



Synthesis, spectroscopy, and thermal study of uranyl unsymmetrical Schiff base complexes

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ABSTRACT

The new uranyl complexes with tetradentate unsymmetrical N_2O_2 Schiff base ligands were synthesized and characterized by IR, UV–vis, NMR and elemental analysis. The DMF solvent is coordinated to uranyl complexes. The thermogravimetry (TG) and differential thermoanalysis (DTA) of the uranyl complexes were carried out in the range of 20–700 °C. The UO_2L^1 complex was decomposed in two and the others were decomposed in three stages. Up to 100 °C, the coordinated solvent was released then the Schiff base ligands were decomposed in one or two steps. Decomposition of synthesized complexes is related to the Schiff base characteristics. The thermal decomposition reaction is first order for the studied complexes.

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1. Introduction

The coordination compounds of uranyl are interesting because of their reactivity, coordination property and their applications in recent years. Salen and salophen Schiff base ligands were applied to separate of actinides from lanthanides in nuclear waste [1–6]. The effect of solvent on the solid structure of salen and the other tetradentate schiff base uranyl compounds was studied well in these compounds [7,8]. The solvents containing oxygen can bind to uranyl as seventh ligands in these complexes. Thermogravimetry (TG) and differential thermoanalysis (DTA) are valuable techniques for studying the thermal behaviour of these compounds [9–13]. The present study is an extension of our work, in which the Schiff bases were prepared by the condensation of 2-hydroxyacetophenone and salicylaldehyde derivatives as starting materials within 1,2-phenylenediamine in two steps [14,15]. The uranyl complexes of synthesized ligands were prepared in DMF solvent (Fig. 1). The newly prepared complexes were identified by IR, NMR, UV–vis spectroscopy and elemental analysis. From thermal decomposition data kinetics parameters were calculated using Coats and Redfern [16] method.

2. Experimental

2.1. Chemicals and apparatus

All of the chemicals and solvents used for synthesis were of commercially available reagent grade and they were used without purification. Infrared spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4000–400 cm^{-1} . The elemental analysis was determined on a CHN–O–Heraeus elemental analyzer. UV–vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. The 1H NMR spectra were recorded in DMSO- d_6 on DPX-400 MHz FT-NMR. Thermogravimetry (TG) and differential thermoanalysis (DTA) were carried out on a PL-1500. The measurements were performed in air atmosphere. The heating rate was kept at 10 °C min^{-1} .

2.2. Synthesis

The Schiff base ligands, L^1 – L^5 , were prepared according to the literature [14,15] and according to the following procedure. At the first stage a tridentate Schiff base ligand was prepared by condensation between 2-hydroxyacetophenone and 1,2-phenylenediamine (1:1 mole ratio) in methanol. The ligand was separated by adding distilled water and purified by recrystallization from methanol. At the second stage the tetradentate Schiff base ligands were prepared by condensation of tridentate ligand and hydroxyaldehydes in methanol and recrystallized by dichloromethane/methanol mixed solvent through the partial evaporation of dichloromethane. The uranyl complexes were synthesized by refluxing a DMF solution of the tetradentate Schiff base ligands and uranylacetate monohydrate. The reaction was continued for 2 h. After adding water the

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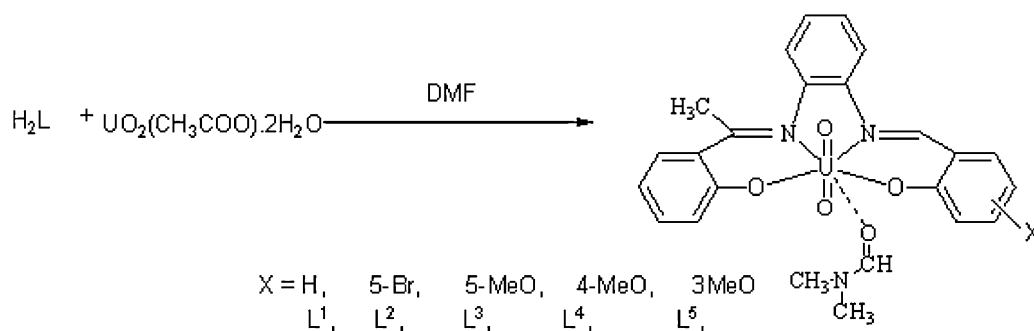


Fig. 1. The structure of uranyl complexes.

