



## Synthesis and Characterization of Ni(II) and Cd(II) Complexes of 4-(4-Nitrophenylazo)-1H-pyrazole-3,5-diamine and 4-(4-Methylphenylazo)-1H-pyrazole-3,5-diamine

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In this study, the diazotized *p*-nitroaniline and *p*-methylaniline were coupled with malononitrile. The ring closure reaction of the obtained products with hydrazine monohydrate yielded 4-(4-methylphenylazo)-1H-pyrazole-3,5-diamine (L<sup>1</sup>) and 4-(4-nitrophenylazo)-1H-pyrazole-3,5-diamine (L<sup>2</sup>). The structure of the ligands has been elucidated by spectroscopic analyses. Then, novel Ni(II) and Cd(II) complexes of the ligands have been synthesized and the structures of these complexes determined by elemental analysis, spectrometric and TGA/DTA methods, molar conductance and magnetic susceptibility measurements. All the complexes were monomeric and diamagnetic. From the elemental analyses and mass spectra data, the complexes were proposed to the formulae [Ni<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(OH)<sub>2</sub>·2Cl·8.5H<sub>2</sub>O, [Cd<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(OH)<sub>2</sub>·2Cl·DMF·3H<sub>2</sub>O, [Ni(L<sup>2</sup>)<sub>2</sub>·2Cl·2DMF·7H<sub>2</sub>O and [Cd<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·2Cl·1.5H<sub>2</sub>O. For the Cd(L<sup>2</sup>) complex octahedral geometry was proposed, but the Ni(L<sup>1</sup>), Ni(L<sup>2</sup>) and Cd(L<sup>1</sup>) complexes show four coordinated structure. The Ni(L<sup>1</sup>), Cd(L<sup>1</sup>) and Cd(L<sup>2</sup>) complexes were found to be dinuclear. On the other hand the Ni(L<sup>2</sup>) complex was found to be mononuclear. All the complexes were found to be (1:2) electrolytes.

**Key Words:** 4-(4-Nitrophenylazo)-1H-pyrazole-3,5-diamine and Metal complexes, 4-(4-Methylphenylazo)-1H-pyrazole-3,5-diamine and Metal complexes, Azodyes complexes.

### INTRODUCTION

In general pyrazole, pyrimidine and its derivatives are known to possess pharmacological activity<sup>1</sup>. Hydrazono-amino-pyrazoles are considered as potential antipyretic and they were found to be effective against some kidney diseases<sup>2</sup>. Metabolic diseases, endocrine functions and oncology are some of the therapeutic areas in which the same compounds comprising the pyrazole ring are being improved. Some of the blockbuster drugs such as viagra, celebrex and acomplia<sup>3,4</sup> stands for the forthcoming examples for the prosperous commercializing of pyrazole containing compounds. They are also used as intermediates in the dyestuff industry<sup>5-17</sup> and there are some patent about these fused heterocyclic compounds<sup>18,19</sup>.

We aimed to obtain potential biological active new compounds. In our previous unpublished work, Ni(II), Cu(II) and Cd(II) complexes of the ligand 4-(2-chlorophenylazo)-1H-pyrazole-3,5-diamine were synthesized in DMF. Furthermore, in our second study Mn(II), Co(III), Ni(II) and Cd(II) complexes of the ligand 4-(2-nitrophenylazo)-1H-pyrazole-3,5-diamine were synthesized in methanol.

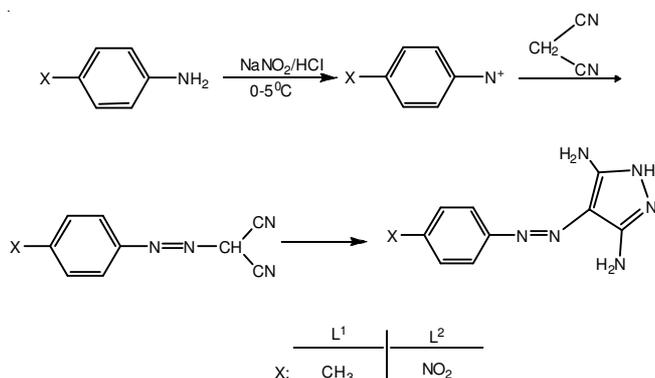
In this work, we have synthesized 4-(4-methylphenylazo)-1H-pyrazole-3,5-diamine (L<sup>1</sup>) and 4-(4-nitrophenylazo)-1H-pyrazole-3,5-diamine (L<sup>2</sup>). Firstly *p*-methylaniline and *p*-nitroaniline were diazotized and coupled with malononitrile then ring closure with hydrazine monohydrate, later their Ni(II) and Cd(II) complexes were synthesized by reaction of NiCl<sub>2</sub>·6H<sub>2</sub>O and CdCl<sub>2</sub>·H<sub>2</sub>O, respectively. Finally, the spectral and magnetic properties and thermal stabilities of all the compounds were studied in detail.

### EXPERIMENTAL

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. The IR spectra were recorded on a Perkin-Elmer Spectrum RX1 FTIR spectrometer on KBr discs in the wave number range of 4000-400 cm<sup>-1</sup>. Electronic spectral studies were conducted on a Shimadzu model 160 UV visible spectrophotometer in the wavelength 1100-300 nm. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using Hg[Co(SCN)<sub>4</sub>] as a calibrant. Thermogravimetric analyses were carried out on

TGA Shimadzu 50 thermal gravimetric analyzer. Molar conductivity was measured with a CMD WPA model 750 conductivity meter, using prepared solution of the complex in DMSO ( $10^{-3}$  M). LC/MS-API-ES mass spectra were recorded using a AGILENT model 1100 MSD mass spectrophotometer.

