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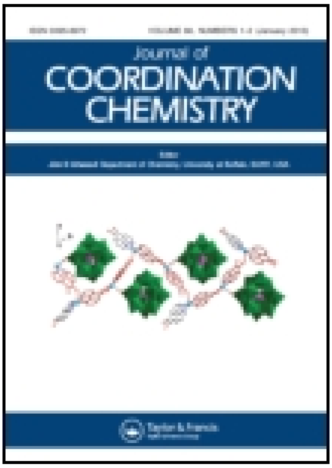

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Synthesis, characterization, thermogravimetry, and structural study of uranium complexes derived from dibasic S-alkylated thiosemicarbazone ligands

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Synthesis, characterization, thermogravimetry, and structural study of uranium complexes derived from dibasic S-alkylated thiosemicarbazone ligands

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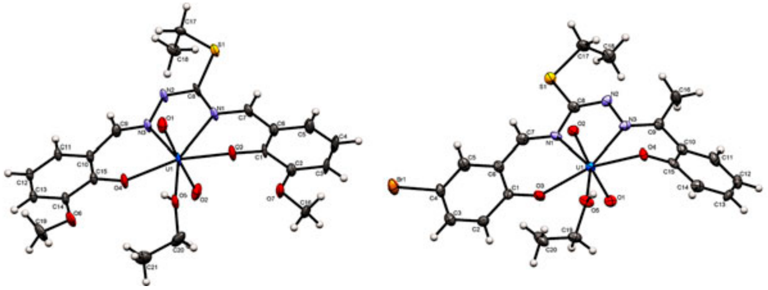

Two pentagonal bipyramidal complexes, ethanol-(*S*-ethyl-N^1,N^4-bis(3-methoxy-2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N′,O,O′)-dioxidouranium(VI) (**1**) and ethanol-(*S*-ethyl-N^1-(2-hydroxyacetophenone)-N^4-(5-bromo-2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N′,O,O′)-dioxidouranium(VI) (**2**), have been prepared and characterized. Their structures have been determined by X-ray crystallography, and the structural parameters are discussed with those observed in related complexes. Electronic absorption, proton magnetic resonance, and FT-IR spectra have been recorded and analyzed. In both complexes, the U(VI) centers are surrounded by N_2O_2 donor ligands, two oxido groups, and one ethanol in a distorted pentagonal bipyramid. The thermal stability of the new complexes has also been determined.

Keywords: Uranium complex; Isothiosemicarbazone; Crystallography; Spectra; Thermal stability

1. Introduction

Schiff base ligands have attracted much consideration in coordination chemistry because of the application of their complexes in medicine, catalysis, nonlinear optics, magnetism, and luminescence [1, 2]. Among the Schiff base ligands, tetradentate N_2O_2 donor Salen-type compounds show applications in the fields of catalysis and nonlinear optical properties [3, 4].

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An important feature of the tetradentate N_2O_2 donors is their ability to form stable complexes with uranium salts [5]. Due to very strong bonding between donors of these ligands and the uranyl group, complex formation leads to high precipitation. Thus, these compounds are of importance for separation of actinides of lanthanides from nuclear waste [6].

Some tetradentate N_2O_2 donors can be synthesized by template reaction of *S*-alkyl isothiosemicarbazones and salicylaldehyde analogs in the presence of transition metal ions Fe (III), Ni(II), Zn(II), Cu(II), Co(II), Pd(II), VO(II), and UO_2(II) [7]. Several studies have shown that the template synthesis of N_2O_2 donor isothiosemicarbazone derivatives with UO_2(II) is effective for complex formation [8].

In this study, we report the preparation of two new complexes of UO_2(II) from tetradentate bis-isothiosemicarbazone ligands within our search for compounds for possible application in the separation of actinides from lanthanides. The crystallization from solution led to pure solid complexes suitable for X-ray measurements. New complexes were characterized by molar conductivity, CHN analysis, FT-IR, and UV–vis spectroscopy as well as with X-ray crystallography. Thermogravimetric analysis is also provided.

2. Experimental

2.1. *Experimental and instrumentation*

H_2L^1 (3-methoxy-2-hydroxybenzaldehyde *S*-ethyl isothiosemicarbazone) was prepared according to our previous report [9]. Other chemicals were of analytical grade and used without purification. FT-IR with samples prepared as KBr pellets; UV–vis at $2 \times 10^{-5}\,M\,L^{-1}$ concentration in EtOH; ^1H NMR spectra in DMSO-d_6; carbon, hydrogen, and nitrogen microanalyses; and Electric conductance measurements were carried out, respectively, on a FT-IR 8400-SHIMADZU spectrophotometer, a SHIMADZU model 2550 UV–vis spectrophotometer, a Bruker BRX 100 AVANCE spectrometer, a Thermo Finnigan Flash Elemental Analyzer 1112EA instrument, and a Metrohm 712 Conductometer.

