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Geometrical structure and potentiometric studies of 5-chloro-2,3-dihydroxy pyridine azo derivatives and their metal complexes

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ABSTRACT

5-Chloro-3-hydroxy-4-(phenylediazenyl)pyridine-2(1H)-one and its derivatives (HL_n) were synthesized and characterized using different spectroscopic techniques. The geometrical structures of the ligands are carried out by HF method with 3-21G basis set. The proton–ligand dissociation constant of the ligands (HL_n) and their metal–ligand stability constants with (Mn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+}) have been determined potentiometrically. The potentiometric studies were carried out in 0.1 M (KCl) and 10% (by volume) DMF–water mixture. The effect of temperature was studied at (298, 308 and 318 K) and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable.

1. Introduction

4-(Aryldiazenyl)pyridine compounds are widely used as analytical reagents, they are capable of forming chelates with a number of metal cations [1], the formation of which is accompanied by change in color, pH, conductivity, and absorption spectra [2]. Azo derivatives have attracted much attention by virtue of their applicability as potential ligands for a large number of metal ions [1]. The 4-(aryldiazenyl)pyridine system is highly reactive and undergoes coupling reaction with diazonium salts to give 4-arylazo derivatives [3]. The azo-derivatives of 4-(aryldiazenyl)pyridine and their metal complexes have wide applications in dye industry as well as analytical reagents for determination of trace metals. It could be useful for some medical and biological applications [4]. Different methods were reported for the synthesis of aryldiazenyl pyridine derivatives [5–7].

In continuation of our previous studies [8,9], we report herein the molecular and electronic structures of 5-chloro-3-hydroxy-4-(phenylediazenyl)pyridine-2(1H)-one and its derivatives (HL_n) using quantum chemical calculations. The dissociation constant of the investigated ligands (HL_n) and the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions at different temperatures were studied. Moreover, the corresponding thermodynamic functions are evaluated and discussed.

2. Materials and methods

2.1. Measurements

All the compounds and solvents were purchased from Aldrich and Sigma and used as received without further purification. Elemental microanalyses of the separated ligands for C, H, and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The ^1H NMR spectra was obtained by Bruker WP 300 MHz using DMSO-d_6 as a solvent containing TMS as the internal standard. IR spectra (KBr discs, 4000–400 cm^{-1}) by Jasco-4100 spectrophotometer.

The molecular structures of the ligands (HL_n) were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBioDraw and optimized using the Perkin Elmer ChemBio3D software. The pH measurements were carried out using VWR Scientific Instruments Model 8000 pH-meter accurate to ± 0.01 units. The pH-meter readings in the non-aqueous medium were corrected [10]. The electrode system was calibrated according to the method of Irving et al. [11]. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M KCl. Potentiometric measurements were carried out at different temperatures. The temperature was controlled to within ± 0.05 K by circulating