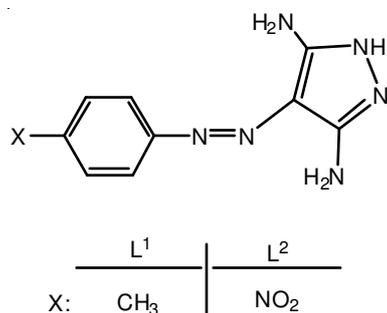
Except the ligand, all the other chemicals and solvents were of analytical grade and used as received. The ligands ( $L^1$  and  $L^2$ ) were synthesized according to **Scheme-I** by the procedure given by literature method<sup>4,15</sup>. In the synthesis of ligands have been occurring azo coupling and ring closure reaction<sup>4,15</sup>.



**Scheme-I:** Synthesis scheme for the preparation of the ligands ( $L^1$ - $L^2$ )

**Preparation of the 4-(4-methylphenylazo)-1H-pyrazole-3,5-diamine ( $L^1$ ):** 4-(4-Methylphenylazo)-1H-pyrazole-3,5-diamine ( $L^1$ ) was prepared by the literature method<sup>4,15</sup>. m.p. 280-282 °C, characteristic IR bands (KBr,  $cm^{-1}$ ):  $\nu(NH_2)$ : 3397 s, 3296 m, 3186 w;  $\nu(aliph\ C-H)$ : 2917 w;  $\nu(N=N)$ : 1607 s;  $\nu(C=N)$ : 1563 s;  $\nu(C=C, phenyl\ ring)$ : 1497 m;  $\delta(NH_2)$ : 1515 m;  $\nu(C-N)$ : 1366 m, 1129 s;  $\delta(NH)$ : 743  $m^{19}$ .

**Preparation of the 4-(4-nitrophenylazo)-1H-pyrazole-3,5-diamine ( $L^2$ ):** 4-(4-Nitrophenylazo)-1H-pyrazole-3,5-diamine ( $L^2$ ) was prepared by the literature method<sup>4,15</sup>. m.p.: 278-281 °C, characteristic IR bands (KBr,  $cm^{-1}$ ):  $\nu(NH_2)$ : 3453, 3378, 3346, 3241 m;  $\nu(Ar\ C-H)$ : 3100 w;  $\nu(C=C, pyrazole\ ring)$ : 1631 m;  $\nu(N=N)$ : 1615 m;  $\nu(C=N)$ : 1563 s;  $\delta(NH_2)$ : 1515 m;  $\nu(C=C, phenyl\ ring)$ : 1492 s;  $\nu(C-N)$ : 1403 s, 1126 m;  $\delta(NH)$ : 745  $m^{19}$ .



**Fig. 1.** Structure of the ligands ( $L^1$ - $L^2$ )

### Preparation of the complexes

**Preparation of the  $[Ni_2(L^1)_2(OH)_2]Cl_2 \cdot 8.5H_2O$ :** The ligand ( $L^1$ ) (0.15 g 0.61 mmol) was dissolved in 15 mL hot DMF in a 100 mL round-bottom flask. A solution of  $NiCl_2 \cdot 6H_2O$  (0.58 g, 2.44 mmol) in 5 mL DMF was added drop wise in 10 min periods with continuous stirring at room

temperature. After 0.5 h, the mixture was blurring and left under reflux for 6 h. Two-third of DMF solvent was vaporized and henna green coloured precipitate was obtained in the mixture (DMF/ $H_2O$ ) (1:5). The precipitated product was filtered off and washed with hot water and hot ethanol and dried at room temperature. The complex was found to be soluble in DMSO. m.p. dec. temp. > 310 °C. Yields: 0.22 g (79 %). Elemental analysis calcd. for  $(C_{20}H_{26}N_{12}O_2Cl_2Ni_2) \cdot 8.5H_2O$  (807.42 g/mol): C, 29.72; H, 5.077; N, 20.80. Found: C, 29.48; H, 4.857; N, 20.51 %. Characteristic IR bands (KBr,  $cm^{-1}$ ):  $\nu(OH, hydroxo\ bridge)$ : 3478 m;  $\nu(H_2O\ hydrate, br)$ : 3380;  $\nu(NH_2)$ : 3324, 3280, 3199 m;  $\nu(N=N)$ : 1606 s;  $\nu(C=N)$ : 1557 vs;  $\delta(NH_2)$ : 1508 m;  $\nu(C-N)$ : 1393 m, 1146 m;  $\delta(N-H)$ : 757 w;  $\nu(M-O)$ : 512 w;  $\nu(M-N)$ : 470 w;  $\Lambda_M^{20,21}$ : 165  $\Omega^{-1} cm^2 mol^{-1}$ . UV-Vis ( $\lambda_{max}, nm$ ) (DMSO): 331.6, 333, 374.5, 537.5, 631. Mass spectra<sup>20,21</sup>: m/z: 809.42  $[M+2H]^{+2}$ .