2.2. *X-ray single-crystal diffraction*

X-ray diffraction data were collected at 120 K with a four-circle diffractometer Gemini of Oxford Diffraction, Ltd., using a sealed X-ray tube with a copper anode. The primary beam was monochromated and collimated with mirrors using the Enhance-Ultra collimator; the diffracted beam was detected with a CCD detector Atlas. Standard data collection strategy of CrysAlis PRO [Agilent Technologies, (2012) CrysAlis PRO. Yarnton, Oxfordshire, England] was used for data collection as well as for data processing. Because of the strong absorption ($\mu \sim 20\,mm^{-1}$), the absorption correction was done carefully combining the correction based on the crystal shape with the one based on the spherical harmonic functions. Crystallographic data are provided in table 1.

The structure was solved by charge flipping using the program Superflip [10], which is part of the program Jana2006 [11]. The structure was refined with ShelXle [12].

Hydrogens attached to carbon were kept in the geometrically derived positions at 0.96 Å from their parent atoms, with isotropic displacement parameter defined as a 1.5 multiple of the parent terminal methyl carbon's U_{eq} and 1.2 multiple of the other carbons.

Table 1. Crystallographic data.

Crystal data		
Chemical formula	$C_{21}H_{25}N_3O_7SU$	$C_{20}H_{22}BrN_3O_5SU$
M_r	701.53	734.41
Crystal system, space group	Triclinic, *P-1*	Triclinic, *P-1*
Temperature (K)	120	120
a, b, c (Å)	8.9722(2), 10.6284(3), 13.4283(3)	9.5571(3), 11.6509(4), 12.1926(4)
α, β, γ (°)	68.272(3), 76.474(2), 76.785(2)	71.762(3), 67.775(3), 67.697(3)
V (Å^3)	1142.16(5)	1139.77(6)
Z	2	2
Radiation type	Cu Kα	Cu Kα
μ (mm^{-1})	21.28	23.27
Crystal size (mm)	0.30 × 0.20 × 0.10	0.20 × 0.11 × 0.06
Data collection		
Diffractometer	Xcalibur, Atlas, Gemini ultra diffractometer	
Absorption correction	Numerical + Multi-scan; *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32	
T_{min}, T_{max}	0.241, 1.000	0.00085, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18,743, 4010, 3970	19,211, 4004, 3818
R_{int}	0.052	0.054
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597	0.597
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.085, 1.20	0.024, 0.062, 1.05
No. of reflections	4010	4004
No. of parameters	256	287
No. of restraints	8	0
H-atom treatment	H atoms treated by constrained refinement	H atoms treated by constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.65, −2.32	1.28, −1.65

For **1**, the disorder of the central bridge was modeled. Two different positions with partial site occupancies 0.8 and 0.2 were found in the maps of electron density. Disordered fragments were then placed in appropriate positions, and all distances between neighboring atoms were restrained as well as angles. Site occupancies were refined for the different parts with the same thermal parameters for the same atoms in various fragments.

2.3. *Synthesis of 2-hydroxyacetophenone S-ethylisothiosemicarbazone (H_2L^2)*

Thiosemicarbazide (0.91 g, 10 mM) and ethyl iodide (1.71 g, 11 mM) were refluxed in ethanol for 3 h until a colorless solution was obtained. Five milliliters ethanolic solution of 2-hydroxyacetophenone (1.36 g, 10 mM) was added and the reflux continued for an extra hour. Finally, $Na_2CO_3 \cdot 10H_2O$ (5.72 g, 20 mM) dissolved in 10 mL water was added to neutralize the produced hydrogen iodide. The neutralization reaction was controlled by pH paper. The light yellow precipitate that separated was washed several times with cold ethanol.

Yield: 2.13 g (90%). M.p. 198 °C. Anal. Calcd for $C_{11}H_{15}N_3OS$ (237.32 g M^{-1}): C, 55.67; H, 6.37; N, 17.71. Found (%): C, 54.24; H, 6.34; N, 17.34. IR (KBr) cm^{-1}: $\nu_{asy}(NH_2)$ 3341vs; $\nu_{sy}(NH_2)$ 3234 ms; ν(OH) 3002vs; ν(CH) 2935–3000vw; ν(C=N) + ν(C=C)1624s, 1582vs, 1543s; ν(C=C) + δ_{ipb}(OH) + $\delta(NH_2)$ 1465s, 1415m; ν(CO) 1253s; ν(N=C–N) 1234m; δ_{oopb}(OH) 743m; $\delta_{oopb}(CH)_{aromatic}$ 698w; ν(CSC) 613w. ^{1}H NMR (100

MHz, DMSO-d_6): $\delta = 11$ (s, 1H, OH; exchanges with D_2O), 7.9 (d, 1H, C^5), 7.6 (dd, 1H, C^3), 7.2 (dd, 1H, C^4), 6.8 (d, 1H, C^2), 4 (s, 2H, NH_2; exchanges with D_2O), 3.1 (q, 2H, C^{10}), 1.3 (t, 3H, C^{11}), 0.9 (s, 3H, C^8). UV/vis (ethanol) λ_{max} nm (log ε, $L\,M^{-1}\,cm^{-1}$): 232 (4.95), 304 (4.81), 343 (4.96). Molar conductivity (1.0×10^{-3} M; EtOH): 12 $\Omega^{-1}\,cm^2\,M^{-1}$.

