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Synthesis and Characterization of Novel Ni(II), Cu(II) and Cd(II) Complexes of 4-(2-Chlorphenylazo)-1*H*-pyrazole-3,5-diamine

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In this study, the diazotized *o*-chloraniline was coupled with malononitrile. The ring closure reaction of the obtained product with hydrazine monohydrate yielded 4-(2-chlorophenylazo)-1*H*-pyrazole-3,5-diamine (L). The structure of ligand has been elucidated by spectroscopic analyses. Then, novel Ni(II), Cu(II), Cd(II) complexes of ligand have been synthesized and the structures of these complexes determined by elemental analysis, spectrometric and TGA/DTA methods and magnetic susceptibility measurements. All complexes were monomeric and diamagnetic. From the elemental analyses and mass spectra data, the complexes were proposed to the formulae $[Ni_2L_2(Cl)_2]\cdot 2Cl\cdot 0.5DMF\cdot 0.5H_2O$, $[Cu_3L_2(Cl)_4(OH)_2(H_2O)_2]\cdot 0.5H_2O$ and $[Cd_3L_2(Cl)_2(OH)_2](Cl)_2\cdot 1.5H_2O$. For the Ni(II) complex square planar and for the Cu(II) complex octahedral geometry were proposed, but the Cd(II) complex includes both four and six coordinated structures. The Cu(II) and the Cd(II) complexes were found to be trinuclear. On the other hand the Ni(II) complex was found to be dinuclear.

Key Words: 4-(2-Chlorphenylazo)-1*H*-pyrazole-3,5-diamine and metal complexes, Azodyes complexes.

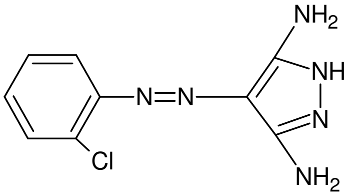
INTRODUCTION

In general pyrazole, pyrimidine and its derivatives are known to possess pharmacological activity and anxiolytic properties. They are also used as intermediates in the dyestuff industry[1-13] and there are some patent about these fused heterocyclic compounds[14,15]. There are lots of study about pyrazole and pyrimidine rings, but there isn't any research about complexes of this dyes.

For this reason we aimed to obtain high biological active new compounds. In the present work, we have synthesized 4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine (L) by reaction of diazotized *o*-chloraniline, malononitrile and hydrazine monohydrate. In the meantime was occurred coupling and ring closure reaction. Then, its Ni(II), Cu(II) and Cd(II) complexes were synthesized by reacting $NiCl_2\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$ and $CdCl_2\cdot H_2O$, respectively. Finally, the spectral and magnetic properties and thermal stabilities of all the compounds were studied in detail.

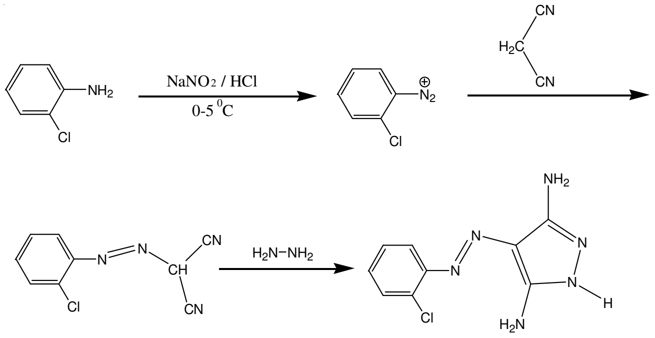
EXPERIMENTAL

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^{1}H NMR spectra were recorded using a model Bruker Avance DPX-400 NMR spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum RX1 FTIR spectrometer on KBr discs in the wave number range of 4000-400 cm^{-1}. Electronic spectral studies were conducted on a Shimadzu model 160 UV visible spectrophotometer in the wavelength 1100-200 nm. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $Hg[Co(SCN)_4]$ as a calibrant. Thermal gravimetric analyses were carried out on TGA Shimadzu model 50 thermal gravimetric analyzer. LC/MS-API-ES mass spectra were recorded using a Agilent model 1100 MSD mass spectrophotometer.



