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A uranium(VI) complex with a tetradentate N^1, N^4 -disalicyliden-Sethylisothiosemicarbazone ligand

Alireza Akbari^a, Ahad Fasihizad^a, Mehdi Ahmadi^{a,*}, Barbara Machura^{b,*}

^aDepartment of Chemistry, Payame Noor University (PNU), 19395-4697, Iran
^bDepartment of Crystallography, Institute of Chemistry, University of Silesia, ul. Szkolna 9, 40-006 Katowice, Poland

^aDr. Mehdi Ahmadi Department of Chemistry, Payame Noor University (PNU), 19395-4697, Iran Tehran Iran Tel/Fax: +98 (513) 4693258 E-mail address: <u>mehdieahmadi@ymail.com</u> ^bProfessor Barbara Machura Department of Crystallography University of Silesia Katowice Poland Tel.: +48322582441; fax: +48322599978. E-mail addresses: basia@ich.us.edu.pl

Abstract:

The Schiff base ligand of bis-(2-hydroxybenzaldehyde)-S-ethylisothiosemicarbazone and its U(VI) complex have been prepared. Their structures were fully characterized by elemental analysis, FT-IR, molar conductivity, UV-Vis and ¹H NMR methods. X-ray diffraction has been used to determine the molecular structure of the uranium complex. The Schiff base complex was found to be pentagonal bipyramidal. The N₂O₂ donor ligand was coordinated to the metal center as a tetradentate binegative agent. Computational studies were performed using the DFT method to estimate the structural preferences in tridentate and tetradentate isothiosemicarbazones. Geometry optimization and natural bond orbital analyses of the UO₂(II) complex have been further discussed in detail. The thermal stabilities of the ligand and its uranium complex have also been determined by thermogravimetric analysis (TGA).

Keyword: isothiosemicarbazone, uranium, X-ray, DFT, TGA

1. Introduction

Isothiosemicarbazones are in the center of research interests, not only for the selective separations of ions [1] but also for their biological properties, which generally arise from their strong chelating ability with metal ions [2,3]. Isothiosemicarbazone compounds are sulfur containing Schiff base materials that have been used for designing tailor-made polydentate ligands [4].

Isothiosemicarbazides have two NH_2 groups. Among them, only the hydrazinic amine group can simply participate in a Schiff base reaction. A metal center with a definite electronic state is needed to dictate the condensation between the thioamide amine group of isothiosemicarbazones and the carbonyl group of aldehyde or ketone compounds. In this way, their interaction is affected by a suitable orientation as a result of their coordination. By means of the metal template process, multidentate ligands can be obtained, the synthesis of which is totally impossible under other conditions [5,6].

It is also documented that the template reaction between aldehyde or ketone compounds and *S*-alkylatedisothiosemicarbazone in alcohol in the presence of the metal ions of V(IV), Mn(II), Fe(III), Ni(II), Zn(II), MoO₂(II) and UO₂(II) can lead to formation of metal complexes containing a tetradentate ligand in high yield [7,8].

By using 2-hydroxobenzaldehyde, an asymmetric N_2O_2 donor ligand, comparable with Salen, can be obtained. Having planar or pseudo-planar conformations of such ligands may enable complexes with the central atom at the center of a charge-transfer system to be formed. These

complexes are suitable for successful applications due to their non-linear optical properties and for use in the field of optoelectronic technologies [9,10].

Uranyl complexes are interesting to researchers because of their high chemical stability, high coordination numbers and low radiological hazard [11]. They have received considerable attention due to their promising luminescent and magnetic properties. Some uranyl complexes have also been used as catalysts in the oxidation of alcohols to ketones and in acyl transfer reactions [12].

The first uranium complex of isothiosemicarbazone was investigated structurally by Leovac *et al.* [13]. From that time until now, many uranium(VI) complexes of isothiosemicarbazones have been synthesized and their structures have been studied by means of spectral methods and X-ray diffraction analysis [14-21]. To the best of our knowledge, however, other analyses like DFT calculations have been rather rarely performed for these systems.

Herein, we first synthesized a reported Ni(II) complex of the tetradentate ligand bis-(2-hydroxybenzaldehyde)-*S*-ethylisothiosemicarbazone by the template process [22]. The tetradentate ligand can be extracted by adding hydrochloric acid. The uranium dioxide complex of the tetradentate ligand was then prepared and characterized by the prevailing methods of FT-IR, UV-Vis, ¹H NMR as well as by single crystal X-ray diffraction. The geometrical parameters, frequency analyses and NBO calculations in the ground state have been calculated by DFT calculations. An additional study was done to examine the thermal stability by TGA.

2. Experimental

2.1 Reagents and physical measurements

All chemicals were of analytical reagent grade and they were used without further purification. FT-IR spectra were measured as KBr pellets in the 400-4000 cm⁻¹ region on a FT-IR 8400-SHIMADZU spectrophotometer. The ¹H NMR spectra were recorded in DMSO- d_6 on a Bruker BRX 300 AVANCE spectrometer. The UV-Vis spectra of the compounds were run in methanol (2 × 10⁻⁵ M) and DMF (10⁻³ M) solutions on a SHIMADZU model 2550 UV-Vis spectrophotometer. C, H and N analyses were carried out using a Thermo Finnigan Flash Elemental Analyzer 1112EA instrument. The molar conductance of 10⁻³ M solutions of the ligands and the metal complexes in DMF were measured at room temperature using a Metrohm 712 conductometer. Thermogravimetric analyses (TGA) were carried out using a TG-50 SHIMADZU under an argon atmosphere over the temperature range 20-800 °C at a heating rate of 10 °C/min.