2.4. *Synthesis of ethanol-(S-ethyl-N^1,N^4-bis(3-methoxy-2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N',O,O')-dioxidouranium(VI) (1)*

Five milliliters ethanolic solution of 3-methoxy-2-hydroxybenzaldehyde *S*-ethyl isothiosemicarbazone (0.253 g, 1 mM) and 3-methoxy-2-hydroxybenzaldehyde (0.15 g, 1 mM) was mixed for 30 min. To the mixture, $UO_2(OAC)_2 \cdot 2H_2O$ (0.424 g, 1 mM) was added as solid. The red solution was obtained immediately and was refluxed for 30 min at 60 °C. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solution in the refrigerator after one week.

Yield: 0.53 g (75%). M.p. 234 °C. Anal. Calcd for $C_{21}H_{25}N_3O_7SU$ (701.53 $g\,M^{-1}$): C, 35.95; H, 3.59; N, 5.99. Found (%): C, 36.04; H, 3.43; N, 5.87. IR (KBr) cm^{-1}: $\nu(OH)_{alcohol}$ 3213 m; ν(CH) 2935–3000w; ν(C=N) + ν(C=C) 1612vs, 1543s; ν(C=C) 1464m, 1435s; ν(CO) 1241 m; ν(N=C–N) 1234ms; ν_{asy}(*trans*-UO_2) 910s; ν_{sy}(*trans*-UO_2) 877m; $\delta_{oopb}(CH)_{aromatic}$ 710m; ν(CSC) 613w. ^1H NMR (100 MHz, DMSO-d_6): $\delta = 13$ (s, 1H, OH; exchanges with D_2O), 8.6 (s, 1H, CH=N), 8.3 (s, 1H, CH=N), 7.9–6.7 (m, 6H, aromatic protons), 4.3 (q, 2H, CH_2, alcohol), 3.8 (s, 3H, CH_3, alcohol), 3.5 (s, 6H, OCH_3), 3.2 (q, 2H, CH_2, S-ethyl), 1.3 (t, 3H, CH_3, S-ethyl). UV/vis (ethanol) λ_{max} nm (log ε, $L\,M^{-1}\,cm^{-1}$): 235 (4.82), 312 (4.13), 360 (3.38), 421 (4.43), 456 (3.45). Molar conductivity (1.0×10^{-3} M; EtOH): 4 $\Omega^{-1}\,cm^2\,M^{-1}$.

2.5. *Synthesis of ethanol-(S-ethyl-N^1-(2-hydroxyacetophenone)-N^4-(5-bromo-2-hydroxybenzaldehyde)-isothiosemicarbazide-N,N',O,O')-dioxidouranium(VI) (2)*

Five milliliters ethanolic solution of 2-hydroxyacetophenone *S*-ethylisothiosemicarbazone (0.237 g, 1 mM) and 5-bromo-2-hydroxybenzaldehyde (0.2 g, 1 mM) was mixed for 30 min. To the mixture, $UO_2(OAC)_2 \cdot 2H_2O$ (0.424 g, 1 mM) was added as solid. The red solution was obtained immediately and was refluxed for 30 min at 60 °C. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solution in the refrigerator after one week.

Yield: 0.46 g (62%). M.p. 223 °C. Anal. Calcd for $C_{20}H_{22}BrN_3O_5SU$ (734.40 $g\,M^{-1}$): C, 32.71; H, 3.02; N, 5.72. Found (%): C, 32.04; H, 3.14; N, 5.47. IR (KBr) cm^{-1}: $\nu(OH)_{alcohol}$ 3213m; ν(CH) 2935–3000w; ν(C=N) + ν(C=C)1602s, 1562s; ν(C=C) 1453 m, 1423s; ν(CO) 1235m; ν(N=C–N) 1221ms; ν_{asy}(*trans*-UO_2) 919s; ν_{sy}(*trans*-UO_2) 885m; $\delta_{oopb}(CH)_{aromatic}$ 698m; ν(CSC) 613w. ^1H NMR (100 MHz, DMSO-d_6): $\delta = 12.8$ (s, 1H, OH; exchanges with D_2O), 8.2 (s, 1H, CH=N), 7.8–6.65 (m, 7H, aromatic protons), 4.2 (q, 2H, CH_2, alcohol), 4 (s, 3H, CH_3, alcohol), 3.2 (q, 2H, CH_2, S-ethyl), 1.3 (t, 3H, CH_3, S-ethyl), 1.1 (s, 3H, $C^{16}H_3$). UV/vis (ethanol) λ_{max} nm (log ε, $L\,M^{-1}\,cm^{-1}$): 238 (4.86), 308 (4.43), 355 (4.02), 402 (4.12), 460 (3.96). Molar conductivity (1.0×10^{-3} M; EtOH): 6 $\Omega^{-1}\,cm^2\,M^{-1}$.