Structure of the ligand (4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine)

Except the ligand, all the other chemicals and solvents were of analytical grade and used as received. The ligand (L) was synthesized according to **Scheme-I** by the procedure



Scheme-I

given by method. In the synthesis of ligand has been occurring azo coupling and ring closure reaction[1,12].

Preparation of the 4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine (L): 4-(2-Chlorphenylazo)-1*H*-pyrazole-3,5-diamine (L) was prepared by the literature method[1,12]. m.p. 208-210 ºC, characteristic IR bands (KBr, ν_{max}, cm^{-1}): (NH_2): 3413, 3342, 3263; (Ar C-H): 3068; (C=C): 1632; (N=N): 1609; (C=N): 1561; (C-N): 1124; δ(N-H): 741[16]; characteristic ^1H NMR peaks (DMSO-d_6, δ ppm): 6.5 (-NH_2, 4H, s), 7.2-7.8 (Ar-CH, m), 10.9 (-NH, s)[17]; UV-vis (λ_{max}, nm) (DMSO): 258, 390[17].

Preparation of complexes

Preparation of the $[Ni_2L_2Cl_2](Cl)_2\cdot0.5DMF\cdot0.5H_2O$: The ligand (4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine) (0.15 g 0.64 mmol) was dissolved in 10 mL hot DMF in a 100 mL round-bottom flask. A solution of $NiCl_2\cdot6H_2O$ (0.61 g 2.56 mmol) in 5 mL DMF was added dropwise in 10 min periods with continuous stirring at room temperature. The dark henna green coloured precipitate was formed after 20 min and left under reflux for 10 h. The resulting yellow-green coloured precipitate was filtered off and washed with hot DMF, H_2O and hot absolute EtOH. The precipitated product was dried at room temperature. The complex was found to be soluble in DMSO. m.p. dec. 290 ºC. Yields: 0.24 g (80 %). Elemental analysis calcd. (%) for $Ni_2C_{18}H_{18}N_{12}Cl_4\cdot0.5DMF\cdot0.5H_2O$: C, 30.08; H; 2.892; N, 22.49. Found (%): C, 30.41; H, 3.123; N, 22.19. Characteristic IR bands (KBr, ν_{max}, cm^{-1}): (NH_2): 3460, 3309, 3195; (Ar C-H): 3061; (C=C):1645; (N=N): 1598; (C=N):1553; (C-N): 1101; δ(N-H): 763; (M-N): 424; UV-vis (λ_{max}, nm) (DMSO): 244, 435. Mass spectra: m/z: 698.42 $[M-Cl + 2H]^+$ [17,18].

Preparation of the $[Cu_3L_2(Cl)_4(OH)_2(H_2O)_2]\cdot0.5H_2O$: The ligand (L) (0.15 g 0.64 mmol) was dissolved in 10 mL hot DMF in a 100 mL round-bottom flask. A solution of $CuCl_2\cdot2H_2O$ (0.43 g 2.56 mmol) in 5 mL DMF was added dropwise in 10 min periods with continuous stirring at room temperature. The dark brown coloured mixture was left under reflux for 10 h. Then the half of solvent (DMF) was vapourized and obtained precipitate in the mixture of DMF/H_2O (1/5) was filtered off. Finally the brown coloured product was washed with hot absolute alcohol and $CHCl_3$ and dried at room temperature. The complex was found to be soluble in DMSO. m.p. dec. > 360 ºC. Yields: 0.29 g (78 %). Elemental analysis calcd. For $(Cu_3C_{18}H_{24}N_{12}Cl_6O_4)\cdot0.5H_2O$: C, 24.42; H, 2.826; N, 18.99. Found (%): C, 24.79; H, 2.764; N, 18.51. Characteristic IR bands (KBr, ν_{max}, cm^{-1}): (OH, hydroxo-bridge): 3505; (NH_2): 3424; (OH, coord. H_2O): 3321; (N=N): 1615; (C=N):1552; (C-N): 1142; δ(N-H): 753; (H_2O, coord.): 857; (M-O): 529; (M-N): 421; UV-vis (λ_{max}, nm) (DMSO): 238, 249, 261, 411, 423. Mass spectra: m/z: 599.08 $[2L + 2Cu-H]^{3+}$ [17,18].