2. 2. X-ray crystal structure determination

The X-ray intensity data of the uranium(VI) complex were collected on a Gemini A Ultra Oxford Diffraction four-circle kappa geometry diffractometer with Atlas CCD detector graphite monochromatic MoK_{α} radiation ($\lambda = 0.71073$ Å) at 293.0(2) K. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [23]. Intensity data were corrected for Lorentz and polarization effects. The absorption correction was introduced by the SCALE3 ABSPACK scaling algorithm [23]. The structure was solved by the Paterson method using SHELXS-97 and refined by full matrix least-squares on F² with SHELXL-97, using anisotropic displacement parameters for the non-hydrogen atoms [24]. The hydrogen atoms were treated as "riding" on their parent carbon atoms and were assigned isotropic temperature factors equal to 1.2 (aromatic) and 1.5 (methyl) times the value of equivalent temperature factor of the parent atom.

Insert Table 1

2. 3. Theoretical calculations

The geometry of the compounds was fully optimized with density functional theory (DFT). All calculations were performed using the B3LYP exchange correlation functional [25]. The calculations were done using the 6-311G**(d,p) [26] basis set for the H, C, N, O and S atoms and the Lanl2dz [27] basis set for the metal center in gas and solution phases with the GAUSSIAN 98 program package [28].

The U(VI) complex and the H₂L ligands, both Z and E isomers and all the deprotonated structures, were fully optimized. No symmetry constraints were applied in the calculations. The optimized structures have been used for the frequency calculations. The lack of negative number of the frequencies showed that the structures were fully optimized. The ground state energies of the Z and E isomers were also calculated in methanol solution using the CPCM model (conductor-like polarizable continuum model) [29]. Analysis of the Natural Bond Orbital (NBO) was done with the NBO-code included in Gaussian 98 [30].

2. 4. Synthesis of 2-hydroxybenzaldehyde S-ethylisothiosemicarbazone H_2L^1

This compound was synthesized by following the literature procedure [5]. 2-Hydroxybenzaldehyde (1.22 g, 10 mmol) and *S*-ethylisothiosemicarbazide (2.47 g, 10 mmol) were refluxed for 1 h. The reaction was completed by the addition of an equivalent amount of Na₂CO₃ (1.06 g, 10 mmol). A yellow precipitate was obtained when the reaction solution was

left to stand overnight. The precipitate was separated and washed several times with cold ethanol and dried in vacuo over silica gel.

Yield: 1.9 g, 85%. M.p.: 155 °C. Anal. Calc. for C₁₀H₁₃N₃OS (223.29 g mol⁻¹): C, 53.79; H, 5.87; N, 18.82. Found (%): C, 35.45; H, 5.72; N, 18.36. FT-IR (KBr, cm⁻¹): v(OH) 3400; v_{as} (NH₂) 3201; v_{as} (NH₂) 3068; v(CH) 2972; v(C=N) + v(C=C) 1589, 1520; v(C=C) 1469, 1450; v(C-O) 1115; v(N-N) 1056; δ_{opb} (C-H) 756. UV-Vis (methanol, λ_{max} , nm (log ε , L mol⁻¹ cm⁻¹)): 213 (4.77), 308 (4.49), 346 (4.56). Molar conductivity (1×10⁻³ mol L⁻¹, MeOH, Ω^{-1} cm² mol⁻¹): 17.

2. 5. Synthesis of (S-ethyl- N^{1} , N^{4} -bis-(2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N',O,O')-nickel(II)

The nickel complex was prepared according to the literature [22]. An ethanolic solution (5 mL) of 2-hydroxybenzaldehyde *S*-ethylisothiosemicarbazone (0.223 g, 1 mmol) and 2-hydroxybenzaldehyde (0.122 g, 1 mmol) were mixed for 30 min in the presence of KOH (0.122 g, 2 mmol). To the mixture, NiCl₂.6H₂O (0.237 g, 1 mmol) was added as a solid. A red solution was immediately obtained. The reaction solution was stirred for 30 min at room temperature. A red crystalline precipitate was obtained which was separated and washed several times with cold ethanol and dried in vacuo over silica gel.

Yield: 0.24 g, 63%. M.p.: 236 °C. Anal. Calc. for C₁₇H₁₅N₃NiO₂S (384.08 g mol⁻¹): C, 53.16; H, 3.94; N, 10.94. Found (%): C, 52.46; H, 3.72; N, 10.71. FT-IR (KBr, cm⁻¹): *v*(CH) 2923; v(C=N) + v(C=C) 1600, 1573,1527; v(C=C) 1427; v(C-O) 1288; v(N-N) 1026; δ_{opb} (C-H) 763. UV-Vis (methanol, λ_{max} , nm (log ε , L mol⁻¹ cm⁻¹)): 225 (5.02), 245 (4.60), 300 (3.99), 393 (4.38). Molar conductivity (1×10⁻³ mol L⁻¹, MeOH, Ω^{-1} cm² mol⁻¹): 24.

2. 6. Synthesis of bis-(2-hydroxybenzaldehyde)-S-ethylisothiosemicarbazone H₂L²

To a 10 mL chloroformic solution of (*S*-ethyl- N^{1} , N^{4} -bis-(2-hydroxybenzaldehyde)isothiosemicarbazide-N,N',O,O')-nickel(II) (0.384 g, 1 mmol), hydrochloric acid 32% (0.22 g, 2 mmol) was added gradually until the red color of the solution became light-green. Water (50 mL) was added to the solution and after vigorous stirring, the organic layer was separated. This was repeated 3 times to ensure the removal of nickel(II) chloride from the organic layer. The chloroform was evaporated and the remaining yellow precipitate was separated and washed several times with cold ethanol and dried in vacuo over silica gel.

