

Synthesis, Characterization and Thermal Studies of a N, N'- bis(2- hydroxy –alpha- methyl benzylidene) Isobutyl Diamine Uranyl (VI) Nitrate [UO₂ (HMBUD)]²⁺

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ABSTRACT

N, N'- bis(2- hydroxy –alpha- methyl benzylidene) isobutyl diamine abbreviated as HMBUD was synthesized and characterized. N, N'- bis(2- hydroxy –alpha- methyl benzylidene) isobutyl diamine Uranyl (VI) nitrate prepared by reaction of nitrate salt of UO₂(NO₃)₂·6H₂O with HMBUD. In this research, some of the inorganic complexes of uranyl with N- donor ligands were synthesized. Complexes were characterized by FT-IR and UV, ¹H NMR, ¹³C NMR spectra, TG/DTG measurements and some physical properties. The results of simultaneous TG-DTG-DTA analyses of the complexes show the final degradation product for these complexes are UO₃. Also the results show chelation causes drastic change in the biological properties of the ligands and also the metal moiety. So the toxic effects of uranyl can be prevented by using chelating agent and complexation of the potentially multidentate ligands.

Key words: N, N'- bis(2- hydroxy –alpha- methyl benzylidene) isobutyl diamine Uranyl (VI) nitrate, Synthesis, Thermal analysis, FT-IR and UV–Visible spectroscopy, Schiff bases.

INTRODUCTION

The coordination chemistry of transition metals with ligands from the uranyl family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metal. In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications.

Nitrogen-containing ligands such as Schiff bases and their metal complexes played an important role in the development of coordination chemistry resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical ¹ and biochemically relevant studies of metal complexes ²⁻⁶ and found wide range of applications. Other kinds of nitrogen-containing

ligands are well-known pyrimidine systems such as purine analogues that exhibit a wide range of biological activities. Fused pyrimidine compounds are valued not only for their rich and varied chemistry, but also for many important biological properties. Among them, the furo-pyrimidine ring system, because of a formal isoelectronic relationship with purine, is of special biological interest. It has numerous pharmacological and agrochemical applications, namely, antimalarials, antifolates, and antiviral, as well as potential radiation protection agents. Recently, some furo-pyrimidines were shown to be potent as cellular endothelial growth factor receptor 2 (VEGFR2) and epidermal growth factor receptor (EGFR) inhibitors. Because of the importance of furo (2,3-d) pyrimidine derivatives, several methodologies for synthesizing them have already been developed. However, many of the synthetic protocols reported so far prolonged reaction times, harsh reaction suffer from disadvantages, such as relying on multistep

reactinos, needing anhydrous conditions, low yields, use of metal-containing reagents, and special instruments or starting materials. Therefore, the development of new and efficient methods for the preparation of furo (2,3-d) pyrimidine derivatives is still strongly desirable⁷. Pyrimidines represent a very interesting class of compounds because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects, for example, as antibacterial, fungicide⁸, antihelmintics, antitubercular, anti-HIV, antidegenerative and hypothermic activities⁸, and herbicides, and have biological activities⁹⁻¹³. It has long been known that metal ions involve in biological processes of life and have been subject of interest. The modes of action of these metal ions are often complex but are believed to involve bonding to the heteroatom of the heterocyclic residues of biological molecules, that is, proteins, enzymes, nucleic acids and so forth¹⁴. From these points of view, it is interesting to study different types of transition metal complexes of these biologically active ligands. In this paper, the synthesis characterization, and antitumor properties of a number of the ligands and uranyl complexes have been studied. In this work, we report the synthesis and structural studies of the ligand and N, N'-bis(2-hydroxy -alpha- methyl benzylidene) isobutyl diamineUranyl (VI) nitrate.

MATERIAL AND METHODS

Solvents were purified by standard methods. All reagents were supplied by Merck and were used without further purification. Melting point was determined in an Electro thermal 9200. The FT-IR spectra were recorded in the range 400–4000 cm^{-1} by KBr disk using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV-Vis spectra in CH_3CN were recorded with a WPA bio Wave S2 100 spectrophotometer. Thermo gravimetric analyses were done on a Perkin Elmer TGA/DTA lab system I (Technology by SII) in nitrogen atmosphere with a heating rate of $20^\circ\text{C}/\text{min}$ from $35-700^\circ\text{C}$. ^1H and ^{13}C -NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

