_5O^+$), $m/z = 93$. All pathways led to the peak at $m/z = 77$ ($C_6H_5{}^+$) followed by further fragmentation at $m/z = 51$ due to $[C_4H_3]^+$.

3.2. *Molar conductance measurements*

The molar conductance values of 10^{-3} M solutions of the complexes in DMF at 25°C were found to be in the range 3.3–54.1 $\mathrm{Ohm^{-1}\,mole^{-1}\,cm^2}$, indicating the non-electrolytic nature of these complexes [20, 21].

3.3. *IR and Raman spectra*

Chelation sites in the complexes were investigated by studying IR and Raman spectra compared to those of the free ligands. Table 4 shows the IR and Raman band assignments for ligands and their complexes.

The IR spectra for **L1** and **L2** showed bands at 3464–3317, 3286–3132 and 1605–1628 $\mathrm{cm^{-1}}$ corresponding to NH-stretching asymmetric, symmetric and scissoring NH_2 vibrations [22], respectively; these bands are very weak in Raman spectra.

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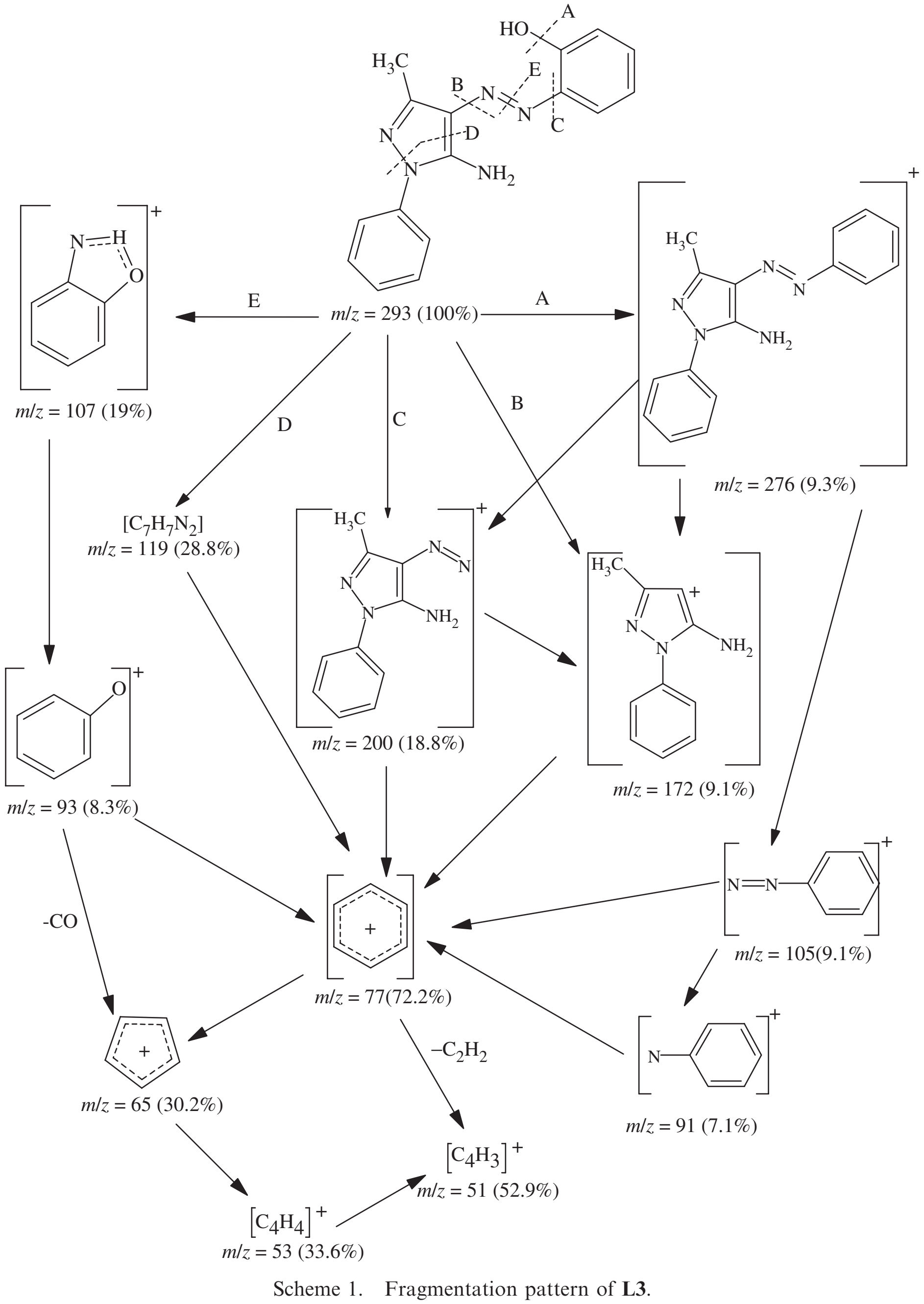