Yield: 0.294 g, 90%. M.p.: 163 °C. Anal. Calc. for $C_{17}H_{17}N_3O_2S$ (327.40 g mol⁻¹): C, 62.36; H, 5.23; N, 12.83. Found (%): C, 61.83; H, 4.98; N, 12.74. FT-IR (KBr, cm⁻¹): v(OH) 3351(m); v(CH)-aromatic 3012-3063(w); v(CH)-Et 2854-2966(w); v(C⁷=N¹) + v(C=C)

1613(m); $v(C=C) + \delta_{ipb}(OH)$ 1573(m); v(C=C) 1485(vs); $v(C^8=N^2) + v(C=C)$ 1454(s); v(CO)1253(m); $v(N=C-N^3) + v(C^2O^2)$ 1211(w); $\delta_{oopb}(OH)$ 812(w); $\delta_{oopb}(CH)$ -aromatic 752(m); v(CSC) 650(w). ¹H NMR (300 MHz, DMSO- d_6) δ , ppm: 10.1 (s, 2H; exchanges with D₂O), 8.3 (s, 1H, C7H), 8.2 (s, 1H, C8H), 7.35 (d, 2H, C5), 7 (dd, 2H, C2, C14), 6.6 (d, 4H, C3, C4, C12, C13), 1.5 (s, 2H, C16), 1.1 (t, 3H, C17). UV-Vis (methanol, λ_{max} , nm (log ε , L mol⁻¹ cm⁻¹)): 213 (5.09), 238 (4.73), 284 (4.74), 335 (4.54), 387 (4.30), 408 (4.27). Molar conductivity (1×10⁻³ mol L⁻¹, MeOH, Ω⁻¹ cm² mol⁻¹): 21.

2. 7. Synthesis of methanol-(S-ethyl- N^{I} , N^{4} -bis-(2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N',O,O')-dioxidouranium(VI)

A methanolic solution (5 mL) of bis-(2-hydroxybenzaldehyde)-S-ethylisothiosemicarbazone (0.327 g, 1 mmol) was gradually added to a methanolic solution (5 mL) of $UO_2(OAC)_2.2H_2O$ (0.424 g, 1 mmol). A red solution was obtained. The reaction solution was stirred for 30 min at 40 °C. Crystals suitable for X-ray analysis were obtained by slow evaporation of the maternal solution in the fridge after one week. They were separated and washed several times with cold methanol and dried in vacuo over silica gel.

Yield: 0.53 g, 85%. M.p. 193 °C. Anal. Calc. for C₁₈H₁₉N₃O₅SU (627.45 g mol⁻¹): C, 34.46; H, 3.05; N, 6.70. Found (%): C, 35.04; H, 3.12; N, 6.87. IR (KBr) cm⁻¹: v(OH)-alcohol 3409(ms); v(CH)-aromatic 3012-3063(w); v(CH)-Et 2854-2966(w); v(C⁷=N¹) + v(C=C) 1589(s); v(C=C) 1550(vs); v(C⁸=N²) + v(C=C) 1435(s); v(CO) 1250(m); v(N=C-N³) + v(C²O²) 1203(m); $v_{asy}(trans$ -UO₂) 910(s); $v_{sy}(trans$ -UO₂) 870(m); δ_{oopb} (CH)-aromatic 756(m); v(CSC) 671(w); v(MO) 586(m); v(MN) 439(m). ¹H NMR (300 MHz, DMSO- d_6) δ , ppm: 9.3 (s, H, OH_{alcohol}; exchanges with D₂O), 8.35 (s, 1H, C7H), 8.25 (s, 1H, C8H), 7.4-6.1 (m, 8H, Ar-CH), 2.75 (s, 3H, C18), 1.5 (s, 2H, C16), 1.4 (t, 3H, C17). UV/Vis (ethanol, λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹)): 222 (4.7), 245 (4.62), 311 (4.53), 394 (4.20), 449 (4.06). Molar conductivity (1.0×10⁻³ M, MeOH, Ω^{-1} cm² mol): 23.

3. Results and discussion

Condensation of 2-hydroxobenzaldehyde with S-ethyl-isothiosemicarbazide gave the Schiff base ligand H_2L^1 . The template reaction of H_2L^1 , 2-hydroxobenzaldehyde and NiCl₂.6H₂O in alkaline solution of MeOH resulted the Ni(II) complex. Hydrochloric acid was added to the chloroformic solution of the nickel complex. Thus, NiCl₂ was extracted and the remaining yellow precipitate corresponding to H_2L^2 was prepared. H_2L^2 was reacted with UO₂(OAC)₂ in methanol and a new uranium complex was synthesized.

The ligands and the complexes are found to be soluble in common organic solvents, like MeOH, DMF and DMSO, but are insoluble in H₂O. The elemental analyses confirm that the complexes are mononuclear and may be formulated as $[Ni(L^2)]$ and $[UO_2(L^2)MeOH]$. Molar conductivity data in 10⁻³M DMF solutions for the ligands and complexes indicate that they are non-electrolytes [31,32].

