Geometrical structure, potentiometric and thermodynamic studies of rhodanine azodye and its metal complexes

A.A. El-Bindary *, A.Z. El-Sonbati, M.A. Diab, Sh.M. Morgan [1]

Department of Chemistry, Faculty of Science, University of Damietta, Damietta 34517, Egypt

ABSTRACT

5-(2,3-Dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) was synthesized and characterized using different spectroscopic techniques. The molecular structures of the ligand are optimized theoretically and the quantum chemical parameters are calculated. The proton–ligand dissociation constants of HL and its metal stability constants with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} have been determined potentiometrically. The potentiometric studies were carried out in 0.1 M KCl and 10% (by volume) DMF–water mixture. At constant temperature the stability constants of the formed complexes decreases in the order Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+}. 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

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1. Introduction

Azodyes play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions [1,2]. The behavior of azodye complexes has attracted the attention of the bioinorganic chemists, since a number of these complexes are recognized to serve as models for biologically important species [3–5]. Azo compounds based on rhodanine, play a central role as chelating agents for a large number of metal ions, as they form a stable six-member ring after complexation with a metal ion. Efforts have been made to carry out detailed studies to synthesize and elucidate the structural and electronic properties of novel families of complexes with rhodanine derivatives as a novel chelating bidentate azodye models. Rhodanine derivatives are a good series of ligands capable of binding metal ions leading to metal complexes with increasing properties. The high stable potential of rhodanine derivative complexes in different oxidation states increased the application of these compounds in a wide range [6,7]. It is known that rhodanine plays an important role in biological reactions [8]. Chemical properties of rhodanine and its derivatives are of interest due to coordination capacity and their use as metal extracting agents [9] also widely the variety of coordination modes of rhodanine azo derivatives and/or pyrazolone derivatives have been demonstrated in a number of complexes. Their biological applications have a considerable interest [10, 11]. Rhodanine and its derivatives are known to possess biological activities such as antimiotic, antidiabetic, antibacterial, hypocholesterolemic,

antiperlipemic, antiviral and antidiabetic in nature and also reported rhodanine derivatives as hepatitis C virus (HCV) protease inhibitor [12–15].

In continuation of our previous work [16–19], we report herein the dissociation constants of 5-(2,3-dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) and the stability constants of its complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} at different temperatures. The corresponding thermodynamic functions are evaluated and discussed. Moreover, the molecular structures of the investigated ligand (HL) are studied and quantum chemical parameters are calculated.