**Preparation of the  $[Cd_2(L^1)_2(OH)_2] \cdot 2Cl \cdot DMF \cdot 3H_2O$ :** The ligand ( $L^1$ ) (0.15 g 0.61 mmol) was dissolved in 15 mL hot DMF in a 100 mL round-bottom flask. A solution of  $CdCl_2 \cdot H_2O$  (0.49 g, 2.44 mmol) in 5 mL DMF was added drop wise in 10 min periods with continuous stirring at room temperature. The brown coloured mixture was formed after 20 min and was left under reflux for 6 h. Two-third of DMF solvent was vaporized and brown coloured precipitate was obtained in the mixture (DMF/ $H_2O$ ) (1:5). The precipitated product was filtered off and washed with hot water and hot ethanol and dried at room temperature. The complex was found to be soluble in DMSO. m.p. dec. 300 °C. Yields: 0.24 g (80 %). Elemental analysis calcd. for  $(C_{23}H_{39}N_{13}O_6Cl_2Cd_2) \cdot (888.82 g/mol)$ : C, 31.05; H, 4.39; N, 20.48. Found: C, 31.09; H, 4.36; N, 20.83 %. Characteristic IR bands (KBr,  $cm^{-1}$ ):  $\nu(OH, hydroxo-bridge)$ : 3480 s;  $\nu(NH_2)$ : 3330 m;  $\nu(H_2O, hydrate.)$ : 3425 br;  $\nu(aliph. C-H)$ : 2917 w;  $\nu(N=N)$ : 1606 s;  $\nu(C=N)$ : 1556 s;  $\nu(C=C)$ : 1497 m;  $\delta(NH_2)$ : 1522 m;  $\nu(C-N)$ : 1384 s, 1153 m;  $\delta(N-H)$ : 738 m;  $\nu(M-O)$ : 515 w;  $\nu(M-N)$ : 460 w.  $\Lambda_M^{20,21}$ : 163  $\Omega^{-1} cm^2 mol^{-1}$ . UV-Vis ( $\lambda_{max}, nm$ ) (DMSO): 372. Mass spectra<sup>20,21</sup>: m/z: 887.82  $[M-H]^+$ .

**Preparation of the  $[Ni(L^2)_2] \cdot 2Cl \cdot 2DMF \cdot 7H_2O$ :** The ligand ( $L^2$ ) (0.15 g, 0.61 mmol) was dissolved in 15 mL hot DMF in a 100 mL round-bottom flask. A solution of  $NiCl_2 \cdot 6H_2O$  (0.58 g, 2.44 mmol) in 5 mL DMF was added drop wise in 10 min periods with continuous stirring at room temperature. The reddish-brown coloured precipitate was formed after 0.5 h and left under reflux for 6 h. One-third of DMF solvent was vaporized. Then, the resulting reddish-brown coloured precipitate was obtained in chloroform and hexane mixture (3:1) was filtered off and firstly washed at the room temperature with hexane and  $CHCl_3$  and then with hot ethanol lastly dried at room temperature. The complex was found to be soluble in DMSO. m.p.: dec. temp. > 310 °C. Yields: 0.21 g (78 %). Elemental analysis calcd. for  $C_{24}H_{46}N_{16}O_{13}Cl_2Ni$  (895.71 g/mol): C, 32.15; H, 5.13; N, 25.01. Found: C, 31.87; H, 4.89; N, 25.43 %. Characteristic IR bands (KBr,  $cm^{-1}$ ):  $\nu(H_2O, hydrate)$ : 3434,  $\nu(NH_2)$ : 3326;  $\nu(C=C, pyrazole\ ring)$ : 1637;  $\nu(N=N)$ : 1602;  $\nu(C=N)$ : 1562;  $\delta(NH_2)$ : 1508;  $\nu(C=C, phenyl\ ring)$ : 1470;  $\nu(C-N)$ : 1381, 1154;  $\delta(N-H)$ : 752;  $\nu(M-N)$ : 469;  $\Lambda_M^{20,21}$ : 167  $\Omega^{-1} cm^2 mol^{-1}$ . UV-Vis ( $\lambda_{max}, nm$ ) (DMSO): 332, 463, 475, 478.4, 541, 550, 574, 628. Mass spectra<sup>20,21</sup>: m/z: 893.71  $[M-2H]^{+2}$ .

**Preparation of the  $[\text{Cd}_2(\text{L}^2)_2(\text{OH})_2(\text{H}_2\text{O})_4]\cdot 2\text{Cl}\cdot 1.5\text{H}_2\text{O}$ :**

The ligand ( $\text{L}^2$ ) (0.15 g 0.64 mmol) was dissolved in 15 mL hot DMF in a 100 mL round-bottom flask. A solution of  $\text{CdCl}_2\cdot\text{H}_2\text{O}$  (0.49 g, 2.44 mmol) in 5 mL DMF was added drop wise in 10 min periods with continuous stirring at room temperature. The reddish-orange coloured mixture was left under reflux for 6 h. One-third of DMF solvent was vapourized and was added 10 mL chloroform. Then, the resulting reddish-orange coloured precipitate was filtered off and firstly washed at the room temperature with hexane and chloroform and then with hot ethanol lastly the precipitated product was dried at room temperature. The complex was found to be soluble in DMSO and (DMF-DMSO) (1:1). m.p.: dec. 300 °C. Yields: 0.23 g (82 %). Elemental analysis calcd. for  $(\text{C}_{18}\text{H}_{28}\text{N}_{14}\text{O}_{10}\text{Cl}_2\text{Cd}_2)\cdot 1.5\text{H}_2\text{O}$  (922.82 (g/mol): C, 23.40; H, 3.359; N, 21.24. Found: C, 23.16; H, 3.087; N, 20.88 %. Characteristic IR bands (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH}$  hydroxo-bridge): 3510 s;  $\nu(\text{NH}_2)$ : 3412, 3346 m;  $\nu(\text{H}_2\text{O}$ , hydrate.): 3385 br;  $\nu(\text{C}=\text{C})$ : 1643 m;  $\nu(\text{N}=\text{N})$ : 1609 m;  $\nu(\text{C}=\text{N})$ : 1563 s;  $\delta(\text{NH}_2)$ : 1520 m;  $\nu(\text{C}-\text{N})$ : 1384 s; 1136 m;  $\delta(\text{N}-\text{H})$ : 741 m;  $\nu(\text{H}_2\text{O}$ , coord.): 801 w;  $\nu(\text{M}-\text{O})$ : 521 w;  $\nu(\text{M}-\text{N})$ : 460 w.  $\Lambda_M^{20,21}$ :  $164 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . UV-Vis ( $\lambda_{\text{max}}$ , nm) (DMSO): 451.5, 464, 466.9 469, 530.5, 540.5, 549.5. Mass spectra<sup>20,21</sup>: m/z: 911.82  $[\text{M}+\text{H}]^+$ .