3.1. General optimization and NBO calculations

The crystal structure of the uranium(VI) complex has been used as the initial geometry for the optimization. Some of important bond lengths and bond angles are given in Table 3, in which the calculated values are in good agreement with the experiment values. A small difference is seen in the bond distances and bond angles. This may be due to the fact that the DFT calculations were performed in the gas phase, whereas the X-ray crystal diffraction was performed in the solid state.

The natural charges from the natural population analyses for the donor atoms and metal atom were calculated in the gas phase. The calculated electronic configurations confirmed electron donation from the donor atoms towards the metal ion. Also, the calculated formal charge on the central ion in the complex was near to +2, quite smaller as compared to the formal oxidation state of the metal (+6), and the net charges on the O1, O2 and O3, O4 atoms are significantly smaller than -2 and -1, respectively.

According to the NBO calculations for the U=O *trans* bonds of the U(VI) complex, there are four σ and π bonding orbitals and four σ^* and π^* antibonding orbitals. The σ bonding orbitals of the {U=O} bonds are polarized mainly on the O1 and O2 atoms (respectively 76.02 and 77.75 %). The metal center and oxygen atoms use 5d and 4f orbitals and 2s and 2p valence orbitals for σ bonds, respectively. The π bonding electrons are also polarized towards the O1 and O2 atoms by 78.30 and 78.30% respectively. In the formation of the U=O π bond, the metal and oxygen atoms use 5d and 4f, and 2p orbitals respectively. Accordingly, the σ^* and π^* antibonding orbitals are polarized toward the central metal ion.

3. 2. Comparison of the structure stability in different forms of the H_2L^1 and H_2L^2 ligands

A DFT study was performed to evaluate the conformational preference in the tridentate (H_2L^1) and tetradentate (H_2L^2) ligands. The optimizations have performed for both *Z* and *E* isomers and their various deprotonated structures. For all the structures, vibrational frequency calculations have been done as a check for the accuracy of the optimizations.

In the solid state, isothiosemicarbazones crystallize in either the *Z* or *E* configuration, while the simultaneous presence of both the *Z* and *E* configurations in the solution phase were reported [33,34]. In the *E* isomer, the N1 and N3 atoms lie in *cis* positions, while in the *Z* isomer they are in *trans* positions with respect to each other [33]. The *E* structure of H_2L^1 is more stable than the *Z* form by 9 and 4 K cal mol⁻¹ in the gas and solution phases respectively. Also, the stability of the *Z* structure of H_2L^2 is significantly higher compared to the *E* form, by 7 and 4 K cal mol⁻¹ in the gas and solution phases respectively.

In the *E* configuration of H_2L^1 , the S atom is generally in a *trans* position with respect to the atom N1. Thus, the N1 and N3 atoms are placed in positions suitable for intramolecular N1...H-N3 hydrogen bonding. The hydrogen bonding interaction is thus preferred to the 1,4 N...S contact, which would take places in the *Z* conformation [34].

In the Z form of $\mathbf{H}_2 \mathbf{L}^2$, the S and N1 atoms are favourably oriented to give an intramolecular through-space 1,4S...N interaction. Also, intramolecular hydrogen bonding within the molecule cannot occur. Thus, the *cis* form becomes more stable than the *trans* form. Adoption of the *cis* form by $\mathbf{H}_2 \mathbf{L}^2$ also forces the phenyl rings far away from each other [34].

For the deprotonated structures of the *cis* and *trans* isomers of H_2L^1 and H_2L^2 , the dideprotonated species have higher energies than the corresponding mono-deprotonated species. This shows that the probability of simultaneous deprotonation of the NH₂ and OH groups in H_2L^1 and O1H and O2H groups in H_2L^2 in the solution is low. Another conclusion indicates that deprotonation in the *E* form of the H_2L^1 firstly occurs at the OH group and then at the NH₂ group. Also, deprotonation in the *Z* form of H_2L^2 firstly occurs at the O1H group and then at the O2H group

3. 3. Infrared spectroscopy

In the FT-IR spectrum of H_2L^1 , the asymmetric and symmetric stretching vibrations of the NH₂ group are observed at 3201 and 3068 cm⁻¹ as sharp bands. The strong band at 3400 cm⁻¹ is characteristic of v(O-H). The peak at 756 cm⁻¹ is attributed to the out of plane bending vibration of the aromatic ring. The peaks at 1589 and 1529 cm⁻¹ are due to the combination of v(C=N) and v(C=C). The stretching vibration of the C-O bond is observed at 115 cm⁻¹ [31].

The FT-IR spectrum of the Ni(II) complex does not show $v_{as}(NH_2)$ and $v_s(NH_2)$, showing the template reaction had been performed successfully. Stretching bands due to v(C=N) + v(C=C) in the spectrum of the Ni(II) complex are recorded at lower frequencies than the corresponding bands of H_2L^1 .

Useful information related to the U(VI) complex formation can be obtained by a comparison between the experimental and theoretical FT-IR spectra. Experimental and theoretical vibrational frequency values of the tetradentate ligand and its U(VI) complex are tabulated in Table 2. The tetradentate ligand and its U(VI) complex belong to the C1 point group and because of their low symmetry, they show a lot of peaks in the infrared spectra. The calculated frequencies were scaled by the suitable scale factor of 0.968 [32].

