



Measurements of thermodynamic parameters for complexation between a tetra-aza macrocycle ligand and some metal cations based on conductometric method



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ABSTRACT

Thermodynamic aspects of complexation process between 14-membered tetra-aza macrocycle ligand and four metal cations were studied in ethanol–water (EtOH–H₂O) binary mixtures at different temperatures by applying conductometric method. In all the cases, the stability constants ($\log K_f$) of 1:1 formed complexes between ligand and cations were obtained by fitting the molar conductivity curves using the Genplot computer program and the formation constant values ($\log K_f$) were generally in the range of 1.41–2.70. The values of thermodynamic parameters, standard enthalpy (ΔH_f°) and standard entropy (ΔS_f°) were obtained from the temperature dependence of the stability constants using the Van't Hoff plots. Complexes in every cases were found to be entropy stabilized, and the selectivity order of all the complexes changes as well as the changes in composition of the solvent mixtures. The experimental data was tested by using artificial neural network (ANN) technique and was in a good agreement with estimated data.

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1. Introduction

The synthesis of azamacrocycles was first proposed by Curtis and House in 1961. Since that time, a vast amount of research on these compounds has been carried out with respect to characterization of the structures and stereochemical dynamics as well as complexation ability of these compounds [1–6]. The organic framework of Curtis macrocycles were formed from the condensation reaction of acetone with diamine complexes containing transition metals [4,7].

Azamacrocyclic compounds received great attention due to the existence of donor nitrogen atoms and their applications in medicinal and modern chemical techniques

such as imaging with radioisotopes, radiotherapy and magnetic resonance imaging, where metal complex with extreme kinetic and thermodynamic stability toward metal release is required [8].

The complexation properties of azamacrocycles are governed mainly by their ring size, since *N*-functionalization of these compounds may enhance their metal-ion selectivity and the stability of metal complexes based on the coordination properties of the pendant arms [9]. The 14-membered tetra-aza macrocyclic ring of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene was already reported to make variety of complexes with copper [10], cobalt [11] and nickel [12]. Generally, Ammonium ions or their derivatives with partially positive charge are known to be good receptors to make complexes with crown ethers, calixarenes, cucurbiturils and porphyrins [13]. However, due to the presence of donor groups which can form semi-rigid cone shapes, they are also able to be used as

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ligands to make complexes with different metal ions [14,15]. The complexation study of tetraaza macrocyclic ligand with different cations in solvent mixtures is important for a better understanding of the mechanism of molecular recognition, biological transport, and other analytical applications. Macrocyclic ammonium salts and their complexation remain competitively under-reported. There are variety of techniques used to study the complexation reaction of macrocyclic compounds with metal ions, such as potentiometry [16–19], calorimetry [20], NMR spectroscopy [21,22], polarography [23] and conductometry [21,24–31]. Among these various techniques, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

The 14-membered tetra-aza macrocycle compound is a fourpodal ligand, which has four donor nitrogen atoms. Two nitrogens in this compound have a partial positive charge due to its salt nature. However, the complexation still occurs by participating of all nitrogens in the mentioned compound [32,33].

One of the main research interests is to study the influence of solvent properties on the thermodynamic aspects of complexation reactions of macrocyclic ligand with different metal cations. This paper describes the 14-membered tetra-aza macrocycle salt of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dibromide (Fig. 1) which first synthesized according to the literature method in a one-step reaction and obtained in crystalline form [32–36]. Subsequently, the findings of a conductometric study of the complexation reaction of Cu^{2+} , Zn^{2+} , Co^{2+} and Fe^{2+} metal cations with macrocyclic ligand in ethanol-water (EtOH–H₂O) binary solution at different temperatures (15, 25, 35 and 45 °C) are reported. Consequently, we studied the effect of solvent properties and the media composition on stoichiometry and selectivity between ligand and cations. The optimized structure of the proposed ligand was obtained by applying a density functional theory (DFT) with the GAUSSIAN 09 software package, and the B3LYP/6-31G basis set.