Scheme 1. Fragmentation pattern of **L3**.

IR spectra of the hydroxyl derivative **L3** showed υ(N–H) as a broad band at 3060–3333 cm^{-1}, broadened due to the stretching vibration of OH attached to the aromatic moiety. Corresponding bands in IR spectra of metal complexes are shifted to lower and higher frequencies in comparison to those of the free ligands (table 4). (N–H) vibration may be merged with broad νOH of water molecules in complexes that

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Table 4. IR (Raman) bands assignment for the ligands and their complexes.

	IR(Raman)								
Compound	$\upsilon\mathrm{NH_2}$	$\upsilon\mathrm{C{=}O}$	$\delta\mathrm{NH}$	$\upsilon\mathrm{N{=}N}$	υC–O	υM–O	υM–N amino	υM–N azo	υM–Cl
L1	3352s (–)	–	1608 (1597)s	1389s (1398)s	–	–	–	–	–
[Co(**L1**)$_2$]	3352 (3344)	–	1597sh (1587)s	1389sh (1368)	–	–	478w (453)	421 (421)	–
[Ni(**L1**)$_2$]	3348 (–)	–	1597sh (1591)s	1400sh (1397)sh	–	–	459w (455)	421 (423)	–
[Cu(**L1**)$_2$]	3367s (–)	–	1577 (–)	1400vs (–)	–	–	478 (–)	– (–)	–
[Zn(**L1**)$_2$]	3298 (–)	–	1597s (1593)s	1396vs (1398)m	–	–	– (454)	409 (412)	–
[Cd(**L1**) · 2Cl]	3302 (–)	–	1609 (–)	1396 (–)	–	–	– (–)	– (–)	–
[Hg(**L1**)Cl · H$_2$O]	3341 (–)	–	1609 (–)	1392 (–)	–	–	478 (–)	425 (–)	–
[Hg(**L1**)$_2$]	3400- 3310b (–)	1744sh –	1593 (–)	1396s (–)	–	–	478 (–)	– (–)	–
L2	3400- 3310b (–)	1747sh (–)	1705 (1710)	1396m (1394)s	1265 (1265)	–	–	–	–
[Co(**L2**) · H$_2$O]	3294 (–)	–	1589sh (1600)s	1381m (1367)s	1311m (1308)s	510 (516)	– (450)	– (410)	–
[Ni(**L2**) · OH]	3200 (–)	1747sh –	1597s (1599)s	1393sh (1393)m	1300s (1298)	517 (519)	459 (447)	– (407)	–
[Cu(**L2**) · OH]	3271 (–)	1747sh (–)	1604 (1622)	1381sh (1386)vs	1303s (1310)	516 (506)	– (446)	424 (427)	–
[Zn(**L2**) · H$_2$O]	3352s (–)	–	– (1597)s	1389 (1370)m	1250 (1265)	510 (510)	459 (451)	405 (420)	–
[Cd(**L2**) · Cl]	3352 (3344)	–	1609s (1586)s	1393s (1389)vs	1258 (1248)	510 (–)	460 (461)	420 (418)	(286)
[Hg(**L2**) · 3H$_2$O]	3300s (3300-3100)	1748 (–)	1601s (1580)s	1354m (1364)vs	1304sh (1272)s	520 (522)	– (450)	– (421)	–
L3	3333w (3245)s	–	1605s (1601)s	1373 (1390)	1248 (1265)	–	–	–	–
[Co(**L3**)Cl] · 2H$_2$O	3282 (–)	–	1632s (1656)	1373 (1404)	1265 (–)	517 (–)	471 (–)	421 (–)	–
[Co(**L3**)$_2$] · H$_2$O	–	–	1620 (–)	1339 (–)	1265 (–)	(–) –	466 (–)	424 (–)	–
[Ni(**L3**) · OH]	3371 (–)	–	1632 (–)	1373 (–)	1257 (–)	(–) –	471 (–)	428 (–)	–
[Cu(**L3**) · OH]	3400- 3310b (–)	–	1600sh (1598)	1400 (1393)s	1269 (1265)	517 (–)	471 (487)	421 (420)	–
[Zn(**L3**) · OH]	3400- 3310b (3358)	–	1566s (1568)s	1339sh (1366)s	1265sh (1251)s	– (525)	470 (496)	417 (421)	–
[Cd(**L3**) · Cl] · 2H$_2$O	3345 (–)	–	1627 (1568)s	1385 (–)	1267 (1258)	513 (517)	– (486)	417 (–)	– (286)
[Hg(**L3**) · Cl] · 2H$_2$O	3352s (–)	–	1597sh (1587)s	1389sh (1368)	–	–	478w (453)	421 (421)	–