Preparation of the $[Cd_3L_2(Cl)_2(OH)_2](Cl)_2\cdot1.5H_2O$: The ligand (L) (0.15 g 0.64 mmol) was dissolved in 10 mL hot DMF in a 100 mL round-bottom flask. A solution of $CdCl_2\cdot H_2O$ (0.52 g 2.56 mmol) in 5 mL DMF was added dropwise in 10 min periods with continuous stirring at room temperature. The dark brown coloured mixture was left under reflux for 10 h. The resulting yellow coloured precipitation was filtered off and washed with DMF and hot absolute alcohol. The precipitated product was dried at room temperature. The complex was found to be soluble in DMSO. m.p. dec. 321 ·C. Yields: 0.34 g (82 %). Elemental analysis calcd. (%) for $(Cd_3C_{18}H_{20}N_{12}Cl_6O_2)\cdot1.5H_2O$: C, 21.31; H, 2.270; N, 16.58. Found (%): C, 20.94; H, 2.346; N, 16.23. Characteristic ^1H NMR peaks (DMSO-d_6, δ ppm): 6.5 (free -NH_2, 2H, s), 5.5 (M-NH_2, 2H, s). Characteristic IR bands (KBr, ν_{max}, cm^{-1}): (OH, hydroxo-bridge): 3542; (NH_2): 3340, 3397; (H_2O, hydrate.): 3447; (Ar C-H): 3061; (C=C): 1645; (N=N): 1598; (C=N): 1555; (C-N): 1385, 1152; δ(N-H): 736; (M-O): 502; (M-N): 416. UV-Vis (ν_{max}, nm) (DMSO): 258, 383. Mass spectra: m/z: 804.82 $[M-Cd^{2+} - 2Cl^- + 2H]^{2+}$ [17,18].

RESULTS AND DISCUSSION

Infrared spectra: The IR spectra of the ligand and its metal complexes were carried out in the range of 4000-400 cm^{-1} and the important bands were given in experimental section.

In the IR spectra of Ni(II) complex, the medium intense and sharp ν(N=N) and intense and sharp ν(C=N) absorption at 1609 and 1561 cm^{-1}, respectively of the metal-free ligand shifted to the lower wavenumber region and observed at 1598 and 1553 cm^{-1}, respectively after complexation. These evidences show that diazonium and pyrazole N atoms are coordinated with the metal ions[19-22].

The stretching vibration bands; ν(NH_2) on the pyrazole ring which found at 3413, 3342 and 3263 cm^{-1} in the free ligand were shifted to higher frequencies and observed at 3460, 3309 and 3195 cm^{-1} in the spectra of the isolated complex[18]. The IR spectrum of the ligand shows two bands at 741 and 1124 cm^{-1} which are assigned to the out-of plane δ(N-H) and ν(C-N) stretching frequencies, respectively. The coordination of the NH_2 group to the metal ion is confirmed by the red shift (763 cm^{-1}) or blue shift (1101 cm^{-1}) in the frequencies of out-of plane δ(N-H) and ν(C-N) bands[23]. Furthermore, the ν(C-N) stretching mode at 1380 cm^{-1} (in the free ligand, 1361 cm^{-1}) is affected to different extends on complexation[24].

New band was found in the IR spectra of the Ni(II) complex at 424 cm^{-1} which was assigned to ν(M-N) stretching vibration, similar values are found in the literature[18,24-28].

