



Geometrical structures, molecular docking, spectroscopic characterization of mixed ligand and Schiff base metal complexes



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ABSTRACT

The mixed ligand mononuclear complexes were synthesized by reaction of $MX_2 \cdot nH_2O$ ($M = Cu(II)$ or $Zn(II)$) with 4-aminoantipyrine (L_p) and heterocyclic base 1,10-phenanthroline (L). Molecular docking was used to predict the binding between the Schiff base ligands (L_1 and L_2) and the receptors of prostate cancer mutant 2q7k-hormone and breast cancer mutant 3hb5-oxidoreductase. Also the corresponding Schiff base mixed ligand complexes were prepared by condensation of mixed ligand complex $[Zn(L_p)(L)]Cl_2$ with 1,2-diaminoethane and/or benzaldehyde. All the compounds have been characterized by elemental analysis, conductance measurements, magnetic moments, spectral (UV-vis, IR, 1H & ^{13}C NMR and ESR) and thermal studies. The IR showed that the ligand (L_p) act as neutral bidentate through the amino nitrogen atom and carbonyl oxygen moiety. The presence of anion, viz., Cl^- , NO_2^- , SO_4^{2-} or NCS^- in the coordination sphere is also inferred by the IR spectral data and conductance measurements. The molar conductivities show that all the complexes are non-electrolytes except Zn(II) complexes. On the basis of electronic spectral data and magnetic susceptibility measurements, suitable geometry has been proposed for each complex. The molecular and electronic structures of the Schiff base ligands (L_1 and L_2) and complexes (**1–4**) are optimized theoretically and the quantum chemical parameters are calculated. It was found that the ligand (L_1) is more stable than the other ligand (L_2). The ESR spectral data of copper complexes provided information about their structure on the basis of Hamiltonian parameters and degree of covalency. ESR calculations support the characterization of the structures of the complex geometries.

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1. Introduction

The studies of Cu(II) complexes have been widely explored for the versatility of their coordination geometries, exquisite color, technical application dependent molecular structures, spectroscopic properties and their biochemical significance. Octahedral Cu(II) complexes of ligands containing mixed electron donors have been studied extensively, due to their potential applications as molecular materials [1]. The chemistry of pyrazolone derivatives has attracted scholarly attention because of its structures and application in derivatives [2]. 4-Aminoantipyrine is key structure in numerous compound of therapeutic importance [3], compounds containing this ring system are known to display diverse pharmacological activities such as potent activity of inhibiting protease-resistant prone protein accumulation [4], anti-tumor necrosis factor activity [5] and inhibition of human telomerase [6]. Copper(II) complexes have also merited much attention in the field of biological study and application [7].

In the last few decades, mixed ligand complexes have been extensively studied in solution as well as in the solid state [8]. Ternary

complexes are found to be more stable than binary complexes. Steric effect and back donation have also been invoked to account for the preferred formation of mixed-ligand complexes [8].

Heterocyclic compounds such as pyridine (Py), 2,2'-bipyridine (bipy), 1,10-phenanthroline (Phen) and related molecules are good ligands due to the presence of at least one ring nitrogen atom with a localized pair of electrons. The successful application of heterocyclic compounds has led to the formation of series of novel compounds with a wide range of physical, chemical and biological properties, spanning a broad spectrum of reactivity and stability [9]. A large number of mixed-ligand complexes involving heterocyclic bases such as Py, bipy and Phen have been reported [7] due to their bioinorganic applications and thermal stability.

Our interest in this area is focused for a considerable time on the investigation of the coordination chemistry of transition metal using azo pyrazolone ligand [10]. This paper reported that the synthesis and characterization of mixed ligand Cu(II) complexes are derived from 4-aminoantipyrine (L_p) as primary ligand and 1,10-phenanthroline (L) as co-ligands. The complexes prepared were characterized particularly by elemental analyses, conductance, magnetic measurements and spectral studies (IR, UV-vis and ESR) as well as thermal analysis. The molecular docking of ligands (L_1 and L_2) is discussed. In addition

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to molecular and electronic structures of the Schiff base ligands (L_1 and L_2) and complexes (**1–4**) are studied. In present work, we reported here the synthesis and characterization of Schiff base complexes of copper(II) derived from the mononuclear mixed ligand complexes.

2. Experimental

Most of the chemicals used in the present investigation were BDH. Materials which are not generally provided into the analar grade were of highest available purity. They included 4-aminoantipyrine (L_p), 1,10-phenanthroline (L), 1,2-diaminoethane, benzaldehyde, $CuCl_2 \cdot 2H_2O$, $Cu(SO_4)_2 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$ and $ZnCl_2 \cdot H_2O$.

2.1. Preparation of metal complexes

2.1.1. Preparation of $[M(L_p)(L)X_2]X_2'$ complexes (**1–3,5**)

Method A: A mixture of (5 mmol) 4-aminoantipyrine (L_p) and (5 mmol) 1,10-phenanthroline (L) dissolved in 50 mL, ethanol was added to an solution of copper salts/Zn(II) (5 mmol). The reaction mixture was refluxed for 2–3 h with constant stirring to ensure the complete formation of the metal complexes. The precipitate was filtered and washed several times with 50% (v/v) ethanol–water to remove any traces of unreacted starting materials. Finally, the filtrate was dried in vacuum desiccators over anhydrous $CaCl_2$.



