

Synthesis and Characterization of Pendant 3-(2-pyridyl) pyrazole based ligands and Investigate Their Complexes of Cu(II), Zn(II), Ni(II), and Ru(II) In Solution

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ABSTRACT

Extend to our interest to design, synthesis and study the coordination behavior of 3-(2-pyridyl)pyrazole based ligands; new ligand containing bidentate chelating 3-(2-pyridyl)pyrazole unit connected to 3-methylbenzyl; 2-(1-(3-methylbenzyl)-1H-pyrazol-3-yl)pyridine (L1), has been synthesized and characterized using 1HNMR and mass spectroscopy. However, we have used 3-methylbenzyl moiety to examine the whole coordination behavior of the ligand in solution. Moreover, the molecular orbitals characterizations of new ligand (L1) have been investigated computationally using hyper chem tools. The ligand (L1) used to prepare Cu(II), Zn(II) and Ru(II) complexes which have been structurally characterized using mass spectroscopy. Dissolve L1-complexes of Zn(II) in CH3CN and Ru(II) in CH3OH revealed that both of Zn(II) and Ru(II) ions coordinated by three units of 3-(2-pyridyl)pyrazole from three different ligands; which confirmed by mass spectroscopy. Moreover, tracking the [Ru(L1)3]2+ in methanoic solution emerged that three peaks assigned belonging to the complex: m 633.48, {Ru(L1)2Cl}+; 601.46, {Ru(L1)2}+and 445.68, {Ru(L1)3}2+. The mass spectrum of dissolved powder in CH3CN shows peak at m/z 388.14 (100%) corresponds to [Cu(L1)2(ClO4)](ClO4)3.H2O. Also, influence of pendant naphthyl group of 2-(1-(naphthalen-2-ylmethyl)-1H-pyrazol-3-yl) pyridine (L2) to Zn(BF4)2, and Ni(BF4)2 have been investigated in solution using same technique.

Keywords: 3-(2-pyridyl) pyrazole; Molecular orbitals; Coordination chemistry; Supramolecular.

INTRODUCTION

Coordination chemistry of 3-(2-pyridyl)pyrazole as organic N-heterocycle bidentate ligands has recently a great progress [1-4]. C.-S. Liu et al. and others were reported one unit of 3-(2-pyridyl)pyrazole-based ligands with different pendant aromatic groups(figure 1) and described their coordination behavior with transition metals [5,4]. Consequently, the coordination behavior 3-(2-pyridyl)pyrazolate with transition metals attracted of coordination chemistry researcher to develop and synthesis this class of coordination site [6]. The bis-(3-(2-pyridyl)pyrazole) class of ligands have been developed and synthesized by group of Ward et al [7,8]. However, the bis-(3-(2-pyridyl)pyrazole) units connected with different linkers and their coordination behavior produced varies architectures structures of supramolecular coordination compounds. Furthermore, the structures of bis-(3-(2-pyridyl) pyrazole) ligands produced aesthetic appealing structure arranged from MnLm; (n=2,4,6,8; m=3,6,9,12). [7,9,10] As example (figure 2), tetradentate ligands L26Py and L13Ph which, on reaction with labile first row transition metal ions reported cube cages with Z(II) and Co(II). However, L26Py with lower ionic radius of Ni(II) reported square [Ni4(L26Py)6](BF4)8 whereas with higher radius of Zn(II) reported cubic cage [Zn8(L26Py)12](ClO4)16.

These structures revealed that each corner connected by three units of 3-(2-pyridyl)pyrazole [7]. Apparently, the coordination behavior of metal complexes in solution may different in solid state [11]. The most surprising differences of coordination behavior between solution and solid state was reported by Ward and et al in [Zn8(L13Ph)12](ClO4)16. The 1HNMR spectrum of [Zn8(L13Ph)12](ClO4)16 in CD3NO2 recorded 90H proton environments consistent with the hexanuclear of "open book" whereas, the crystal structure of [Zn8(L13Ph)12](ClO4)16 reported cube coordination cage [11].

Notably, metal complexes have been synthesized and reported with ligands L1Ph, L3Py, L1NaPh and Cu(II), Cd(II), Ag(I) and Zn(II).As example, reaction of L3Py with Ag(I) produced crystal structure consists of ClO4- in 1D chain cations {[AgL3Py]+}∞. The crystal structure showed Ag(I) coordinate with three donor atoms two from pyridyl-pyrazole and one from the pendant pyridyl ring

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Figure 1. Chemical Structure of some pendant aromatic ligands L1Ph and L3Py, L1NaPh, L2NaPh and L8Qu.[4] [5]



Figure 2. - Chemical Structure of some bis-(3-(2-pyridyl)pyrazole) ligands L13Ph and L26Py [11].



Scheme 1. Synthesis of 2-(1-(3-methylbenzyl)-1H-pyrazol-3-yl)pyridine (L¹)



Figure 3. 3-D view of 2-(1-(3-methylbenzyl)-1H-pyrazol-3-yl)pyridine (L1)



Figure 4. shows the crystal structure of L2. The ligand synthesized by Najar and et al. in same manner of L1[4]. Chemical structure of 2-(1-(naphthalen-2-ylmethyl)-1H-pyrazol-3-yl) pyridine (L2)

of another ligand formed distorted trigonal planar coordination geometry [5]. In the present paper we have been reported a new pyridyl-pyrazole ligand attached to electron donating group(EDG). Its coordination behavior has been study by mass spectroscopy.