In the IR spectra of Cu(II) complex, the medium intense and sharp ν(N=N) and intense and sharp ν(C=N) absorptions shifted to the higher wavenumber and lover wavenumber and observed at 1615 and 1552 cm^{-1}, respectively after complexation. These evidences show that diazonium and pyrazole N atoms are coordinated with the metal ions[19,20]. The shift to higher frequency region of ν(N=N) can be explained with the presence of the electronegative groups and affects the donor capacity of the N-atom[20].

In the IR spectra the medium intense band at 3424 cm^{-1} which assigned to the NH_2 stretching vibration shifted to higher frequencies. The other ν(NH_2) vibrations are hidden under ν(OH) stretching frequency of the water and the hydroxo-bridge[21]. The coordination of the NH_2 group to the metal ion is confirmed by the red shift (753 cm^{-1}) and (1142 cm^{-1}) in the frequencies of out-of plane δ(N-H) and ν(C-N) bands[22,23]. In a addition, the ν(C-N) stretching mode at 1380 cm^{-1}) (in th free ligand, 1361 cm^{-1}) is affected to different extends on complexation[24].

In the IR spectra observed broad band at 3321 cm^{-1} which attributed to ν(OH) of H_2O and supported peak by 857 cm^{-1} is due to the coordinated water molecules[17,24,29].

Moreover, the presence of a sharp signal at 3505 cm^{-1} in the Cu(II) complex can be assigned to the OH stretching frequency of the hydroxo-bridge[30].

The absorption bands assigned to the (M-O) and (M-N) stretching frequencies of the complex were observed at 529 and 421 cm^{-1}, respectively[17,24-28,31].

In the IR spectra of Cd(II) complex, the intense and sharp ν(N=N) and medium intense and sharp ν(C=N) shifted to the lower wavenumber region and observed at 1599 and 1555 cm^{-1}, respectively after complexation. These evidences show that diazonium and pyrazole N atoms are coordinated with the metal ions[19-21].

The stretching vibration bands; ν(NH_2) on the pyrazole ring were shifted to higher frequencies and observed at 3340 and 3397 cm^{-1} in the spectra of the isolated complex[17,24]. The IR spectrum of the ligand shows two bands at 741 and 1124 cm^{-1}, which are assigned to the out-of plane δ(N-H) and ν(C-N) stretching frequencies. The coordination of the NH_2 group to the metal ion is confirmed by the blue shift (736 cm^{-1}) or red shift (1152 cm^{-1}) in the frequencies of out-of plane δ(N-H) and ν(C-N) bands[23]. Moreover, the ν(C-N) stretching mode at 1385 cm^{-1}) (in the free ligand, 1361 cm^{-1}) is affected to different extends on complexation[24].

In the lower frequency region some metal-sensitive bands appeared at 502 and 416 cm^{-1} for complex which are due to ν(M-O) and ν(M-N), respectively, similar values found in the literature[17,24-28,31].

In the IR spectra of the Ni(II) and the Cd(II) complexes, the stretching band ν(C=C) which observed at 1632 cm^{-1} in the free ligand shifted to the higher frequence region and observed at 1645 cm^{-1}. 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[20].

The conclusive evidences in the IR spectra of all complexes indicate that the ligand behaves as a terdentate ligand and the coordinating sites are -NH_2 and N atom of the pyrazole ring and -N=N- moiety.

The coordinated halogen in the complexes shows a far IR absorption peak in the range 294-230 cm^{-1}, which may be attributed to ν(M-Cl)[26,32]. However, the IR spectra of the complexes, (M-Cl) bands could not be observed, which we have studied in 4000-400 cm^{-1} range.

In the Ni(II) and Cd(II) complexes of the ligand (L), the chloride ions are coordinate with the metal ions (Figs. 1 and 3). In the Cl^- test with $AgNO_3$, we were observed precipitation of white AgCl salt immediately as an evident. Therefore, these complexes have been including free Cl^- ion[26].