**RESULTS AND DISCUSSION**

**Infrared spectra:** The IR data of the ( $\text{L}^1$ ) and ( $\text{L}^2$ ) ligands and their metal complexes were given in experimental section.

In the IR spectra of the isolated Ni(II) and Cd(II) complexes of the ligands ( $\text{L}^1$ ), the characteristic stretching vibration bands are at 3330-3199  $\text{cm}^{-1}$   $\nu(\text{NH}_2)$  and 1508, 1522  $\text{cm}^{-1}$   $\delta(\text{NH}_2)$ , respectively. In the free ligand ( $\text{L}^1$ ), the intense and sharp  $\nu(\text{C}=\text{N})$  stretching vibration band is observed at 1563  $\text{cm}^{-1}$ . In the Ni(II) and Cd(II) complexes, these bands appear at lower frequency in 1557, 1556  $\text{cm}^{-1}$  regions, respectively, confirming the involvement of the  $\text{C}=\text{N}$  moiety in complexes formation<sup>20,21</sup>. The  $\delta(\text{NH}_2)$  band of the free ligand ( $\text{L}^1$ ) are shifted considerably to lower wave number (1515  $\text{cm}^{-1}$ ) supporting coordination of the ligand to the Ni(II) ion *via* the amino nitrogen atom<sup>20-23</sup>. In the IR spectra of the Cd(II) complex of the ligand ( $\text{L}^1$ ), the stretching vibration bands at 3330  $\text{cm}^{-1}$   $\nu(\text{NH}_2)$  and 1522  $\text{cm}^{-1}$   $\delta(\text{NH}_2)$  on the pyrazole ring were shifted to higher frequencies<sup>20</sup>. The IR and spectroscopic data, therefore, suggest that the ligand is coordinated to the Ni(II) and Cd(II) ions *via* the amino nitrogen and the  $\text{C}=\text{N}$  moiety.

The new absorption bands assigned to the M-O (bridging  $\text{OH}^-$ ) and M-N stretching frequencies of the Ni(II) and Cd(II) complexes of  $\text{L}^1$  were observed at 512, 515 and 470, 460  $\text{cm}^{-1}$ , respectively<sup>20,22-24</sup>. Moreover, the presence of a sharp signals at 3478 and 3480  $\text{cm}^{-1}$  in the Ni(II) and Cd(II) complexes can be assigned to the OH stretching frequency of the hydroxo-bridge<sup>25</sup>. On the other hand, the spectra of the Ni(II) and Cd(II) complexes of  $\text{L}^1$  exhibited broad and a medium intense new bands at 3380, 3425  $\text{cm}^{-1}$ , respectively, due to  $\nu(\text{OH})$  of hydrated water molecules<sup>20,21,24,26</sup>. The presence of lattice water is also confirmed by thermogravimetric analyses.

IR spectrum of the ligand ( $\text{L}^2$ ) exhibited a band 3453-3241  $\text{cm}^{-1}$  attributed to  $\nu(\text{NH}_2)$  band. The band observed at

1515  $\text{cm}^{-1}$  in the free ligand assigned to  $\delta(\text{NH}_2)$  is shifted to lower or higher frequencies in Ni(II) and Cd(II) complexes. The other  $\nu(\text{NH}_2)$  stretching vibrations are overlap under  $\nu(\text{OH})$  stretching frequency (3434  $\text{cm}^{-1}$ , br) of hydrated water molecules<sup>27</sup>.

The solid state IR spectra of the complexes compared with those of the ligand ( $\text{L}^2$ ) indicate that the  $\text{N}=\text{N}$  band 1615  $\text{cm}^{-1}$  is shifted to lower values (1602, 1609  $\text{cm}^{-1}$ , respectively) for Ni(II) and Cd(II) complexes. Further evidence of the metal ions was shown by the appearance of weak low frequency new bands 469 and 460  $\text{cm}^{-1}$  which can be assigned for  $\nu(\text{Ni}-\text{N})$  and  $\nu(\text{Cd}-\text{N})$ <sup>20-24,26</sup>. These changes suggest that amine group and  $-\text{N}=\text{N}-$  moiety are involved in metal ion coordination<sup>20,21,26,27</sup>.

In the spectra of the Ni(II) and Cd(II) complexes of  $\text{L}^2$  exhibited broad and a medium intense new bands at 3434, 3385  $\text{cm}^{-1}$ , respectively, due to  $\nu(\text{OH})$  of hydrated water molecules<sup>20,21,24,26</sup>. The new absorption bands assigned to the (coord.  $\text{H}_2\text{O}$ ) and M-O (bridging  $\text{OH}^-$ ) stretching frequencies of the Cd(II) complex of  $\text{L}^2$  were observed at 801 and 521  $\text{cm}^{-1}$ , respectively<sup>20, 22-24</sup>.

Moreover, the presence of a sharp signal at 3510  $\text{cm}^{-1}$  in the Cd(II) complex can be assigned to the OH stretching frequency of the hydroxo-bridge<sup>25</sup>. The infrared spectra of ligand ( $\text{L}^2$ ) showed band at 1631  $\text{cm}^{-1}$  assigned to the  $\nu(\text{C}=\text{C})$  vibration. However, in the spectra of the Ni(II) and the Cd(II) the  $\text{C}=\text{C}$  band shifted to the higher region 1637, 1643  $\text{cm}^{-1}$ , respectively<sup>28,29</sup>. This phenomenon may be correlated with the decrease in the electronic density of the pyrazole ring. At the same time, the donor character of the nitrogen atom in the M-N bond has been increasing<sup>29</sup>.

