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Research Article

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Transition metal complexes of 2-(substituted-1*H*-pyrazole-4-yl)-1*H*-benzo[*d*]imidazoles: Synthesis and characterization

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ABSTRACT

Four novel monodentate 2-(3′-(4″-sub-aryl)-1′-phenyl-1H-pyrazole-4-yl)-1H-benzo[d]imidazole ligands (La-d) have been synthesized via the cyclocondensation of o-phenelyndiamine with 1,3-disubstituted pyrazole aldehydes by adding oxidizing agent ceria ammonium nitrate as catalyst in presence of hydrogen peroxide in alcoholic media. The non chelated Cu(II) and Ni(II) complexes of newly synthesized monodentate 2-substituted benzimidazole (La-d) ligands were prepared in 1:2-metal:ligand stoichiometry. The monodentate behavior of the ligand was confirmed on the basis of spectral studies. The Ni(II) complexes exhibits tetrahedral geometry where as Cu(II) complexes exhibits square planar geometry around the metal center.

Key words: Monodentate 1*H*-benzimidazole, Non chelated Cu(II) and Ni(II) complexes, Pyrazole aldehydes.

INTRODUCTION

The coordination ability of a number of monodentate benzimidazole derivatives has been reported in past literature [1-6]. Numerous complexes involving d-block metals and imidazole derivatives are well known [7-13] and there is enormous interest in the transition metal complexes of imidazole and its derivatives as ligands [14-18]. Parasitic and antiviral activities of benzimidazoles and some substituted benzimidazole compounds have been widely investigated in medicinal fields. In medicine, drugs based on benzimidazoles and benzimidazole derivatives have been patented, due to their antiviral and antihelmintic activity [19]. In metallurgy, benzimidazole has been used as a corrosion inhibitor [20].

Benzimidazole as its 5,6-dimethyl derivative is present in vitamin, B_{12} and related biomolecules. Coordination complexes of benzimidazole derivatives with transition metals have been used in attempts to prepare structural and spectroscopic models of the active sites of some metalloenzymes [21]. Reaction of the benzimidazole ligands with hydrated copper(II) and nickel(II) salts in ethyl alcohol led us to the formation of monodentate benzimidazole complexes $M(La\text{-}d)_2Cl_2$ (Where, M = Cu(II) and Ni(II). The synthesized benzimidazole ligands (La-d) are an *N*-monodentate ligand that contains one donor group of relevance to the coordination of metal centers. In the present paper, we reported the synthesis and structural characterization of the dichloro-bis(La-d)metal(II) complexes.

EXPERIMENTAL SECTION

Reagents and Material

All procedures were carried out by using standard solvents and chemicals without further purification which were commercially available and used as purchased. The IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer using KBR discs. The ^{1}H NMR spectra were measured in DMSO-d_6 solutions on the Bruker Av spectrophotometer (400 MHz) using TMS as an internal reference. The mass spectra were recorded on the Shimadzu GC-MS QP2010 Gas Chromatograph. The TG analysis curves were obtained on the Perkin Elmer the Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA) model at a heating rate of 20 °C per minute. The Electronic spectra were recorded in DFM solution on a Shimadzu UV mini-1240 spectrophotometer. Molar conductance of all the complexes was performed on an Elico conductivity bridge (type CM82T). The magnetic moment of all the complexes were measured by Guoy balance at room temperature using $CuSO_4.5H_2O$ as callibrant. All the synthesized compounds were micro analyzed satisfactorily for C, H and N on Euro EA Elemental Analyzer, EA-3000, RS-232.

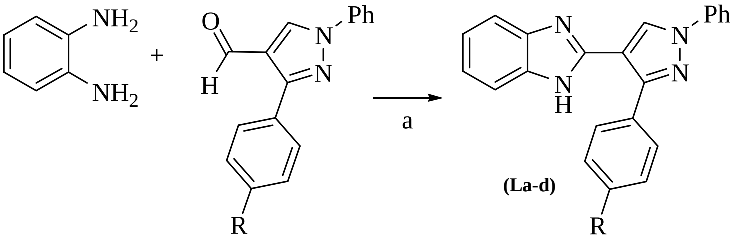
Preparation of ligands

Synthesis of 1-phenyl-3-(4′-sub-aryl)-1*H*-pyrazole-4-carbaldehydes

1-phenyl-3-(4′-sub-aryl)-1*H*-pyrazole-4-carbaldehydes were synthesized as previous published method [22-25].

