

Synthesis and Spectroscopic Investigation of a Schiff Base with Uranium (VI) Ion

F. M. Morad, M. M. El-agaily and A. A. Maihub*

Chemistry Department, Faculty of Science, Garyounis University, Benghazi, Libya,

**Chemistry Department, Faculty of Science, Alfateh University, Tripoli, Libya*

Summary. A chelate of Uranium (VI) Schiff base (derived from Salicylaldehyde and L-Cysteine) has been synthesized and investigated using different physical techniques; in particular, (C, H, N and S), molar conductance, magnetic moment, infrared, electronic and mass spectra. The (C, H, N and S) data show the formation of 1:1 [M:L] ratio. The molar conductance measurement reveals the presence of a non-electrolytic nature. The infrared spectrum shows the proper chelation between the free Schiff base and U(VI) ion. The magnetic moment measurement and electronic spectral data confirm the expected geometrical structure for the chelate. The mass spectral data illustrate the fragmentation of the prepared free Schiff base.

Introduction

Salicylaldehyde and cysteine compounds are bidentate ligands and have many applications in chemistry and medicine. The used ligands have a good ability to form large number of chelates with most transition and non-transition metal ions. Maihub et.al.⁽¹⁾ prepared some transition metal chelates with Schiff base derived from salicylaldehyde and primary amines. The chemical investigation of these chelates were carried out by using several techniques such as; elemental analysis, molar conductivity, thermal analysis and spectroscopic studies. Some new transition metal complexes of the Schiff base quinoxaline-2-carboxalidine-2-aminophenol (HQAP) have been synthesized and characterized by using different techniques.⁽²⁾ The complexes have empirical formulae of $[\text{Mn}(\text{QAP})_2]$, $[\text{Mn}(\text{QAP})_2\text{Cl}]$, $[\text{Ni}(\text{QAP})_2]$ and $[\text{Cu}(\text{QAP})_2]$. Tetrahedral geometries have been suggested for Mn(II), Co(II), Ni(II) and Cu(II) complexes. An octahedral dimeric structure has been assigned for Fe(III) complex. It has been found that the HQAP acts as a bidentate ligand. Hassan.⁽³⁾ Synthesized of some Co(II) and Fe(III) Schiff base complexes derived from Isatin and some α -amino acids. The synthesized complexes were identified by chemical analysis and physical studies.

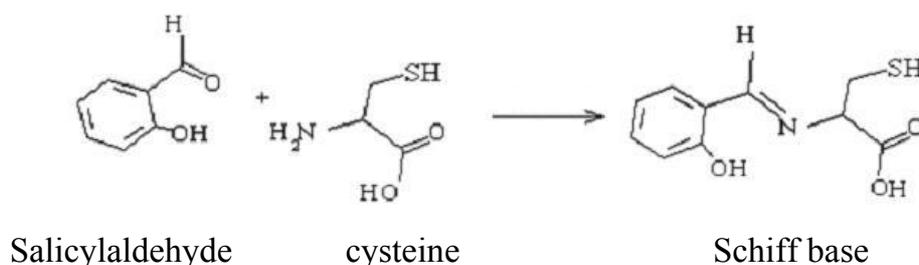
This paper aims to prepare and investigate the chemical geometry of the uranium (VI) Schiff base complex derived from salicylaldehyde and cysteine.

Experimental

All chemicals used in this investigation were reagent pure of BDH or Aldrich. All organic solvents were obtained as pure grade materials from BDH. Water used was always double distilled.

Preparation of Schiff base

The Schiff base was prepared as follows: Sodium hydroxide (10 mmol; 0.4g) was dissolved in methanol (25cm³) and Cysteine; 10 mmol was added to it. The mixture was stirred magnetically at room temperature. When the mixture became homogeneous, (10 mmol; 1.22g) of Salicylaldehyde (25 cm³) was added. After two minutes the mixture was evaporated to 20% of its original volume and 1 cm³ of CH₃COOH was added immediately. After two hours, Yellow crystals appeared. The crystals were filtered and washed with ethanol, recrystallized from hot methanol to give yellow crystals and dried at room temperature with 80% yield and It's purity was confirmed by TLC technique.



