

Synthesis and characterization of Mn(II), Au(III) and Zr(IV) hippurates complexes

Moamen S. Refat^{a,*}, Sabry A. El-Korashy^b, Ahmed S. Ahmed^a

^a Department of Chemistry, Faculty of Education, Port Said, Suez Canal University, Mohamed Ali Street, Port Said, Egypt

^b Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt

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Abstract

Mn(II), Au(III) and Zr(III) complexes with *N*-benzoylglycine (hippuric acid) (abbreviation hipH) were synthesized and characterized by elemental analysis, molar conductivity, magnetic measurements, spectral methods (mid-infrared, ¹H NMR, mass, X-ray powder diffraction and UV/vis spectra) and simultaneous thermal analysis (TG and DTG) techniques. The molar conductance measurements proved that all hippuric acid complexes are non-electrolytes. The electronic spectra and magnetic susceptibility measurements were used to infer the structures. The IR spectra of the ligand and its complexes are used to identify the type of bonding. The kinetic thermodynamic parameters such as: E^* , ΔH^* , ΔS^* and ΔG^* are estimated from the DTG curves. The free ligand and its complexes have been studied for their possible biological antifungal activity.

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1. Introduction

Amino acids and their compounds with different metal ions play an important role in biology, pharmacy and industry [1]. Hippuric acid, (hippH), *N*-benzoylglycine, benzoylaminoacetic acid, one of the amino acids, present in the urine of herbivorous animals; also in smaller amounts in human urine [2]. Liebig [3] is the first who discover the compound named hippuric acid which was isolated from equine urine and in contrast to benzoic acid, it contains nitrogen. Hippuric acid is synthesized in the liver as derivative of glycine as a metabolite of benzoic acid urinary excretion [4].

Coordination chemists have been interested for many years in the donor properties of amino acids as models for metal–protein interaction and recent studies have also emphasized the reactivity of coordinated amino acids in the hope of finding simple and easily interpretable models of reactivity of some biological system which contain metals [5].

Further, a great deal of attention has been paid recently to the close relationships between metals, or their complexes, and carcinogenesis and some metal complexes are used in anti-cancer therapy. In cancer chemotherapy amino acids assume

a remarkable importance [6], and when discussing the possibility of introducing an amino acid into an anticancer drug, it is very important to know whether the amino acid forms metal complexes and in particular, any special metal complexes.

Hippuric acid is a monocarboxylic acid with three types of donor site: the nitrogen and oxygen atoms of the amide group, and the oxygen atom of the carboxylic acid group.

The literature reveals that the hippuric acid is potentially capable of forming coordinate bonds with many metal ions through a carboxylic oxygen atom as a monodentate or bound through the carboxylic oxygen atoms as a bidentate [7–18]. The NH group of L coordinates to the central metal atom only in some complexes [5,19]. Infrared spectroscopy has been widely used as a powerful means for this purpose, a shift in the carboxylic stretching vibrations to lower wave numbers is usually taken to indicate a metal–oxygen bond [17]. X-ray crystal structure determination for some metal hippuric complexes [Cd(hip)₂(cyt)(H₂O)]₂ [7] and [Cu₂(OH)(H₂O)-(bipy)₂(Am-hip)](NO₃)₂·4H₂O [8] have been reported and indicated that the hippurate anions coordinated to cadmium(II) and copper(II) as a bidentate via the two oxygen atoms of carboxylic group after being deprotonated.

The present investigation was undertaken to study the course of the reaction of hippuric acid with Mn(II), Au(III) and Zr(IV) and the products were characterized. The thermal stabilities and the kinetic parameters data were calculated as well as the antibio-

* Corresponding author.

E-mail address: mrefat@yahoo.com (M.S. Refat).

logical screening of these complexes and the free ligands against different fungi species have been reported.

2. Experimental

2.1. Materials and instrumentation

All chemicals were reagent grade and were used without further purification. Hippuric acid was purchased from Fluka Chemical Co., $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, KAuCl_4 and ZrCl_4 from (Merck Co.).

Carbon and hydrogen contents were determined using a Perkin-Elmer CHN 2400 in the Micro-analytical Unit at the Faculty of Science, Cairo University, Egypt. The metal content was found gravimetrically by converting the compounds into their corresponding oxides.

IR spectra were recorded on Bruker FTIR spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) in KBr pellets. The UV–vis spectra were determined in the DMSO solvent with concentration ($1.0 \times 10^{-3}\text{ M}$) for the free ligand and its complexes using Jenway 6405 Spectrophotometer with 1 cm quartz cell, in the range 200–800 nm. Molar conductivities of freshly prepared $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ DMSO solutions were measured using Jenway 4010 conductivity meter.