The conclusive evidences in the IR spectra of the Ni(II) and Cd(II) complexes of the ligand ( $\text{L}^1$ ) indicate that the ligand behaves as a bidentate ligand and the coordinating sites are N atom of  $-\text{NH}_2$  group and on the pyrazole ring  $\text{C}=\text{N}$  moiety.

On the other hand, in the IR spectra of the Ni(II) and Cd(II) complexes of the ligand ( $\text{L}^2$ ) indicate that the ligand behaves as a bidentate ligand and the coordinating sites are N atom of  $-\text{NH}_2$  group on the pyrazole ring and  $-\text{N}=\text{N}-$  moiety.

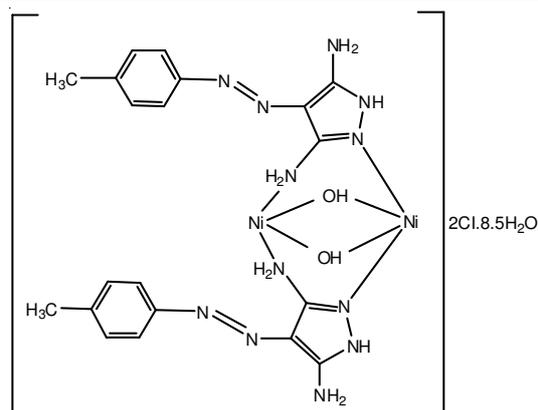
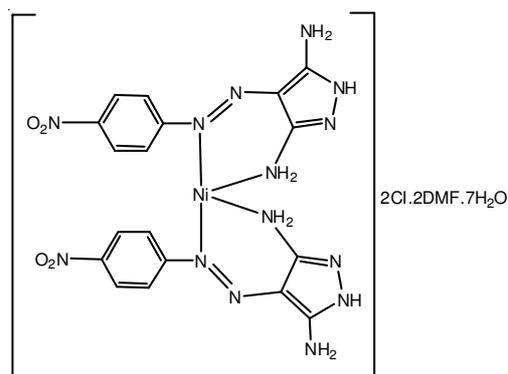
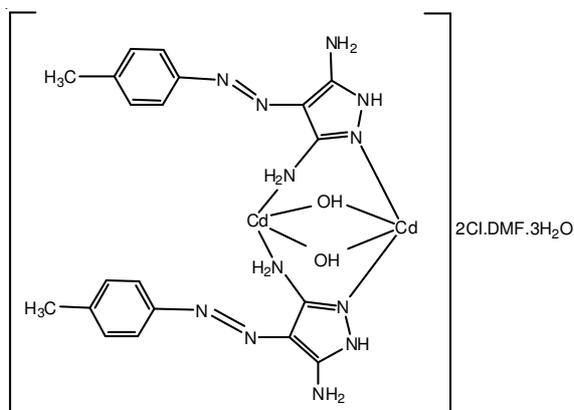
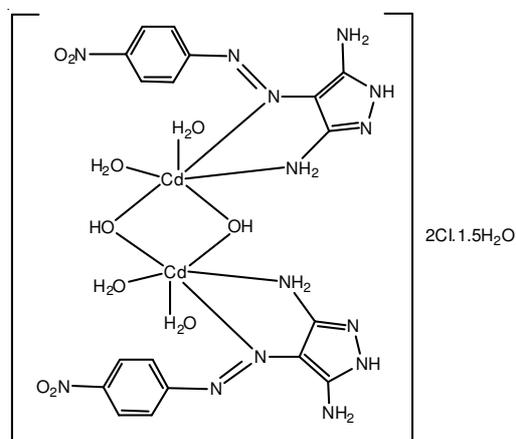
The coordinated halogen in the complexes shows a far IR absorption peak in the range 294-230  $\text{cm}^{-1}$ , which may be attributed to  $\nu(\text{M}-\text{Cl})$ <sup>26,30</sup>. However, the IR spectra of the complexes, (M-Cl) bands could not be observed, which we have studied in 4000-400  $\text{cm}^{-1}$  range.

In the Ni(II) and Cd(II) complexes of the ligands ( $\text{L}^1$  and  $\text{L}^2$ ), the chloride ions are coordinate with the metal ions (Figs. 2-5). In the Cl- test with  $\text{AgNO}_3$ , we observed precipitation of white  $\text{AgCl}$  salt immediately as an evident. Therefore, these complexes have been including free  $\text{Cl}^-$  ions<sup>26</sup>.

**Magnetic, electronic spectral and conductivity studies:**

All the complexes were found (at 294 K) diamagnetic by the magnetic measurements. The square planar geometry of the Ni(II) complex of either two ligands causes diamagnetic character<sup>31</sup>.

The absorption band attributable to *d-d* transition in the spectra of Ni( $\text{L}^1$ ) and Ni( $\text{L}^2$ ) complexes observed a broad shoulders centered at about 15924  $\text{cm}^{-1}$  (628 nm) and 15848  $\text{cm}^{-1}$  (631 nm), respectively. This absorption is due to the square planar geometry of the diamagnetic Ni(II) complex<sup>32</sup>.

Fig. 2. Suggested structure of Ni(II) complex of the ligand ( $L^1$ )Fig. 3. Suggested structure of Ni(II) complex of the ligand ( $L^2$ )Fig. 4. Suggested structure of Cd(II) complex of the ligand ( $L^1$ )Fig. 5. Suggested structure of Cd(II) complex of the ligand ( $L^2$ )

The molar conductivity measurements of all complexes were recorded in DMSO ( $1 \times 10^{-3}$  M), which is in the range  $163\text{--}167 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . All complexes of the ligands behave as 1:2 electrolyte. Therefore, these complexes have been included free  $\text{Cl}^-$  ions<sup>20,21</sup>.

