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Synthesis and Characterization of Cu(II), Ni(II) and Cd(II) Complexes With 3,5-Diamino-4-(4-Bromo-Phenylazo)-1H-Pyrazole

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Abstract

3,5-Diamino-4-(4-bromo-phenylazo)-1H-pyrazole (L) ligand have been synthesized from 2-(4-bromo-phenylazo)malononitrile and hydrazine hydrate. Complexes of this ligand with Cu(II), Ni(II) and Cd(II) chloride were prepared. The structures of the ligand and its complexes are proposed based on the elemental analyses, IR, ^{1}H and ^{13}C NMR spectra, UV-Vis. spectra, thermogravimetric analyses (TGA), differential thermal analyses (DTA) and magnetic susceptibility measurements. Magnetic moments, along with electronic spectral data, suggest octahedral geometry for the Ni(II), for the a tetrahedral structure Cd(II) complex, whereas, square-planar structure has been proposed for the Cu(II) complex. Thermal decomposition of complexes ended with metal oxide as a final product.

Keywords: 3,5-Diamino-4-(4-bromo-phenylazo)-1H-pyrazole, Hydrazine Hydrate, Cu(II), Ni(II) and Cd (II) charide

INTRODUCTION

Diamines have been widely used as ligands in asymmetric synthesis [1]. Also, several biologically active entities are known to contain diamine moieties. The diamine derivatives are reported to have analgesics activity [2]. Further, they are used in the determination of mercury in natural waters [3], production of colored thermoplastic resins and cross-linked epoxy resins [4], determination of selenium by instrumental methods, prevention of corrossion [5], pressure-sensitive color imagin technologies [6], powdered hair dyes [7], cation-exchange copolymerizations and some antiallergenes of medical use [8]. Complexes formed by the reactions of diamines with transition metals have a wide range of applications [9].

It is important to use amines containing at least two nitrogens since they produce quite stable complexes with transition metals [10]. Amines and their derivatives (monodental, bidental, etc.) have been known to produce stable complexes with transition metals [11]. A lot of amine complex compounds have been synthesized and their properties (carcinogenic, optical and biological activities) established [12].

MATERIALS AND METHODS

The chemicals were purchased from Merck used without purification. The electronic spectra of the ligand and the complexes in the UV-VIS region were recorded in DMF solutions using a Shimadzu UV-1700 Spectrophotometer. The IR spectra of the ligand and the complexes were recorded with Perkin Elmer precisely Spectrum One using KBr pellets in the region of 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker, 300 MHz in DMSO-d$_6$, magnetic suscebtibilities were determined at room temperature on a Sherwood Scientific MKI model balance. The elemental analyses were conducted on a Leco 932 CHNS-o instrument. Thermal analyses were recorded on a Shimadzu TA60-WS.

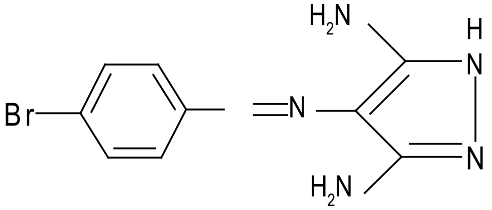

Figure. 1. Structure of the ligand (L)

Synthesis of 3,5-diamine-4-(4-bromo-phenylazo)-1H-pyrazole (L)

Hydrazine hydrate (0.59 g, 0.01 mol) was added to a solution of 2-(4-bromo-phenylazo)malononitrile (1.7 g, 0.01 mol) and pyridine 0.5 mL in 30 mL ethanol. The reaction mixture was heated under reflux for 3-4 h, then cooled to room temperature. The separated solid was filtered, washed with water, dried and recrystallized from ethanol to give a pale yellow solid 3,5-diamino-4-(4-bromo-phenylazo)-1H-pyrazole. (Found: C, 38.28 %; H, 3.00 %; N, 29.68 %; calculated: C, 38.45 %; H, 3.20 %; N, 29.90 %). The yield was 60 %.