Preparation of Schiff base complex

The uranium (VI) Schiff base complex under study was prepared by mixing 25 cm³ of methanol containing sodium hydroxide (20 mmol; 0.8 g) of the Schiff base (0.01; 3.10 g) with the same volume of the same solvent of UO₂(NO₃)₂·6H₂O (5.02 g). The mixture was refluxed for three hours, then its volume was evaporated up to 75% of its original volume and the residue was left to cool and filtered by section. The final product was recrystallized from methanol/ethanol mixture.

Measurement

The elemental analyses of the prepared complex have been performed at micro analytical unit, Cairo-University CHNS elemental analyzer. The molar conductivity was carried out in DMF solvent using conductivity meter model CMD 650 digital at Chemistry department, Garyounis University. The infrared spectrum of the complex was scanned in the range of 4000-500 cm^{-1} as KBr disk using IFS-25DPUS/IR spectrometer (Bruker) 1998Y. The electronic spectrum of the complex under study was measured in CHCl_3 solvent using a Perkin–Elmer lambda 4 β spectrophotometer. The mass spectrum was carried out to show the possible fragmentations of the free Schiff base using Q 1000 EXGC-MS A Shimadzu spectrometer at 70 eV and MA energy using a direct insertion probe at temperature 90-110 $^{\circ}\text{C}$. The TLC technique was used to confirm the purity.

Results and Discussion

The obtained elemental analysis data of the prepared complex (C% 22.20, H% 2.48, N% 2.61 and S% 6.41) are in a good agreement with the theoretical values (C% 22.05, H% 2.20, N% 2.02 and S% 6.90). The data display the formation of the complex in the ratio of 1:1 [M: L].

The molar conductance value of the prepared complex in 10^{-3} M DMF solvent was $4.85 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that this complex is non-electrolytic nature.⁽⁴⁾ This value suggests that no anions are exist outside the coordination sphere.

The infrared spectrum of the complex under investigation (Fig.1) exhibits a broad band at 3403 cm^{-1} is assigned to the existence of water molecules,⁽⁶⁾ and bands at 1630 and 1601 cm^{-1} are attributed to $\nu(\text{-C=N})$ and $\nu(\text{COOH})$ vibrations. The shifting of these bands to higher frequency suggest their participation in complexation through nitrogen and oxygen atoms with uranium metal ion.⁽⁷⁾ There is no evidence that the -SH group of the amino acid is participated in complexation. The same spectrum shows two bands at 425 and 672 cm^{-1} due to the appearance of $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations.⁽⁸⁾ The appearance of these two bands support the involvement of

azomethine and hydroxyl group of the Salicylaldehyde and carboxylic group of the cysteine.

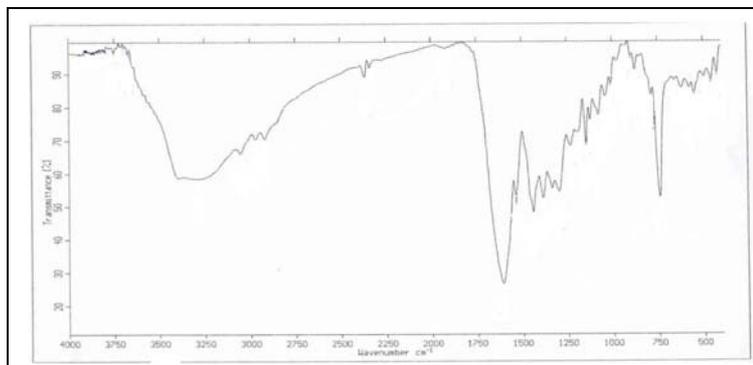


Fig. 1. Infrared spectrum of cysteine schiff base complex

The electronic spectral data of the present complex (Fig.2), which is recorded in chloroform, displays bands at 432 nm (23148 cm^{-1}) corresponding to charge transfer transition. The magnetic moment value of this complex reveals the presence of a diamagnetic character. Based on the obtained data, an octahedral structure was suggested.⁽⁹⁾