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance in the micro analytical laboratory, faculty of science, Mansoura University, Egypt using Gouy method.

Calibration: Two very good solid calibrants are used: $\text{Hg}[\text{Co}(\text{CNS})_4]$ and $[\text{Ni}(\text{en})_3](\text{S}_2\text{O}_3)$. They are easily prepared pure, do not decompose or absorb moisture and pack well. Their susceptibilities at 20°C are 16.44×10^{-6} and 11.03×10^{-6} c.g.s. Units, decreasing by 0.05×10^{-6} and 0.04×10^{-6} per degree temperature raise respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields, while the nickel compound with lower susceptibility and density is suitable for higher field [20]. Here we are used $\text{Hg}[\text{Co}(\text{CNS})_4]$ only as calibrant. ^1H NMR spectrum of the free acids and Au^{3+} complexes were recorded on Varian Gemini 200 MHz spectrometer using $\text{DMSO-}d_6$ as solvent and TMS as an internal reference. The purity of the ligand and $[\text{Zr}(\text{hip})_2\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ complexes were checked from mass spectra at 70 eV by using AEI MS 30 mass spectrometer. The X-ray powder diffraction analyses were carried out by using Philips Pw 1370 X ray generator. Radiation was provided by copper target (Cu/Ni) high intensity X-ray tube operated at 40 kV and 20 MA. Divergence slit and the receiving slit were 1 and 0.1, respectively. Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 ml min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ using a Shimadzu TGA-50H thermal analyzer.

2.2. Synthesis of metal complexes

A general method is: the desired weight of the free ligand was dissolved in 30 ml methanol and the solution was adjusted to pH 7.0 by addition of methanolic solution of sodium hydrox-

ide. The metal salts were dissolved in 20 ml of methanol and then the prepared solutions were slowly added to the solution of the ligand under magnetic stirring. After heating for about 1 h, the pH of each solution was then adjusted to 7.0 again by addition of methanolic solution of sodium hydroxide. The obtained precipitates were filtered off, wash with hot methanol and dried at 60°C .

2.2.1. Synthesis of hippurate complexes

2.2.1.1. $[\text{Mn}(\text{hip})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (I, $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Mn}$) complex. Hippuric acid (0.716 g, 4.0 mmol) was added to 30 ml methanol and the pH of the solution was adjusted at 7.0, then 10 ml methanolic solution of (0.396 g, 2.0 mmol) of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ was added with continuously stirring, after heating the mixture was titrated with methanolic sodium hydroxide (0.1 M) to adjust pH at 7.0. The precipitate was settle down and filtered off, washed several times by minimum amounts of hot methanol and dried under *vacuo* over anhydrous CaCl_2 .

2.2.1.2. $[\text{Au}(\text{hip})_3] \cdot 3\text{H}_2\text{O}$ (II, $\text{C}_{27}\text{H}_{30}\text{N}_3\text{O}_{12}\text{Au}$) complex. A similar procedure as that described for complex (I) was carried out, by mixing (0.537 g, 3.00 mmol) of hippuric acid with KAuCl_4 (0.377 g, 1.0 mmol).

2.2.1.3. $[\text{Zr}(\text{hip})_2\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ (III, $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Cl}_2\text{Zr}$) complex. A cream complex, $[\text{Zr}(\text{hip})_2\text{Cl}_2] \cdot 4\text{H}_2\text{O}$ was prepared during the reaction of (0.716 g, 4.0 mmol) hippuric acid with (0.233 g, 1.0 mmol) of ZrCl_4 by a method similar to that used for the preparation of (I) complex.

2.3. Antifungal investigation

For these investigations the hole well method was applied. The investigated isolates of fungi were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm^3) was homogenized in the tubes with 9 cm^3 of melted (45°C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The holes (diameter 4 mm) were done in the cool medium. After cooling in these holes, $2 \times 10^{-3}\text{ dm}^3$ of the investigated compounds were applied using a micropipette. After incubation for 7 days in a thermostat at $25\text{--}27^\circ\text{C}$, the inhibition (sterile) zone diameters (including disc) were measured and expressed mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the fungi under investigation.

The antifungal activities of the investigated compounds were tested against *Aspergillus flavus ps.*, *Fusarium solani ps.* and *Penicillium verrucosum ps.* In the same time with the antifungal investigations of the complexes, the free ligand was also tested, as well as the pure solvent. The concentration of each solution was $1.0 \times 10^{-3}\text{ mol dm}^{-3}$. Commercial DMSO was employed to dissolve the tested samples.

3. Results and discussion

The complexes are air-stable, hygroscopic, with higher melting points, insoluble in H_2O and most of organic solvents, but partly soluble in DMSO and DMF.

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