contain water. IR spectra of **L1–L3** showed υN=N as a medium band at 1396–1373 cm^{-1} [23], Raman spectra showed this band as strong at 1398–1390 cm^{-1}. IR and Raman spectra of **L1** complexes showed υN=N at slightly higher frequencies, while the complexes of **L2** and **L3** showed this band at lower frequency. These shifts, as well as elongation in N=N bond length in comparison to those of the free ligands (as will be discussed later in the X-ray section), indicate involvement of the azo group in coordination with the metal ion ($M \leftarrow N$) [24]. IR (Raman) spectra of **L2** showed a sharp band at $1705\,cm^{-1}$ ($1710\,cm^{-1}$), assigned to C=O stretching vibration. Complexes of **L2** showed a very weak band at $1743–1747\,cm^{-1}$ assigned for υC=O revealing participation of carboxylate in chelation. **L2** complexes show bands at $1489–1500\,cm^{-1}$ assigned to the symmetrical COO^- which appeared in the ligand at $1504\,cm^{-1}$; asymmetric COO^- band at $1420–1300\,cm^{-1}$ [25] is obscured by υC=C. This band is not observed in the Raman spectra of the complexes. Three new bands appeared in the far IR and (Raman) spectra of the complexes at 510–520 (506–525), 459–478 (446–486) and 405–425 (407–423) cm^{-1} due to υM–O, M–N of azo group and M–N of amino, respectively. Raman spectra of [Cd(**L2**)·Cl], [Cd(**L3**)·Cl]·$2H_2O$ and [Hg(**L3**)·Cl]·$2H_2O$ showed an additional band at $286\,cm^{-1}$ which may be assigned to (M–Cl) stretching mode [26].

3.4. *^{1}H-NMR spectroscopy*

^{1}H-NMR spectra of the ligands and their Zn^{2+}, Cd^{2+}, and Hg^{2+} complexes (figure 2) showed signals at δ 2.4 and δ 2.5 ppm corresponding to CH_3 protons attached to the pyrazole [27, 28] and CH_3 protons of DMSO [25]. The spectra of **L2** and **L3** showed distinct signals at δ 3.3 and 10.6 ppm attributed to COOH and OH protons which disappeared on deuteration [25]. Such bands are disappeared in Zn^{2+}, Cd^{2+}, and Hg^{2+} complexes confirming participation of carboxylic and hydroxyl groups in chelation. Multiplet signals at 6.9–8.0 ppm are assigned to nine aromatic and two amino protons. Integration of the spectra of the Zn^{2+}, Cd^{2+} and Hg^{2+} complexes in this range show participation of NH_2 group in chelation. The ^{1}H-NMR spectra of [Hg(**L1**)Cl·H_2O], [Zn(**L2**)·H_2O], [Hg(**L2**)·$3H_2O$], [Cd(**L3**)·Cl]·$2H_2O$ and [Hg(**L3**)·Cl]·$2H_2O$ exhibit a new sharp signal at 3.4 ppm corresponding to water molecules that exist in the formed complexes [29].

3.5. *Thermogravimetric (TG) analysis*

TGA has been performed to examine the presence and nature of water molecules and to study the thermal stability of the formed complexes. Thermal data of the prepared complexes are depicted in table 5. The obtained TG thermograms exhibited several mass loss steps. The initial weight loss occurring within the temperature range 50–150°C is attributed to the loss of water of hydration. The mass loss exhibited at 150–200°C is due to coordinated water molecules in the complexes. All complexes yield metal oxides as the final residue except [Cd(**L2**)Cl] and [Cd(**L3**)·Cl]·$2H_2O$ that yield $CdO + CdCl_2$ as the final residue. Metal content estimated from titration with EDTA confirmed the obtained data.

