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Bioactive complex compound of zinc (II) with a Schiff base derived from L-tryptophan[☆]

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Abstract:

Amino acid Schiff bases and their first-row transition metal complexes were reported to exhibit fungicidal, bactericidal, antiviral and antitumor activity. In addition, tryptophan, an essential amino acid in human nutrition, is an important and frequently used starting material in the chemical synthesis of a range of pharmaceuticals. A potentially bioactive complex compound of Zn(II) with a Schiff base ligand derived from tryptophan was synthesized and characterized using the data obtained from elemental analysis, molar conductivity, IR, electronic, emission spectra and thermal analysis. The IR spectra confirmed the *in situ* obtaining of the Schiff base ligand and its coordination to the zinc ion through the deprotonated carboxylate oxygen atom, the azomethine nitrogen atom and the Ar-O-R etheric oxygen atom. The low molar conductivity value of the complex compound indicated this to be non-electrolyte. The emission spectrum suggested that this complex compound has the luminescent properties.

Keywords: tryptophan Schiff base, IR spectra, bioactive metal complexes

1. INTRODUCTION

Amino acid Schiff bases and their first-row transition metal complexes were reported to exhibit fungicidal, bactericidal, antiviral and antitubercular activity [1].

[☆] Paper presented at the XVIIth Edition of the National Chemistry Symposium, Craiova, Some Schiff bases [2] synthesized from salicylaldehyde, 2,4-dihydroxy-benzaldehyde, glycine and L-alanine and their metal complexes of Cu(II), Ni(II), Zn(II) and Co(II) possess antitumor activity with the following order of reactivity Ni>Cu>Zn>Co. The Schiff bases derived from 2-hydroxy-1-naphthaldehyde and an amino acid (glycine, alanine, phenylalanine, histidine, tryptophan) and their manganese (III) complexes show antimicrobial activity [3]. In addition, tryptophan, an essential amino acid in human nutrition, is an important and frequently used starting material in the chemical synthesis of a range of pharmaceuticals. Some of its derivatives are potent drugs [4].

The aim of the present study is to present the synthesis and characterization of a potentially bioactive complex compound of Zn(II) with a Schiff base ligand derived from L-tryptophan. The IR spectra confirmed the *in situ* obtaining of the Schiff base ligand and its coordination to the zinc ion through the deprotonated carboxylate oxygen atom, the azomethine nitrogen atom and the Ar-O-R etheric oxygen atom.

2. MATERIALS AND METHODS

All the chemicals used were of analytical reagent grade and were obtained from Sigma Aldrich or Merck. They included 1,3-bis(2′-formylphenyl)-1,3-dioxapropane, tryptophan, potassium hydroxide, zinc (II) acetate and methanol, ethanol, ethyl ether, dimethylformamide (DMF) as solvents.

Synthesis of the zinc complex, $[Zn_2(C_{39}H_{34}O_6N_4)(OAc)_2(H_2O)_4]$:

The Zn(II) complex compound was obtained by template synthesis since any attempt to isolate the free Schiff base ligand was unsuccessful, because it is easily hydrolyzed in contact with water. A solution of 1,3-bis(2′-formylphenyl)-1,3-dioxapropane (0.2 g, 0.7 mmol) in 5 mL methanol was added, dropwise, to a mixture of L-tryptophan (0.286 g, 1.4 mmol) and KOH (0.078 g, 1.4 mmol) in 25 mL methanol. The resulting mixture was refluxed for 3h and then 1.4

mmol of zinc acetate in methanol (10-15 mL) were added under continuous stirring. The reaction mixture was stirred under reflux for another 4h and left standing overnight. The obtained colored product was separed by filtration, washed with distilled water, ethanol, ethyl ether and dried under vacuum.

This complex compound was characterized using the data obtained from elemental analysis, molar conductivity, IR, electronic, emission spectra and thermal analysis.

3. RESULTS AND DISCUSSION

The orange binuclear complex compound of Zn(II) was synthesized by template condensation of the methanolic solutions of the 1,3-bis(2′-formylphenyl)-1,3-dioxapropane, L-tryptophan (in alkaline medium) and zinc acetate in a 1:2:2 molar ratio, with medium yield. This compound was insoluble in common organic solvents and in water, but soluble in DMF and DMSO. The low molar conductivity value of the complex compound ($9{,}7\ \Omega^{-1}\cdot cm^{2}\cdot mol^{-1}$) indicated this to be non-electrolyte [5] of the $[Zn_2L(OAc)_2(H_2O)_4]$ type, where L′ = $(C_{39}H_{34}O_6N_4)^{2-}$.

