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Spectroscopic characterization of metal complexes of novel Schiff base. Synthesis, thermal and biological activity studies

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ABSTRACT

Novel Schiff base (HL) ligand is prepared via condensation of 4-aminoantipyrine and 2-aminobenzoic acid. The ligand is characterized based on elemental analysis, mass, IR and ^{1}H NMR spectra. Metal complexes are reported and characterized based on elemental analyses, IR, ^{1}H NMR, solid reflectance, magnetic moment, molar conductance and thermal analyses (TGA, DrTGA and DTA). The molar conductance data reveal that all the metal chelates are non-electrolytes. IR spectra show that HL is coordinated to the metal ions in a uninegatively tridentate manner with NNO donor sites of the azomethine N, amino N and deprotonated caroxylic-O. From the magnetic and solid reflectance spectra, it is found that the geometrical structures of these complexes are octahedral. The thermal behaviour of these chelates shows that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps. The activation thermodynamic parameters, such as, E^*, ΔH^*, ΔS^* and ΔG^* are calculated from the DrTG curves using Coats–Redfern method. The synthesized ligands, in comparison to their metal complexes also were screened for their antibacterial activity against bacterial species, *Escherichia Coli*, *Pseudomonas aeruginosa*, *Staphylococcus Pyogones* and *Fungi* (Candida). The activity data show that the metal complexes to be more potent/antibacterial than the parent Shciff base ligand against one or more bacterial species.

1. Introduction

The Schiff base ligands with sulphur and nitrogen donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [1–4]. Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhance their activities [5], as has been reported for pathogenic fungi [6]. There is a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have been shown to exhibit interesting physical and chemical properties [7] and potentially useful biological activities [8]. Many reports are available for the preparation and properties of model copper complexes which mimic copper-containing metalloproteins such as hemocyanine and tyrosinase. Two noticeable properties of copper proteins are an intense absorption band [9] near 600 nm and relatively high copper(II)/copper(I) reduction potentials [7]. Attention was particularly focused on their correlation with the active site of metalloenzymes and metalloproteins containing dinuclear metallocenters in order to elucidate the factors that determine the reversible binding and activation of O_2 in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity [9]. Schiff bases [10] were still regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their noteworthy contributions to single molecule-based magnetism, material science [11], catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation [12], their industrial applications [13], complexing ability towards some toxic metals [14]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and unexpensive determinations of different organic and inorganic substances [15]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

The present study describes the chelation behaviour of Schiff base derived from the condensation of 4-aminoantipyrine with 2-aminobenzoic acid (HL) towards some transition elements, which may help in more understanding of the mode of chelation of HL towards metals. For this purpose the complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), UO_2(II), Mn(II) and Th(IV) ions with HL are studied in solution and in the solid state. The stability constants are evaluated and structure of the studied complexes is elucidated using elemental analyses, IR, ^{1}H NMR, solid reflectance, magnetic

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moment, molar conductance, and thermal analyses (TGA, DrTGA and DTA) measurements. The biological activity of the parent Schiff base and its metal complexes is reported.

2. Experimental

2.1. Materials and reagents

All chemicals used were of the analytical reagent (AR) grade, and of highest purity available. They included 4-aminoantipyrine (Sigma) and 2-aminobenzoic acid (Aldrich). Cu(II)$Cl_2 \cdot 2H_2O$ (Sigma), Co(II)$Cl_2 \cdot 6H_2O$ and Ni(II)$Cl_2 \cdot 6H_2O$ (BDH); $MnCl_2$ (sigma), $ThCl_4$ (Aldrich), $ZnCl_2 \cdot 2H_2O$ (Ubichem), $UO_2(AcO)_2 \cdot 2H_2O$ (Sigma) and $FeCl_3 \cdot 6H_2O$ (Prolabo) were used. Organic solvents used included absolute ethyl alcohol, diethylether and dimethylformamide (DMF). These solvents were spectroscopic pure from BDH. Hydrogen peroxide and chloride, carbonate and hydroxide salts of sodium (A.R.) were used. Hydrochloric and nitric acids (Merck) were used. De-ionized water collected from all glass equipments was usually used in all preparations.

2.2. Solutions

Fresh stock solution of 5×10^{-3} M ligand was prepared by dissolving the accurately weighed amount of 0.161 g/L in the appropriate volume of absolute ethanol. 5×10^{-3} M Stock solutions of the metal salts (Fe(III), 0.271 g/L; Co(II), 0.238 g/L; Ni(II), 0.238 g/L; Cu(II), 0.218 g/L; Zn(II), 0.219 g/L; UO_2(II), 0.50 g/L, Mn(II), 0.170 g/L and Th(IV), 0.316 g/L) were prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of de-ionized water. The metal salt solutions were acidified and standardized by the recommended procedures [16].

