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The asymmetric ONNO complexes of dioxouranium(VI) with N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazones derived from 3,5-dichlorosalicylaldehyde: Synthesis, spectroscopic and structural studies

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ABSTRACT

Two uranyl complexes having the composition $[UO_2(L)DMSO]$ were synthesized using salicyl- and 3,5-dichlorosalicylaldehyde-*S*-propyl-thiosemicarbazones as starting materials. The *S*-propyl-thiosemicarbazidato structures in the complexes are N^1-3,5-dichlorosalicylidene-N^4-salicylidene and N^1-salicylidene-N^4-3,5-dichlorosalicylidene. The stable solid complexes were characterized by means of elemental analysis, IR and ^{1}H NMR spectroscopies, and the single crystal X-ray diffraction technique. The two complexes, with the same formula, crystallize in different space groups. In the title complexes, the uranium atom is seven-coordinated in a distorted pentagonal-bipyramidal geometry involving an ONNO donor set of the thiosemicarbazidato ligand and an oxygen atom of a DMSO molecule. The two apical positions of the pentagonal bipyramid are occupied by the two oxygen atoms of the *trans*-dioxouranium group. The relative orientations of the DMSO and *S*-propyl groups in both complexes are somewhat different due to different crystal packing.

1. Introduction

Tuberculosis activity of some thiosemicarbazones and chemotherapeutic effective platin complexes of thiosemicarbazide derivatives were reported in the 1950s [1–4]. Since then many articles on the biologic potential of thiosemicarbazones and their metal complexes have been published. Transition metal complexes obtained from thiosemicarbazones have antitumor [5–7], cytotoxic [8–10], antifungal [11–14], antiviral and even anti-HIV effects [15–18]. Additionally, anticonvulsant [19], anti-malarial [20], anti-amoebic [21,22] and antioxidant properties [23] have been mentioned.

The lesser known features of thiosemicarbazones are that they are suitable compounds for bio-sensors [24–26] and non-linear optical materials [27–29]. Some thiosemicarbazones are good reagents for analytical purposes because of their polydentate functions [30–32]. 2,4-Dihydroxy-, 4,4′-dihydroxy- and 2-hydroxy-4-methoxy-5-sulfonyl-benzophenone thiosemicarbazones are selective analytical reagents for the spectrophotometric trace analysis of Cu(II) [33], Rh(III) [34] and Mo(IV) [35], respectively. Besides, bis-thiosemicarbazones are tetra- or pentadentate ligands having a high analytical capability [36].

Thiosemicarbazones can behave as mono-, bi- or tridentate ligands, coordinating to metal atoms through the sulfur, azomethine nitrogen and heteroatom of the condensed aldehyde or ketone. Some derivatives, which were synthesized by metal-directed condensation of *S*-alkyl-thiosemicarbazones with carbonyl compounds, are tetradentate ligands [37–39]. The N_2O_2-type complexes of thiosemicarbazones are synthesized using Fe(III) [40,41], Co(II) [42,43], Ni(II) [44,45], Cu(II) [46,47], Zn(II) [48,49], Pd(II) [50] and VO(IV) [51,52] as template ions. The dioxouranium(VI) ion can be also used to obtain chelate complexes of tetradentate N^1,N^4-diarylidene-*S*-alkyl-thiosemicarbazone ligands. However, studies related to uranium complexes are in limited number [53–56].

In our previous works, long-chain alcohol solvated dioxouranium(VI) complexes of N^1,N^4-diarylidene-*S*-alkyl-thiosemicarbazones were investigated [55,56]. We present here two DMSO solvated dioxouranium(VI) complexes of N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazones having a 3,5-dichlorosalicylidene moiety on the N^1 (**1**) or N^4 (**2**) nitrogen atom of the thiosemicarbazone backbone (Fig. 1). The asymmetric N_2O_2 complexes were characterized by elemental analysis, IR and ^{1}H NMR spectroscopies. The molecular structures of **1** and **2** were determined by single crystal X-ray diffraction.