The broad and medium band observed at 3321 cm^{-1} in the IR spectrum of the Zn(II) complex compound was assigned to the stretching vibrations of O-H group from the coordinated water molecules. The medium band at 3412 cm^{-1} in this IR spectrum can be attributed to the N-H stretching vibration of tryptophan moiety and a strong band at 1625 cm^{-1} may be attributed to C=N stretching vibration [6]. The IR spectrum of the Zn(II) complex showed a band at 1600 cm^{-1} which can be assigned to $\nu_{asym}(COO^{-})$ stretching vibration. This band also appears in the IR spectrum of tryptophan at 1592 cm^{-1}. A medium band at 1383 cm^{-1} in the IR spectrum of the complex and at around 1415 cm^{-1} in the IR spectrum of tryptophan can be also attributed to $\nu_{sym}(COO^{-})$ stretching vibration. These results confirm the ligand coordination to the zinc ion through the oxygen atom of amino acid deprotonated carboxylate. In the spectrum of the complex, a medium band at 1241 cm^{-1} was due to ν_{asym}(Ar-O-C) stretching vibrations and a weak band at 1077 cm^{-1} was due to ν_{sym}(Ar-O-C) stretching vibrations. This last band is found in the spectrum of dialdehyde at 1104 cm^{-1}. These results provide evidence for the coordination through the Ar-O-R etheric oxygen atom. The band present at 583 cm^{-1} in spectrum of complex may be assigned to ν(Zn-O) stretching vibrations.

The spectrum of the complex also showed a band at 427 cm^{-1} corresponding to ν(Zn-N) stretching vibrations, which give insight into the coordination of the azomethine nitrogen to the zinc ion [7]. Therefore, the IR spectra confirm the *in situ* obtaining of the Schiff base ligand and its coordination to the zinc metal ions through the deprotonated carboxylate oxygen, the azomethine nitrogen and the Ar-O-R etheric oxygen atoms.

The photoluminescent behaviour of Zn(II) complex compound was investigated in the solid state at ambient temperature and this exhibited emission maxima at 471 nm and additional shoulder peak at 520 nm upon excitation at 390 nm. The luminescence of this compound should be assigned to the $\pi \rightarrow \pi^*$ intraligand transitions [8].

Elemental analysis and thermogravimetric analysis results were in good agreement with the proposed composition of the studied compound.

On the basis of all these results, the proposed structure for the zinc complex compound is presented in Figure 1.

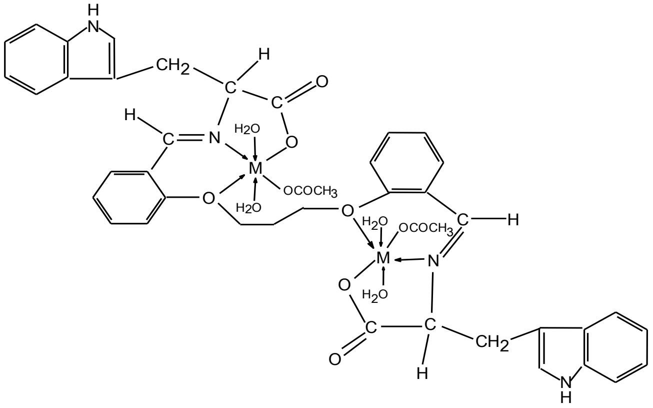

Figure 1. The proposed structure for the metal complex compound (M = Zn).

4. CONCLUSION

In this study was presented the synthesis and characterization of a potentially bioactive Zn(II) binuclear complex compound with a Schiff bases derived from tryptophan. The IR spectra confirm the *in situ* obtaining of the Schiff base ligand and its coordination to the zinc ions through the deprotonated carboxylate oxygen atom, the azomethine nitrogen atom and the Ar-O-R etheric oxygen atom.

The low molar conductivity value of the complex indicated this to be non-electrolyte. Thermogravimetric analysis results were in good agreement with the proposed composition of the complex. The emission spectrum suggested that this compound has the luminescent properties.

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