Dilute solutions of the metal ions and Schiff base under study of 2.5×10^{-6} M, 1×10^{-6} M, 2.5×10^{-5} M, 1×10^{-5} M, and 1×10^{-4} M were prepared by accurate dilution. For potentiometric studies, all solutions of metal ions were prepared by dissolving the calculated amount of their salts in the least amount of water, then ethanol was added to the appropriate volume. Standard 0.1N sodium carbonate solution was prepared from dried sodium carbonate. 0.1N hydrochloric acid was prepared and standardized using sodium carbonate. 1.00 M sodium chloride solution was also prepared. A 1:1 sodium hydroxide solution was prepared from A.R. product and stored in a well steamed waxed tall glass cylinder for some days with occasional shaking to obtain a carbonate free sodium hydroxide solution. The clear solution was filtered through a sintered glass funnel G4. Solutions of the required molarity were prepared by dilution and then standardized by recommended procedure [16].

2.3. Instruments

pH measurements were carried out using 716 DMS Titrino Metrohm connected with 728 Metrohm Stirrer. Elemental microanalyses of the separated solid chelates for C, H and N were performed in the Microanalytical Center, Cairo University. The analyses were repeated twice to check the accuracy of the analyzed data. The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, E = 3406). Infrared spectra were recorded on a PerkinElmer FT-IR type 1650 spectrophotometer in wave number region 4000–200 cm^{-1}. The spectra were recorded as KBr pellets. The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS–MS Hewlett-Packard instrument in the Microanalytical Center, Cairo University. The ^1H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) and the spectra extended from 0 to 15 ppm. The thermal analyses (TGA and DTA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10 °C min^{-1} using Shimadzu TGA-50H and DTA-50H thermal analyzers.

2.4. Procedures

2.4.1. Potentiometric measurements

The potentiometric measurements were carried out at 25 °C and ionic strength μ = 0.1 M by the addition of appropriate amounts of 1 M sodium chloride solution. The pH-meter was calibrated before each titration using standard buffers. The ionization constants of the investigated Schiff base and the stability constants of their metal chelates with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), UO_2(II), Mn(II) and Th(IV) ions were determined potentiometrically using the technique of Sarin and Munshi [17]. For this purpose three solution mixtures of total volume 50 mL were prepared. Thus,

(A) 3 mL of standard HCl (0.10 M) + 5 mL 1 M NaCl + 25 mL ethanol and the volume was completed up to 50 mL with distilled water.
(B) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 25 mL 0.001 M of ethanolic solution of the Schiff base (HL) and the volume was completed to 50 mL with distilled water.
(C) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 25 mL 0.001 M of ethanolic solution of the Schiff base + 5 mL 0.001 M metal ion solution and the volume was completed to 50 mL with distilled water.

The above three mixtures were titrated potentiometrically against standard sodium hydroxide solution (0.10 M). The molarities of HCl and NaOH were checked every day before the titrations. The appropriate volume of ethanol was added so as to keep the ratio 50% (v/v) ethanol/water, constant to ensure the complete solubilities of the Schiff base during the titration. The three curves obtained were referred to as: (A) acid titration curve, (B) ligand titration curve and (C) complex titration curve.

2.4.2. Synthesis of Schiff base (HL)

Hot solution (60 °C) of 4-aminoantipyrine (5 g, 24.88 mmol) was mixed with hot solution (60 °C) of 2-aminobenzoic acid (3.41 g, 24.88 mmol) in 50 mL ethanol. The resulting mixture was left under reflux for 2 h and the formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride. The brownish yellow products were produced in 88% yield.

2.4.3. Synthesis of metal complexes

The metal complexes of the Schiff base, HL were prepared by the addition of hot solution (60 °C) of the appropriate metal chloride or acetate (1 mmol) in an ethanol–water mixture (1:1, 25 mL) to the hot solution (60 °C) of the Schiff base (0.203 g, 1 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for 1 h whereupon the complexes precipitated. They were collected by filtration and purified by washing with an ethanol–water mixture (1:1) and diethyl ether. The analytical data for C, H and N were repeated twice.

2.5. Determination of the metal content of the chelates

An accurately weighed portion of the different chelates ranged from 10 to 30 mg was placed in Kjeldahl flask. A measured volume of concentrated nitric acid ranged from 5 to 10 mL was added initially to the powdered chelates, to start the fast wet oxidation digestion. This mixture had been digested by a gradual heating with dropping