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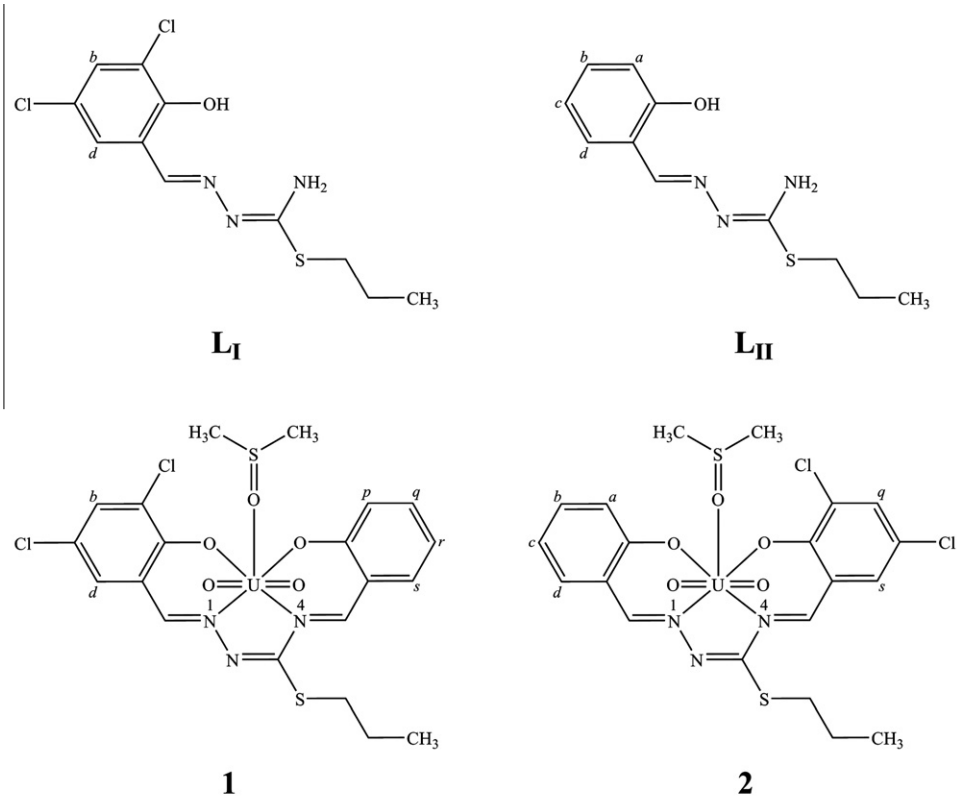

Fig. 1. The DMSO solvated dioxouranium(VI) complexes.

2. Materials and methods

2.1. Physical measurements

All chemicals were analytical reagent grade and used as commercially purchased without further purification. The elemental analyses were determined on a Thermo Finnigan Flash EA 1112 Series Elemental Analyser. FT-IR spectra of the compounds were recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets at room temperature. The ^1H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer, relative to $SiMe_4$, using $CDCl_3$. Magnetic measurements were carried out at room temperature by the Gouy technique with an MK I model device obtained from Sherwood Scientific, using $CuSO_4{\cdot}5H_2O$ as a calibrant. The molar conductivities of the complexes were measured in 10^{-3} M DMSO solution at 25 ± 1 °C using a digital WPA CMD 750 conductivity meter.

2.2. Syntheses

2.2.1. N^1-arylidene-S-propyl-thiosemicarbazones

The N^1-3,5-dichlorosalicylidene-*S*-propyl-thiosemicarbazone (**L_I**) and N^1-salicylidene-*S*-propyl-thiosemicarbazone (**L_{II}**) ligands were synthesized by the reaction of salicylaldehyde or 3,5-dichlorosalicylaldehyde with *S*-propyl-thiosemicarbazide, according to the procedure described by Yamazaki [57]. The physical constants of the ligands were consistent with the published data. The color, yield (%), m.p. (°C), elemental analysis, IR (KBr, cm^{-1}) and ^1H NMR (ppm) data of the ligands are as follows:

L_I: Yellow, 77, 133–134, *Anal.* Calc. for $C_{11}H_{15}Cl_2N_3OS$: C, 43.15; H, 4.28; N, 13.72; S, 10.47. Found: C, 43.08; H, 4.32; N, 13.69; S, 10.56%. IR: ν(OH) 3102, $\nu_{as}(NH_2)$ 3476, $\nu_s(NH_2)$ 3276, $\delta(NH_2)$ 1651, ν(C=N) 1632, 1562, ν(C–O) 1181. ^1H NMR (500 MHz, $CDCl_3$): 12.24 (br.s, 1H, OH), 8.35, 8.21 (s, *syn*/*anti*: 2/1, 1H, C*H*=N), 7.34 (dd, J = 2.44, J = 7.32, 1H, *b*), 7.15 (dd, J = 2.44, J = 15.13, 1H, *d*), 5.11 (s, 2H, NH_2), 3.07, 2.92 (t, J = 7.32, i:2:1, 2H, S–CH_2), 1.75, 1.64 (m, i:2/1, 2H, –CH_2–), 1.08, 1.03 (t, J = 7.32, i:1/2, 3H, CH_3).

L_{II}: Yellow, 75, 150–151, *Anal.* Calc. for $C_{11}H_{15}N_3OS$: C, 55.67; H, 6.37; N, 17.71; S, 13.51. Found: C, 55.56; H, 6.52; N, 17.67; S, 13.59%. IR: ν(OH) 3106, $\nu_{as}(NH_2)$ 3426, $\nu_s(NH_2)$ 3303, $\delta(NH_2)$ 1643, ν(C=N)1605, 1585, ν(C–O) 1150. ^1H NMR (200 MHz, $CDCl_3$): 11.74, 11.56 (s, i:2/3, 1H, OH), 8.45–8.31 (s, *syn*/*anti*: 2/1, 1H, C*H*=N), 5.09, 4.92 (s, i:4/1, 2H, NH_2), 7.34 (dd, J = 1.46, J = 7.81, 1H, *d*), 7.28 (d, J = 7.81, 1H, *b*), 7.00 (t, J = 7.81, 1H, *c*), 6.93 (dd, J = 2.44, 1H, *a*), 3.02 (m, 2H, S–CH_2), 1.64 (m, 2H, –CH_2–), 0.99 (t, J = 7.32, 3H, CH_3).

2.2.2. Complexes **1** and **2**

Complex **1** was synthesized using N^1-3,5-dichlorosalicylaldehyde-*S*-propyl-thiosemicarbazone (**L_I**). 0.29 g of **L_I** (1 mmol) and salicylaldehyde (0.1 ml, 1 mmol) were solved in 25 ml of DMSO, and the mixture was added to a solution of $UO_2(CH_3COO)_2{\cdot}2H_2O$ (0.40 g, 1 mmol) in 25 ml of DMSO. The reaction mixture was then allowed to stand at room temperature to give a solid product. After two weeks, red crystals were collected by filtration and washed twice with 5 ml of DMSO. The fine crystals were recrystallized from DMSO and dried for 12 h in air.

Complex **2** was obtained from N^1-salicylaldehyde-*S*-propyl-thiosemicarbazone (**L_{II}**) and 3,5-dichlorosalicylaldehyde as starting materials. The color, yield (%), m.p. (°C), μ_{eff} value(BM), Λ (in 10^{-3} M DMSO, $ohm^{-1}\,cm^2\,mol^{-1}$), elemental analysis, IR (KBr, cm^{-1}) and ^1H NMR (ppm) data of the dioxouranium (VI) complexes are as follows:

1: Red; 52, 231–232, 0.08, 8.8, *Anal.* Calc. for $C_{20}H_{21}Cl_2N_3O_5S_2U$ (756.46 g): C, 31.75; H, 2.80; N, 5.55; S, 8.48. Found: C, 31.01; H, 2.70; N, 5.55; S, 8.90%. IR: ν(C=N) 1601, 1574, 1551, ν(C–O)

Table 1
Crystal data and structure refinement parameters for complexes **1** and **2**.