3. Results and discussion

The template reactions of **H_2L^1** and 3-methoxy-2-hydroxybenzaldehyde as well as **H_2L^2** and 2-hydroxyacetophenone with hydrated dioxidouranium(II) acetate in ethanol gave two new complexes of uranium(VI). The complexes are stable in air, fairly soluble in methanol, ethanol, DMF, and DMSO; sparingly soluble in acetone and diethyl ether; and insoluble in water and n-hexane. The analytical data are in accord with the proposed structures. The molar conductivity data are consistent with the nonelectrolytic nature of the compounds [13].

3.1. *X-ray crystallography*

Single-crystal X-ray diffraction provided insight into the structure of the complexes. Their plots with the atom labeling are shown in figures 1 and 2. Selected bond lengths and angles are given in table 2. In both complexes, the bis-isothiosemicarbazone ligands coordinate as tetradentate N_2O_2 donors, chelating to the uranyl ions. The equatorial positions are occupied by the tetradentate ligands and oxygen of coordinated solvent. The apical positions of the strongly distorted pentagonal-bipyramid are completed by uranyl oxygens.

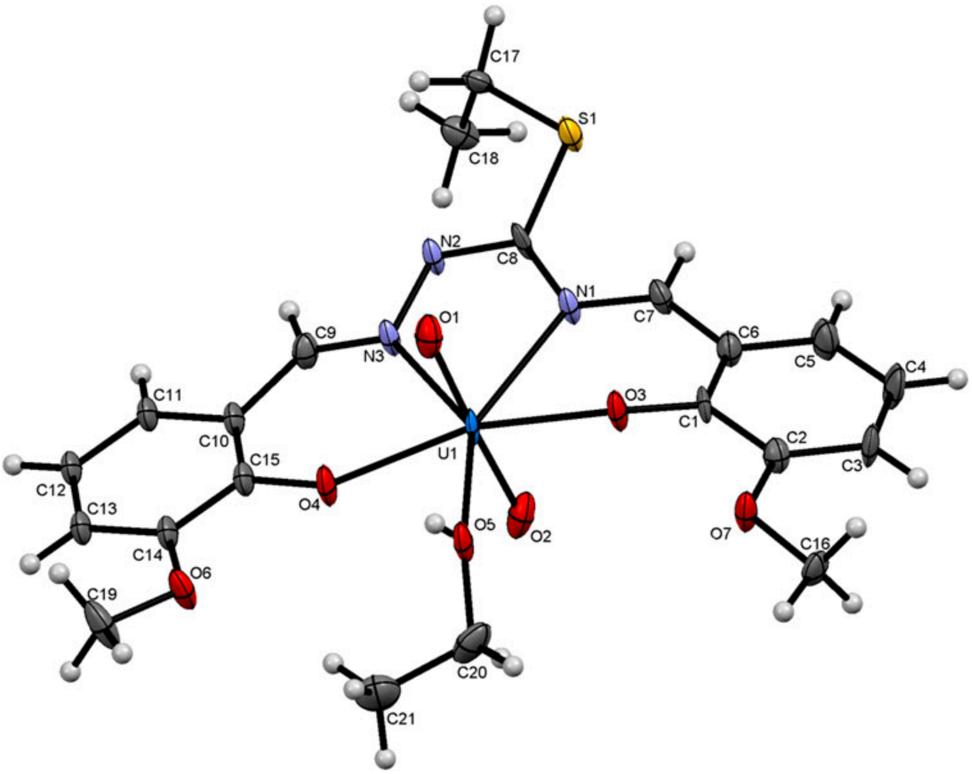


Figure 1. View of **1** showing the atomic numbering and 50% probability displacement ellipsoids.

