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Synthesis and Characterization of Zn(II) Complex of a Tripodal Tetradentate (N_4) Ligand and a Theoretical Study

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A slightly modified method for synthesis of a previously known tetradentate (N_4) tripodal ligand, $N(CH_2CH_2NH_2)_2(CH_2C_5H_4N)$ (L_{22py}), is reported. A new zinc(II) complex, $[Zn(L_{22py})](ClO_4)_2$, is prepared from the direct reaction of the latter ligand and $ZnCl_2$ in equimolar ratio followed by addition of excess amount of $NaClO_4$. The resulting complex is characterized by microanalysis, IR, ^1H NMR and ^{13}C NMR spectra. The *ab initio* calculations on $[Zn(L_{22py})]^{2+}$ show that all nitrogen donor atoms of the ligand are coordinated to the metal ion.

Key Words: *ab initio*, **Tetradentate ligands, Tripodal complexes.**

INTRODUCTION

Zinc(II) is present at the active sites of various enzymes in living systems and plays a central role in catalysis and gene expression[1-5]. Most of these zinc-containing enzymes are involved in hydrolysis reactions with the Zn(II) ions acting as a Lewis acid or playing a structural role[6]. From crystal structure, the active site coordination environment of the metal ion is well known for several enzymes. Catalyses of the hydrolysis of amides and carboxylate and phosphate esters by both mono- and multi-nuclear Zn(II) synthetic complexes and zinc-containing metalloenzymes are known[7]. In aqueous solution and in small-molecule complexes, species containing zinc(II) with coordination number six is common. It is the flexibility of coordination number and coordination polyhedra that may enable zinc(II) to reveal its essential catalytic function as during a reaction this will enable a substrate to bind to the metal without releasing another group from the coordination sphere. In order to elucidate the mechanism of zinc(II) involvement in hydrolytic enzymes, small-molecule complexes have been synthesized[8]. Herein, the synthesis and characterization of mononuclear zinc(II) complex with a tetradentate (N_4) ligand containing pyridinyl group is reported.

EXPERIMENTAL

Diethylenetriamine and 2-picolylchloride hydrochloride were obtained from Merck Company and were used without further purification. Bis(2-phthalimidoethyl)amine was prepared by the literature method[9]. IR and NMR spectra were measured on Perkin-Elmer FT-IRGX and Bruker FT-NMR 500Hz spectrometers, respectively.

Computational methods

The geometries of $[ZnL]^{2+}$ species at gas phase were fully optimized at both the Hartree-Fock and DFT (B3LYP)[10] levels of theory using Gaussian 98 set of programs[11]. At first, this complex was optimized using the standard LanL2MB basis set[12] and then the resulting structures were used for further calculations using standard 3-21G* basis set for ligand atoms and LanL2DZ for metal ion[13, 14]. The latter resulting structures were also used for similar calculations using 6-31G* basis set for ligand atoms[15]. Therefore, this complex was fully optimized with six different methods. Vibrational frequency analyses, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Calculations were performed on a Pentium-PC computer with 2400 MHz processor. A starting molecular mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program[16].

Preparation of bis(2-aminoethyl)(pyridine-2-ylmethyl)amine (L_{22py})

Step 1: Preparation of bis(2-phthalimidoethyl)(pyridine-2-ylmethyl)-amine: Bis(2-phthalimidoethyl)amine (5 g, 13.76 mmol) was suspended in 50 cm^3 of water with stirring and pH was adjusted to between 11.5 and 12 by addition of NaOH (5 M). The reaction mixture was kept at room temperature and 2-picolyl chloride (2.26 g, 13.76 mmol) was added. Then the mixture was stirred for 3 d. The mixture was evaporated by rotary evaporation to give dark oil and then EtOH (80 cm^3) was added to give a white powder. Yield: 5.4 g (90%). ^1H NMR δ_H (D_2O) 2.9 (t, 4H), 3.5 (t, 4H), 3.9 (s, 2H), 7.3 (m, 8H), 7.6 (m, 4H). ^{13}C NMR δ_C (D_2O) 33.7, 53.2, 54.0, 122.5, 123.4, 125.4, 126.0, 133.7, 134.0, 147.2, 152.0, 168.0.

Step 2: Preparation of ligand L_{22py}: Bis(2-phthalimidoethyl)(pyridine-2-ylmethyl)amine (5 g) was dissolved in 6 N HCl (100 cm^3) and heated under reflux for 24 h to remove the protection group. The phthalic acid and inorganic salts (NaCl), which formed on cooling, were filtered off and the filtrate was evaporated to small bulk and poured into absolute EtOH. The resulting viscous precipitate was washed with absolute EtOH and dried in vacuum to give a brown powder. Yield: 1 g (27%). ^1H NMR δ_H (D_2O), 3.0 (t, 4H), 3.2 (t, 4H), 4.2 (s, 2H), 8.1 (m, 2H), 8.8 (m, 2H) ^{13}C NMR δ_c (D_2O) 36.3, 50.2, 54.4, 126.2, 127.1, 141.1, 147.2, 152.1.