**Thermal studies:** The thermal stability of the complexes was investigated by a combination of TGA and DTA. The thermal stability of the complexes curves were obtained at a heating rate of  $15 \text{ }^\circ\text{C}/\text{min}$  in a nitrogen atmosphere over a temperature range of  $20\text{--}800 \text{ }^\circ\text{C}$ . The thermal data are summarized in Table-1. The results are in good agreement with the theoretical formula suggested by the mass spectra and the elemental analyses. The mass losses for complexes were calculated within the corresponding temperature ranges.

The Ni(II) complex which has the general formula  $[\text{Ni}_2(\text{L}^1)_2(\text{OH})_2]\text{Cl}_2 \cdot 8.5\text{H}_2\text{O}$  exhibits two decomposition steps. The decomposition curve of Ni(II) complex begins by a step at  $50\text{--}365 \text{ }^\circ\text{C}$ , displaying (% experimental mass 22.40; calculated mass 23.16) mass loss corresponding to the removal of 8.5 moles hydrated water molecule and  $2\text{OH}^-$  (bridging  $\text{OH}^-$ )<sup>20,21,25,28,33</sup>. The second stage ending at  $365\text{--}395 \text{ }^\circ\text{C}$ , the mass loss is assigned to the elimination of  $2\text{HCl}$  molecules as the free  $\text{Cl}^-$  ion in the complex (% experimental mass 9.60; calculated mass 9.04)<sup>26,34</sup>. The DTA curve of the complex exhibits two exothermic peaks at  $370$  and  $450 \text{ }^\circ\text{C}$ . The decomposition stage of the complex is irreversible<sup>26,35</sup>.

The decomposition curve of  $[\text{Cd}_2(\text{L}^1)_2\text{Cl}_2(\text{OH})_2] \cdot \text{DMF} \cdot 3\text{H}_2\text{O}$  begins by a step at  $48\text{--}275 \text{ }^\circ\text{C}$ , displaying (% experimental mass 13.92; calculated mass 14.28) mass loss corresponding to the removal of  $3\text{H}_2\text{O}$  (hydrated water molecules) and  $\text{DMF}$ <sup>20,21,26,29</sup>. The second stage ending at  $275\text{--}290 \text{ }^\circ\text{C}$ , the mass loss is assigned to the  $2\text{OH}^-$  (bridging  $\text{OH}^-$ ) ions in the complex (% experimental mass 3.48; calculated mass 3.83)<sup>25,32</sup>. The third step within the temperature range of  $290\text{--}345 \text{ }^\circ\text{C}$  correspond to the removal of  $2\text{HCl}$  ( $\text{Cl}^-$  free ion) molecules as deduced from mass loss calculations (experimental mass loss of 8.69 %, calculated mass loss 8.21 %)<sup>26,34</sup>. The DTA curve of the complex exhibits two exothermic peaks at  $290$  and  $710 \text{ }^\circ\text{C}$ . The two stages of the complex decomposition are irreversible<sup>26,35</sup>.

The Ni(II) complex which has the general formula  $[\text{Ni}(\text{L}^2)_2] \cdot 2\text{Cl} \cdot 2\text{DMF} \cdot 7\text{H}_2\text{O}$  exhibits two decomposition steps. The first decomposition step in the temperature range  $40\text{--}290 \text{ }^\circ\text{C}$  (% experimental mass 30.37; calculated mass 29.57) this may be attributed to the loss of  $7\text{H}_2\text{O}$  (hydrated water molecules) and  $2\text{DMF}$ <sup>20,21,26,29</sup>. The second step within the temperature range of  $290\text{--}345 \text{ }^\circ\text{C}$  correspond to the removal of  $2\text{HCl}$  ( $\text{Cl}^-$  free ion) molecules as deduced from mass loss calculations (experimental mass loss of 8.70 %, calculated mass loss 8.15 %)<sup>26,34</sup>. The DTA curve of the complex exhibits two exothermic peaks at  $345$  and  $440 \text{ }^\circ\text{C}$ . The two stages of the complex decomposition are irreversible<sup>26,35</sup>.

The decomposition curve of  $[\text{Cd}_2(\text{L}^2)_2(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 2\text{Cl} \cdot 1.5\text{H}_2\text{O}$  begins by a step at  $45.0\text{--}334.5 \text{ }^\circ\text{C}$ , displaying (the experimental mass loss of 14.44 % agrees well with the calculated mass loss of 14.41 %) mass loss corresponding to the removal of  $1.5\text{H}_2\text{O}$  (hydrated water),  $4\text{H}_2\text{O}$  (coordinated water) and  $2\text{OH}^-$  (bridging  $\text{OH}^-$ ) ions<sup>20,21,25,32</sup>. The second decomposition step in the temperature range  $334.5\text{--}350.9 \text{ }^\circ\text{C}$ , the