One of the significant differences seen between the IR spectra of H_2L^2 and its U(VI) complex is due to the presence of more strong bands at 910 and 870 cm^{-1} for the metal complex. They are due to $v_{asy}(trans-UO_2)$ and $v_{sy}(trans-UO_2)$. Theoretical values are disclosed at 901 and 861 cm⁻¹. The ligand band at 1253 cm⁻¹ (calculated at 1263 cm⁻¹) assigned to v(C-O), shifts to 1250 cm⁻¹ (calculated at 1245 cm⁻¹) on complexation, confirming involvement of the oxygen atoms in the complex formation [8]. The infrared spectrum of the tetradentate ligand shows a v(OH) band at 3351 cm⁻¹ while in the calculation it is determined at 3431 cm⁻¹. The absence of this band in the infrared spectrum of the U(VI) metal complex indicates deprotonation of the hydroxyl group during the chelation. The sharp intense bands at 1613 and 1485 cm⁻¹ in the spectrum of H_2L^2 can be assigned to $v(C^7=N^1) + v(C=C)$ and $v(C^8=N^2) + v(C=C)$ [7]. A downward shift in v(C=N) is observed upon coordination, indicating that the nitrogen atoms of the azomethine groups are involved in the coordination. The uranium complex shows a broad band at 3409 cm⁻¹ in the experiment and at 3531 cm⁻¹ in the calculation, which can be assigned to v(OH) of the coordinated solvent molecule. The new bands present at 586 and 439 cm⁻¹ are due to metal-oxygen and metal-nitrogen stretching vibrations. The calculations disclose these bands at 559 and 411 cm⁻¹.

Insert Table 2.

3. 4. UV-Vis study

The electronic absorption spectra of $\mathbf{H}_2 \mathbf{L}^1$ and $\mathbf{H}_2 \mathbf{L}^2$ and their Ni(II) and U(VI) complexes in MeOH solution have been recorded in the region 800-200 nm. The electronic spectrum of $\mathbf{H}_2 \mathbf{L}^1$ displays two absorption bands at 213 and 308 nm. They can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine (C=N) group. Another band at 346 nm is most probably due to the $n \rightarrow \pi^*$ transitions of the azomethine and thioamide groups [9].

The electronic spectrum of $\mathbf{H}_2 \mathbf{L}^2$ has some extra bands in comparison with $\mathbf{H}_2 \mathbf{L}^1$. They can be due to the extra benzene ring and the formation of a new azometinic C=N moiety. Three intense bands appeared at 213, 238 and 284 nm in the UV-Vis spectrum of $\mathbf{H}_2 \mathbf{L}^2$, which are assignable to $\pi \rightarrow \pi^*$ transitions of the benzene rings. These bands show a red shift in the spectra of the complexes [8]. The $n \rightarrow \pi^*$ transitions of the azomethine and thioamide moieties

are displayed at 335, 387 and 408 nm. Three $n \rightarrow \pi^*$ transitions within the ligands are omitted in the spectra of the complexes and only one band for the $n \rightarrow \pi^*$ transition is observed at 393 and 394 nm in the UV-Vis spectra of the Ni(II) and U(VI) complexes, respectively [10]. By comparison of the electronic spectra of the ligands with their Ni(II) and U(VI) complexes, it is clearly obvious that some bands show blue or red shifts which can be considered as evidence for the complex formation. Additionally, new bands are observed in the spectra of the complexes corresponding to certain ligand to metal and metal to ligand charge transitions.

3. 5. ¹H NMR spectroscopy

Scheme 1 can be applied for the assignment of the proton resonances. The ¹H NMR spectra (300 MHz, δ in ppm) of H_2L^2 and its diamagnetic UO₂(II) complex were recorded in DMSOd₆. The aromatic ring protons of the ligand are detected at 7.35, 7 and 6.6 ppm, while the aromatic ring protons for the complex consist of a set of multiplets in the range 7.4-6.1 ppm (m, 8H, Ar-CH). The signal of the OH protons for the free ligand disappear in the spectrum of the complex, showing coordination take places through the deprotonated phenolic oxygen atoms. Also, the upfield shift of the azomethinic proton signals in the spectrum of the complex with respect to the corresponding value of the free ligand reveals coordination through the azomethinic nitrogen atoms. The signals related to the protons of the alcohol molecule in the spectrum of the complex suggest that the molecule is not coordinated to the uranium center in the presence of DMSO as the ¹H NMR solvent.

Insert Scheme 1.

3. 6. Thermogravimetry

The thermal analyses of the tetradentate N_2O_2 donor ligand and its uranium complex were performed to obtain information about their thermal stability. Thermogravimetric studies were done in the temperature range 20-1000 °C at a heating rate of 10 °C min⁻¹. The TG curves are depicted in Fig. 1. Fig. 2 shows the partial mass losses with the assignments at each decomposition stage, based on mass calculations. The obtained results are in good agreement with the theoretical values suggested from the C, H and N analysis.

The ligand gives a decomposition pattern of three stages. The first stage, in the region 163-184 °C, corresponds to the evolution of the S-ethyl moiety, with a found mass loss of 18.16% (calcd. 18.67%). The second stage, in the temperature range 203-2236 °C, is related to the loss of the C=N-N=C-N=C fragment, with a found mass loss of 24.86% (calcd. 25.37%). The final stage of the thermal decomposition of the ligand is attributed to the loss of two C₆H₆OH

fragments, with a found mass loss of 57.83% (calcd. 57.48%), within the temperature range 245-294 °C.

The complex gives a decomposition pattern of two stages. The first stage, within the temperature range 198-263 °C, corresponds to the evolution of S-ethyl and MeOH molecules, with a found mass loss of 15.00% (calcd. 14.84%). The second stage, within the temperature range 293-468 °C, is attributed to the loss of the remaining parts of the ligand, with a found mass loss of 43.33% (calcd. 42.60%), leaving the final residuum U_3O_8 with a weight 43.08% (calc. 44.73%), which is stable from 468 to 1000 °C.

