Spectrochimica Acta Part A 76 (2010) 253–258

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis and characterization of tin(II) complexes of fluorinated Schiff bases derived from amino acids

Har Lal Singh*

Department of Chemistry, Faculty of Engineering & Technology, Mody Institute of Technology and Science, On NH-11, Lakshmangarh, Sikar 332311, Rajasthan, India

ARTICLE INFO

Article history:
Received 18 November 2009
Received in revised form 15 March 2010
Accepted 17 March 2010

Keywords:
Schiff bases
Metal complexes
Spectral studies
Antibacterial activity

ABSTRACT

New tin(II) complexes of general formula $Sn(L)_2$ (L = monoanion of 3-methyl-4-fluoro-acetophenone phenylalanine L^1H, 3-methyl-4-fluoro-acetophenone alanine L^2H, 3-methyl-4-fluoro acetophenone tryptophan L^3H, 3-methyl-4-fluoro-acetophenone valine L^4H, 3-methyl-4-fluoro-acetophenone isoleucine L^5H and 3-methyl-4-fluoro-acetophenone glycine L^6H) have been prepared. It is characterized by elemental analyses, molar conductance measurements and molecular weight determinations. Bonding of these complexes is discussed in terms of their UV–visible, infrared, and nuclear magnetic resonance (^1H, ^{13}C, ^{19}F and ^{119}Sn NMR) spectral studies. The ligands act as bidentate towards metal ions, via the azomethine nitrogen and deprotonated oxygen of the respective amino acid. Elemental analyses and NMR spectral data of the ligands with their tin(II) complexes agree with their proposed square pyramidal structures. A few representative ligands and their tin complexes have been screened for their antibacterial activities and found to be quite active in this respect.

1. Introduction

Schiff bases continue to occupy an important position as ligand in metal coordination chemistry, even almost a century later [1–7]. Amino acids and their compounds with different metal ions play an important role in biology, pharmacy and industry [8–13]. A number of in vivo studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation. Such interaction of transition metal ions with amino acids and peptides is of immense biologically importance [14–16]. It has been reported that metal complexes of amino acid Schiff bases with transition metals possess anticarcinogenic [17], antimicrobial [18] and antitumor [19] activity.

Due to its small steric size, fluorine has been used as a replacement for hydrogen in many biologically active molecules, including amino acids [20]. Once introduced the strong carbon fluorine bond is particularly resistant to metabolic transformations, and the electronegativity of fluorine can have a significant effect on the basicity or acidity of neighboring groups and on the electron distribution, and can change the overall reactivity and stability of a molecule [21]. Fluorine incorporation in heterocycles is known to affect the course of the reaction besides influencing the biological activity [22]. It has been observed that introduction of a fluorine atom to heterocycles may act as a pharmocophore, enhancing pharmacological properties of the compound to their non-fluorinated analogues [23].

In the present studies, ligand (L^1H–L^6H) is obtained by the condensation reaction between amino acids (phenylalanine, alanine, glycine, valine, isoleucine and tryptophan) and 3-methyl-4-fluoro-acetophenone with this hope that it may provide us valuable theoretical information for exploring metal-based bacteriostatic and carcinostatic pharmaceuticals with high efficacy and low toxicity. In this effort, we have also introduced an azomethine (>C=N–) linkage with the concern that it may permit a notable variety in the remarkable chemistry and behavior of such compounds. The synthesized amino acid derived compounds (L^1H–L^6H) have been exposed to act as bidentate towards divalent metal atom solely through the azomethine nitrogen and carboxylate oxygen forming a stable five member chelate ring. The structures of the ligands are shown in Fig. 1.

2. Experimental

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. Melting points were determined in open glass capillary and are uncorrected.

2.1. Preparation of the ligands

The ligands were synthesized by the condensation of 3-methyl-4-fluro acetophenone (0.904 g, 5.94 mmol) with the amino acids

* Tel.: +91 1573225001; fax: +91 1573225042.
E-mail addresses: hlsingh9@rediffmail.com, harlalsingh@hotmail.com.

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doi:10.1016/j.saa.2010.03.029

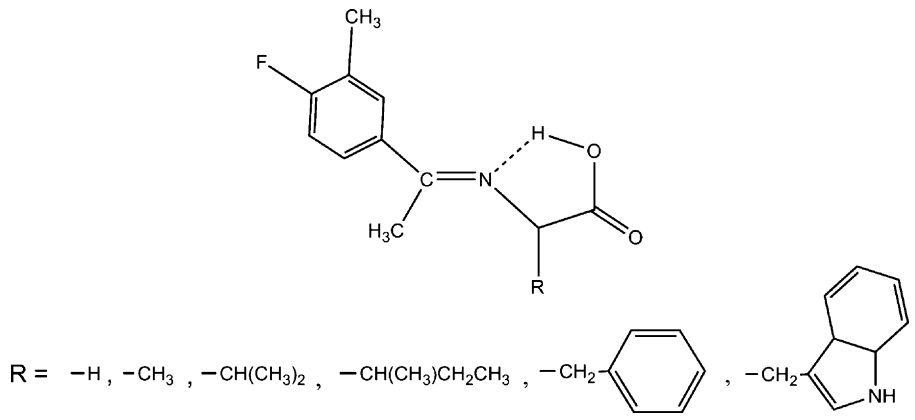

Fig. 1. Structure of the ligands.