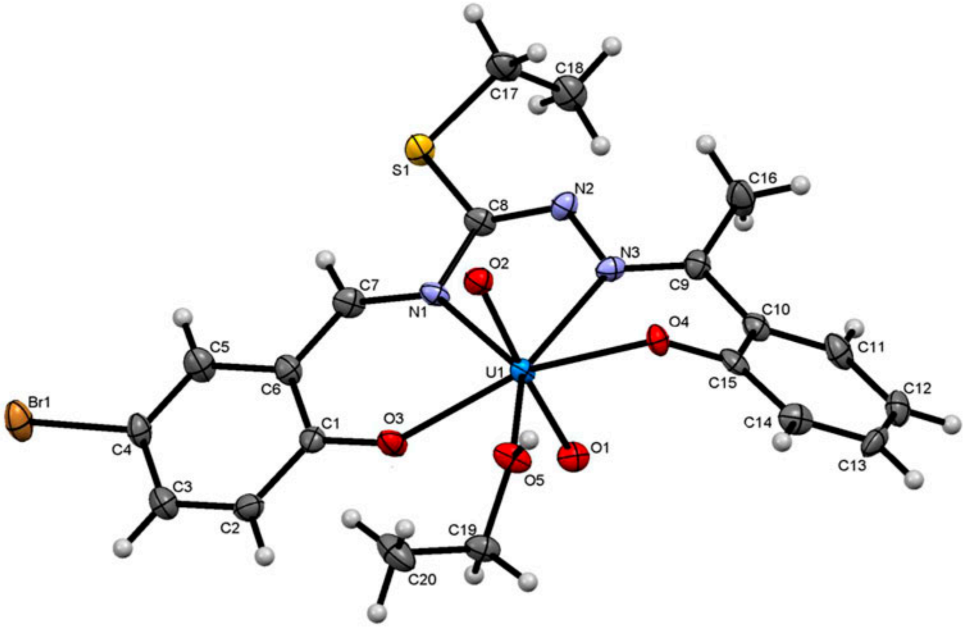


Figure 2. View of **2** showing the atomic numbering and 50% probability displacement ellipsoids.

Table 2. Selected bond distances (Å) and angles (°) of **1** and **2**.

Type	1	2	Type	1	2
U1–O1	1.787(6)	1.773(4)	O1–U1–O2	177.4(2)	176.4(2)
U1–O2	1.800(6)	1.777(4)	N3–U1–N1	62.4(4)	62.9(1)
U1–O3	2.284(4)	2.255(4)	N1–U1–O3	70.7(3)	70.8(1)
U1–O4	2.232(4)	2.263(4)	O3–U1–O5	77.8(2)	78.9(1)
U1–O5	2.454(4)	2.410(4)	O5–U1–O4	78.8(2)	80.1(1)
U1–N1	2.54(1)	2.588(5)	O4–U1–N3	70.6(3)	70.1(1)
U1–N3	2.49(4)	2.535(4)	O1–U1–N3	87.5(4)	84.3(2)
N1–C7	1.30(1)	1.315(7)	O1–U1–N1	91.2(3)	98.5(2)
N3–C9	1.30(2)	1.300(6)	O1–U1–O3	88.5(2)	86.2(2)
N2–C8	1.31(2)	1.287(7)	O1–U1–O5	89.7(2)	94.5(1)
N1–C8	1.42(2)	1.413(5)	O1–U1–O4	91.6(2)	89.5(2)
N3–N2	1.41(1)	1.416(7)	O2–U1–N3	92.9(4)	92.8(2)
C1–O3	1.305(7)	1.305(7)	O2–U1–N1	86.7(3)	82.0(2)
C15–O4	1.335(6)	1.339(5)	O2–U1–O3	89.4(2)	97.4(2)
C20–O5	1.427(9)	1.446(5)	O2–U1–O5	91.3(2)	86.9(1)
S–C8	1.73(1)	1.758(6)	O2–U1–O4	91.0(2)	87.5(2)
S–C17	1.802(8)	1.811(5)	N3–U1–O5	149.1(3)	150.2(1)
C17–C18	1.53(2)	1.487(8)	N1–U1–O5	148.4(3)	145.9(1)
C7–C6	1.435(8)	1.432(6)	O3–U1–O4	156.6(2)	158.1(1)
C6–C1	1.409(9)	1.415(8)	U1–O3–C1	134.5(4)	145.4(3)
C9–C10	1.451(7)	1.471(8)	U1–O4–C15	147.2(3)	121.5(3)
C10–C15	1.389(5)	1.420(8)			

The U1–O3 and U1–O4 bond distances in the complexes are shorter than U1–N1 and U1–N3 distances, whereas the deprotonated oxygen is typically a stronger donor than the azomethine nitrogen. This may also be due to the electronic influence imposed by the anionic *trans* ligands [7]. The U–O(phenolic) and U–N(imine) bond lengths are similar to the previously observed values in this class of uranium(VI) complexes. The U=O bond distances are from 1.746(5) to 1.770(8) Å, much shorter than the equatorial U–O bond lengths, indicating multiple bond order. The U=O bond distances are in accord with the average value [8]. N2 and C8 are significantly out of the pentagonal plane, as indicated by the torsion angle N1C8N2N3 = 3.55° in **1** and 2.98° in **2**. N2 and C8 deviate, respectively, from this plane by 0.344 and 0.257 Å in **1**, and 0.551 and 0.342 Å in **2**. The central ions in **1** and **2** deviate from the pentagonal plane by 0.013 and 0.032 Å, respectively.

The angles around U are not equivalent and are 62.4(4)°–78.8(2)° for **1** and 62.9(1)°–80.1(1)° for **2**, thus departing from the angle 72° in an ideal pentagon. The distortion of ideal pentagonal-bipyramidal geometry is also manifested by the O(oxo)–U–O,N angles ranging from 86.7(3)° to 92.9(4)° for **1** and 82.0(2)° to 98.5(2)° for **2**. The dihedral angle between the UN_2O_3 plane and the plane including the metal and the two axial O atoms is 89.78° for **1** and 89.48° for **2**.

The dihedral angles 22.33° and 52.38° for the phenolic parts of the ligands show propeller-like conformation of these moieties. These values are higher than the earlier reported values [13]. Such distortion in the uranium complexes, including bis-isothiosemicarbazones, may occur due to the large radius of uranium without putting significant strain on the back bone of the ligand [14].