Insert Fig. 1. Insert Fig. 2.

3.7.X-ray study

X-ray diffraction provided detailed structural parameters for the studied complex. The ortep plot with the atom numbering is shown in Fig. 3. Selected bond lengths and bond angles are tabulated in Table 3. In order to compare the structural futures of the new U complex with similar compounds, we tabulated some data from the Cambridge Structural Database (CSD) in Tables 4 and 5. The parameters used for comparison are explained in Scheme 2.

The complex contains a N^1 , N^4 -disalicyliden-S-ethyl-thiosemicarbazone ligand with a *trans*-UO₂ ion and one methanol molecule. [*Trans*-UO₂(L)(MeOH)] crystallizes in the Pbca space group with unit cell parameters a = 22.287(3) Å, b = 15.6245(14) Å, c = 11.4339(16) Å, $a = 90^\circ$, $\beta = 11.4339(16)^\circ$, $\gamma = 11.4339(16)^\circ$, with eight molecules in the unit cell. The pentagonal-bipyramidal geometry of the complex is easily seen in Fig. 3. Two imine nitrogen atoms (N1 and N3) and two phenolic oxygen atoms (O3 and O4) from the tetradentate thiosemicarbazone ligand and one oxygen atom (O5) from the coordinated methanol molecule form a pentagon, while the two oxo groups (O1 and O2) occupy axial sites [5].

Coordination of the teteradentate ligand to the metal center results in one six-membered and to two five-membered chelate rings. Similar to the studied complex here, in U-based isothiosemicarbazone complexes the six-membered chelate rings show a half-chair conformation, but the conformation of the five-membered chelate ring may be planar or not, due to the some electron delocalization in the thiosemicarbazide group. The orientations of the coordinated solvents and S-alkyl groups in the uranyl complexes are somewhat different, probably due to different crystal packing.

The U1-O3, U1-O4, U1-N1 and U1-N3 bond distances in the tetradentate ligand are 2.28(1), 2.22(1), 2.57(2) and 2.54(2) Å. From Table 4, the U-O and U-N bond distances are in the region previously published for uranium isothiosemicarbazone complexes (e.g., in the

complexes of dimethylsulfoxide-(*S*-ethyl- N^{1} , N^{4} -bis-(2-hydroxybenzaldehyde)isothiosemicarbazide-N,N',O,O')-dioxidouranium(VI), with U1-O3/4 of 2.25 Å on average and U1-N1/3 of 2.58 Å on average [14], and ethanol-(*S*-methyl- N^{1} , N^{4} -bis-(2hydroxybenzaldehyde)-isothiosemicarbazide-N,N',O,O')-dioxidouranium(VI), with U1-O3/4 of 2.24 Å on average and U1-N1/3 of 2.56 Å on average [13]).

However, the U1-O5 bond length is longer than those in $[UO_2(L^2)DMSO]$, with the parent organic ligand. This is due to the different nature of the coordinated solvents. Subsequently, the U1-N1 and U1-N3 bond lengths in the $[UO_2(L^2)DMSO]$ complex are longer than in the studied complex here, imposed by the *trans* effect of the DMSO ligand. As can be seen in Table 3, the uranium-oxygen bond distances in the complex are shorter than the uraniumnitrogen bond distances, based on the hard and soft acid-base concept explained by Pearson. The U=O1 and U=O2 bond distances are 1.76(1) Å, much shorter than the equatorial U-O bond lengths, including the multiple bond order. A search in the Cambridge Structural Database (CSD) demonstrates the coordination environments around the uranyl cations have very little effect on the U=O bond lengths.

The apical U1-O2/3 bond distances are in good accordance with the values reported previously for seven-coordinated uranyl complexes (e.g., in the complexes of 1-nonanol-(*S*-methyl- N^{I} -(3,5-dichlorosalicylidene)- N^{4} -(2-hydroxybenzaldehyde)-isothiosemicarbazide-

N,N',O,O')-dioxidouranium(VI), with U1-O2/3 of 1.76 Å on average [15], and allyl alcohol-(S-propyl- N^1 , N^4 -bis-(5-bromosalicylidene)-isothiosemicarbazide-N,N',O,O')-

dioxidouranium(VI) with U1-O2/3 of 1.76 Å on average [16]

The atoms N1, N3, O3, O4, O5 and U1 deviate from the pentagonal plane by 0.309, 0.354, 0.24, 0.14, 0.05 and 0.02 Å. Atoms N1, N3 and O3 are significantly out of the pentagonal plane, as indicated by the torsion angle O3N1N3O4 of 32.17° . The central ion in the complex is approximately located on the pentagonal plane. From Table 5, this is in common with similar structures. The two oxo atoms O1 and O2 of the uranyl moiety lie *trans* to each other, as indicated by the O1=U1=O2 angle of 178.9° .

In an ideal pentagonal-bipyramidal geometry, each of the five angles subtended at the equatorial plane must be 72°. The angles around the U atoms are not equivalent and stand in the interval $61.8(5)-81.34(4)^\circ$, showing significant distortion [13]. Distortion of the ideal pentagonal-bypiramidal geometry is also well detectable by the O(oxo)-U-O,N angles, that are in the region 85.8(5) to $94.1(5)^\circ$. The dihedral angle between the UN₂O₃ plane and the plane including the metal and two axial O atoms is 87.55° .