Parameter	**1**	**2**
CCDC deposition no.	779460	779461
Color/shape	red/prism	red/prism
Chemical formula	$[UO_2(C_{18}H_{15}Cl_2N_3O_2S)(C_2H_6OS)]$	$[UO_2(C_{18}H_{15}Cl_2N_3O_2S)(C_2H_6OS)]$
Formula weight	756.45	756.45
Temperature (K)	296	293
Wavelength (Å)	0.71073 Mo Kα	0.71073 Mo Kα
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
Unit cell parameters		
a, *b*, *c* (Å)	12.1231(4), 8.2287(2), 25.4627(7)	8.2289(3), 23.2894(10), 26.2836(13)
α, β, γ (°)	90, 94.421(2), 90	90, 90, 90
Volume (Å^3)	2532.53(12)	5037.2(4)
Z	4	8
D_{calc} (g/cm^3)	1.984	1.995
μ (mm^{-1})	6.821	6.859
Absorption correction	integration	multi-scan
T_{min}, T_{max}	0.330, 0.541	0.176, 0.504
F(0 0 0)	1440	2880
Crystal size (mm^3)	0.22 × 0.14 × 0.07	0.50 × 0.20 × 0.10
Diffractometer/measurement method	STOE IPDS II/ω scan	Rigaku RAXIS-RAPID/ω scan
Index ranges	$-15 \leqslant h \leqslant 15$, $-10 \leqslant k \leqslant 10$, $-32 \leqslant l \leqslant 32$	$-9 \leqslant h \leqslant 9$, $-27 \leqslant k \leqslant 27$, $-31 \leqslant l \leqslant 31$
θ Range for data collection (°)	$1.60 \leqslant \theta \leqslant 26.78$	$2.74 \leqslant \theta \leqslant 25.00$
Reflections collected	32010	91085
Independent/observed reflections	5390/4329	4336/4291
R_{int}	0.0695	0.0904
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5390/75/336	4336/80/335
Goodness-of-fit on F^2	1.044	1.095
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.0923$	$R_1 = 0.0684$, $wR_2 = 0.1318$
R indices (all data)	$R_1 = 0.0509$, $wR_2 = 0.0978$	$R_1 = 0.0692$, $wR_2 = 0.1324$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	1.033, −1.245	2.358, −2.303
Extinction coefficient	0.00087 (13)	–

1139, ν(CH)$_{aliph.}$ 2956, 2921, $\nu_{sym}(UO_2)$ 865, $\nu_{asym}(UO_2)$ 915. ^{1}H NMR (500 MHz, $CDCl_3$): 9.62 (s, 1H, C*H*═N), 9.29 (s, 1H, C*H*═N), 7.16 (br.s, 1H, *b*), 7.68 (d, *J* = 2.93, 1H, *d*), 7.40 (d, *J* = 2.93, 1H, *p*), 7.76 (dd, *J* = 1.98, *J* = 8.79, 1H, *q*), 6.85 (t, *J* = 7.32, 1H, *r*), 7.64 (d, *J* = 7.81, 1H, *s*), 3.39 (t, *J* = 7.32, 2H, S–C*H*$_2$), 1.94 (m, 2H, –C*H*$_2$), 1.18 (t, *J* = 7.32, 3H, CH_3), 3.22 (s, 6H, C*H*$_3$ for DMSO).

2: Red; 58, 255–256, 0.04, 9.2, *Anal.* Calc. for $C_{20}H_{21}Cl_2N_3O_5S_2U$ (756.46 g): C, 31.75; H, 2.80; N, 5.55; S, 8.48. Found: C, 31.20; H, 2.89; N, 5.61; S, 8.98%. IR: ν(C═N) 1597, 1585, 1551, ν(C–O) 1143, ν(CH)$_{aliph.}$ 2956, 2914, $\nu_{sym}(UO_2)$ 896, $\nu_{asym}(UO_2)$ 958. ^{1}H NMR (500 MHz, $CDCl_3$): 9.45 (s, 1H, C*H*═N), 9.40 (s, 1H, C*H*═N), 7.00 (d, *J* = 8.30, 1H, *a*), 7.63 (t, 1H, *b*), 6.76 (t, *J* = 7.80, 1H, *c*), 7.54 (d, *J* = 7.80, 1H, *d*), 7.77 (d, *J* = 2.93, 1H, *q*), 7.48 (d, *J* = 2.44, 1H, *s*), 3.38 (t, 2H, *J* = 7.32, S–C*H*$_2$), 1.92 (m, 2H, *J* = 7.32, –C*H*$_2$–), 1.14 (t, *J* = 7,32, 3H, C*H*$_3$), 3.19 (s, 6H, C*H*$_3$ for DMSO).