Synthesis of the Cu(II), Ni(II) and Cd(II) complexes of ligand (L)

3,5-Diamino-4-(4-bromo-phenylazo)-1H-pyrazole (L) 0.25 g (0.89 mmol) was dissolved in 15 mL DMF. A solution 1.00 mmol of the metal chloride [$CuCI_2.2H_2O$ (0.17 g), $NiCI_2.6H_2O$ (0.24 g)] and 2.00 mmol of the metal chloride [$CdCI_2.H_2O$ (0.40 g)] in 30 mL methanol was added dropwise with continuous stirring over the course of 10 min at room temperature. Then, the reaction mixture was stirred for 4 h at 110°C. The mixture was collapsed by water, and obtained solids was filtered, washed with water and dried at room temperature. Spectral data and magnetic measurements results are given in Table 1 and 2.

The ligand and complexes were prepared by the general reactions shown below.

$L + CuCl_2.2H_2O \rightarrow [LCuOH_2] + 2HCl$

$2L + NiCl_2.6H_2O \rightarrow [L_2NiCl_2] + 6H_2O$

$L + 2CdCl_2.H_2O \rightarrow [LCd_2Cl_4] + 2H_2O$

L: $C_9N_6H_9Br$

Table 1. The Colors, Formulas, Formula Weight, Yields, Elemental Analyses and Magnetic Susceptibility of the Ligand and Its Complexes

			Elemental Analyses Calculated (Found) %			
Compounds	F.W g/mole	Yield (%)	C	H	N	μ eff (B.M.)
Ligand (L) (Pale yellow)	280.90	60	38.45	3.20	29.90	—
($C_9H_9N_6Br$)			(38.28)	(3.00)	(29.68)	
$[L_2NiCl_2].H_2O$ (Dark Green)	709.41	56	30.43	2.82	23.68	3.37
($C_{18}H_{20}N_{12}OBr_2NiCl_2$)			(29.98)	(3.11)	(24.08)	
$[LCu(OH)_2].DMF$ (Black)	451.45	53	31.90	3.99	21.71	1.46
($C_{12}H_{18}N_7O_3BrCu$)			(31.42)	(3.29)	(21.44)	
$[LCd_2Cl_4]$ (Yellow)	647.52	52	16.68	1.39	12.97	Dia.
($C_9H_9N_6BrCd_2CI_4$)			(16.42)	(1.70)	(12.89)	

RESULTS AND DISCUSSION

3,5-Diamino-4-(4-bromo-phenylazo)-1H-pyrazole (L) has been synthesized with 2-(4-bromo-phenylazo)malononitrile and hydrazine hydrate. Then, ligand (L) on reaction with $CuCI_2.2H_2O$, $CdCI_2.H_2O$ and $NiCI_2.6H_2O$ yields complexes corresponding to the formulas L, $[LCu(OH)_2].DMF$, $[L_2NiCl_2].H_2O$ and $[LCd_2Cl_4]$ (Fig. 1, 2, 3 and 4).

The analytical data for the ligand and its metal comlexes are listed in Table 1. The results of the elemental analyses show that the metal to ligand ratio in the Cu(II), Ni(II) and Cd(II) complexes are 1:1, 1:2 and 2:1, respectively. The ligand is soluble in common organic solvents. But its metal complexes are generally soluble in DMF and DMSO.