3.6. *Electronic absorption spectra*

3.6.1. Electronic absorption spectra of the ligands in ethanol. The electronic absorption spectra for 5×10^{-5} M ethanolic solution of (**L1**–**L3**) ligands were scanned between

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200–700 nm, showing four bands at 206–209 nm, 214–216 nm, 238–242 nm and 370–408 nm assigned to π–π* transitions within the phenyl moiety (^1L_a-1_A) [30, 31], π–π* transitions within the pyrazole ring [27], low energy π–π* electronic transition of the phenyl moiety (^1L_b-1_A) [32] and π–π* electronic transition of the conjugated π–system of the hydrazone influenced by charge transfer through the molecule [33], respectively. **L2** shows an additional band at 317 nm ascribed to

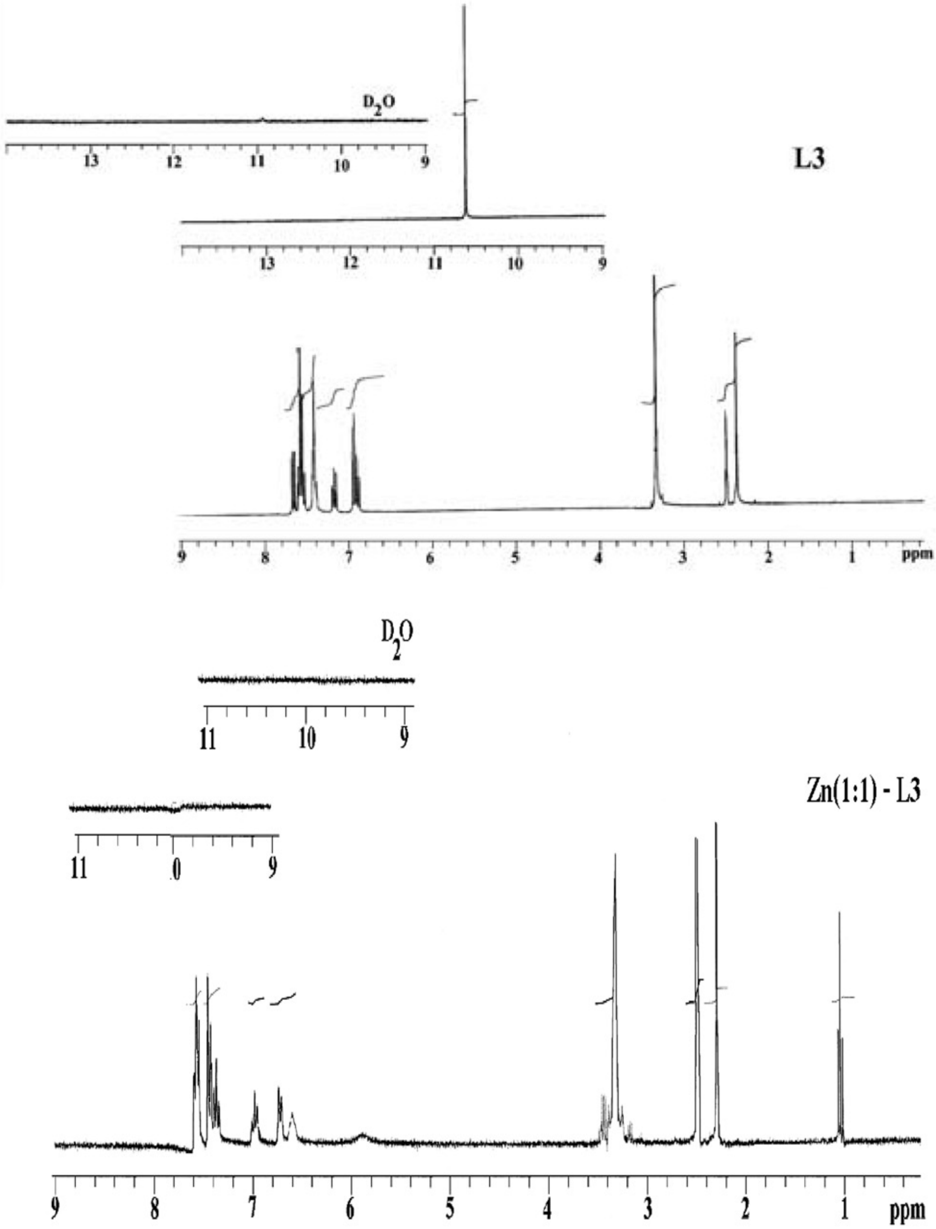

Figure 2. ^{1}H-NMR spectra for **L3** and its Zn complex.