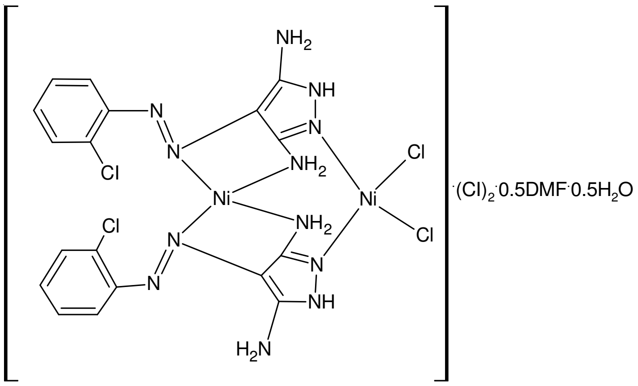


Fig. 1. Suggested structure of the square planar Ni(II) complex of the ligand, (4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine)

^{1}H NMR Spectra: The ^{1}H NMR spectra of the ligand and the Cd(II) complex were recorded in DMSO-d_6 and listed in the experimental section. In the spectra of the ligand observed signal at 6.5 ppm is due to NH_2 protons (s, 4H). Moreover, in the ^{1}H NMR spectra of the Cd(II) complex a new signal was found at 5.5 ppm which was assigned to M-NH_2 protons (s, 2H). The shift to lower field may be correlated with the decrease in the electronic density of the NH_2-group and the coordination of the NH_2 group to the metal ion is confir-med. On the other hand, the signal of the free NH_2 protons was observed at 6.5 ppm (s, 2H) and wasn't changed[17,33].

Magnetic susceptibility: The observed room temperature magnetic moment value for the trinuclear Cu(II), Cd(II) complexes and the dinuclear Ni(II) complex were found to be diamagnetic. The diamagnetic behaviour of the trinuclear Cu(II) complex could be explained by a very strong antiferromagnetic interaction in the Cu-Cu pair[18,34]. The square planar geometry of the Ni(II) complex causes diamagnetic character.

Thermal studies: The thermal stability of the complexes were investigated using TGA. The thermogravimetric analysis were carried out (Table-1) at a heating rate of 15 ºC/min in a nitrogen atmosphere over the temperature range of 20-800 ºC. The decomposition and weight losses of Ni(II), Cu(II) and Cd(II) complexes were occurred at the temperature ranges of 29.2-370.0, 35.4-350.0 and 36.5-433.0 ºC, respectively. The results are in good agreement with the theoretical formula suggested by the mass spectra and the elemental analyses. The weight losses for complexes were calculated within the corresponding temperature ranges.

The decomposition curve of $[Ni_2L_2Cl_2](Cl)_2·0.5DMF·0.5H_2O$ begins by a step at 29.2-280.0 ·C, displaying (percentage experimental weight 5.92; calculated weight 5.85) weight loss corresponding to the removal of 0.5 DMF and 0.5 H_2O[17,27,31,35]. The second stage ending at 290-350 ºC, the weight loss is assigned to the elimination of 2HCl molecules, because of the free Cl^- ions in the complex (percentage experimental weight 9.26; calculated weight 9.38)[26,28]. The third step (350.0-370.0

TABLE-1
THERMAL DATA OF THE COMPLEXES

Compounds	Weight loss %, decomposition	Calcd. (%)	(Found %) group	Total weight loss % calcd. (found)
	First step (ºC)	Second step (ºC)	Third step (ºC)	
$[Ni_2L_2Cl_2](Cl)_2·0.5DMF·0.5H_2O$ 777.92 (g mol^{-1})	29.2-280 5.85, (5.92) $0.5H_2O$ + 0.5DMF	290-350 9.38, (9.26) 2HCl, ($2Cl^-$ free ion)	350-370 9.38, (9.28) 2HCl, ($2Cl^-$ coord.)	24.61, (24.46)
$[Cu_3L_2(Cl)_4(OH)_2(H_2O)_2]·0.5H_2O$ 884.62 (g mol^{-1})	35.4-230 8.93, (7.78) $0.5H_2O$, (hydrate) + $2H_2O$, (coord.) + $2OH^-$, (bridging)	230-280 8.25, (9.07) 2HCl, (coord. $2Cl^-$)	280-350 8.25, (9.05) 2HCl, ($2Cl^-$ bridging)	25.43, (25.90)
$[Cd_3L_2(Cl)_2(OH)_2](Cl)_2·1.5H_2O$ 1013.23 (g mol^{-1})	36.5-280 6.02, (5.93) $1.5H_2O$ + $2OH^-$ (bridging)	280-335 7.20, (7.39) 2HCl, ($2Cl^-$ free ion)	335-433 7.20, (7.41) 2HCl, ($2Cl^-$ bridging)	20.42, (20.73)