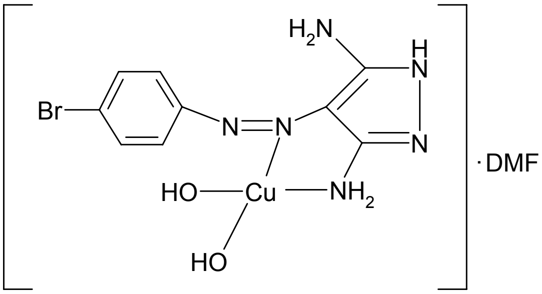

Figure. 2. Suggested structure of the Cu(II) complex

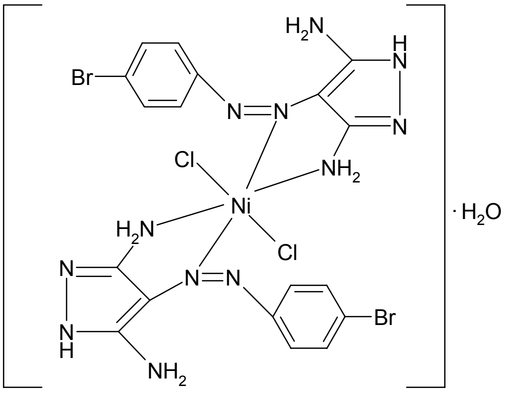

Figure. 3. Suggested structure of the Ni(II) complex

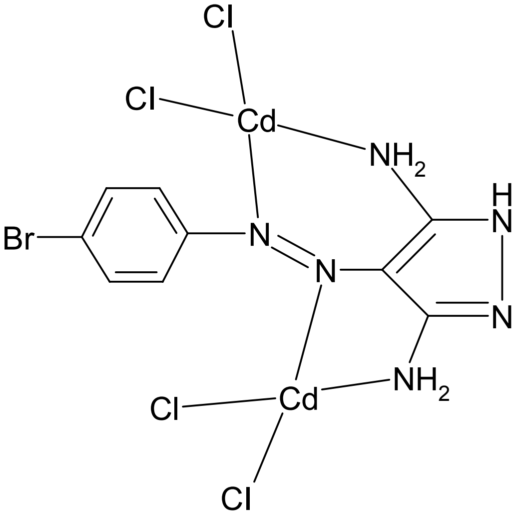

Figure. 4. Suggested structure of the Cd(II) complex

Magnetic Data and UV-VIS Spectra

The Cu(II), Ni(II) complexes are paramagnetic and their magnetic susceptibility values are 1.46, 3.37 B.M., respectively. Cd(II) complex is diamagnetic.

The UV-vis spectra of the ligand and complexes were recorded in DMF solution in the wavelength range from 1000-200 nm. In the spectrum of the ligand, bands in the 26316-29421 cm^{-1} range are assigned to the $n \rightarrow \pi^*$ transitions of the azo group. During the formation of the complexes, these bands are shifted to lower wavelength, suggesting that the nitrogen atom of the azo group is coordinated to the metal ion. The bands in the 33362-40241 cm^{-1} range are attributed to the $\pi \rightarrow \pi^*$ transition of the benzene and pyrazol ring. In the spectra of complexes, these bands are slightly to lower wavelength [13].

The magnetic moment value of the Cu(II) complex fall in the range observed for Cu(II) complex with one unpaired spin (1.46 B.M.). The electronic spectrum of this complex shows a shoulder at 19842 cm^{-1} assignable to the $^2B_{1g} \rightarrow {}^2E_g$ transition, suggesting a square-planar geometry around the Cu(II) ion [14,15].

The electronic spectra of the Ni(II) complex showed d-d bands in the region 10115 and 26280-26410 cm^{-1} $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$, respectively, consistent with their well-defined octahedral configuration [15,16,17]. The band 30215 cm^{-1} was assigned to metal → ligand charge transfer. The magnetic measuraments (3.37 B.M.) showed two unpaired electrons per Ni(II) ion suggesting also an octahedral geometry for the Ni(II) complexes [18-21].

The electronic spectra of the Cd(II) complex showed an absorbtion band at 16750 cm^{-1} attributed to the L → M (charge transfer) transition, which could be tetrahedral or square-planar structure, but it must be tetrahedral structure because CI^- ions have bulky radius [22].

Infrared Spectra

Important IR bands of the ligand and its complexes are given in Table 2. The IR spectrum of the complexes are compared with those of the 3,5-Diamino-4-(4-Bromo-phenylazo)-1H-pyrazole (L) in order to determine the coordination sites that may involve in chelation. There are some guide peaks, in the spectra of the ligand, which are of good help for achieving this goal. The position and/or the in tensities of these peaks are expected to be changed upon chelation. The IR spectrum of ligand contains characteristic bands at 3405, 3333 and 3245 cm^{-1} assigned to $\upsilon(NH_2)$ and (N-H) groups, in the IR spectrum of the Cu(II) and Ni(II) complexes one of the NH_2 group isn't shifted and the other $\upsilon(NH_2)$ vibration shifted to lower frequences (3385 and 3380 cm^{-1}) is due to metal coordinate to the only one NH_2 group [23,24], Further the IR spectrum of the ligand exhibits a band 1588 cm^{-1} attributed to δ(N-H) band. In the IR spectrum of Cd(II) complex two of the $\upsilon(NH_2)$ vibrations are shifted to lower frequency. The band observed at 1588 cm^{-1} in the free ligand assigned to δ(NH) is shifted to lower frequences after forming the complexes [25]. This suggests that this amine group is involved in metal ion coordination [26]. This spectrum change was supported this coordination.