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the *n*–*π** transition of carbonyl (C=O) and azo (N=N) groups within the *π*–electronic system.

3.6.2. Electronic absorption spectra of complexes in DMF and magnetic susceptibility.

The electronic absorption spectra of 5×10^{-5} M of **L1**–**L3** and their complexes have been recorded in DMF at room temperature in the range 280–700 nm (figure 3). The free ligands **L1**–**L3** exhibited intense bands at 375, 395 and 420 nm, respectively, due to intra-ligand electronic transition *π*–*π**. The spectra of metal chelates showed a red shift for this band that can be attributed to charge transfer (L-M CT). Additional bands in the region 503–654 nm are ascribed to d–d transitions of the metal

Table 5. Thermal analysis data of complexes of **L1**, **L2** and **L3** substituent with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions.

	Water of hydration			Water of coordination			% of metal residue		
		Water loss%			Water loss%				
Formula	Temp up to °C	Calcd	Found	Temp up to °C	Calcd	Found	Temp up to °C	Calcd	Found
$[Cu(L1)_2]$	–	–	–	–	–	–	710	20.61	22.60
$[Zn(L1)_2]$	–	–	–	–	–	–	541	13.17	13.50
$[Hg(L1)_2]$	–	–	–	–	–	–	800	28.7	26.50
$[Co(L2)H_2O]$	–	–	–	200	4.55	5.00	470	18.91	19.35
$[Ni(L2)OH]$	–	–	–	–	–	–	600	18.86	20.77
$[Cu(L2)OH]$	–	–	–	–	–	–	600	19.84	19.00
$[Zn(L2)\cdot H_2O]$	–	–	–	190	4.47	4.54	490	20.20	19.88
$[Cd(L2)\cdot Cl]$	–	–	–	–	–	–	800	33.24	33.00
$[Hg(L2)3H_2O]$	–	–	–	200	9.42	9.48	600	37.73	36.26
$[Co(L3)_2]\cdot H_2O$	40	2.72	3.57	–	–	–	600	11.33	12.81
$[Co(L3)Cl]\cdot 2H_2O$	75	8.50	8.99	–	–	–	600	17.71	18.30
$[Ni(L3)OH]$	–	–	–	–	–	–	600	20.30	21.06
$[Cu(L3)OH]$	–	–	–	–	–	–	600	21.33	23.14
$[Zn(L3)OH]$	–	–	–	–	–	–	600	25.98	25.89
$[Cd(L3)\cdot Cl]\cdot 2H_2O$	67	7.57	5.90	–	–	–	700	32.73	33.45

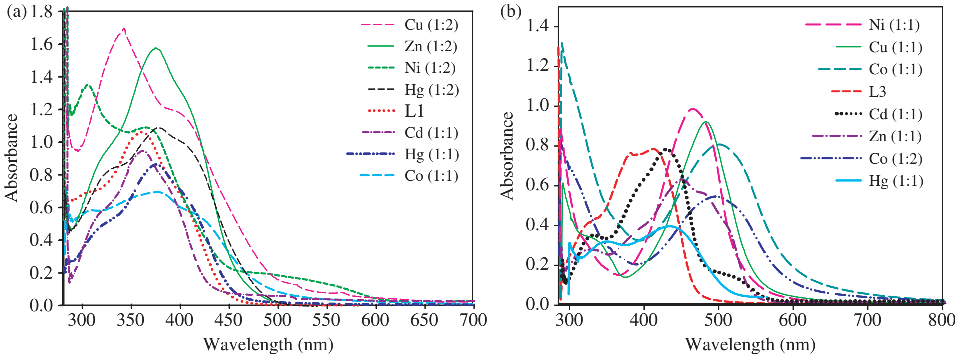

Figure 3. Electronic absorption spectra of 5×10^{-5} M of **L1** (a) and **L3** (b) and their complexes in DMF.