ºC) ascribed to the removal of coordinated $2Cl^-$ ions as 2HCl by weight loss of (percentage experimental weight 9.28; calculated weight 9.38)[26,28]. The DTA curve of the complex exhibits two exothermic peak at 380.1 and 454.2 ºC. The two stages of the complex decomposition are irreversible[26,36].

The Cu(II) complex which has the general formula $[Cu_3L_2(Cl)_4(OH)_2(H_2O)_2]·0.5H_2O$ exhibits three decomposition steps. The first decomposition step in the temperature range 35.4-230.0 ºC, the experimentally found weight loss is 7.78 % (calculated weight loss 8.93 %), this may be attributed to the loss of 0.5 mol H_2O molecules of hydration, two coordinated water molecules and two OH^- ions[17,18,26,31]. The second step within the temperature range of 230.0-280.0 ºC correspond to the removal of 2HCl ($2Cl^-$ coordinated) molecules as deduced from weight loss calculations (experimental weight loss of 9.07 %, calculated weight loss 8.25 %)[26,28]. The third step was occurred at the temperature range of 280.0-350.0 ºC. The calculated and found weight loss indicated the successive departure group to be 2HCl ($2Cl^-$ bridging) mainly, the experimentally found weight loss of 9.05 % (calculated weight loss 8.25 %)[26,28]. The DTA curve of the complex exhibits three exothermic peak at 291.6, 475 and 508.3 ºC. The three stages of the complex decomposition are irreversible[26,36].

The decomposition curve of $[Cd_3L_2(Cl)_2(OH)_2](Cl)_2·1.5H_2O$ begins by a step at 36.5-283 ºC, displaying (the experimental weight loss of 5.93 % agrees well with the calculated weight loss of 6.02 %) weight loss corresponding to the removal of 1.5 H_2O and $2OH^-$ [17,26,31]. The second decomposition step in the temperature range 283.0-335.0 ºC, the experimentally found weight loss is 7.39 % (calculated weight loss of 7.20 %) this may be attributed to the weight loss of the elimination of 2HCl molecules because of the free Cl^- ions in the complex[26,28]. The final decomposition step in the temperature range 335.0-433.0 ºC shows elimination of 2HCl molecules ($2Cl^-$ bridging) (experimental weight loss of 7.41 %, calculated weight loss 7.20 %)[26,28]. The DTA curve of the complex exhibits two exothermic peak at 362.5 and 491.7 ºC. The two stages of the complex decomposition are irreversible[26,36].

Mass spectra: The mass spectra of the Ni(II), Cu(II) and Cd(II) complexes peaks attributable to the related cationic molecular ions m/z: 698.92 $[M-Cl + 2H]^{3+}$, m/z: 599.08 $[2L + 2Cu - H]^{3+}$ and m/z: 804.82 $[M-Cd^{2+}-2Cl^- + 2H]^{2+}$, respectively. The observed free ligand peaks for Ni(II), Cu(II) and Cd(II) complexes are m/z: 238.65, 238.50 and 238.75 $[L + 2H]^+$, respectively[17,18]. The mass spectra data of the complexes were given in detail in the Table-2. The values in the table which posses 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 and magnetic data enable to us propose the possible structures which are shown below in Figs. 1-3[30,37].