The spectra of the Cu(II) and Ni(II) complexes exhibited intense broad bands at 3454-3310 cm^{-1} due to υ(OH) lattice water or hydroxo group [27].

The IR spectra of all complexes showed a shift of the N=N streching bands at 1479-1476 cm^{-1} to lower wavenumbers by 18-21 cm^{-1} indicating coordination of a nitrogen atom of the azo-group to the metal ion [28].

The infrared spectrum Cu(II), Ni(II) and Cd(II) and shows new bands of 496, 480 and 475 cm^{-1} assignable to (M-N) bands of stretching vibration, respectively [29]. The spectra of Cu(II) exhibit new band 518 cm^{-1} characteristic of υ(Cu-O), supporting our suggestion for the mononuclear nature of $[LCu(OH)_2].DMF$ in the hydroxo complex [30].

The IR spectra of chloro complexes display an additional new band at 355-325 cm^{-1}, assigned to υ(M-CI) [31]. In the IR spectrum of the complexes (M-CI) bands could'nt be observed, that we study in 4000-400 cm^{-1} range.

^1H and ^{13}C NMR Data

The ^1H-NMR spectra of ligand (L) has been carried out in DMSO-d_6 at room temperature. The ^1H-NMR spectra (in DMSO-d_6) of the ligand showed signals at 6.16 (s, 2H, NH_2), 6.40 (s, 2H, NH_2), 7.76 (d, J=11.4, 2H, ArH), 7.47 (d, J=8.7, 2H, ArH) and 10.10 (s, 1H, NH). The NH and NH_2 signals dissapear on addition of D_2O.

The signals due to NH_2 protons are either shielded or deshielded in case of $[LCd_2CI_4]$ complex confirming non-deprotonation and throught nitrogen of azo group in this complex [32].

^{13}C- NMR spectrum of ligand each carbon atom, namely C_1, C_2, C_3, C_4, C_5, C_6 and C_7 Fig.5 has resonances, 123,130, 122, 132, 114, 152 and 151 ppm, respectively.

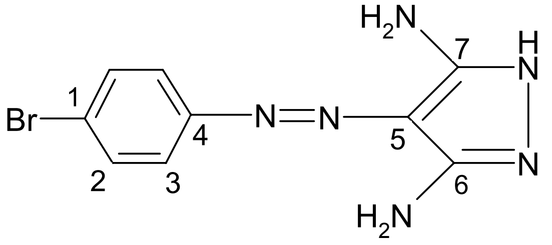

Figure. 5. Structure of the ligand

Thermal Studies

The thermal stability of the complexes was investigated using TGA and DTA. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were obtained at a heating rate of 15 °C/ min. in nitrogen atmosphere over a temperature range of 1000-25 °C.

The curves obtained for Cd(II) showed thermal stability 180.42 °C, whereas the Ni(II) and Cu(II) complexes are thermally stable up to 36.5 °C and 41.5 °C, respectively. The decomposition curve of Cd(II) complex begins by a step at 180.42-270.76 °C displaying 21.48 % weight loss corresponding to the removal 4Cl atoms. (Calculated 21.89 %) [33].

Table 2. Spectral Data of 3,5-Diamino -4-(4-Bromo-Phenylazo)-1H-Pyrazole (L) and Its Complexes