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ions of the complexes. Chelates with formula [Co(**L1**)$_2$], [Co(**L2**) $\cdot$ H_2O], and [Co(**L3**) $\cdot$ Cl] $\cdot$ 2H_2O showed broad bands at 19,880, 20,181 and 19,960 cm^{-1}, respectively, due to $^4A_2 \rightarrow {}^4T_1(P)$. The magnetic moment values are 5.3, 4.6 and 4.8 B.M., respectively. A tetrahedral geometry is suggested for these chelates [34]. On the other hand, [Co(**L3**)$_2$] $\cdot$ H_2O showed a band at 19,960 cm^{-1} due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$ indicating octahedral geometry [35], confirmed by its magnetic moment of 3.80 B.M. Spin orbit coupling may contribute to the high magnetic values of the cobalt complexes [36].

The electronic spectra for [Ni(**L1**)$_2$], [Ni(**L2**) $\cdot$ OH] and [Ni(**L3**) $\cdot$ OH] showed bands at 27,100, 19,880 and 21,482 cm^{-1}, respectively, assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions which are in good agreement for square planar geometry [37]. [Ni(**L1**)$_2$] and [Ni(**L2**) $\cdot$ OH] had magnetic moments of 2.04 and 1.15 B.M., respectively. This deviation from diamagnetism may result from the slight distortion of the planar geometry as shown by X-ray crystallographic analysis for [Ni(**L1**)$_2$]; we did not attempt to fit this data. [Ni(**L3**) $\cdot$ OH] was diamagnetic, in good agreement with square planar geometry [38].

The electronic spectra of [Cu(**L1**)$_2$], [Cu(**L2**) $\cdot$ OH] and [Cu(**L3**) $\cdot$ OH] showed bands at 23,474, 23,094 and 20,855 cm^{-1}, respectively, assigned to $^2B_{1g} \rightarrow {}^2E_g$. The position of the bands with their magnetic moment values 2.13, 1.87 and 2.03 B.M. are assigned to square planar complexes [38].

Zn(II), Cd(II) and Hg(II) complexes exhibited electronic transitions at 31,298–26,212 cm^{-1} corresponding to ligand-metal charge transfer, probably π–π* [39]. The electronic spectra of [Zn(**L1**)$_2$], [Zn(**L2**) $\cdot$ H_2O] and [Zn(**L3**) $\cdot$ OH] exhibited additional broad bands at 26,420, 23,094 and 22,573 cm^{-1}, respectively, assigned to tetrahedral geometry for these chelates [40]. Magnetic moments of Zn(II), Cd(II) and Hg(II) complexes revealed their diamagnetic nature.

3.7. *Crystal structure of [Ni(L1)$_2$]*

[Ni(**L1**)$_2$] crystallizes in the monoclinic space group $P2_1/c$. Its crystallographic structure and schematic numbering of its atoms is illustrated in figure 4. Selected bond lengths and angles are listed in table 6. Packing diagram in the unit cell [Ni(**L1**)$_2$] is illustrated in figure 5.

The X-ray diffraction revealed that the investigated pyrazole derivative **L1** is bidentate *via* azo and amino nitrogens. The geometry around nickel atom is probably best described as being slightly distorted square planar, where the bond angles around the Ni atom N(3)–Ni(1)–N(5), N(3)–Ni(1)–N(10), N(9)–Ni(1)–N(5) and N(9)–Ni(1)–N(10) are 90.80, 88.45, 90.28 and 93.40°, respectively. The coordination environment around the nickel deviates from linearity with bond angles that make the tetragonal plane Ni(1)–N(3)–N(2), 129.98°(14); Ni(1)–N(5)–C(15), 123.1°(2); Ni(1)–N(10)–C(14), 124.4°(2) and Ni(1)–N(9)–N(6), 128.49°(15). The remaining N–Ni–N angles, N(3)–Ni(1)–N(9) and N(5)–Ni(1)–N(10), are 169.66°(7) and 163.59°(8), respectively. The angular distortion may be due to steric crowding provided by the phenyl groups [42].