Synthesis of the $[\text{UO}_2(\text{HMBUD})]^{2+}$

For synthesis of the $[\text{UO}_2(\text{HMBUD})]^{2+}$ to a magnetically stirred of ligand (0.45g, 1.4mmol) in acetonitrile (10ml) was added uranyl (VI) nitrate (0.69g, 1.4mmol) at room temperature. The reaction mixture was further stirred for 3 hours to ensure the completion and precipitation of the formed complex. The precipitated solid complex was filtered and washed several times with diethyl ether to remove any traces of the unreacted starting materials. Yield, 85%. Anal.Mp: 225°C . ^1H NMR (DMSO): 6.8-8 (CH

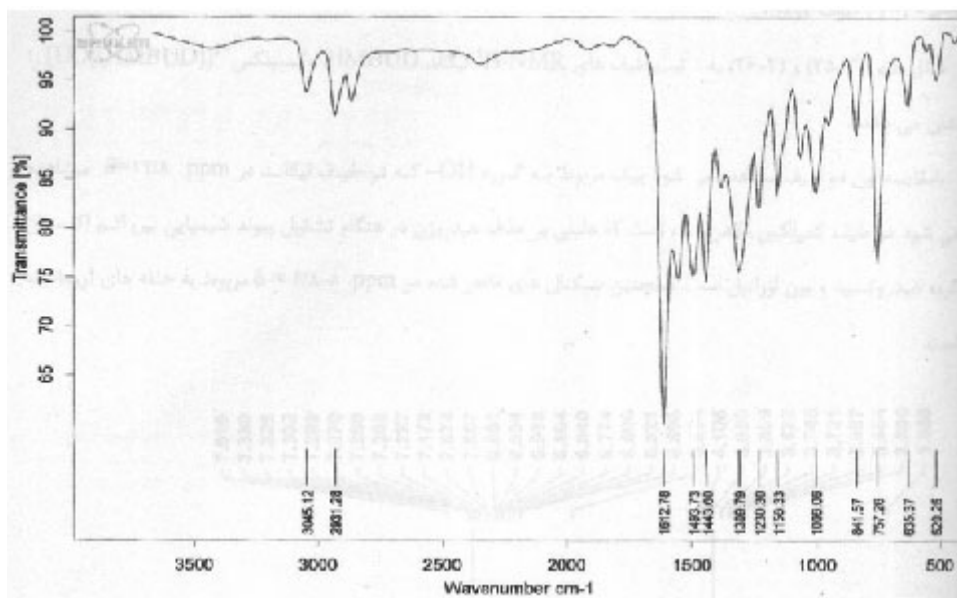


Fig. 1: FTIR spectrum of HMBUD (KBr Disk)

phenol), 2.7 (CH₃), 3.1 (CH₂), FT-IR (KBr, cm⁻¹): 1287s (ν C-N), 1622 s (ν C=N), 2929 br(ν OH), 572 m (ν U-O), 464m (ν U-N), 921 s (ν O=U=O), UV-vis (DMSO): λ_{max} 260nm(ε 22000), 320nm(ε 10000), 410nm(ε 3600)(Figure 1-9). [UO₂ (HMBUD)]²⁺ is soluble in acetone, DMF and DMSO and insoluble

in water, methanol, Acetonitrile, dichloro methane, diethyl ether and hexane and little soluble in chloroform and ethanol. Figure 10, 11 shows Chemical structures of HMBUD and [UO₂ (HMBUD)]²⁺.

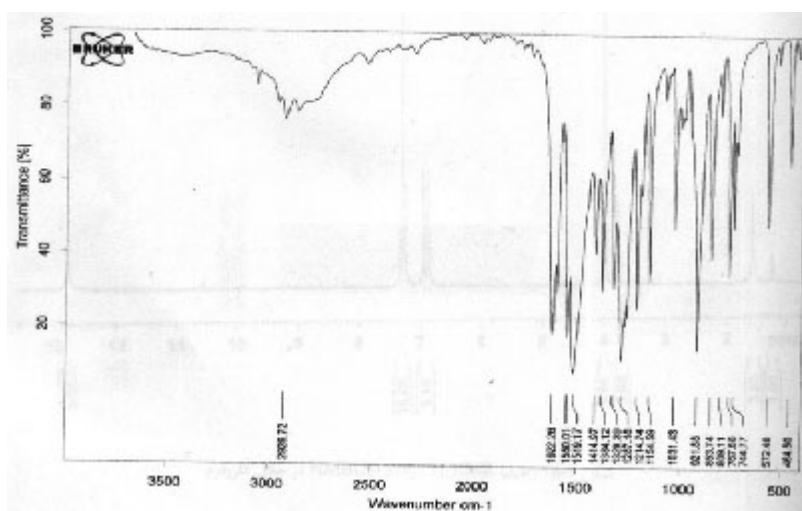


Fig. 2: FTIR spectrum of [UO₂ (HMBUD)]²⁺(KBr Disk)