2. Materials and methods

2.1. Preparation of the ligand

5-(2,3-Dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) was prepared previously [20] by coupling an equimolar amounts of 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one and 2-thioxo-4-thiazolidinone (Fig. 1). In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid was added to 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one (0.01 mol). To the resulting mixture stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazolidinone, in 10 ml of pyridine. Immediately, the orange precipitate formed was filtered through sintered glass crucible, washed several times by distilled water. The crude products was purified by recrystallization from hot ethanol, yield ~77% then dried in vacuum desiccator over anhydrous P_2O_5. The
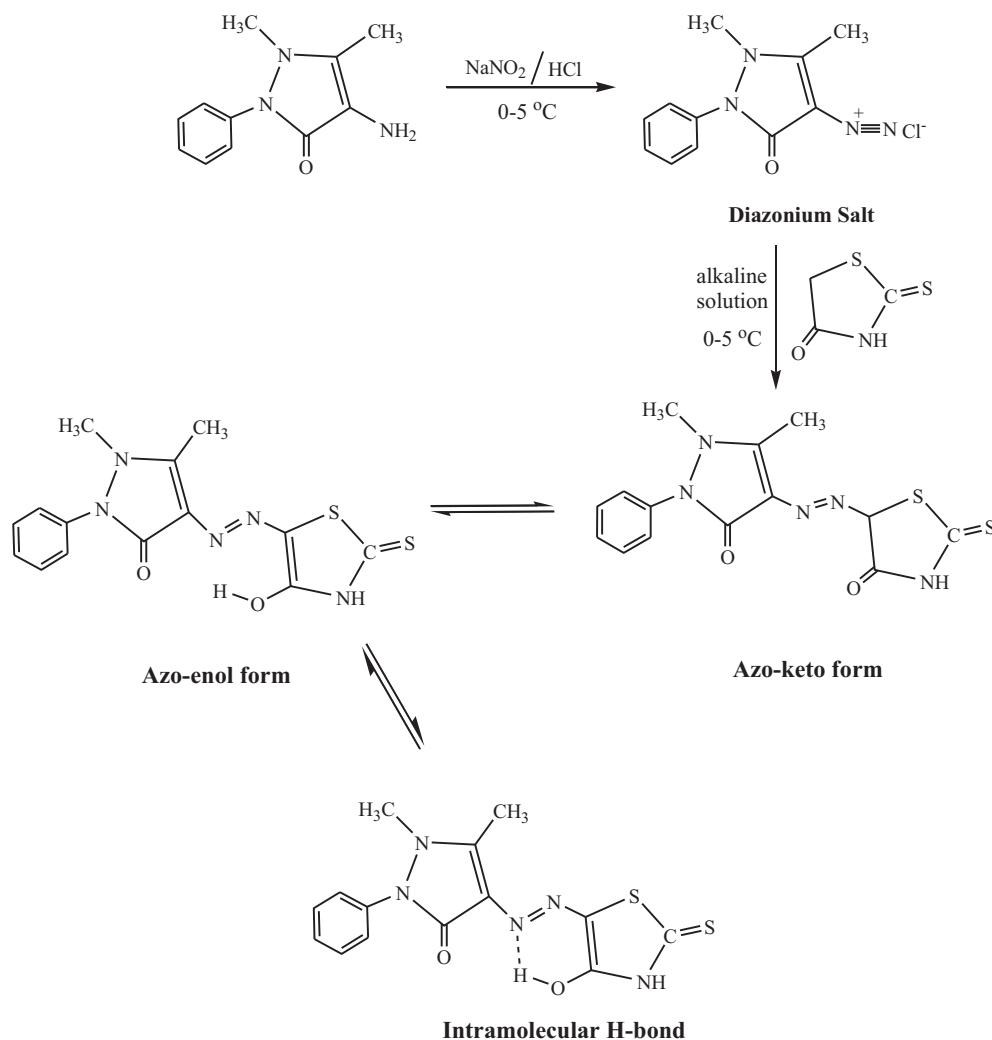
Fig. 1. The formation mechanism of rhodanine azodye (HL).

structure of formed ligand (HL) was established by IR, ^{1}H NMR and X-ray spectroscopes.

2.2. Potentiometric studies

A ligand solution (0.001 M) was prepared by dissolving an accurately weighted amount of the solid in DMF. Metal ion solutions (0.0001 M) were prepared from metal chlorides in bidistilled water and standardized with EDTA [21]. Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free NaOH solution in 10% (by volume) DMF–water mixture was used as titrant and standardized against oxalic acid.

The apparatus, general conditions and methods of calculation were the same as in previous work [16–19]. The following mixtures (i)–(iii) were prepared and titrated potentiometrically at 298 K against standard 0.002 M NaOH in a 10% (by volume) DMF–water mixture:

i) 5 cm^3 0.001 M HCl + 5 cm^3 1 M KCl + 5 cm^3 DMF.
ii) 5 cm^3 0.001 M HCl + 5 cm^3 1 M KCl + 5 cm^3 0.00 l M ligand.
iii) 5 cm^3 0.001 M HCl + 5 cm^3 l M KCl + 5 cm^3 0.001 M ligand + 10 cm^3 0.0001 M metal chloride.

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for the temperatures of 308 and 318 K. All titrations have been carried out between pH 4.0–11.0 and under nitrogen atmosphere.

2.3. Measurements

All the compounds and solvents used were purchased from Aldrich and Sigma and used as received without further purification. The IR spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. The ^{1}H NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d$_6$ as the solvent and TMS as an internal reference. X-ray diffraction analysis of the ligand (HL) powder form was recorded on X-ray diffractometer in the range of diffraction angle $2\theta° = 4$–70°. This analysis was carried out using CuKα radiation ($\lambda = 1.541874$ Å). The applied voltage and the tube current are 40 kV and 30 mA, respectively.

The calculations of geometry optimization were performed using Perkin Elmer ChemBio 3D software by HF method with 3–21 G basis set [20]. Geometry optimization option was employed to obtain the most stable structure.

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 [22]. The electrode system was calibrated according to the method of Irving et al. [23]. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of