Synthesis of 2-(3′-(4″-sub-aryl)-1′-phenyl-1*H*-pyrazole-4-yl)-1*H*-benzo[*d*]imidazoles (La-d)

A mixture of *o*-phenylenediamine (0.01 mol) and pyrazole aldehyde (0.01 mol) were allowed to reflux with stirring in alcohol until all the solid dissolve, to the reaction mass hydrogen peroxide (30 %, 10 ml) and Ceric Ammonium Nitrate (CAN) (0.001 mol) were added. Reaction was monitored by TLC (Solvent system, Hexane : Ethyle acetate- 4:1). After completion of the reaction, the reaction mass was poured into ice water, filtered with suction produced the benzimidazole ligands in 75-80 % yield (Scheme 1).



^{a}Reaction and conditions: CAN, H_2O_2, Me-OH
R = -4-H, -4-OCH_3, -4-OH, -4-NO_2

Scheme 1: Synthetic scheme of benzimidazole ligands (La-d)

2-(1′,3′-Diphenyl-1*H*-pyrazol-4-yl)-1*H*-benzo[*d*]imidazole (La)

Yield: 70%, m.p. 200 °C, IR (KBr) νcm^{-1}: 3350, 3196, 3053, 2983, 1693, 1643, 1599, 1560, 1498, 1452, 1371 and 1303. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm: 7.18-7.97 (dd and m, 14H, aromatic proton), 9.07 (s, 1H, pyrazole proton), 12.63 (s, 1H, imidazole proton). Mass *m/z*: 335.

2-(3′-(4″-Methoxyphenyl)-1′-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzo[*d*]imidazole (Lb)

Yield: 78%, m.p. 150 °C, IR (νcm^{-1}, KBr): 3346, 3161, 3047, 1654, 1643, 1543, 1529, 1213 and 1024. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm: 3.80 (s, 3H, methoxy proton), 7.00-8.00 (dd and m, 13H, aromatic protons), 9.07 (s, 1H, pyrazole proton), 13.02 (s, 1H, imidazole proton). Mass *m/z*: 365.

2-(3′-(4″-Hydroxyphenyl)-1′-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzo[*d*]imidazole (Lc)

Yield: 69%, m.p.: 200 °C, IR (KBr) νcm^{-1}: 3500, 3441, 3387, 3350, 3090, 3030, 1693, 1643, 1599, 1498, 1473, 1452, 1371 and 1303. Mass m/z: 351. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm: 5.12 (s, 1H, hydroxyl proton), 6.75-7.11 (dd and m, 13H, aromatic proton), 8.81 (s, 1H, pyrazole proton), 12.83 (s, 1H, imidazole proton).

2-(3′-(4″-Nitrophenyl)-1′-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzo[*d*]imidazole (Ld)
Yield: 73%, m.p.: 230 °C, IR (νcm^{-1}, KBr): 3340, 3167, 3076, 3036, 1689, 1602, 1560, 1504, 1477, 1402, 1346 and 1259. ^{1}H NMR (400 MHz, DMSO-d_6) δ in ppm: 7.24-8.02 (dd and m, 13H, aromatic proton), 9.12 (s, 1H, pyrazole proton), 13.02 (s, 1H, imidazole proton). Mass m/z: 380 (M-1).

Preparation of complexes

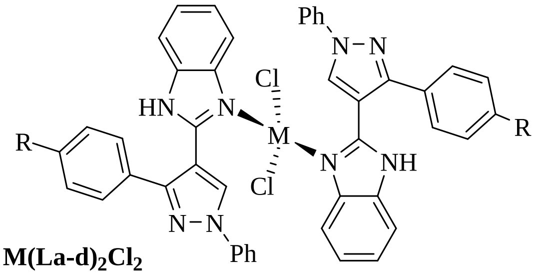
Hot solution of hydrated metal chloride (0.01 mol) in absolute ethanol was added to the hot solution of the ligand (La-d) (0.02 mol) in the same solvent (50 ml). The resulting mixture was stirred under reflux for several days whereupon the complex precipitate. Dark colored crystals were collected by filtration, washed with a distilled water and methanol.

RESULTS AND DISCUSSION

Synthesis

Eight novel Cu(II) and Ni(II) complexes of 2-substituted benzimidazole ligands (La-d) were synthesized and characterized. The monodentate ligands (La-d) linked directly to metal ion through tertiary nitrogen atom of imidazole ring, which have a lone pair of electron to form a coordinate covalent bond. In forming of the coordination bond the metal ion attracts the electrons of the imidazole ring of tertiary nitrogen. All the complexes are insoluble in common organic solvents such as alcohols and acetone but highly soluble in DMF and DMSO.