Preparation of $[Zn(L_{22py})](ClO_4)_2$ complex

$L_{22py}\cdot 3HCl$ (0.1 g, 33 mmol) and NaOH (0.039 g, 0.99 mmol) were mixed and heated under reflux for 1 h in EtOH (15 cm^3) solution. Then NaCl, which formed on cooling, filtered off and $ZnCl_2\cdot 4H_2O$ (0.1 g, 0.33 mmol) dissolved in MeOH (5 cm^3) was added to the filtrate. The reaction mixture was stirred at 50–60°C for 1 h. The solvent was evaporated to small bulk and after cooling, an excess amount of $NaClO_4$ was added. The white crystals of product were obtained by slow diffusion of diethyl ether to above solution. Yield: 0.04 g (26%). % Anal. Calcd. (Found) for $C_{10}H_{18}N_4O_8Cl_2Zn$: C, 26.19 (26.13); H, 3.95 (3.96); N, 12.21 (11.96). IR (cm^{-1}, Nujol): 3361, 3305, 3242 and 3165 (ν(N—H) *str.*), 1606 and 1573 (ν(C=N) and/or ν(N—H) binding), 1090 (vs, ν(Cl—O) *str.*), 622 (s, ν(Cl—O) binding). ^1H NMR δ_H (D_2O) 2.7 (m, 4 H), 2.8 (m, 4 H), 4.1 (s, 2 H), 7.4 (m, 2 H), 7.9 (t, 1 H), 8.5 (s, 1 H). ^{13}C NMR δ_C (D_2O) 37.8, 52.6, 57.6, 125.1, 125.4, 142.0, 148.6, 157.1.

RESULTS AND DISCUSSION

The ligand L_{22py} was prepared as hydrochloride salt by the literature method[17] with slight modification in two steps. Herein, in contrast to the previously reported methods the protected form of ligand (Fig. 1) was also isolated. The successful *in situ* reaction of protected triamine with 2-picolyl chloride and formation of ligand in its protected form is confirmed by the lack of N—H stretching band of the initial protected amine at about 3324 cm^{-1} in the IR spectrum. Furthermore, the ^1H NMR and ^{13}C NMR spectra of this product clearly confirm its formation and purification. The IR and NMR spectra of the ligand L_{22py} which is the product of acidic hydrolysis of its protected form are also completely consistent with its structure and formulation.

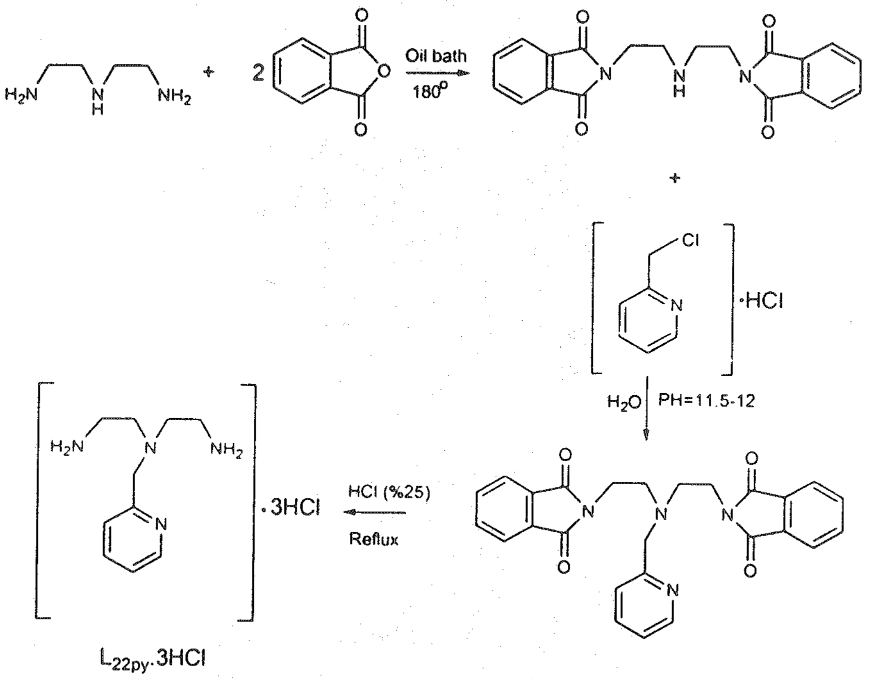

Fig. 1

Complex synthesis

The $[Zn(L_{22py})](ClO_4)_2$ complex was readily synthesized by the reaction of neutralized L_{22py} tripodal ligand with zinc(II) ion and characterized by micro-analysis, IR, ^1H NMR and ^{13}C NMR spectra. The presence of two pairs of sharp ν(N—H) bands in the IR spectrum of the $[Zn(L_{22py})](ClO_4)_2$ complex is consistent with the existence of two primary amine groups. The stretching bands of pyridine C═N group and bending bands of primary amine groups appear, as expected, at about 1573–1606 cm^{-1}. ^{13}C and ^1H NMR spectra of this complex are completely consistent with its formulation and are similar to those of the ligand except that, as expected, there are small shifts in the corresponding peaks.