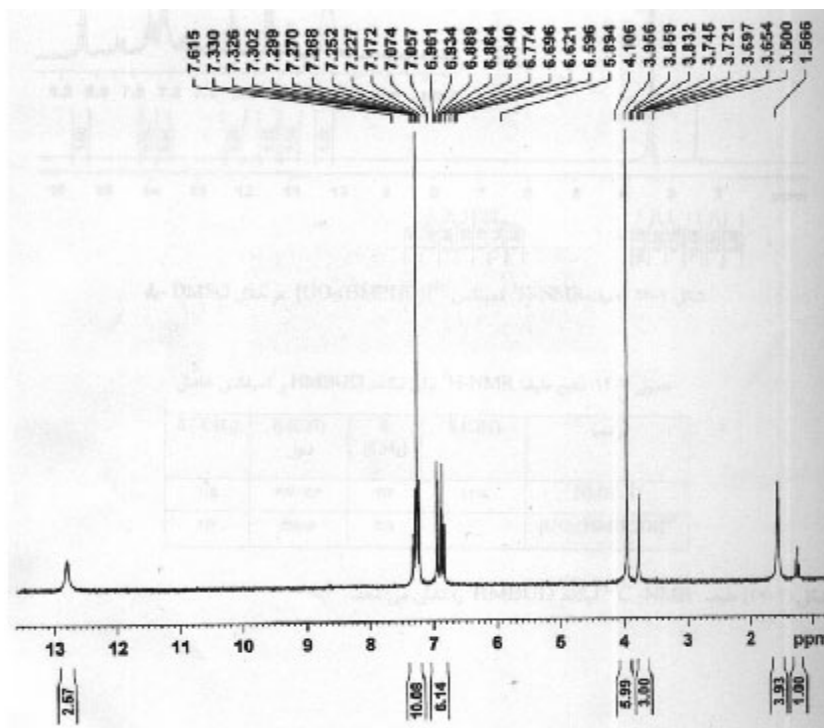


Fig. 3: ¹H- NMR spectrum of HMBUD

Analysis of HMBUD Ligand

Anal:%69. Calcd of $C_{20}H_{24}N_2O_2$; C;74.09, H; 7.4, N; 8.63; found: C; 80.11, H. 8.20, N; 9.12. Mp192-194 °C, $^1\text{H-NMR}$ (DMSO): 6.7-7.6 (CH phenol), 1.5 (CH₃), 3.6 (CH₂), 12.8 (OH), FT-IR (KBr, cm^{-1}): 1309s (v C-N), 1612 s (v C=N), 2931br(v

OH), UV-vis (DMSO): λ_{max} 268nm(ϵ 28000), 355nm(ϵ 10000). HMBUD is soluble in acetonitrile, DMSO, chloroform, dichloro methane and diethyl ether and insoluble in acetone, water, methanol, ethanol and hexane and little soluble DMF.