METHOD

Experimental

Caution!

Metal perchlorate salts are potentially explosive; it should be prepared in small quantities and handled with care.

Materials and Solvents: Metal salts and organic reagents were purchased from Sigma Aldrich or Alfa Aesar. 1H NMR spectra were recorded on a Bruker - 400 MHz spectrometer. EI mass spectra were recorded with full scan ms [40.00-1000.0]. 3-(2-Pyridyl)pyrazole was synthesized by reported procedures[4]. All the other reagents for synthesis were commercially available and used as received.

Synthesis of Ligand L1: A mixture of 3-methylbenzylbromide (1.00 g, 5.40 mmol), 3-(2-pyridyl)pyrazole (0.789 g, 5.40 mmol), aqueous NaOH (10M, 10 mL) and tetrahydrofuran (THF) 50mL was heated at reflux with stirring for 23h. After cooling, the organic layer was washed with water and then dried over MgSO4. The residue was purified by column chromatography on silica gel eluting with, ethyl acetate to give L1 as an off white solid in 90% yield. ESMS: m/z 249.23(80%). 1HNMR (400MHz,CDCl3) :2.248(3H,s, CH3), 5.87(2H, s, CH2), 6.80 (1H, d,pyrazolylH4), 6.98 (1 H, m, benzyl H4),7.08 (1 H, m, benzyl H2), 7.07 (1H, d, pyazolyl H5),7.08 (1 H, m, benzyl H6) , 7.43 (1 H, m, benzyl H5), 7.59(1 H, t, pyridyl H5), 8.02(1H, t, pyridyl H4), 8.40 (1H, d,pyridyl H3),8.56 (1 H, d, pyridyl H6).

Complexes of pyridyl-pyrazole ligands: Zn-complex of L1: A solution of Zn(ClO4)2.6H2O (0.032 g 0.086 mmol) in MeOH (7 cm3) was added to a solution of L (0.025 g, 0.100 mmol) in CH2Cl2 (7 cm3) .The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH2Cl2, and dried in vacuo to give [Zn (L1) 3] (ClO4)2 as a white powder in 90% yield. EI-MS: m/z 412.15 (80%).

Cu-complex of L1: A solution of Cu(ClO4)2.6H2O (0.032 g, 0.086 mmol) in MeOH (7 cm3) was added to a solution of L1 (0.025 g, 0.100 mmol) in CH2Cl2 (7 cm3). The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH2Cl2, and dried in vacuo to give green powder in 70% yield. EI-MS: m/z 388.14 (100%).

Ru-complex of L1: To 50 mL test tube was added 2-(1-(3-methylbenzyl)-1H-pyrazol-3-yl)pyridine (80 mg, 0.321 mmol), RuCl3.6H2O (24 mg, 0.1 mmol), ethanol (6mL) and H2O (2 mL). This solution was stirred overnight at 80 oC, during which time solution color changed from dark brown to yellow. The solvent was then removed via rotary evaporation and the residue purified via passage through a Sephadex-20 column eluted with methanol to give [Ru(L1)3]Cl2 as a tan solid. EI-MS: m/z 445.66 (40%).

Zinc complex of L2: A solution of Zn(BF4)2.6H2O (83.79 mg 0.35 mmol) in MeOH (7 cm3) was added to a solution of L (100 mg, 0.0.35mmol) in CH2Cl2 (7 cm3) .The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH2Cl2, and dried in vacuo to give J Phys Chem Biophys, Vol. 10 Iss. 3 No: 290

[Zn (L1) 3](BF4)2 as a white powder in 90% yield. EI-MS: m/z 412.15 (80%).

Nickel complex: A solution of Ni(BF4)2.6H2O (59.57 mg, 0.175 mmol) in MeOH (7 cm3) was added to a solution of L1 (50 mg, 0.175 mmol) in CH2Cl2 (7 cm3). The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH2Cl2, and dried in vacuo to give pink powder in 70% yield. EI-MS: m/z 388.14 (100%).

RESULT

L1; synthesis of new ligand. The synthesis reaction of the ligand is shown in Scheme 1; it was prepared by reaction of 3-(2-pyrazol-1-yl) pyridine with 1-(chloromethyl)-3-methyl benzene under basic conditions using phase transfer reaction. The 3-(2-pyrazol-1-yl) pyridine pendant to toluene ring. The ligand is bidentate with one bidentate chelating site. The methyl group substitution on benzyl ring could affect the ligand solubility in organic solvent to give the whole picture to examine the solution behavior of the compounds.