TABLE-1  
 TGA DATA OF THE COMPLEXES

Compounds Molecular weight (g/mol)	Mass loss %, Calc. (Found) Decomposition Group			Total mass loss % Calc. (Found)
	First step (°C)	Second step (°C)	Third step (°C)	
$[\text{Ni}_2(\text{L}^1)_2(\text{OH})_2] \cdot 2\text{Cl} \cdot 8.5\text{H}_2\text{O}$ 807.42	50.0-365.0 23.16, (22.40) 8.5 H <sub>2</sub> O+2OH <sup>-</sup> (OH <sup>-</sup> bridging)	365.0-395.0 9.04, (9.60) 2HCl, (Cl <sup>-</sup> free ion)		32.20, (32.00)
$[\text{Cd}_2(\text{L}^1)_2(\text{OH})_2] \cdot 2\text{Cl} \cdot \text{DMF} \cdot 3\text{H}_2\text{O}$ 888.82	48.0-275.0, 14.28, (13.92) 3H <sub>2</sub> O+DMF	275.0-290.0 3.83, (3.48) 2OH <sup>-</sup> (bridging)	290.0-345.0 8.21, (8.69) 2HCl, (Cl <sup>-</sup> free ion)	26.32, (26.09)
$[\text{Ni}(\text{L}^2)] \cdot 2\text{Cl} \cdot 2\text{DMF} \cdot 7\text{H}_2\text{O}$ 895.71	40.0-290.0 29.57, (30.37) 7H <sub>2</sub> O+2DMF	290.0-345.0 8.15, (8.70) 2HCl, (Cl <sup>-</sup> free ion)		38.52, (38.27)
$[\text{Cd}_2(\text{L}^2)_2(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 2\text{Cl} \cdot 1.5\text{H}_2\text{O}$ 922.82	45.0-334.5 14.41, (14.44) 5.5 H <sub>2</sub> O+2OH <sup>-</sup> (OH <sup>-</sup> bridging), (4H <sub>2</sub> O coord.)	334.5-350.9 7.91, (8.33) 2HCl, (Cl <sup>-</sup> free ion)		22.32, (22.77)

 TABLE-2  
 MASS SPECTRA DATA OF THE COMPLEXES

Compound Formula weight (g/mol)	MS/EI	Assignment
$[\text{Ni}_2(\text{L}^1)_2(\text{OH})_2] \cdot 2\text{Cl} \cdot 8.5\text{H}_2\text{O}$ 807.42	809.42 655.42 (calc.) 655.16 (found) 217.00 (calc.) 217.00 (found)	$[\text{M}+2\text{H}]^{+2}$ ; $[\text{M}-8.5\text{H}_2\text{O}+\text{H}]^+$ ; $[\text{L}+\text{H}]^+$
$[\text{Cd}_2(\text{L}^1)_2(\text{OH})_2] \cdot 2\text{Cl} \cdot \text{DMF} \cdot 3\text{H}_2\text{O}$ 888.82	887.82 217.00 (calc.) 217.12 (found)	$[\text{M}-\text{H}]^+$ ; $[\text{L}+\text{H}]^+$
$[\text{Ni}(\text{L}^2)] \cdot 2\text{Cl} \cdot 2\text{DMF} \cdot 7\text{H}_2\text{O}$ 895.71	893.71 248.00 (calc.) 248.08 (found)	$[\text{M}-2\text{H}]^{+2}$ ; $[\text{L}+\text{H}]^+$
$[\text{Cd}_2(\text{L}^2)_2(\text{OH})_2(\text{H}_2\text{O})_4] \cdot 2\text{Cl} \cdot 1.5\text{H}_2\text{O}$ 922.82	923.82 248.00 (calc.) 248.08 (found)	$[\text{M}+\text{H}]^+$ ; $[\text{L}+\text{H}]^+$

experimentally found mass loss is 8.33 % (calculated mass loss of 7.91 % ) this may be attributed to the elimination of 2HCl molecules because of the free Cl<sup>-</sup> ions in the complex<sup>26,34</sup>. The DTA curve of the complex exhibits two exothermic peaks at 334.5 and 449.1 °C. The two stages of the complex decomposition are irreversible<sup>26,35,36</sup>.

**Mass spectra:** The mass spectra of the Ni(II), Cd(II) complexes of the ligand (L<sup>1</sup>) peaks attributable to the related molecular ions m/z: 809.42  $[\text{M}+2\text{H}]^{+2}$  and m/z: 887.82  $[\text{M}-\text{H}]^+$ , respectively. The mass spectra of the Ni(II), Cd(II) complexes of the other ligand (L<sup>2</sup>) peaks attributable to the related molecular ions m/z: 893.71  $[\text{M}-2\text{H}]^{+2}$  and m/z: 923.82  $[\text{M}-\text{H}]^+$ , respectively. The observed free ligand (L<sup>1</sup>) peaks for (Ni(II) and Cd(II) complexes<sup>20,21</sup> m/z: 217.00 and 217.12  $[\text{L}+\text{H}]^+$ . The observed free ligand (L<sup>2</sup>) peaks for every to complexes similar<sup>20,21,36</sup> m/z: 248.08  $[\text{L}+\text{H}]^+$ . The mass spectra data of the complexes were given in detail in the Table-2. The values in the table which have high abundance were reported.

**Structural interpretation:** Single crystals of the complexes could not be isolated from any solutions, thus no definite structure could be described. However, the analytical, spectroscopic molar conductance and magnetic data enable to us propose the possible structures which are shown in Fig. 2-5.

## Conclusion

As a general conclusion, in the Ni(II) and Cd(II) complexes of the ligands (L) behaves as bidentate ligand and coordinating sites for Ni(L<sup>2</sup>) and Cd(L<sup>2</sup>) complexes are N atom of -NH<sub>2</sub> group on the pyrazole ring and -N=N- moiety. But coordinating

sites for the Ni(L<sup>1</sup>) and Cd(L<sup>1</sup>) complexes are N atom of C=N moiety and N atom of -NH<sub>2</sub> group on the pyrazole ring.

From the reflectance spectra and magnetic moment measurements, the geometrical structures of the Ni(L<sup>1</sup>), Cd(L<sup>1</sup>) and Ni(L<sup>2</sup>) complexes were proposed to be square planar geometry. On the other hand, the Cd(L<sup>2</sup>) complex includes octahedral geometry.