All the complexes were synthesized in the reaction of warm ethanolic solution of the $CuCl_2.2H_2O$ and $NiCl_2.6H_2O$ with benzimidazole ligands (La-d) in a 1:2 mole ration. It should be noticed that the reaction of all the metal ions yielded bis (La-d) metal complexes. The analysis of complexes, magnetic moment and molar conductivity data are summarized in Table 1. The molar conductivity values of Cu(II) and Ni(II) complexes indicate that these complexes behave as non electrolytes. The proposed structure of complexes is given in Figure 1.



$M(La\text{-}d)_2Cl_2$

R = 4-H, 4-OCH_3, 4-OH, 4-NO_2
M = Cu(II) and Ni(II),

Figure 1: Proposed structure of $M(La\text{-}d)_2Cl_2$ metal complex

Table 1: Physical characteristics and analytical data of the metal complexes

Complex	Color	μ_{eff} (BM)^b	Λ^a	Metal % Cacld.(Found)
$Cu(La)_2Cl_2$	Dark blue	1.70	11.94	7.87 (7.71)
$Cu(Lb)_2Cl_2$	Yellow green	1.68	14.48	7.33 (7.23)
$Cu(Lc)_2Cl_2$	Blue	1.74	16.55	7.57 (7.43)
$Cu(Ld)_2Cl_2$	Dark brown	1.71	17.71	7.08 (6.95)
$Ni(La)_2Cl_2$	Greenish blue	4.00	12.30	7.31 (7.23)
$Ni(Lb)_2Cl_2$	Light green	3.94	10.82	6.81 (6.68)
$Ni(Lc)_2Cl_2$	Dark green	4.02	8.58	7.03 (6.90)
$Ni(Ld)_2Cl_2$	Dark red	3.89	15.25	6.58 (6.45)

^{a}*($\Omega^{-1}cm^2mol^{-1}$) Molar conductance in DMF solution 1×10^{-3} M at 30 ℃*
^{b}*Measurement were performed at 27 ℃*

Infrared spectra

The infrared spectra of the all ligands exhibits the bands at 3387-3161 cm^{-1} which assigned to ν(N-H) stretching vibrations. The band emerging at 1693-1654 cm^{-1} about to ν(C=N) vibrations of benzimidazole ring [26,27]. Substituted phenyl groups of pyrazole moiety in all ligands shows the ring stretching vibrations at 3090-2983. The IR spectra of investigated complexes are similar to those of the corresponding ligands. There are some significant changes between the metal complexes and their free ligand. The co-ordination mode and sites of the ligand to the metal ion was investigated by comparing the infrared spectra of the free ligand with its metal complexes. The stretching vibrations for the N-H and C=N bonds in metal complexes are shifted to 3372-3150 cm^{-1} and 1660-1612 cm^{-1} in metal complexes. Upon co-ordination, it is note worthy that the peaks in the range of 1660-1612 cm^{-1} attributed to ν(C=N) vibration originating form *N*-3-imidazole ring, which is shifted by 30-10 cm^{-1} on complexion, indicating co-ordination of *N*-3-atom to metal ion ν(M-N) observed near about at 501-445 cm^{-1} and ν(N-Cl) observed at 440-400 cm^{-1}. The values of all the ligands and complexes are assigned in Table 2.

Table 2: Selected IR frequencies of ligands (La-d) and their complexes $M(La\text{-}d)_2Cl_2$

Comp^d	ν(C-NH)	ν(C=N)	ν(N-M)	ν(M-Cl)
La	3350	1693	-	-
Lb	3346	1654	-	-
Lc	3387	1654	-	-
Ld	3340	1693	-	-
$Cu(La)_2Cl_2$	3343	1660	453	421
$Ni(La)_2Cl_2$	3330	1668	478	422
$Cu(Lb)_2Cl_2$	3340	1631	428	403
$Ni(Lb)_2Cl_2$	3345	1639	422	400
$Cu(Lc)_2Cl_2$	3372	1642	445	432
$Ni(Lc)_2Cl_2$	3358	1643	472	435
$Cu(Ld)_2Cl_2$	3342	1659	450	400
$Ni(Ld)_2Cl_2$	3348	1670	501	412