The intermolecular hydrogen bonds present in the complexes are summarized in table 3. In both cases, the molecules have donor and acceptor groups and form centrosymmetric dimers, through an interaction between O–H donors of the coordinated solvent and the phenolato O^- acceptor. The ring patterns are $R^2_2(14)$ for **1** (figure 3) and $R^2_2(8)$ for **2** (figure 4).

3.2. *Spectral properties*

Asymmetric and symmetric vibrations of the NH_2 groups are observed at 3234–3521 cm^{-1} in the infrared spectra of the ligands. Their absence in FT-IR spectra of the complexes suggests successful template reactions [15]. FT-IR spectra of the ligands display a broad band at 3000–3132 cm^{-1}, due to ν(OH). After coordination, the stretching vibration of the OH also disappears. The coordination of the azomethinic nitrogens to the metal centers is accompanied with a shift of ν(C=N) + ν(C=C) in the IR spectra to lower frequency [16]. The ν(CO) band is also shifted to lower frequency, indicating that the phenolic oxygens take part in coordination. Finally, bands due to ν_{asy}(*trans*-UO_2) and ν_{sy}(*trans*-UO_2) are at 910 and 877 cm^{-1} in **1** and at 919 and 885 cm^{-1} in **2** [8].

^{1}H NMR spectra of the compounds were recorded in DMSO-d_6. The signals of the azomethinic protons of the complexes are at lower fields than the ligands, showing increased electron density after complexation. The chemical shift of the OH of ethanol in the ^{1}H NMR spectra of the complexes shows that the solvents are coordinated. Signals due to phenolic protons are not observed in the spectra of the complexes, indicating that the

Table 3. Hydrogen bond distances (Å) and angles for **1** and **2**.

		D–H…A	d(D–H)	d(H…A)	∠(DHA)
Complex **1**	O–H…O	2.787	0.793	2.060	152.47
Complex **2**	O–H…O	2.616	0.769	1.869	163.33

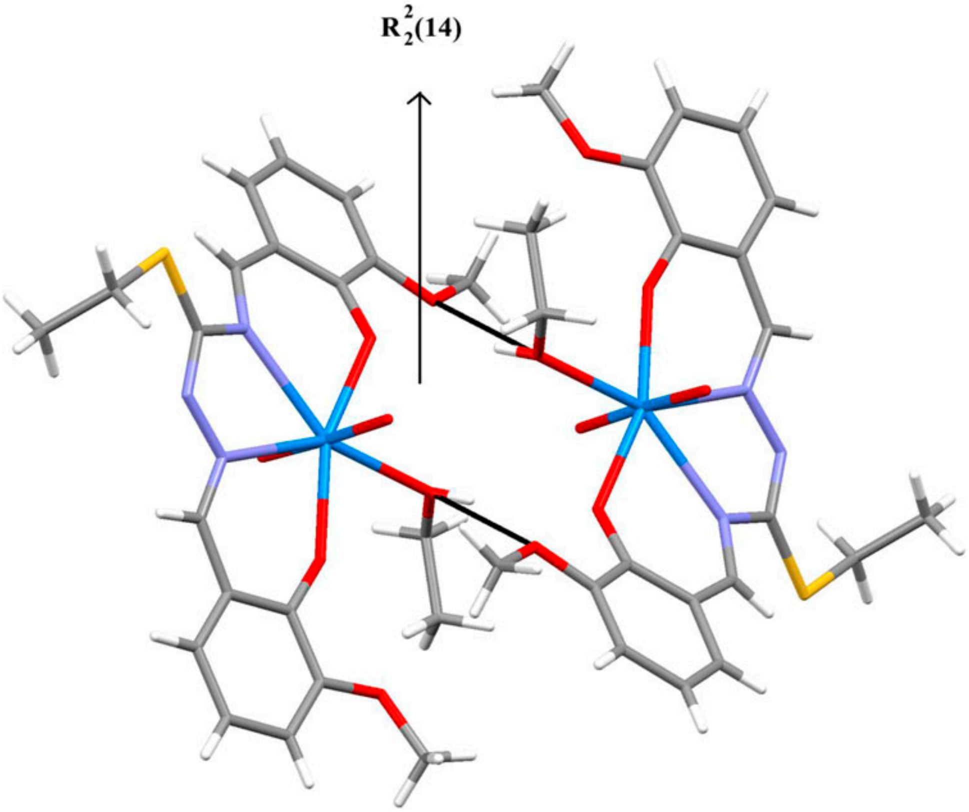


Figure 3. Centrosymmetric H bonded dimer in **1**. H bonds are represented by dashed thick lines.

coordination takes place through oxygen. The aromatic proton signals are observed as multiplets at 7.9–6.7 ppm in **1** and at 7.8–6.65 ppm in **2**. The signals related to S-ethyl moieties appear at the same chemical shifts in both spectra of the ligands and complexes, since sulfur does not participate in complexation.