Compounds	Spectral Data
Ligand (L)	IR: υ/cm^{-1}: 3405 (NH$_2$), 3333 (NH$_2$), 3245 (NH), 3080-3060 (aromatic C-H), 1610 (C=N), 1494 (-N=N-), 1356 (C-N), 690 (C-Br) IR: δ /cm^{-1}: 1588 (NH) ^{1}H-NMR (DMSO-d$_6$), δ: 10.10 (s,1H, NH) D$_2$O exchangeable, 7.76 (d, J=11.4 Hz, 2H, PhH), 7.47 (d, J=8.7 Hz, 2H, PhH), 6.16 (s, 2H, NH$_2$) D$_2$O exchangeable and 6.40 (s, 2H, NH$_2$) D$_2$O exchangeable. ^{13}C- NMR (DMSO-d$_6$), δ: 123 (C$_1$),130 (C$_2$), 122 (C$_3$), 132 (C$_4$), 114 (C$_5$), 152 (C$_6$) and 151 (C$_7$)
[LCu(OH)$_2$].DMF	IR: υ/cm^{-1}: 3446 (OH), 3385 (NH$_2$), 3331 (NH$_2$), 3246 (NH), 3078 (aromatic C-H), 1605 (C=N), 1476 (-N=N-), 1342 (C-N), 686 (C-Br), 496 (M-N) IR: δ /cm^{-1}: 1557 (NH)
[L$_2$NiCI$_2$].H$_2$O	IR: υ/cm^{-1}: 3454-3410 (OH), 3380 (NH$_2$), 3334 (NH$_2$), 3243 (NH), 3075 (aromatic C-H), 1607 (C=N), 1479 (-N=N-), 1332 (C-N), 688 (C-Br), 486 (M-N) IR: δ /cm^{-1}: 1555(NH)
[LCd$_2$CI$_4$]	IR: υ/cm^{-1}: 3388 (NH$_2$), 3320 (NH$_2$), 3244 (NH), 3078 (aromatic C-H), 1606 (C=N), 1476 (-N=N-), 1346 (C-N), 681 (C-Br), 475 (M-N) IR: δ /cm^{-1}: 1560 (NH)

The DTA curve of the Cd(II) complex exhibits endothermic peak 200.00 °C corresponding to the loss of Cl atoms.

At the temperature range 270.76-900.35 °C mass loss occured due to the formation of intermediate species through the decomposition of the organic moiety of the complex and this continious till a constant weight is obtained where a metalic oxide resude is formed (Found: 42.96 % Calculated: 43.38 %). The DTA curve shows exothermic peak maxima 634.00 °C.

The Ni(II) complex was stable up 36.55 °C and its decomposition started at this temperature. In the decomposition process of the Ni(II) complex at 36.55-150.32 °C corresponds to the loss of water molecules of hydration [34].

The DTA curve of the Ni(II) complex exhibits endothermic peak 100.15 °C corresponding to the loss of hydration water (Found: 2.22 % Calculated: 2.54 %). The IR spectra of the apperance of a broad band in the region 3454-3310 cm^{-1} due to the υ(OH) frequency of water of hydration. This water content was also identified by the elemental analys [30,35]. In the temperature range 150.32-280.64 °C a mass loss occured corresponding to a loss of 2Cl atoms (Found: 9.62 % Calculated: 9.99 %) [25].

At the temperature range 280.64-800.50 °C, mass loss occured due to the formation of intermediate species through the decomposition of the organic moiety of the complex (Found: 78.52 % Calculated: 79.19 %). The product at 800.50 °C is the corresponding metal oxides. The DTA curve shows two exothermic peak maxima 490.60 °C and 570.10 °C.

In the TGA curve of the Cu(II) complex 23.70 % weight loss was observed at 41.50- 350.25 °C. This shows that Cu(II) complexes contain 2 mole of hydroxo groups and 1 mole of DMF of crystallization per complex molecule (Found: 23.69 % Calculated: 23.70 %). The IR spectra of the complex are characterized by the appearance of a broad band in the region 3446 cm^{-1}, due to the υ(O-H).

The DTA curve of the Cu(II) complex exhibits endothermic peaks 100.23 and 280.10 °C corresponding to the loss of hydroxy ligands and DMF [28,36]. This hydroxy groups and DMF were also identified by the elemental analyses.

The subsequent step 350.25-800.10 °C corresponds to the removal of the organic part of the ligand leaving metal oxide as a residue (Found: 78.52 % Calculated: 79.19 %) The DTA curve shows exothermic peak maxima 520.50 °C.

Single cyrstal 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 us to propose the possible structured.

Table 3. Thermal decomposition of the metal complexes

Compounds	Step	Decomp. Temperature (ºC)	Weight Loss Calculated (Found), %	Residue
$[LCu(OH)_2]$. DMF	1 2	41.50-350.25 350.25-800.10	23.70(23.69) 62.22(61.48)	CuO
$[L_2NiCI_2].H_2O$	1 2 3	36.55-150.32 150.32-280.64 280.64-800.50	2.54(2.22) 9.99(9.62) 79.19(78.52)	NiO
$[LCd_2CI_4]$	1 2	180.42-270.76 270.76-900.35	21.89(21.48) 43.38(42.96)	2CdO

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