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## REFERENCES

- A.A. Bekhit, A. Hymete, A. Bekhit El-Din, D. Alaa, Y. Ashenafi and H. Aboul-Enein, *Mini Rev. Med. Chem.*, **10**, 1014 (2010); J.K. Gupta, A. Chaudhary, R. Dudhe, K. Varuna, P.K. Sharma and P.K. Verma, *Int. J. Pharm. Sci. Res.*, **1**, 34 (2010) and references therein;
- J. Elguero, P. Goya, N. Jagerovic and A.M.S. Silva, *Targets Heterocycl. Syst.*, **6**, 52-98 (2002) and references therein.
- Z. Zhang, Antipreparation of Hydrazonodiaminopyrazoles with Antiproliferative Activity, US Patent 2003060453.
- H. Elnagdi, S.M. Fahmy, E.M. Zayed and M.Z.M.A. Ilias, *Naturforsch. B*, **31**, 795 (1976).
- G. Auzzi, F. Bruni, A. Costanzo, L.P. Vettori, R. Pirsino, M. Corrias, G. Banchelli and L. Raimondi, *J. Med. Chem.*, **26**, 1706 (1983).
- R. Robins, D.E. O'Brien, T. Novinson and R.H. Springer, *Ger. Patent*, **2**, 257,547 (1972); *Chem. Abstr.*, **79**, 78840 (1973).
- H.Y. Wen, *Dyes Pigments*, **64**, 223 (2005).
- T.P. Chen and W.I. Jing, *Dyes Pigments*, **64**, 259 (2005).
- M.H. Elnagdi, E.M. Kandeel, E. Zayed, K. Mohamed and Z.J. El-Shahat, *Heterocycl. Chem.*, **14**, 155 (1977).

10. M.H. Elnagdi, S.M. Fahmy, E.A.A. Hafez, M.R.H. Elmoghayar and S.A.R. Amer, *J. Heterocycl. Chem.*, **16**, 1109 (1979).
11. G. Zvilichovsky and D. Mordechai, *J. Chem. Soc. Perkin Trans. I*, 11 (1983).
12. K.Z. El-Shatat, A.F. Mohamed, E.N. Elshahira, S. Magda and M.H. Elnagdi, *J. Chem. Soc. Perkin Trans. I*, 1499 (1985).
13. H.A. Elfahham, G.E.H. Elgemeie, Y.R. Ibraheim and M.H. Elnagdi, *Liebigs Ann. Chem.*, 819 (1988).
14. K.Z. El-Shatat, *J. Chem. Res. Synop.*, 290 (1995).
15. T.P. Chen and W.I. Jing, *Dyes Pigments*, **74**, 578 (2007).
16. K. Vladimir, C. PetR, F. Iveta, S. Jan and K. George, *J. Med. Chem.*, 6500 (2006).
17. S. Junpei and N. Masayuki, Japan Patent, 03,176190 (1991); *Chem. Abstr.*, **116**, 13456 (1992).
18. C. Junji and K. Hiroyuki, Japan Patent, 03,143686 (1991); *Chem Abstr.*, **116**, 22879 (1992).
19. I. Sener, F. Karci, E. Kilic and H. Deligoz, *Dyes Pigments*, **62**, 141 (2004).
20. R. Adiguzel, Z. Ergin and M. Sekerci, *Asian J. Chem.*, **22**, 3895 (2010).
21. S. Ilhan, H. Temel, I. Yilmaz and M. Sekerci, *Polyhedron*, **26**, 2795 (2007).
22. G.G. Mohamed and N.E.A. El-Gamel, *Spectrochim. Acta*, **61A**, 1089 (2005).
23. M.S. Masoud, M.F. Amira, A.M. Ramadan and G.M. El-Ashry, *Spectrochim. Acta*, **69A**, 230 (2008).
24. F. Hu, X. Yin, J. Lu, Y. Mi, J. Zhuang and W. Luo, *J. Coord. Chem.*, **63**, 263 (2010).
25. H. Golchoubian and R.Z. Zarabi, *Polyhedron*, **28**, 3685 (2009).
26. N. Turan and M. Sekerci, *Heteroatom. Chem.*, **21**, 14 (2010).
27. G.G. Mohamed, N.E.A. El-Gamel and F. Texidor, *Polyhedron*, **20**, 2689 (2001).
28. J. Ponsa, A. Chadghan, J. Casabo, A. Alvarez-Larena, J.F. Piniella, X. Solans, M. Font-Bardia and J. Ros, *Polyhedron*, **20**, 1029 (2001).
29. A.Z. El-Sonbati, R.M. Issa and A.M. Abd-El Gawad, *Spectrochim. Acta*, **68A**, 134 (2007).
30. M.S. Nair and R.S. Joseyphus, *Spectrochim. Acta*, **70A**, 749 (2008).
31. V. Yilmaz, S. Hamamci, O. Andac, C. Thone and W. Harrison, *Transition Met. Chem.*, **28**, 676 (2003).
32. N.V. Loginova, T.V. Koval'chuk, G.I. Polozov, N.P. Osipovich, P.G. Rytik, I.I. Kucherov, A.A. Chernyavskaya, V.L. Sorokin, O.I. Shadyro, *Eur. J. Med. Chem.*, **43**, 1536 (2008).
33. C.M. Sharaby, G.G. Mohamed and M.M. Omar, *Spectrochim. Acta*, **66A**, 935 (2007).
34. G.G. Mohamed and C.M. Sharaby, *Spectrochim. Acta*, **66A**, 949 (2007).
35. N. Turan and M. Sekerci, *Synth. React. Inorg. Met-Org. Chem.*, **39**, 637 (2009).
36. R. Adiguzel, H. Esener, Z. Ergin, E. Aktan and M. Sekerci, *Asian J. Chem.*, **23**, 1846 (2011).