^{1}H NMR spectra

The ^{1}H NMR spectrum of 2-(3′-(4″-sub aryl)-1′-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzo[*d*]imidazole (La-d) in DMSO-d_6 solution confirms their structures. All 1*H*-benzo[*d*]imidazole ligands displays a singlet broad peak at 13.02-12.63 δ ppm due to the secondary amine –NH group the imidazole ring proton, which is the confirmation of the formation of imidazole ring. Further, more singlet were observed in all NMR spectra in the range of 9.12-8.81 δ ppm assigning the pyrazole ring proton for –CH group. The double dublets and multiplets of aromatic ring protons were observed in the range of 6.75-8.02 δ ppm. The ^{1}H NMR spectra of the complexes are nearly similar to their analogous ligands. The ^{1}H NMR spectrum of complexes conformed that ligand is an *N*-monodentate one donor ligand because the secondary amine proton peak were present in all ^{1}H NMR spectra of complexes, moreover, there was no major difference in δ values between ligand protons and complexes protons, the intensity of peaks were increased may be due to double characteristic peak of both attached ligands. It is indicates that there is no formation of any new bond by losing protons rather than coordinate covalent bond by lone pair of electron of tertiary nitrogen of imidazole ring.

Electronic spectra

The UV-visible spectrum of the free ligands shows two adsorption bands near about at 263 and 311 nm of $M(La\text{-}d)_2Cl_2$ complexes. The visible spectrum of all complexes in *N*,*N*-dimethylformamide is displays broad and weak bands at 660-800 nm. The predictable difference between tetrahedral and square planar complexes in respect of their electronic spectra is that the bands obtained for tetrahedral complexes is in higher range than those of square planar complexes. The Ni(II) complexes are shows bands at 730-770 nm showing $^3T_{1g} \rightarrow {}^3T_{2g}$, $^3T_{1g} \rightarrow {}^3A_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ transitions which are higher than the Cu(II) complexes whose shows bands at 640-670 nm demonstrating $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_g \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions. The observed transitions for the Ni(II) and Cu(II) complexes suggest the tetrahedral and square planar environment respectively around the metal ions. The shoulder type low laying absorption bands are appeared at 400-489 nm due to the ligand metal charge transfer transition in all the complexes.

Magnetic properties

A suggestion of the most probable stereochemistry of the synthesized Cu(II) and Ni(II) complexes is given by its magnetic moment. The effective magnetic moments of Ni(II) and Cu(II) complexes were measured in DMF solution at room temperature. The Ni(II) complexes usually have a tetrahedral configuration. The magnetic value of Ni(II) complexes fall in expected range (μ_{eff} = 3.89-4.02 BM) suggesting the tetrahedral stereochemistry. While the μ_{eff} value for Cu(II) complexes observed in the range of (μ_{eff} = 1.68-1.74 BM) suggests the square planar geometry around Cu(II) ions [28]. The magnetic properties of all the complexes are given in Table 1.

Thermal analysis

TGA graphs of complexes shows four weight-loss steps in the range 30-1000 °C. The initial weight loss start in the range 80-195 °C is attributed to the elimination of lattice and/or coordinated water molecules. In the temperature range 220-455 °C, the mass loss is in a good agreement with the loss of one molecule of the ligand. The second step of the thermal decomposition in the temperature range 460-750 °C is associated with the loss of second molecule of the ligand [29]. The last step of the exclusion is leading to complete decomposition for the conversion of metal oxide (CuO and NiO) as a final product from which the metal content was calculated.

CONCLUSION

The ligands 2-(3′-(4″-sub ary)-1′-phenyl-1*H*-pyrazole-4-yl)-1*H*-benzo[*d*]imidazoles (La-d) formed with Cu(II) and Ni(II) complexes in the empirical formula $M(La\text{-}d)_2Cl_2.nH_2O$ (M = Cu, Ni, La-d = 2-substituted benzimidazole ligands, n = 0, 1 or 2). The complexes were synthesized and characterized by elemental analysis of the metal, molar conductivity, magnetic susceptibility, IR spectra, ^{1}H NMR spectra electronic spectra and thermogravimetric analysis. Cu(II) and Ni(II) complexes behave as non electrolytes in 10^{-3} M DMF solution, Cu(II) complexes have a square planar stereochemistry while Ni(II) complexes possess tetrahedral configuration. The configurations of complexes are realized by coordination of tertiary nitrogen of imidazole ring and it is confirmed from the ^{1}H NMR spectra of complexes that novel benzimidazole lligands are monodentate and non-chelated in nature.

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