The phenolic parts of the ligand are not planar and show a propeller-like conformation with respect to each other, as can be seen by the dihedral angle of 42.42°. This may be due to the large radius of the uranium ion, without putting significant strain on the backbone of the ligand. The propeller-like conformation of the complex is also detectable by considering the angles between the mean planes U1-N1-C7-C6-C1-O3 and U1-N3-C9-C10-C15-O4, which is calculated to be 29.51°. This distortion in the uranium complexes, including bis-isothiosemicarbazones, is common (see Table 5) [8].

The dihedral angles between the pentagon plane of O5-O3-N1-N3-O4 and the benzene rings planes of C1-C2-C3-C4-C5-C6 and C14-C15-C10-C11-C12-C13 are 31.48 and 43.32° respectively, indicating a non-planar disposition of the tetradentate isothiosemicarbazone ligand. As can be seen from the values of folding of the chelating rings 1, 2 and 3 along N1...N3, N1...O3 and N3...O4 respectively, it is clearly obvious the ligand is coordinated to the uranium center in a concave way and this is in common with most tetradentate N₂O₂ donor isothiosemicarbazone complexes (see Scheme 2 and Table 5).

The intermolecular hydrogen bonds detected in the crystal structure of the complex are summarized in Table 6. The molecule has the donor as well as the acceptor group and forms centrosymmetric dimers through an interaction between the O5-H5A donor of the coordinated methanol solvent and the O⁻ acceptor of the phenolato group. The ring pattern is $R^2_2(8)$ (Fig. 4.).

The studied complex $[UO_2(L^2)MeOH]$ links with a neighbouring complex and forms an O-H...O hydrogen bond using the hydroxyl group of the MeOH ligand and the phenolic oxygen atom of the adjacent molecule. However, the reported complex $[UO_2(L^2)DMSO]$ with the parent organic ligand does not show this intermolecular interaction due to absence of a hydroxyl group [14].

Insert Table 3.

Insert Table 4.

Insert Table 5.

Insert Table 6.

Insert Scheme 2.

Insert Fig. 3.

Insert Fig. 4.

4. Conclusion

This study presents the successful synthesis and characterization of a new tetradentate isothiosemicarbazone ligand and its UO₂(II) complex. Based on the spectral and structural data, it was found that the ligand coordinates to the metal center as a tetradentate N₂O₂ donor. The uranium complex adopts a pentagonal bipyramidal geometry and has a propeller-like conformation. Results from DFT calculations for the structural preference reveal that H_2L^1 (tridentate) and H_2L^2 (tetradentate) adopt the *E* and *Z* forms respectively. According to the NBO calculations, the N and O donor atoms of H_2L^2 transmit electrons towards the central U(VI) metal ion. Also, in the *trans*-UO₂ fragment, the σ and π bonding orbitals and the σ^* and π^* antibonding orbitals are polarized toward the ligand and metal ion respectively. Thermogravimetric analysis showed the thermal decomposition results in the metal oxide U₃O₈ as the final residue.

Finally, the uranium complex is air-stable and is soluble in most solvents. These may lead to a trend for researchers to develop its applications in biological and catalytic activities [35,36]. DFT calculations can be applied successfully to predict the structural geometry and interpret the natural bond orbital analyses [37,38].

Supplementary data

CCDC 1510074 contains the supplementary crystallographic data of the complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Figure captions:

Scheme 1. A key for the assignment of the proton resonances.

Scheme 2. Schematic of U(VI) isothiosemicarbazones as a key to the quantities in Tables 3 and 4.

Fig. 1. Thermal decomposition diagrams.

Fig. 2. The proposed mechanisms for thermal decomposition.

Fig. 3. Ortep diagram of the complex. Thermal ellipsoids are drawn at the 30% probability level.

Fig. 4. Centrosymmetric H bonded dimer in the complex. H bonds are represented by dashed thick lines.







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 U_3O_8



6





Empirical formula	$C_{18}H_{19}N_3O_5SU$
Formula weight	627.45
Temperature [K]	293.0(2)
Wavelength [Å]	0.71073
Crystal system	Orthorhombic
Space group	Pbca
	a = 22.287(3)
Unit cell dimensions [Å, °]	b = 15.6245(14)
	c = 11.4339(16)
Volume [Å ³]	3981.6(9)
7.	8
- Calculated density [Mg/m ³]	2.093
Absorption coefficient $[mm^{-1}]$	8 293
F(000)	2368
Crystal size [mm]	$0.164 \ge 0.111 \ge 0.037$
) rongo for data collection [0]	3 52 to 25 05
range for data conection [*]	3.52 to 25.05
index renges	$-20 \ge 11 \ge 21$
index ranges	-18≤ K≤ 13
	$-13 \le 1 \le 10$
Reflections collected	10822
ndependent reflections	3518 [R(int) = 0.0777]
Completeness to $2\theta = 25.05^{\circ}$ [%]	99.8
Max. and min. transmission	1.000 and 0.23380
Data / restraints / parameters	3518 / 2 / 258
Goodness-of-fit on F ²	1.110
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0798, $wR2 = 0.1666$
R indices (all data)	R1 = 0.1312, $wR2 = 0.1843$
Largest diff. peak and hole [e $Å^{-3}$]	2.145 and -1.837

Table 1. Crystal data and structure refinement for the uranium complex.