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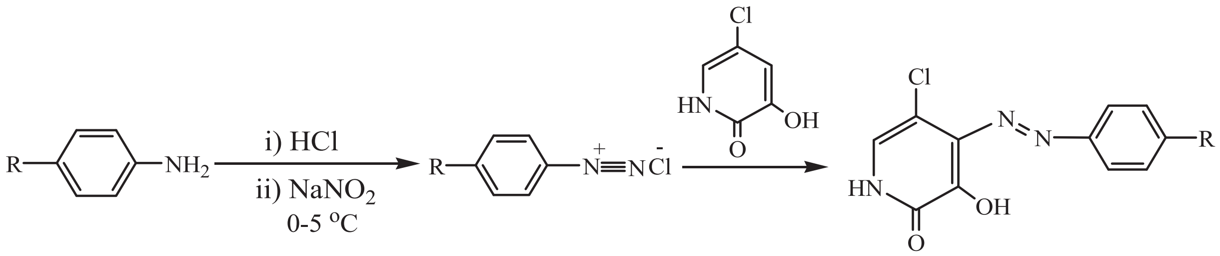
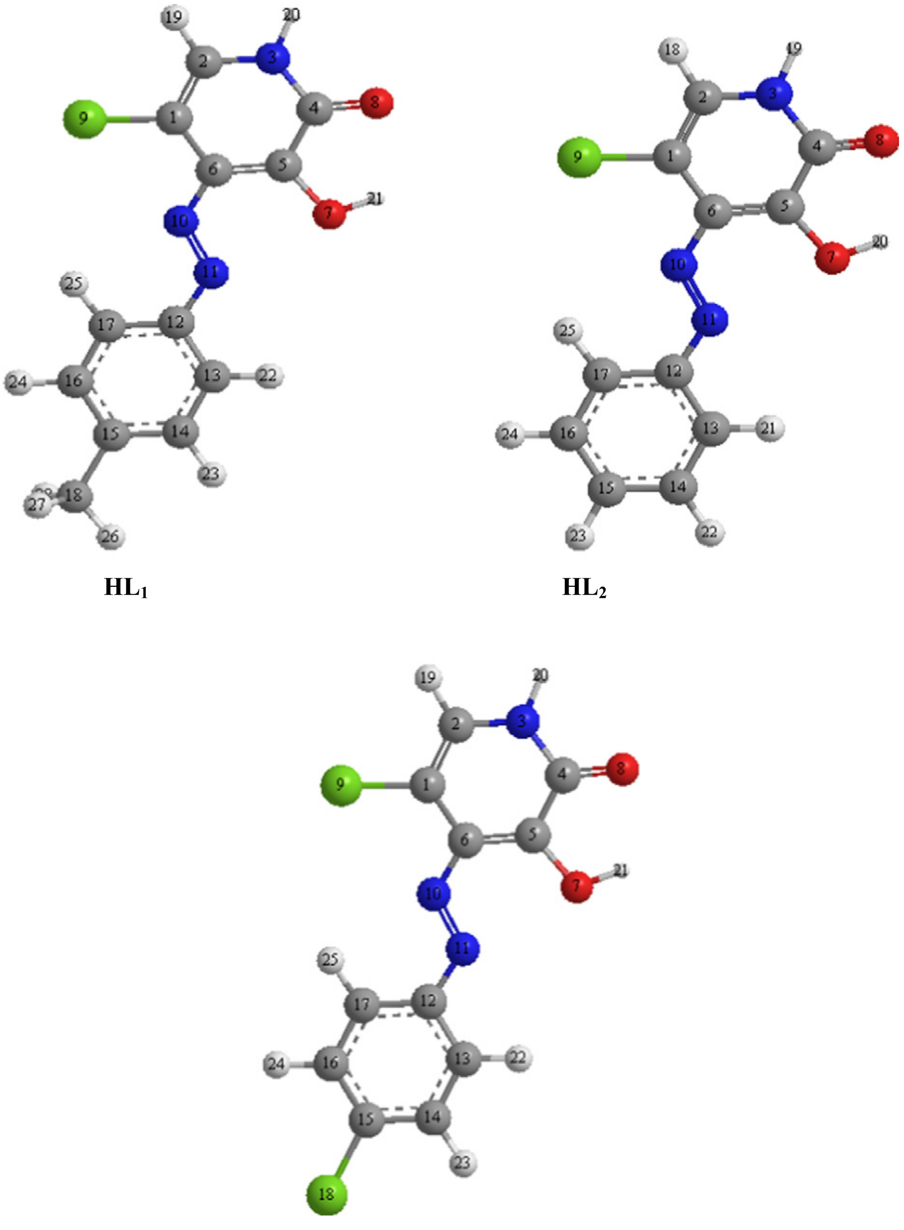


$R = -CH_3$ (HL_1), -H (HL_2) and -Cl (HL_3)

Fig. 1. Structure of the investigated ligands (HL_n).



HL₁

HL₂

HL₃

Fig. 2. The calculated molecular structures of the investigated ligands (HL_n).