Electronic spectra of the compounds were recorded in ethanol. The UV–vis spectra of the ligands show the $\pi\rightarrow\pi^*$ transitions near 230 nm. This band displays red shift in the spectra of the complexes [17]. The azomethine and isothioamide $n\rightarrow\pi^*$ transitions are at 300 and 340 nm in spectra of the free ligands. The complexes display these peaks at 310 and 360 nm with red shifts ascribed to coordination of azomethine fragment. The charge transfer bands assigned to N→M and O→M occur at 421 nm (4.43) and 456 nm (3.45) for **1** and at 402 nm (4.12) and 460 nm (3.96) for **2** [15].

3.3. *TGA study*

TG analyses were performed from 27 to 1000 °C. Thermal decompositions of **1** and **2** occur at 245–494 °C and 220–507 °C, respectively, with the proposed mechanisms shown in scheme 1.

The thermal decomposition of **1** takes place in four steps (theoretical values in parentheses). The 6.3% (6.5%) weight loss corresponding to loss of ethanol occurs at 245–263 °C. The

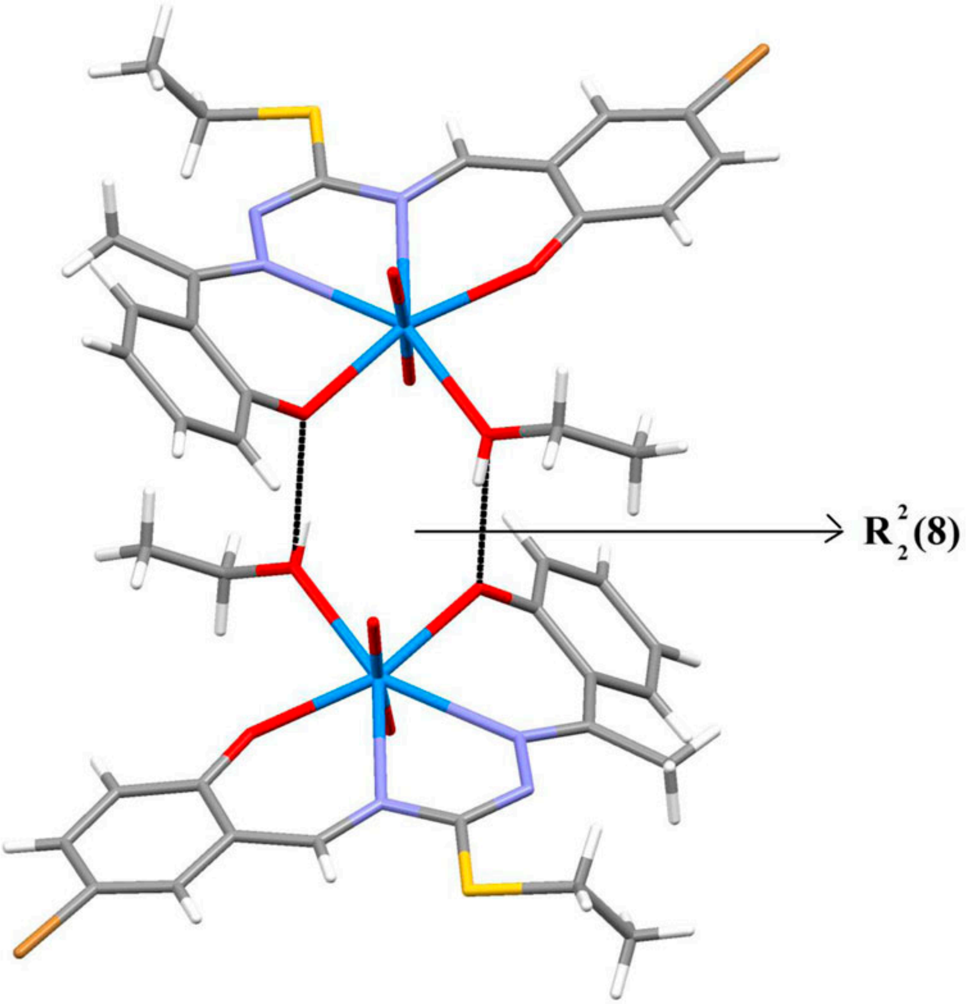
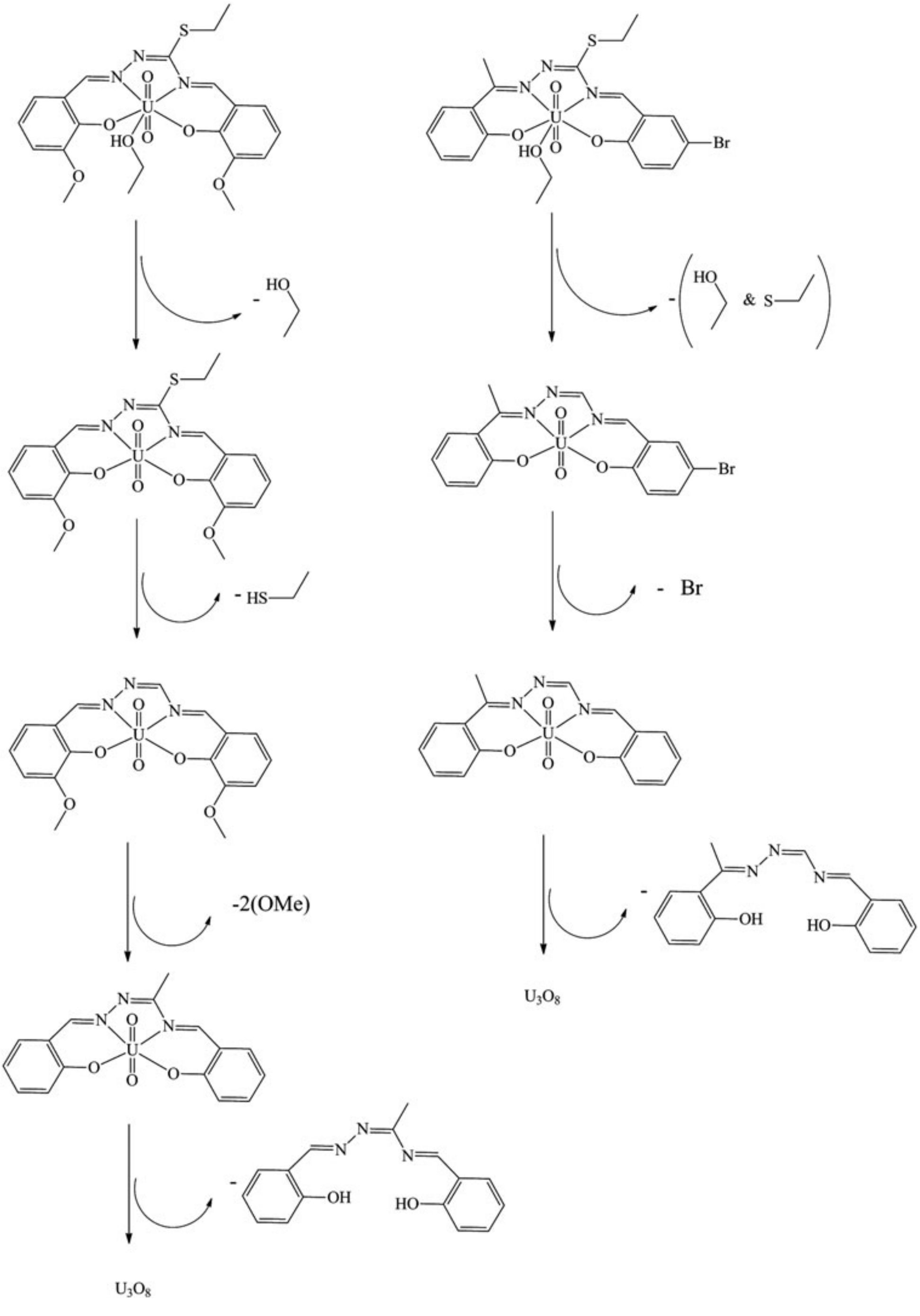