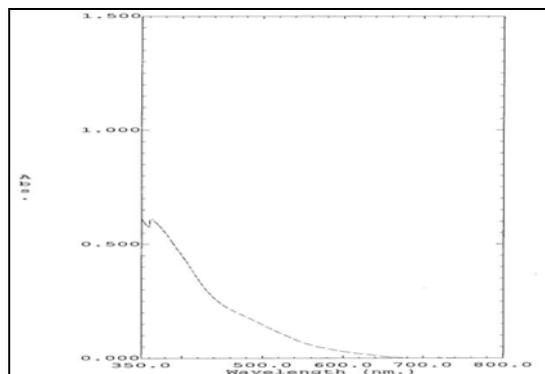


Fig .2. Electronic spectrum of cysteine Schiff base complex

The mass spectra is one of the modern spectroscopic techniques used to measure the relative molecular weights with very high accuracy, from these can be deduced exact molecular formulae.⁽¹⁰⁾ Also, it can detect within a molecule the places at which it prefers to fragment, from this can be deduced the presence of recognizable groupings within the molecule. The mass spectral fragmentation data of the Schiff base (Fig.3) are shown in the scheme. For the free Schiff base, the m/e^+ at 256

corresponding to loss of water molecules and reach to a stable compound at m/e^+ 64, which is C_4H_2N .

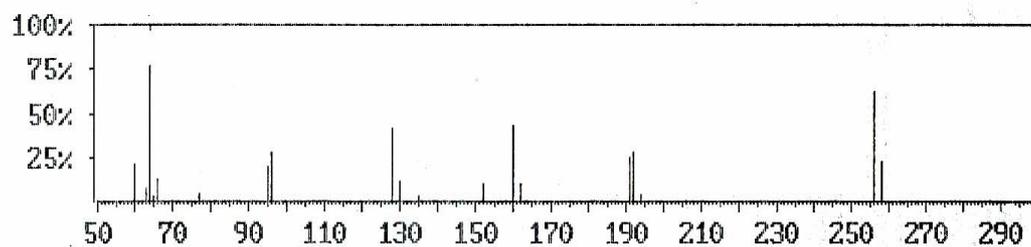
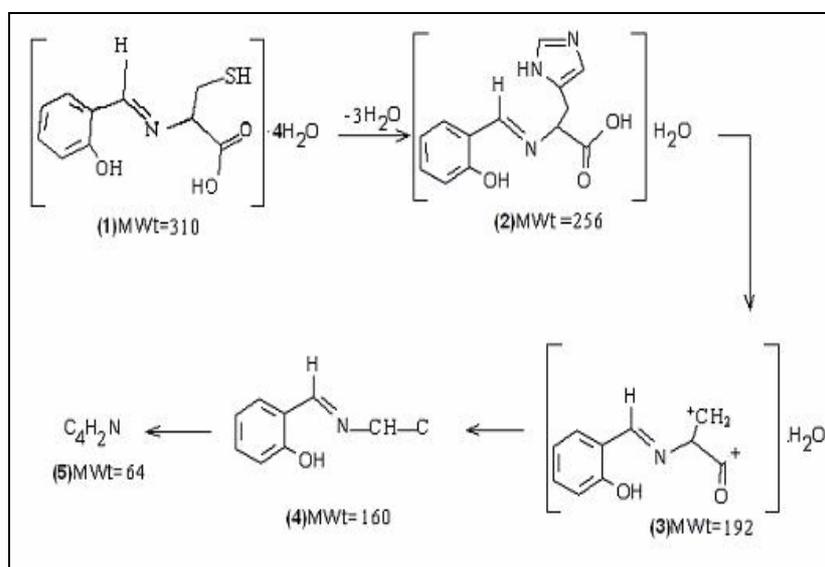
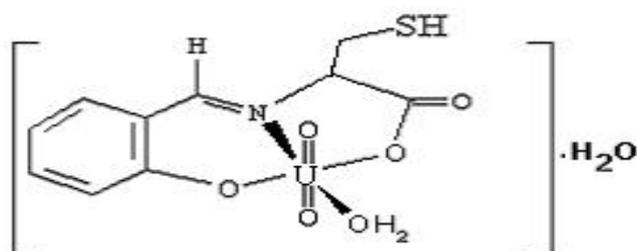


Fig. 3. Mass spectrum of cysteine Schiff base



Scheme: Mass spectrum of cysteine Schiff base

From the previous chemical analyses, we can suggest the following chemical structure for the prepared complex.



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