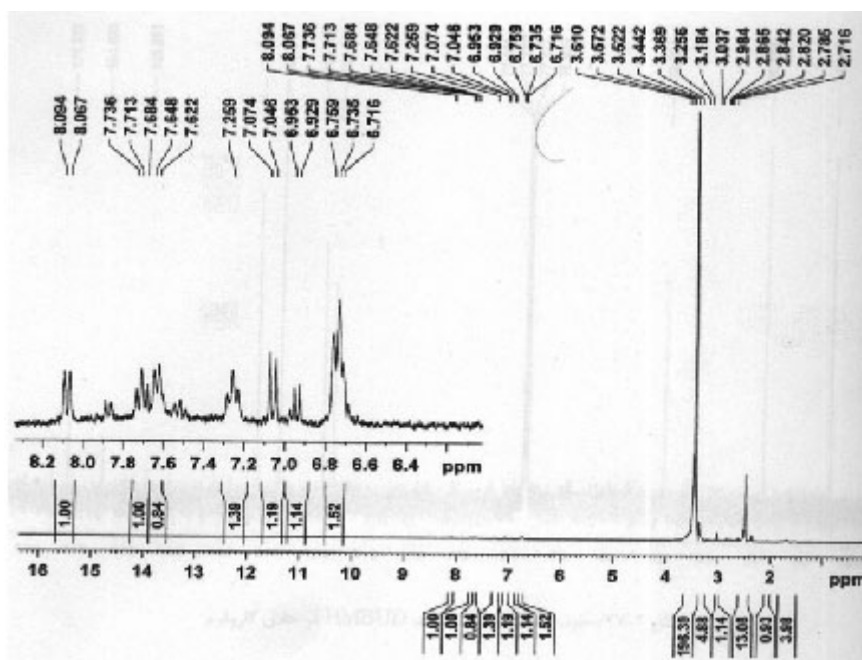


Fig. 4: $^1\text{H-NMR}$ spectrum of $[\text{UO}_2(\text{HMBUD})]^{2+}$

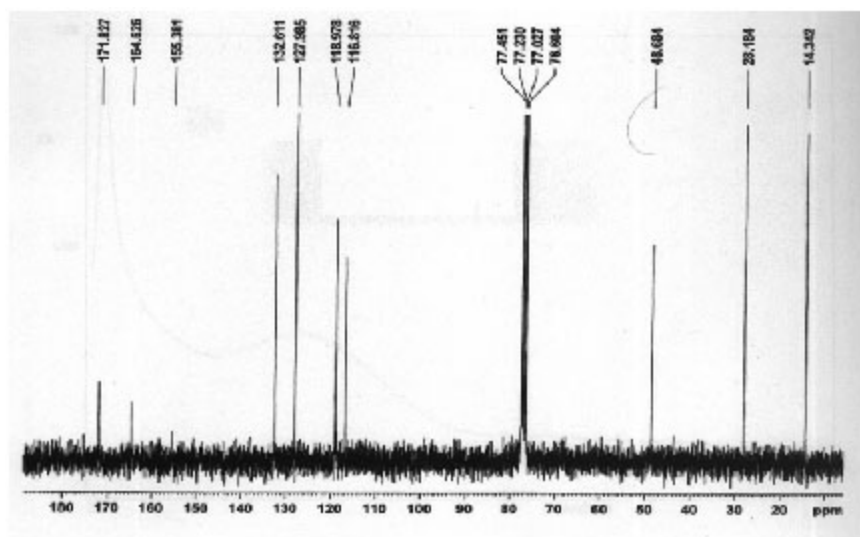


Fig. 5: $^{13}\text{C-NMR}$ spectrum of HMBUD

RESULTS

Preparation of Ligand and complex

In this paper, we report a new method of the synthesis of N, N'- bis(2- hydroxy –alpha- methyl benzylidene) isobutyl diamineUranyl (VI) nitrate. The compound was obtained by reaction of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMBUD and was synthesized

through a one-step reaction. Our procedure for producing compound has some advantages. For example, there is no side product in preparing $[\text{UO}_2(\text{HMBUD})]^{2+}$ in our method, the reaction is quite fast and does not require any severe conditions such as high pressure or high temperature, and it is not sensitive to air. Compounds were characterized by several techniques using FT-IR, UV-Visible and

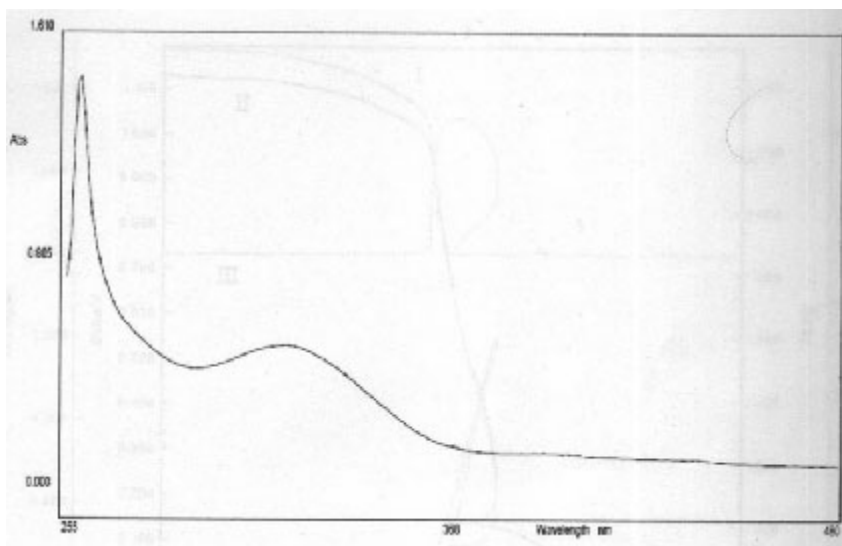


Fig. 6: UV/Vis spectrum of HMBUD(DMSO, 5×10^{-4} M)