Figure 4. Centrosymmetric H bonded dimer in **2**. H bonds are represented by thick lines.

second step with weight loss of 8.7% (8.7%) at 263–312 °C is attributed to loss of the S-ethyl moiety. Two OMe fragments separate at 342–368 °C with weight loss of 9% (8.8%). Finally, the remainder of the organic part is lost at 408–494 °C (weight loss of 38.5% (40%)). The residue is U_3O_8 with the residual weight 38.5% (40%), which is stable above 494 °C.

The TGA shows that **2** decomposed in three stages. Simultaneous, losses of S-ethyl fragment and ethanol occur at 220–341 °C with a weight loss of 14.9% (14.6%). The halide with a weight loss of 10.9% (10.9%) takes place at 367–383 °C. The third stage is a slow process occurring at 392–507 °C, which is due to loss of the remainder of the ligand with a weight loss of 41% (40.2%). The final residue is U_3O_8 as indicated by the residual weight of 39% (38.2%), which is stable above 507 °C.



Scheme 1. The proposed mechanisms for the thermal decomposition of uranium complexes.

4. Conclusion

Two new uranium(VI) complexes were prepared by template reactions of $UO_2(OAC)_2 \cdot 2H_2O$, isothiosemicarbazone, and an aldehyde. The complexes were air-stable and non-electrolytes in EtOH. The complexes were characterized by CHN, FT-IR, UV–vis, ^1H NMR, and TGA as well as X-ray crystallography. It was found that the complexes were [$UO_2L \cdot EtOH$], where L is dibasic N_2O_2 donor. The ligands are ONNO quadridentate and coordinated to metal centers as dianion chelates. The thermal decomposition of the complexes by TGA analyses showed that the complexes were stable to 230 °C, and after complete decomposition, metal oxide U_3O_8 remained as the residue above 500 °C.

Supplementary material

CCDC 990588 and 990589 contain the supplementary crystallographic data of the complexes. 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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