_

H_2L^2		U co	mplex	
Exp. ^a	Scaled.	Exp.	Scaled.	Assignment.
-	-	439(m)	411	V(MN)
-	-	586(m)	559	<i>V</i> (MO)
650(w)	635	671(w)	642	V(CSC)
752(m)	734	756(m)	764	$\delta_{\text{oopb}}(\text{CH})$ -aromatic
812(w)	801	-	-	$\delta_{\text{oopb}}(\text{OH})$
-	-	870(m)	861	$V_{sy}(trans-UO_2)$
-	-	910(s)	901	$V_{asy}(trans-UO_2)$
1211(w)	1241	1203(m)	1227	$\mathcal{V}(N=C-N^3) + \mathcal{V}(C^2O^2)$
1253(m)	1265	1250(m)	1245	<i>V</i> (CO)
1454(s)	1427	1435(s)	1463	$\mathcal{V}(C^8=N^2) + \mathcal{V}(C=C)$
1485(vs)	1493	1550(vs)	1567	V(C=C)
1573(m)	1600	-	-	$\mathcal{V}(C=C) + \delta_{ipb}(OH)$
1613(m)	1603	1589(s)	1592	$\mathcal{V}(\mathbf{C}^7 = \mathbf{N}^1) + \mathcal{V}(\mathbf{C} = \mathbf{C})$
2854-2966(w)	2914-3023	2854-2966(w)	2904-3011	V(CH)-Et
3012-3063(w)	3062-3121	3012-3063(w)	3024-3131	V(CH)-aromatic
3351(m)	3431	-	-	<i>V</i> (OH)
-	-	3409(ms)	3531	v(OH)-alcohol

Table 2. The experimental and calculated IR vibrational frequencies of the tetradentate ligand and its U(VI) complex.

^a Wavenumbers (cm⁻¹)

Abbreviation: vs; very strong, s; strong, m; medium, w; weak, sy; symmetric, asy; asymmetric, v; stretching, δ ; bending, oopb; out of plane bending; ipb; in plane bending.

Bond lengths	X-ray	Optimized ^a	Optimized ^b	Bond angles	X-ray	Optimized ^a	Optimized ^b
U1-01	1.76(1)	1.78	1.79	O2-U1-O1	178.9(6)	177.8	176.2
U1-O2	1.76(1)	1.78	1.79	O2-U1-O4	90.5(5)	89.7	89.5
U1-O3	2.28(1)	2.29	2.25	O2-U1-O3	85.8(5)	89.4	89.7
U1-O4	2.22(1)	2.26	2.26	01-U1-O4	89.2(5)	91.6	90.6
U1-05	2.41(1)	2.58	2.55	O1-U1-O3	94.1(5)	90.2	91.7
U1-N3	2.54(2)	2.55	2.58	O3-U1-N1	69.9(4)	71.9	71.1
U1-N1	2.57(2)	2.58	2.56	N1-U1-N3	61.8(5)	63.2	62.2
C7-N1	1.28(3)	1.30	1.30	N3-U1-O4	71.3(5)	71.5	70.8
N1-N2	1.43(2)	1.39	1.39	O4-U1-O5	79.4(5)	85.6	82.4
N2-C8	1.26(3)	1.28	1.29	O5-U1-O3	81.3(4)	72.4	73.0
C8-N3	1.42(3)	1.40	1.40				
N3-C9	1.31(3)	1.30	1.30				
C15-O4	1.32(2)	1.30	1.30				
C1-03	1.32(2)	1.30	1.31				
C8-S1	1.72(2)	1.78	1.78				
^a gas phase							
^b solution phase	e						
1							

Table 3. Selected bond lengths (Å) and bond angles (°) of the complex [trans-UO₂(L)(MeOH)].

Table 4. Comparison of the	chelated ligand geometries	(Å and °) for the [a	trans-UO ₂ (L)(MeOH)] complex.

	Fold of ring	Fold of ring	Fold of ring	Angle	Angle	Angle	Distance of	
	1 along	2 along	3 along	between the	between the	between the	The metal	
	N^1N^3	N^1O^3	$N^{3}O^{4}$	mean planes	mean planes	mean planes	from the	
				of rings 1	of rings 1	of rings 2	pentagon	
				and 2	and 3	and 3	plane of	
							O3-N1-N3-	
							O4-X	
1	1.96	15.66	20.76	13.41	16.10	29.51	0.02	
2	7.48	4.88	22.56	15.85	20.71	31.98	0.03	
3	2.56	19.77	17.53	10.35	16.85	27.05	0.02	
4	4.14	1.39	10.96	7.07	10.81	15.53	0.00	
¹ U comp ² CCDC ³ CCDC ⁴ CCDC	4.14 entry EPIJET (Re entry KAZKED (entry VAXKAG (1.39 f. [8]). Ref. [5]). Ref. [23]).						

Table 5. Conformational angles (°) for the [*trans*-UO₂(L)(MeOH)] complex.

0.9(1) 1.8(1) 2.64(2) 161(16) 1-x, 1-y, 1-z			D-H····A	d(D-H)	d(H···A)	d(D····A)	<(DHA)	Symmetry code on A atom
		official and a second	D5-H5O3	0.9(1)	1.8(1)	2.64(2)	161(16)	1-x, 1-y, 1-z
		office of the second se						21
								6
								9
							~	
						dr.		
				<i>Q</i> `				

Table 6. Hydrogen bonds for [trans-UO_2(L)(MeOH)] [Å and $^\circ\).$

- A uranium complex of a tetradentate isothisemicarbazone ligand is synthesized.
- Structure analysis, spectral, TG and DFT studies are performed.
- Accepter The uranium(VI) ion adopts a pentagonal bipyramidal geometry. •