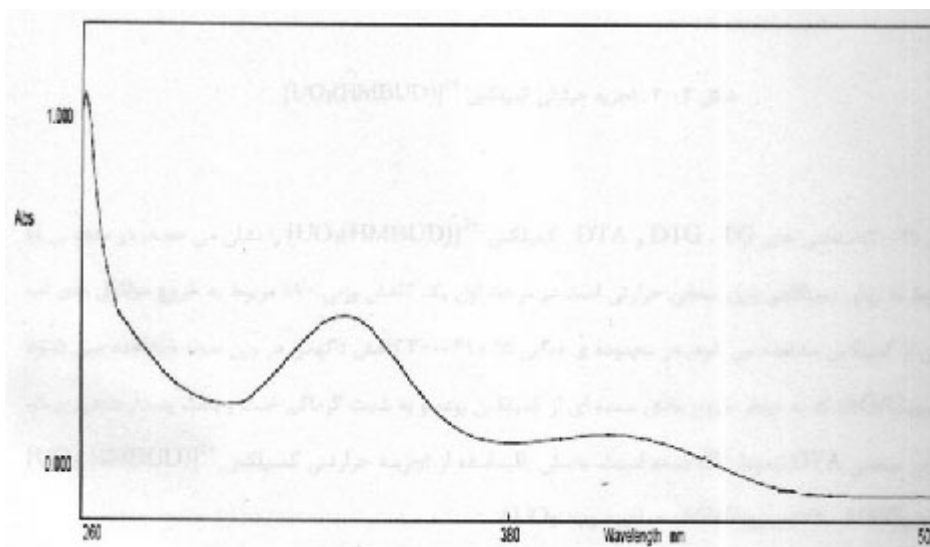


Fig. 7: UV/Vis spectrum of $[\text{UO}_2(\text{HMBUD})]^{2+}$ (DMSO, 5×10^{-4} M)

NMR spectra Thermal analysis were studied for these compounds. The $[\text{UO}_2(\text{HMBUD})]^{2+}$ has 225 °C melting points respectively. It is soluble in acetone, DMF and DMSO and insoluble in water, methanol, Acetonitrile, dichloro methane, diethyl ether and hexane and little soluble in chloroform and ethanol. The spectral data of the complexes have good relationship with the literature data. The IR spectra of the Schiff base show characteristic bands due to $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ in the region 2931 cm^{-1} ,

(1612, 1309) cm^{-1} respectively. The strong band in the region 1612, 1309 cm^{-1} in the IR spectra of the Schiff base are assigned to $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{N})$ respectively. In the case of U(VI) complex we observed the following changes. The bands appeared around 572, 464, 921, 1287, 1622, 2929 cm^{-1} due to $\nu(\text{U}-\text{O})$, $\nu(\text{U}-\text{N})$, $\nu(\text{O}=\text{U}=\text{O})$, $\nu(\text{C}-\text{N})$, $\nu(\text{C}=\text{N})$, $\nu(\text{OH})$ IR spectra of ligand (HMBUD) show a broad medium intensity band in the region 2931 cm^{-1} due to OH.