Ab initio and DFT studies

The geometry of $[Zn(L_{22py})]^{2+}$ cation was also fully optimized with six different methods at both the Hartree-Fock (HF) and density functional B3LYP levels of theory.

Selected calculated bond lengths and bond angles of this complex are given in Table-1. The results of methods studied here are close to each other and show that the two primary amino groups as well as pyridine nitrogen and single tertiary nitrogen donor atoms are arranged at apices of a significantly distorted tetrahedron (Fig. 2). A similar structure has been experimentally determined for a zinc complex of a tripodal tetradentate ligand L_{333}, $[Zn(L_{333})](ClO_4)_2$ $\{L_{333} = N(CH_2CH_2CH_2NH_2)_3\}$, in which the distortion from tetrahedral geometry is less significant[18]. The calculated $Zn-NH_2$ bond distances in $[Zn(L_{22py})]^{2+}$ are similar to corresponding bond distances in $[Zn(L_{333})]^{2+}$. In both complexes the Zn-N(tertiary) bond distance is longer than other Zn-N bond distances. For $[Zn(L_{333})](ClO_4)_2$ complex the X-ray crystal structure analysis it has been shown that the metal ion is not completely encapsulated by tripodal ligand but neither the chloride anions nor the water molecules are bound to the Zn(II) ion. The closest contact of metal ion with any potential donor atom, other than amine nitrogens, in the latter complex is distance from an oxygen atom of one of the two perchlorate ions (Zn-O 2.91 Å). As can be seen in Fig. 1 in the case of $[Zn(L_{22py})]^{2+}$ cation the metal is not completely encapsulated by ligand and it is probable that another donor atom, for example an oxygen atom of the two perchlorate anions, is coordinated to metal ion (or at least having a weak bonding interaction).

TABLE-1
SELECTED CALCULATED BOND LENGTH (Å) AND BOND ANGLES (°) FOR $[Zn(L_{22py})]^{2+}$ COMPLEX

	Computational level[a]					
	LanL2MB		3-21G* (LanL2DZ for Zn)		6-31G* (LanL2DZ for Zn)	
Bond lengths:						
Zn-N (1)	2.084	**2.091**	2.097	**2.108**	2.147	**2.078**
Zn-N (7)	2.067	**2.091**	2.064	**2.084**	2.097	**2.030**
Zn-N (9)	2.006	**2.033**	2.031	**2.054**	2.046	**1.985**
Zn-N (11)	2.067	**2.091**	2.065	**2.084**	2.098	**2.031**
Bond angles:						
N(1)-Zn-N (7)	87.9	**88.6**	88.6	**88.7**	86.2	**89.5**
N(1)-Zn-N (9)	87.5	**87.9**	86.5	**86.6**	85.2	**88.2**
N(1)-Zn-N (11)	87.9	**88.6**	88.6	**88.7**	86.2	**89.5**
N(7)-Zn-N (9)	115.2	**115.4**	114.6	**114.9**	113.9	**115.7**
N(7)-Zn-N (11)	129.6	**129.1**	130.9	**130.2**	131.2	**128.8**
N(9)-Zn-N (11)	114.8	**115.2**	114.1	**114.5**	113.4	**115.4**

[a] The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold.

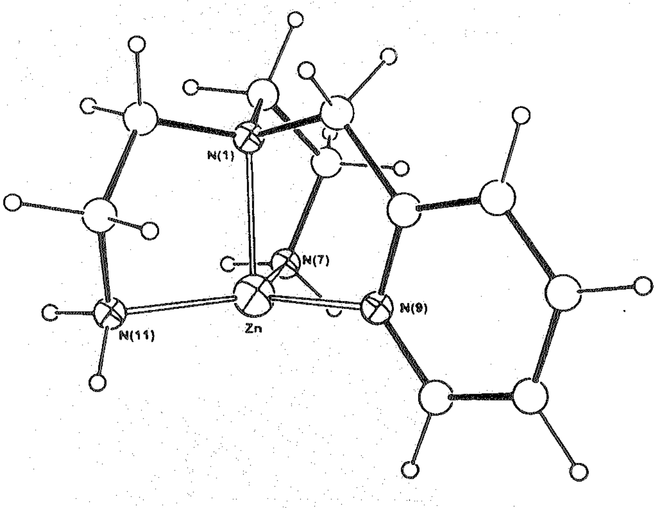

Fig. 2

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