DISCUSSION

Complexes

Complexes of pyridyl-pyrazole ligand (L1) with Zn(II): Complexes [Zn(L1)3](ClO4)2; was prepared by reaction of Zn(ClO4)2.6H2O and ligands L1. The complex formed by dissolve Zn(ClO4)2.6H2O in MeOH and Ligand in CHCl3. The participated was filtered of and washed with MeOH and CHCl3 and dried. The white powder was dissolved in CH3CN and full scanned using ES-MS to give peaks at: 412.15, {Zn(L1)(ClO4)}; 577.50, {Zn(L1)2}; 647.57, {Zn(L1)2(ClO4)}.

Complexes of L1 with Ru(II): Complexes [Ru(L1)3]Cl2; was prepared by reaction of RuCl3.5H2O4 and ligands L1.The residue purified via passage through a Sephadex-20 column eluted with methanol. Evaporated the solvent gives the tan powder. The powder dissolved in MeOH and scanned with ES-MS to gives peaks at: 633.48, {Ru(L1)2Cl}+; 601.46, {Ru(L1)2}2+; 445.68, {Ru(L1)3}2+.

Complexes of L2 with Zn(II): Zinc complex; was prepared by reaction of Zn(BF4)2.6H2O and ligands L2. The complex formed by dissolve Zn(BF4)2.6H2O in MeOH and Ligand L2 in CHCl3. The participated was filtered of and washed with MeOH and CHCl3 and dried. The white powder was dissolved in CH3CN and full scanned using ES-MS to give peaks at: 634.31, {Zn(L2)}; 577.50, {Zn(L2)2BF4}; 922.17, {Zn(L2)3}.

Complex of L2 and Ni(BF4)2: The Nickel complex of L2 was prepared in exactly the same manner as L2-Zn complex but starting from Ni(BF4)2. The pink powder was dissolved in CH3CN and full scanned using ES-MS to give peaks at: 320.286, {Ni(L2)2}; 691.69, {Ni(L2)BF4}; 914.97, {Ni(L2)3}.

Computational investigation of molecular orbitals for L1: Personal acer desktop PC with Windows XP, a 2.93 GHz Intel (R) core (TM) 2 Duo CPU, and 4.00 GB of RAM was used to run all the calculations. Semi-empirical PM3 quantum chemical calculation was carried out by the Hyper Chem (version 8) TM 8.0 Molecular Modeling program[12]with root mean square (RMS) gradient 0.1 kcal/Åmol using Polak Ribiere algorithm. The calculations for all compounds runs using semi-empirical-geometry optimization-PM3 methods [13]. In our calculations, we have been Appling PM3geometry optimization using semi-empirical methods. The used methods were of the most common and popular computational protocols in our group [13,14]. The calculated data listed in the tables below.

Structure optimization: The geometrical optimization have been applied in order to minima the internal energy of molecular structure. However, within the geometry optimization the molecular symmetry calculated and preforming both of molecular symmetry and asymmetry properties [15]. Thus, all of calculation parameters for compound obtained based on optimal geometry.

Frontier molecular orbital (FMO)

Molecular orbitals and compound reactivity: Molecular orbital energy can be used to determine the most important properties of chemical compound. The high occupied molecular orbital abbreviate as (HOMO) and Low unoccupied molecular orbital (LUMO) can be used to describe molecular stability using the difference between HOMO-LUMO as the most stable molecule has low energy gap (ΔE) and vice versa. However, chemical reactivity of molecular compounds and be detected using HOMOM/ LUMO; the shorter LUMO- HOMO gap is considered as the high reactivity. Moreover, the molecules stability and reactivity can be measured based on the EHOMO/ELUMO gap where; molecule with high Egap have a low stability so it has a low reactivity [16]. The HOMO is level of energy where the electrons accommodate in and has ability to give these electrons such as an electron donor. On the other hand, LUMO can be through the innermost orbital containing free places to accept electron. Additionally, most of reactivity descriptors such as electrophilicity (ω), the chemical potential (μ), electronegativity (χ), hardness (η) and softness (S) can be determined using some relationship with HOMO and LUMO energy orbital. The ionization energy (I) and electron affinity (A) can be determined using -EHOMO and -ELUMO values respectively [15]. Also hardness, softness parameters and Fukai Index can be used as indicator for stability of molecules. However, direct relationship between polarizability, hardness and stability of molecules. The minimum polarizability and minimum hardness indicate the more stable [15]. Additionally, the polarization of molecules usually effected by the energy gap; molecules with low energy gap tend to be easy to polarize [16]. Thus, we can observe that the ligand recorded Softness (S) at 0.232 and Hardness (η) at 4.301, ionization energy (I) at 8.861and electron affinity (A) at 0.259, chemical potential (μ) at -4.56, electrophilicity (ω) at 44.716, and electronegativity (γ) at 4.56. However, the polarization of molecules usually effected by the Egap; molecules with high energy gap tend to be hard to polarize[16]

CONCLUSION

As a result of this research, a new bidentate organic ligands 2-(1-(3-methylbenzyl)-1H-pyrazol-3-yl)pyridine and its coordination compounds with Cu(II), Zn(II) and Ru(II) were synthesized. The characterization of ligands was based on 1HNMR and mass spectroscopy. The characterization of coordination compounds in solution was based on mass-spectroscopy. Tracking the complexes in solution revealed that the three complexes conduct different behavior.

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No potential conflict of interest was reported by the authors.

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