(1.213–0.446 g, 5.94 mmol) (glycine, alanine, phenylalanine, valine, isoleucine and tryptophan) in 1:1 molar ratio using methanol (120 ml) as the reaction medium and were then, it was refluxed for 6–8 h. After this it was put on cooling at room temperature and the solid products were obtained. The excess solvent was removed on a rotary evaporator. It was dried further and then purified by recrystallization from same solvent (Table 1).

2.2. Syntheses of tin(II) complexes

To tin(II) acetate (0.275 g, 1.16 mmol) was added to the calculated amount of the ligands (0.785–0.485 g, 2.32 mmol) in 1:2 molar ratio in dry benzene (90 ml), methanol (30 ml) mixture as solvent in an oxygen-free nitrogen atmosphere. The contents were refluxed on a fractionating column for 6–8 h and the acetic acid librated in the reaction was removed azeotropically with solvent. Excess solvent was removed under reduced pressure and the compound was dried in vacuum at $45 \pm 5\,^{\circ}C$ after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from methanol (Table 2). The purity of the compounds was checked by TLC using silica gel-G as an adsorbent.

2.3. Analytical methods and spectral measurements

Tin was determined gravimetrically as SnO_2. Nitrogen was determined by Kjeldahl's methods. Molar conductance measurements were made in anhydrous dimethylformamide at $45 \pm 5\,^{\circ}C$ using a Systronics conductivity bride model 305. Molecular weight determinations were carried out by the Rast camphor method.

The electronic spectra were recorded in DMSO on a Toshniwal spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer in the region 4000–400 cm^{-1}. ^{1}H NMR and ^{19}F NMR were recorded on a Jeol (model FX 90Q) using DMSO-d_6 as solvent at 89.55 MHz and 84.25 MHz, respectively. ^{13}C NMR was recorded on a 90 MHz Jeol (FX 90Q) NMR spectrometer using dry DMSO as the solvent at 84.25 MHz. TMS was used as internal reference for ^{1}H NMR and ^{13}C NMR and hexafluorbenzene as external reference for ^{19}F NMR. The ^{119}Sn NMR spectra with proton noise decoupling were recorded on a 90 MHz Jeol spectrometer using dry DMSO as the solvent at 22.7 MHz and tetramethyltin (TMT) as an external standard.

2.4. Antibacterial tests

The antibacterial tests were carried out using a paper disk diffusion method [24–25] at 100 mg/l concentration, in nutrient agar medium, against five microorganisms. *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus*. Streptomycin was used as a reference compound for antibacterial activities. These bacterial strains are used because they are known as common pathogens of human beings.

2.5. Tests procedure

The agar broth was melted using a hot water bath then cooled to $45\,^{\circ}C$ and then about 30–50 ml of based media were poured into each of the Petri dishes and the solution was allowed to solidify. The bacterial culture was then sprayed over each plate. The discs having a diameter of 4 mm were soaked in these solutions. These discs were placed on the appropriate medium previously seeded with organisms in Petri dishes and stored in an incubator at $28 \pm 2\,^{\circ}C$. The inhibition zone around each disc was measured after 24 h.

3. Result and discussion

The reactions of tin(II) acetate with these ligands have been carried out in 1:2 molar ratios using anhydrous benzene and absolute methanol in 3:1 ratio as solvent. These reactions proceed with the liberation of acetic acid, which was azeotropically removed, are indicated below (Scheme 1).

The reactions in Scheme 1 were found to be quite facile and could be completed in 6–8 h of refluxing. All these complexes are intensively coloured and solids. They are insoluble in common organic solvents and only soluble in DMF and DMSO. Molar conductance values of the complexes in DMF (10^{-3} M solution at $25\,^{\circ}C$) were 18–25 $\Omega^{-1}\,cm^2\,mol^{-1}$, indicating, their non-electrolytic nature. The elemental analyses data (Table 2) agree with the proposed formulae for the ligands and also confirmed the $Sn(L)_2$ (Fig. 6) composition of the tin(II) chelates.

3.1. Electronic spectra

The spectra of the ligands and their complexes were recorded in dry DMSO. The various bands observed were assigned to interligand and charge transfer of n–π* transitions according to their energies and intensities. A band due to the)C=N– chromophore in the spectrum of ligand at 390 nm (π–π* transition) shifts to a lower wavelength in the spectra of tin complexes and appears at 380 nm in the complexes. This clearly indicates the coordination of azomethine nitrogen to the tin atom. It was found that the elec-

$$Sn(OOCCH_3)_2 + 2\overset{\frown}{N\ O}H \xrightarrow[\text{reflux 6-8 hr}]{\text{dry } C_6H_6+CH_3OH} Sn(\overset{\frown}{N\ O})_2 + 2CH_3COOH$$

where $2\overset{\frown}{N\ O}H$ represents the donor system of the Schiff bases

Scheme 1.