Conclusion

As a general conclusion, the ligand (L) behaves as terdentate ligand through $-NH_2$ and N atom on the pyrazole ring and -N=N- moiety in case of Ni(II), Cu(II) and Cd(II) complexes. From the reflactance spectra and magnetic moment measurements, the geometrical structure of the Ni(II) and Cu(II) complexes were proposed square planar and octahedral geometry. On the other hand, the Cd(II) complex includes both 4 and 6 coordinated structure.

TABLE-2
MASS SPECTRAL DATA OF THE COMPLEXES

Compound formula, weight	MS/EI	Assigment
$[Ni_2L_2Cl_2](Cl)_2·0.5DMF·0.5H_2O$ 777.92 (g mol^{-1})	698.92	$[M-Cl+2H]^{3+}$
	238.65 (found)	$L+2H]^{2+}$
	238.50 (calc.)	
	–	$Ni_2(Cl)_2^{2+}$ or $Ni_2(OH)_2^{2+}$, *
$[Cu_3L_2(Cl)_4(OH)_2(H_2O)_2]·0.5H_2O$ 884.62 (g mol^{-1})	599.08	$[2L + 2Cu - H]^{3+}$
	238.5 (calcd. and found)	$[L+2H]^{2+}$
	198.50 (found)	$Cu_2(Cl)_2^{2+}$ (Cl-bridge), (^{63}Cu or
	198.70 (found)	^{65}Cu)
	199.10 (found)	
	199.40 (found)	
	198.08 (calcd.)	
$[Cd_3L_2(Cl)_2(OH)_2](Cl)_2·1.5H_2O$ 1013.23 (g mol^{-1})	804.82	$[M-Cd^{+2} - 2Cl^-+2H]^{2+}$
	238.70 (found)	$[L+2H]^{2+}$
	238.50 (calcd.)	
	258.90 (found)	$Cd_2(OH)_2^{2+}$ (OH-bridge)
	258.82 (calcd.)	

*This peak wasn't observed in the Ni(II) complex.

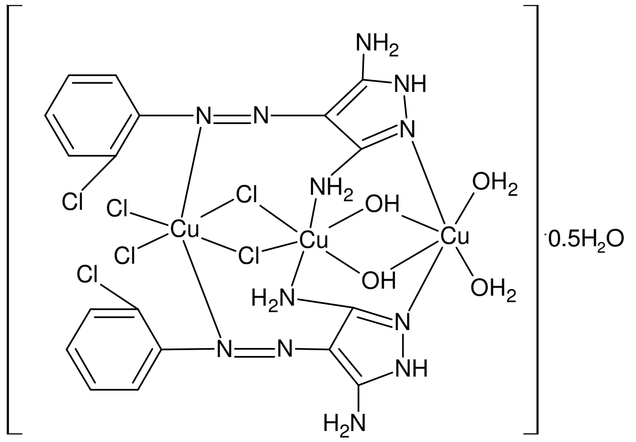


Fig. 2. Suggested structure of the octahedral Cu(II) complex of the ligand, (4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine)

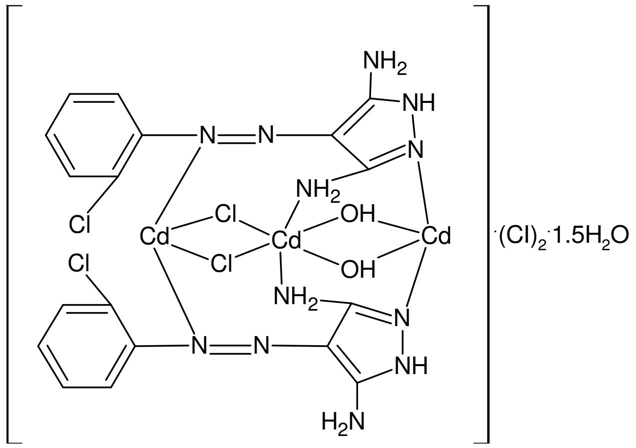


Fig. 3. Suggested structure of the four and six coordinated Cd(II) complex of the ligand, (4-(2-chlorphenylazo)-1*H*-pyrazole-3,5-diamine)

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