The N(2)–N(3) and N(6)–N(9) bond lengths are 1.311(2) and 1.309(2) Å, respectively. Comparisons for the free ligand are not available; free arylazo heterocyclic compounds are about 1.25 Å [41]. This elongation of the N–N bond length in the complex may be taken as evidence for azo group coordination with the nickel atom. Ni–N(3) and Ni–N(9) bond lengths are 1.917(2) and 1.929(2) Å, respectively, whereas Ni–N(5) and Ni–N(10) bond lengths are 1.865(2) and 1.861(2) Å, respectively, indicating that

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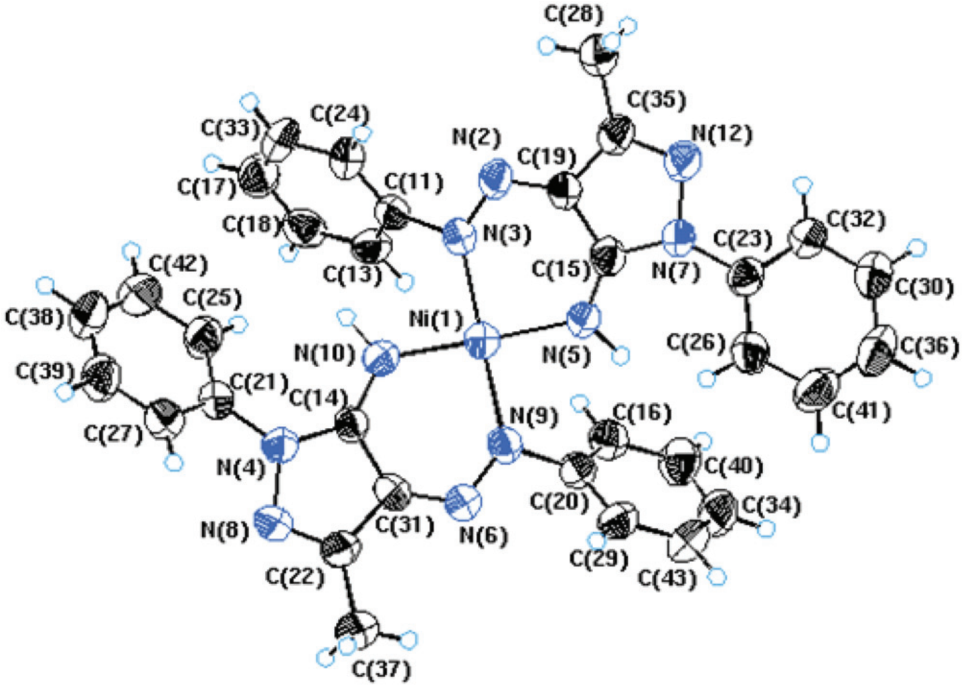

Figure 4. Single crystal X-ray structure of [Ni(**L1**)$_2$].

Table 6. Selected bond lengths (Å) and angles (°) of [Ni(**L1**)$_2$].

Bond lengths	(Å)	Bond angles	(°)
Ni1–N3	1.917 (2)	N3–Ni1–N5	90.80 (8)
Ni1–N5	1.865 (2)	N3–Ni1–N9	169.66 (7)
Ni1–N9	1.929 (2)	N3–Ni1–N10	88.45 (8)
Ni1–N10	1.861 (2)	N5–Ni1–N9	90.28 (8)
N2–N3	1.311 (2)	N5–Ni1–N10	163.59 (8)
N2–C19	1.335 (3)	N9–Ni1–N10	93.40 (8)
N3–C11	1.433 (3)	Ni1–N3–N2	129.98 (14)
N4–N8	1.414 (2)	N6–N9–C20	109.0 (2)
N4–C14	1.363 (3)	N2–N3–C11	110.3 (2)
N4–C21	1.419 (3)	N7–N12–C35	105.9 (2)
N5–C15	1.306 (3)	N12–N7–C23	118.2 (2)
N6–N9	1.309 (2)	Ni1–N5–C15	123.1 (2)
N6–C31	1.329 (3)	N4–N8–C22	104.2 (2)
N7–N12	1.423 (2)	N8–N4–C21	118.9 (2)
N7–C15	1.364 (3)	N4–C14–N10	130.9 (2)
N7–C23	1.417 (3)	N9–N6–C31	119.3 (2)
N8–C22	1.312 (3)	N7–C15–C19	105.4 (2)
N9–C20	1.441 (3)	C31–C22–C37	126.5 (2)
N10–C14	1.313 (3)	Ni1–N9–N6	128.49 (15)
N12–C35	1.299 (3)	Ni1–N9–C20	122.3 (2)
C14–C31	1.418 (3)	C19–C35–C28	126.5 (2)
C15–C19	1.427 (3)	N9–N6–C31	119.3 (2)
C22–C31	1.414 (3)	N9–C20–C16	118.5 (2)
C22–C37	1.503 (3)	C16–C20–C29	119.6 (2)
C28–C35	1.483 (3)	Ni1–N10–C14	124.4 (2)
N5–H5	0.960 (2)	N5–N3–C13	126.29 (10)
N10–H10	0.960 (2)	N4–C14–C31	104.7 (2)