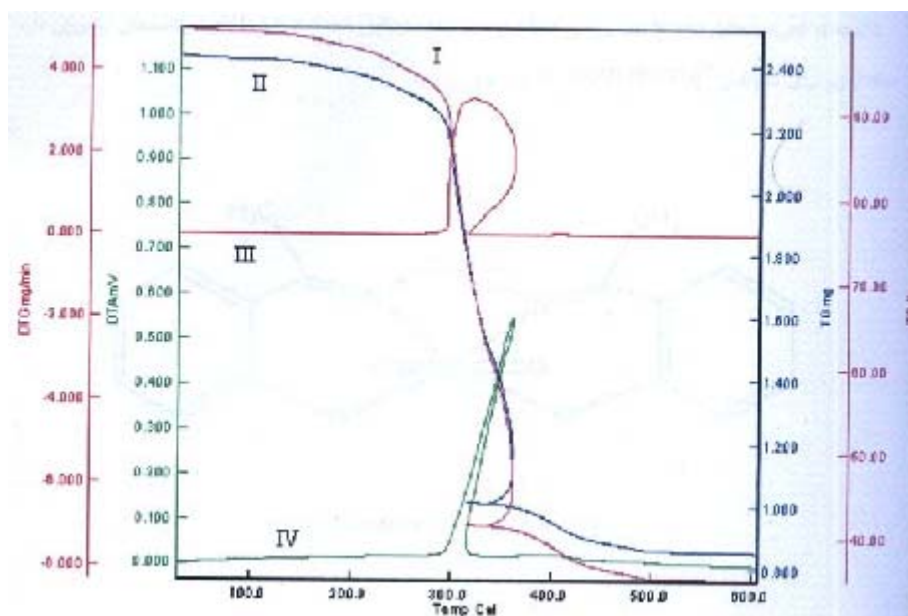


Fig. 8: Thermal analysis data of $[\text{UO}_2(\text{HMBUD})]^{2+}$

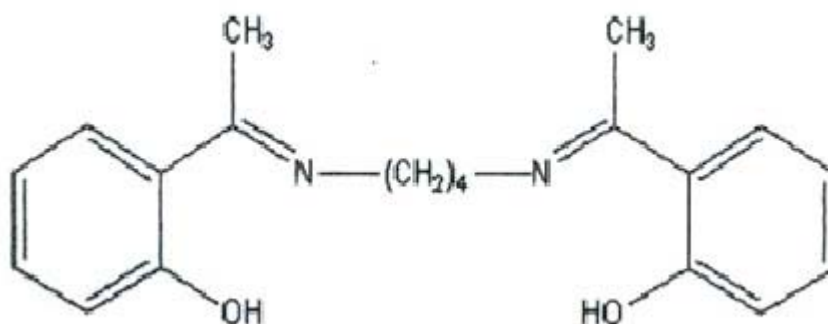


Fig. 9: Chemical structure of HMBUD

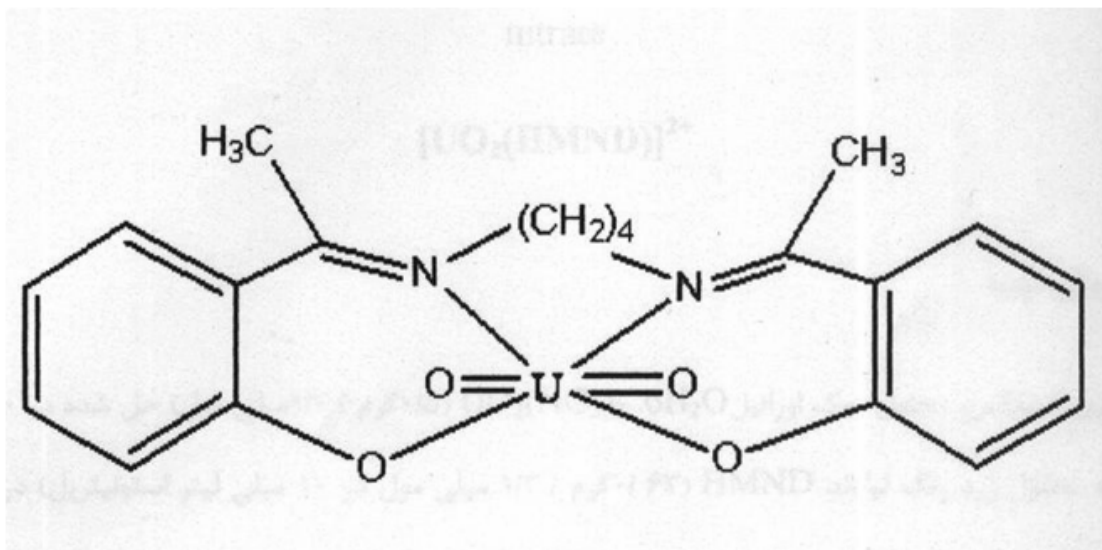


Fig. 10: Chemical structure of $[UO_2(HMBUD)]^{2+}$

Thermo gravimetric analyses

The thermal properties of these compounds were investigated by thermo grams (TG, DTG and DTA). Figure 9 shows TGA and DTA curves for $[UO_2(HMBUD)]^{2+}$. In the temperature range from 300-410°C, 60% weight losing was observed which was related to the loss of most parts of compound.

DISCUSSION

In this research, some of the inorganic complexes of uranyl with N- donor ligands were

synthesized. Complexes were characterized by FT-IR and UV, 1H NMR, ^{13}C NMR spectra, TG/DTG measurements and some physical properties. The results of simultaneous TG-DTG-DTA analyses of the complexes show the final degradation product for these complexes are UO_3 .

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