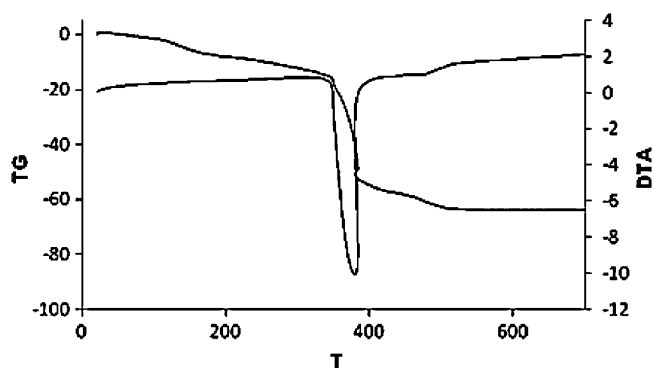


Fig. 2. The TG and DTA of UO_2L^4 complex.

brown precipitate appeared. The precipitate was filtered, washed with water and dried in vacuum.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis (Table 1) is in good agreement with those calculated for the proposed formula.

3.2. IR characteristics

The IR spectra of the uranyl Schiff base complexes synthesized here are listed in Table 2. The IR spectra of the complexes exhibit several bands in the 400–4000 cm^{-1} region.

The characteristic C=N bond appears in 1597–1607 cm^{-1} region for the synthesized complexes respectively [14,15]. The C=N stretching in the complexes is generally shifted to a lower frequency relative to the free Schiff base ligands, indicating a decrease in the C=N bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair [14,15,17].

Table 1
Elemental analysis data for the uranyl complexes.

Compounds	Found (calc.) (%)		
	C	H	N
UO_2L^1	42.74(42.00)	3.03(2.83)	4.95(4.66)
UO_2L^2	37.69(37.05)	2.81(2.35)	4.71(4.11)
UO_2L^3	42.96(41.90)	3.38(3.01)	4.95(4.44)
UO_2L^4	42.81(41.90)	3.28(3.01)	4.81(4.44)
UO_2L^5	43.50(41.90)	3.42(3.01)	5.01(4.44)

The band at 895–899 cm^{-1} is assigned to $\nu(\text{O}=\text{U}=\text{O})$. This band is observed as a new peak for the complexes and is not observed in the spectrum of free ligands [14,15,18]. Also $\nu(\text{CO})$ of DMF solvent appears at 1648 cm^{-1} .

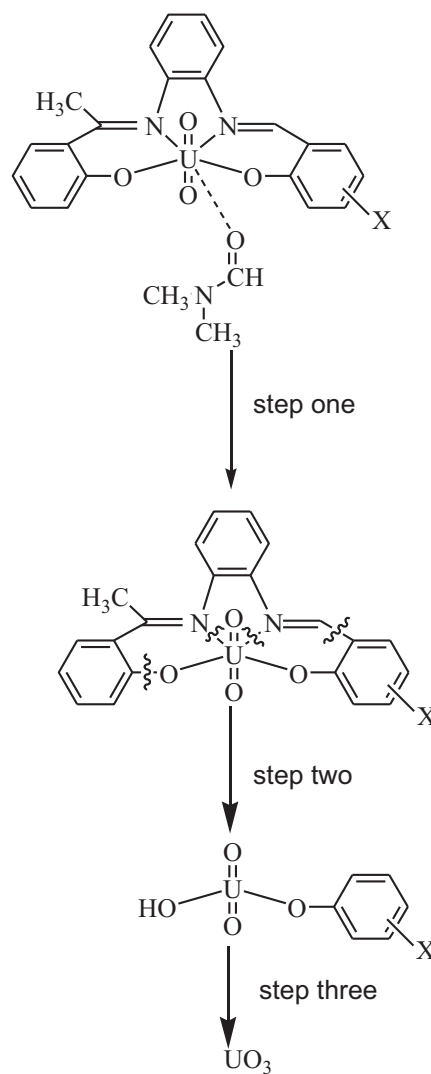


Fig. 3. The proposed decomposition pathway of the uranyl complexes.

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