

Synthesis, characterization and thermal studies on metal complexes of new azo compounds derived from sulfa drugs

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Abstract

Four new azo ligands, L1 and HL2–4, of sulfa drugs have been prepared and characterized. $[\text{MX}_2(\text{L1})(\text{H}_2\text{O})_m] \cdot n\text{H}_2\text{O}$; $[(\text{MX}_2)_2(\text{HL2 or HL3})(\text{H}_2\text{O})_m] \cdot n\text{H}_2\text{O}$ and $[\text{M}_2\text{X}_3(\text{L4})(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$; M = Co(II), Ni(II) and Cu(II) (X = Cl) and Zn(II) (X = AcO); $m = 0-4$ and $n = 0-3$, complexes were prepared. Elemental and thermal analyses (TGA and DTA), IR, solid reflectance spectra, magnetic moment and molar conductance measurements have accomplished characterization of the complexes. The IR data reveal that HL1 and HL2–3 ligands behave as a bidentate neutral ligands while HL4 ligand behaves as a bidentate monoionic ligand. They coordinated to the metal ions via the carbonyl O, enolic sulfonamide $-\text{S}(\text{O})\text{OH}$, pyrazole or thiazole N and azo N groups. The molar conductance data reveal that the chelates are non-electrolytes. From the solid reflectance spectra and magnetic moment data, the complexes were found to have octahedral, tetrahedral and square planar geometrical structures. The thermal behaviour of these chelates shows that the water molecules (hydrated and coordinated) and the anions are removed in a successive two steps followed immediately by decomposition of the ligand in the subsequent steps. The activation thermodynamic parameters, such as, E^* , ΔH^* , ΔS^* and ΔG^* are calculated from the TG curves applying Coats–Redfern method.

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Keywords: Sulfa drugs; Metal complexes; IR; Conductance; Solid reflectance; Magnetic moment; Thermal analysis

1. Introduction

Aromatic sulfonamide derivatives exhibit a range of bioactivities, including anti-angiogenic [1,2], anti-tumor [2,3], anti-inflammatory and anti-analgesic [4], anti-tubercular [5], anti-glaucoma [6], anti-HIV [7], cytotoxic [8], anti-microbial [9] and anti-malarial [10] agents. The synthesis of metal sulfanilidie compounds had received much attention due to the fact that sulfanilamides were the first effective chemotherapeutic agents to be employed for the prevention and cure of bacterial infections in humans. The pharmacological activity of these types of molecules is often enhanced by complexation with metal ions [11,12]. The anti-bacterial activity of sulfonamides is confined only to microorganisms which synthesize their own folic acid [13]. The effectiveness of burn treatment seemed to depend not only in the presence of metal ion but also crucially on the nature of the material to which the metal ion is

bound [14]. Certain theories had been advanced advocating that a major portion of drug action occurred through complexation [15].

The importance of metal ions in biological systems is well known. One of the very interesting features of metal coordinated systems is the concerted spatial arrangement of the ligands around the metal ions. Among metal ions of biological importance, the Cu(II) ion presents a high number of complexes with distortion [16]. Metal complexes of sulfonamide ligands incorporating additional donor atoms from iminomethyl and phenol groups [17], iminomethyl and thiophenol groups [18] or pyridine groups [19,20] had been investigated recently.

In continuation to our work on sulfa drugs [21–23], this article involves the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with four new azo sulfa drugs had been described. The solid products were characterized by elemental and thermal analyses, IR, molar conductance, magnetic moment and solid reflectance spectra measurements. The thermal decomposition of the complexes is also used to infer the structure and the different thermodynamic activation parameters are calculated.

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2. Experimental

All chemicals used in the preparation of the complexes and in solution studies were of the highest purity available. They included 4-aminobenzenesulfonamide (**1a**), 4-amino-*N*-1,3-thiazol-2-ylbenzenesulfonamide (**1b**), 4-amino-*N*-pyrimidin-2-ylbenzenesulfonamide (**1c**) and 4-amino-*N*-[amino(imino)methyl]benzenesulfonamide (**1d**) supplied from Sigma. Cobalt acetate tetrahydrate (BDH), copper and zinc acetate dihydrate (ProLab), and nickel chloride hexahydrate (BDH). Ethylenediaminetetracetic acid (EDTA) disodium salt, zinc oxide (Analar), and ammonium chloride and hydroxide (Merck) were used as received. The organic solvents used included absolute ethyl alcohol (BDH) and diethyl ether and dioxane (Aldrich).

Elemental analyses (C, H, N, S and M) were performed in the Microanalytical Center at Cairo University. The analyses were repeated twice. ^1H NMR spectra were carried out in $\text{DMSO-}d_6$ at 300 MHz on Varian Mercury VX spectrometer using TMS as an internal standard. The IR spectra were recorded using 1430 Perkin-Elmer FT-IR spectrometer and in wave number region $4000\text{--}400\text{ cm}^{-1}$. The spectra were recorded as KBr disks. The molar magnetic susceptibilities of the powdered samples were measured using the Faraday method (magnetic susceptibility balance–Sherwood) were made by Pascal's constant using $\text{Hg}[\text{Co}(\text{SCN})_4]$ calibrant. The diffuse reflectance spectra were recorded using Shimadzu 3101pc spectrophotometer. The spectra were recorded as BaSO_4 disks. The molar conductance measurements of the complexes were carried out in DMF using a Genway 4200 conductivity meter. pH measurements were carried out using GENWAY 3020 pH meter. Thermal analyses (TGA and DTA) of the complexes were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ using Shimadzu TGA-50 H and DTA-50 Hz. The percent weight loss was measured from the ambient temperature up to $1000\text{ }^\circ\text{C}$. Highly sintered $\alpha\text{-Al}_2\text{O}_3$ was used as a reference. Metal contents of the complexes were determined by titration against standard EDTA after complete decomposition of the complexes with aqua regia in a 50 mL digestion flasks.