M = Cu(II) at X = Cl (**1**), NO_3 (**2**), SO_4 (**3**), M = Zn(II) at X = nil, $X' = Cl$ (**5**)

2.1.2. Preparation of Cu(II) isothiocyanate complex (**4**)

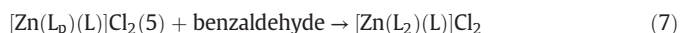
Method B: A methanolic solution (5 ml) of $Cu(NO_3)_2 \cdot 6H_2O$ (1 mmol) in the same solvent followed by addition of 4-aminoantipyrine (L_p) (1 mmol), 1,10-phenanthroline (L) (1 mmol) and NH_4NCS (1 mmol) in warm methanol. The resultant mixture was refluxed for 3 h. The product obtained was filtered washed with methanol and dried under vacuum over $CaCl_2$.



The obtain mixed ligand complexes are $[M(L_p)(L)X_2]X_2'$ (**1–5**). **Scheme 1(I)** represents the proposed chemical structure of mixed ligand complexes.

2.1.3. Preparation of complexes (**6, 7**)

A solution of complex $[Zn(L_p)(L)Cl_2]$ (**5**) (1.0 mmol) in DMF (10 mL) was added to a solution of 1,2-diaminoethane/benzaldehyde (1.0 mmol) in DMF/ethanol (v/v %). The resulting mixture was stirred whilst heating for ~5 h. The solid obtained after the addition of an aqueous solution of ethanol was filtered, washed with distilled water and followed by diethyl ether and dried in vacuum as complexes $[Zn(L_1)(L)Cl_2]$ (**6**)/ $[Zn(L_2)(L)Cl_2]$ (**7**) (**Scheme 1(II)**).



All the complexes were recrystallization from 1:1:1 molar ratio solution of methanol and benzene. The purity of the complexes was checked by thin layer chromatography (TLC). The yield of complexes = ~ 45–65%.

2.2. Measurements

Elemental microanalyses of the separated ligands and solid chelates for C, H, and N were performed in the Microanalytical Center, Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the analyzed data. The metal content in the complexes was estimated by standard methods [11,12]. The 1H NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with $DMSO-d_6$ as the solvent and TMS as an internal reference. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. Ultraviolet–visible (UV–vis) spectra of the compounds were recorded in nuzol solution using a Unicam SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [13] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\text{eff}} = 2.84 [T_M^{\text{cor.}}]^{1/2}$. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10 °C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, $10 \times 5 \times 2.5$ mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. ESR measurements of powdered samples were recorded at room temperature using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenyl picrylhydrazyle (DPPH) as a reference material. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA. In the study simulates the actual docking process in which the ligand–protein interaction energies are calculated using a Docking Server [14,15]. Docking calculations were carried out on 2q7k-hormone and 3hb5-oxidoreductase protein models. Essential hydrogen atoms, Kollman united atom type charges, and solvation parameters were added with the aid of AutoDock tools [16]. Affinity (grid) maps of $20 \times 20 \times 20$ Å grid points and 0.375 Å spacing were generated using the Autogrid program [17]. Auto Dock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively. The molecular structures of the compounds were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBio Draw and optimized using Perkin Elmer ChemBio3D software [18,19]. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}) and HOMO–LUMO energy gap (ΔE) for the investigated molecules were calculated.

3. Results and discussion

3.1. General

The formation of novel mixed ligand complexes Cu(II)/Zn(II) with organic compounds has long been recognized. However, the Schiff base mixed ligand complexes have not studied yet, although they may be an area of interest. The elemental analyses agree quite well with the speculated structure of the complexes (**Table 1**). The results of elemental analyses; (**Table 1**), suggest that the complexes are formed in 1:1:1 [Metal]:[Primary ligand]:[Co-ligand] ratio and they proposed to have the general formulae $[M(L_p)(L)X_2]X_2'$ (M = Cu(II) at X = Cl (**1**), NO_3 (**2**), SO_4 (**3**), NCS (**4**), $X' = \text{nil}$; M = Zn(II) at X = nil, $X' = Cl$ (**5**), $[Zn(L_1)(L)Cl_2]$ (**6**) and $[Zn(L_2)(L)Cl_2]$ (**7**) formed in 1:1:1 [Metal]: [mixed ligand complex]:[Co-ligand] ratio.

The ligand has N_3O cores (nitrogen of NH_2 , keto O-atom present in the pyrazolone ring and two azomethine nitrogen atoms in 1,10-phenanthroline) to coordinate metal ions. There are variable binding possibilities to metal ions for ligand structural form (see **Scheme 1(I)**). All mixed ligand complexes of Cu(II) and Zn(II) ions (**1–5**) have 1:1:1 metal-to-ligands stoichiometry, as shown in **Scheme 1(I)**. Moreover, the analytical data of metal chelates (**Table 1**) indicates that the metal

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