2. Experimental

2.1. Reagents and apparatus

Copper (II) nitrate hexa hydrate (Merck), zinc (II) nitrate hexa hydrate (Hamburg), cobalt (II) nitrate hexa hydrate and ferrous (II) chloride hexa hydrate (Sigma Aldrich) were used without further purification. Acetone, ethanol (Sigma Aldrich) of the highest purity and deionized distilled water were used as solvents. The Thermo Scientific Orion Versastar conductivity apparatus was utilized and connected to the thermostatted water bath (Julabo F12) to keep the temperature constant to within ± 0.01 °C during the experiment. To evaluate the electrolytic conductance, a cell comprising two platinum electrodes with cell constant of 0.99 cm^{-1} was used and an alternating potential was applied. The cell was calibrated using a standard solution of KCl (0.1000 M) each time prior to application.

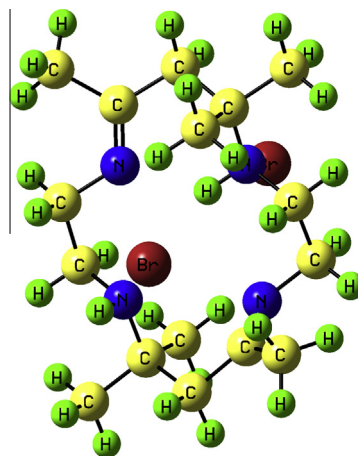


Fig. 1. The optimized structure of the ligand (L).

2.2. Synthesis of ligand (L)

The macrocyclic tetraaza ligand was prepared according to the literature methods with slightly modification [4]. The reflux reaction of stoichiometric amounts of ammonium bromide (0.01 mol, 0.534 g) and ethylenediamine (0.01 mol, 0.601 g) was performed in 30 ml acetone. Single crystals were obtained from the solution with a yield of 83% after one day of evaporation at room temperature.

The structure of the ligand was characterized by elemental analysis, infrared, UV–Vis, ¹H and ¹³C NMR spectroscopies. Elemental analysis for C₁₆H₄₀N₄O₃Br₂: Calc. (C: 38.72; N: 11.29; H: 8.12%), Found. (C: 38.2; N: 11.4; H: 8.2%); IR(KBr): 1234.1 (C–N), 1672.5 (C=N), 3454.6 (NH), 3009.5 (CH₃) cm⁻¹; ¹H NMR (ppm., CD₃OD), δ H: 1.5 (s, 12H, C–(CH₃)₂); 2.1 (s, 6H, C–CH₃); 2.8 (s, 4H, C–CH₂–C); 3.3 (m, 4H, CH₂–CH₂); 3.8 (m, 4H, CH₂–CH₂); 5.1 (s, 2H, NH₂). ¹³C NMR (ppm., CD₃OD), δ C: 175.9 (N=C–C); 58.4 (C–C–N); 40.0 (C–CH₂–C); 23.46 (N=C–CH₃); 47.7 (C=N–CH₂); 44.80 (N–CH₂–C); 21.66 (C–(CH₃)₂).

2.3. Methodology

Two types of cationic and ligand (L) solutions were prepared in this study. 25 ml of metallic salt solutions (copper (II), zinc (II), cobalt (II), and ferrous (II)) with a concentration of 5.0×10^{-5} M were placed in the water-jacketed cell containing a magnetic stirrer of constant stirring speed for each experiment. The water-jacketed cell was connected to the circulating water bath in order to maintain a constant temperature. The actual calibration associated with conductometric cell was created by using KCl solution. The conductivity constant was computed using the equation associated with Lind, Zwolennik along with Fuoss [37]. A known amount of the ligand (L) with a concentration of 2.5×10^{-3} M was added dropwise using a micropipette, over a period of two minutes. The conductance value was recorded after each addition of the ligand (L). Addition of the ligand (L) was continuous, until the desired ligand-to-cation mole ratios were achieved. The variations of stability constant, $\log K_f$, between the ligand and the chosen

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