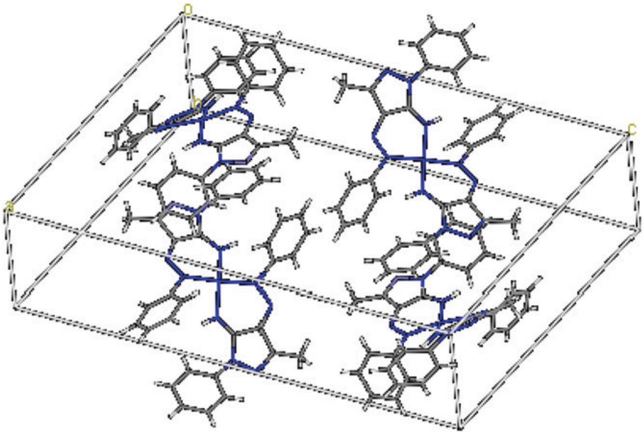

Figure 5. Packing diagram in the unit cell of [Ni(**L1**)$_2$].

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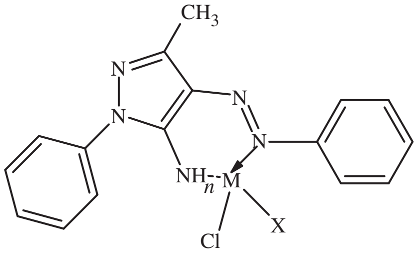
Ni atom is strongly coordinated to the two nitrogen donors of each ligand in addition to sthe interaction between Ni and the N = N π cloud [42].

4. Conclusion

Based on the results it can be concluded that:

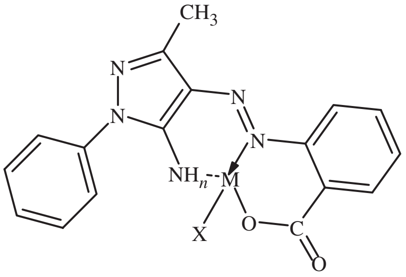
1. Unsubstituted phenylazo pyrazole derivative **L1** is a monobasic bidentate ligand in all of its chelates by deprotonation of the amine, except for Cd (1 : 1) complex where the two positive charges on Cd are neutralized with two Cl$^-$ ions.
2. **L2** is a dibasic tridentate ligand *via* azo, amino and carboxylate when coordinated with Co(II), Zn(II) and Hg(II). Where it is monobasic tridentate ligand, Ni(II), Cu(II) and Cd(II) complexes, it binds through its carboxylate group.
3. **L3** is a monobasic tridentate ligand via azo, amino and hydroxyl group in all of its complexes.

The structure of the investigated chelates can be represented by the following structures.



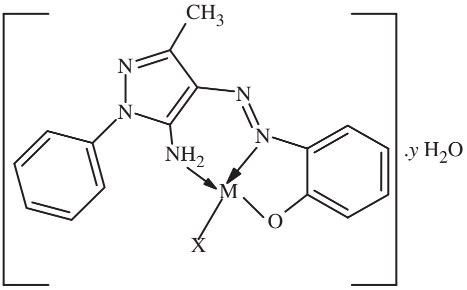
M	X	*n*
Cd	**Cl**	**2**
Hg	**H$_2$O**	**1**

1 : 1 complexes for L1



M	X	*n*
Co, Zn	**H_2O**	**1**
Hg	**$3H_2O$**	**1**
Ni, Cu	**OH**	**2**
Cd	**CI**	**2**

1 : 1 complexes for L2



M	X	*y*
Co, Cd, Hg	**CI**	**2**
Ni, Cu, Zn	**OH**	–

1 : 1 complexes for L3

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Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 606777 for [Ni(**L1**)$_2$]. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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