2.1. Preparation of the azo ligands (L1 and HL2–4)

A solution of the appropriate 4-aminobenzenesulfonamide (**1a**), 4-amino-*N*-1,3-thiazol-2-ylbenzenesulfonamide (**1b**), 4-amino-*N*-pyrimidin-2-ylbenzenesulfonamide (**1c**) and 4-amino-*N*-[amino(imino)methyl]benzenesulfonamide (**1d**) (0.01 mol) in 30 mL hydrochloric acid (30%, v/v) was treated with a cold saturated solution of sodium nitrite (0.013 mol), with stirring in ice-bath for 15 min, after that the cold solutions were added to a cold solution of 2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (**3**) (0.01 mol) in ethanol (30 mL) containing 2.0 g of sodium acetate. The reaction mixtures were stirred in ice-bath for 1 h. The solid products that formed were filtered off, washed with cold water, dried and crystallized from the proper solvent to give 4-[2-(5-oxo-1,3-diphenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-hydrazino]benzenesulfonamide (L1), 4-[2-(5-oxo-1,3-diphenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-

hydrazino]-*N*-1,3-thiazol-2-yl-benzenesulfonamide (HL2), 4-[2-(5-oxo-1,3-diphenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-hydrazino]-*N*-pyrimidin-2-ylbenzenesulfonamide (HL3) and *N*-[amino(imino)methyl]-4-[2-(5-oxo-1,3-diphenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)-hydrazino]benzenesulfonamide (HL4), respectively.

2.2. Preparation of solid complexes

Metal complexes were synthesized by the addition of a hot ethanolic solution ($60\text{ }^\circ\text{C}$) of the appropriate metal chloride or acetate (25 mL, 0.1 mmol) to a hot ammoniacal ethanolic solution (25 mL) of azo ligands (25 mL, 0.05 mmol). The resulting mixture was stirred under reflux for 2 h and left to cool whereby the complexes were precipitated. The solid complexes were filtered, washed firstly by ethanol and then by diethyl ether and dried in vacuum desiccator over anhydrous calcium chloride.

3. Results and discussion

3.1. Preparation and characterization of the ligands

It has been found that the reaction of 4-aminobenzenesulfonamide (**1a**) with nitrous acid (NaNO_2/HCl) afforded the diazonium salt 2a, which underwent coupling reaction with 2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (**3**) to yield the azo coupling product L1. The structure of L1 was elucidated based on elemental (Tables 1S and 2S in supplementary data) and spectral data. The ^1H NMR spectrum of L1 (Table 3S in supplementary data) indicated the signals of 4*H*-pyrazole and NH at $\delta = 3.49$ and 13.62 ppm, respectively, indicated that the structure of L1 is present in a mixture of the two tautomeric forms the azo and the hydrazo form. Its IR spectra (Tables 4S and 5S in supplementary data) showed the absorption bands of NH_2 , $\text{C}=\text{O}$ and $\text{N}=\text{N}$ at 3356 , 3264 , 1656 and 1547 cm^{-1} , respectively. In the same way, **1b–d** underwent diazotization and coupling with **3** to give HL2–4, as shown in Scheme 1. Compounds L1 and HL2–4 are separated in high yield (80–85%).

The aim of this study is to investigate the chelating properties of different new azo ligands towards some biologically important metals like Co(II), Ni(II), Cu(II) and Zn(II) and assign the possible structures of these complexes. The results of the elemental analyses (C, H, N, S and metal content) with the proposed molecular formulae are presented in Tables 1S and 2S in supplementary data. The results obtained are in good agreement with those calculated for the suggested formulae. 2:1 (M: L2 or L3 or L4) solid chelates are isolated and found to have the general formulae $[(\text{MX}_2)_2(\text{HL2 or HL3})(\text{H}_2\text{O})_m]\cdot n\text{H}_2\text{O}$ and $[\text{M}_2\text{X}_3(\text{L4})(\text{H}_2\text{O})]\cdot n\text{H}_2\text{O}$; M = Co(II), Ni(II) and Cu(II) (X = Cl) and Zn(II) (X = AcO); $m = 4$ and $n = 0\text{--}3$. While L1 form 1:1 (M:L1) complexes with the formula $[\text{MX}_2(\text{L1})(\text{H}_2\text{O})_m]\cdot n\text{H}_2\text{O}$; M = Co(II), Ni(II) and Cu(II) (X = Cl) and Zn(II) (X = AcO); $m = 0\text{--}2$ and $n = 0\text{--}2$. The solid complexes are prepared and characterized by different tools of analyses like IR, molar conductance, magnetic moment, solid reflectance and thermal analyses (TGA and DTA) to through more light on the coor-

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