2.3. X-ray analysis

The intensity data for complex **1** were collected on a STOE IPDS II diffractometer at 296 K, while crystallographic measurements for complex **2** were carried out on a Rigaku RAXIS RAPID diffractometer at 293 K. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and the ω-scan technique were used. The structures were solved by direct methods using SHELXS-97 [58] and refined through the full-matrix least-squares method using SHELXL-97 [59], implemented in the WINGX [60] program suite. All H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.96 and 0.97 Å for CH, CH_3 and CH_2 groups, respectively. The displacement parameters of the H atoms were fixed at $U_{iso}(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl) of their parent atoms. In both complexes, the dimethylsulfoxide moieties show positional disorder and the refined site-occupancy factors of the disordered parts, *viz.* O5A/S2A/C19A/C20A and O5B/S2B/C19B/C20B, are 0.650(4)/0.350(4)% for complex **1** and 0.59(6)/0.41(6)% for complex **2**. The disordered atoms were refined using the following restraints: SIMU, DELU and SADI [59]. For complex **1**; Data collection: X-AREA [61], cell refinement: X-AREA, data reduction: X-RED32 [61]. For complex **2**; Data collection: PROCESS-AUTO [62], cell refinement: PROCESS-AUTO, data reduction: CRYSTALSTRUCTURE [63]. Details of the data collection conditions and the parameters of the refinement process are given in Table 1. The general-purpose crystallographic tool PLATON [64] was used for the structure analysis and presentation of the results.

3. Results and discussion

The thiosemicarbazones, $\mathbf{L_I}$ and $\mathbf{L_{II}}$, obtained as crystalline powders, were soluble in alcohols and donor solvents such as DMSO. The interaction of the *S*-propyl-thiosemicarbazone, aldehyde and uranylacetate in equivalent amounts yielded the chelate complexes **1** and **2**, having the composition $[UO_2(L)DMSO]$. The complexes obtained in DMSO are stable in air, and are soluble in alcohols and chlorinated hydrocarbons. Complexes **1** and **2** are non-electrolytes in DMSO, with low conductance values of 8.8 and 9.2 ohm^{-1} cm^2 mol^{-1}, respectively.

3.1. Spectroscopic characterization

The template reactions of the *S*-alkyl-thiosemicarbazones and a 2-hydroxy aldehyde can be easily monitored by means of IR and ^{1}H NMR spectra. In the IR spectra of the template compounds, the NH_2 and 2-OH bands of the thiosemicarbazones disappeared due to the condensation on the formation of complexes **1** and **2**. After condensation, the ν(C═N) bands of the *S*-propyl-thiosemicarbazones shifted to lower energies by *ca.* 8–30 cm^{-1} and also a new azomethine band, (N^4═C), appeared in the region 1585–1551 cm^{-1} due to condensation of the thioamide nitrogen and aldehyde.

In the ^{1}H NMR spectra of $\mathbf{L_I}$ and $\mathbf{L_{II}}$, the expected chemical shift values were monitored for the aromatic, azomethine and *S*-propyl protons, and even the *syn–anti* and *cis–trans* isomer peaks of these protons [65]. The appearance of a second signal at around 9.50 ppm, which is a singlet and equivalent to one proton integral value, indicates a new azomethine group (N^4=CH) because of the template formations. The ^{1}H NMR spectra of complexes **1** and **2** did not show any isomers, probably as these moieties have been partially fixed because of the template reaction.

Consequently, from the analytical and spectral data it becomes evident that the free NH_2 group and 2-hydroxy-aldehyde gave a new imine group and formed the N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazidato ligand by the template effect of the uranyl ion.

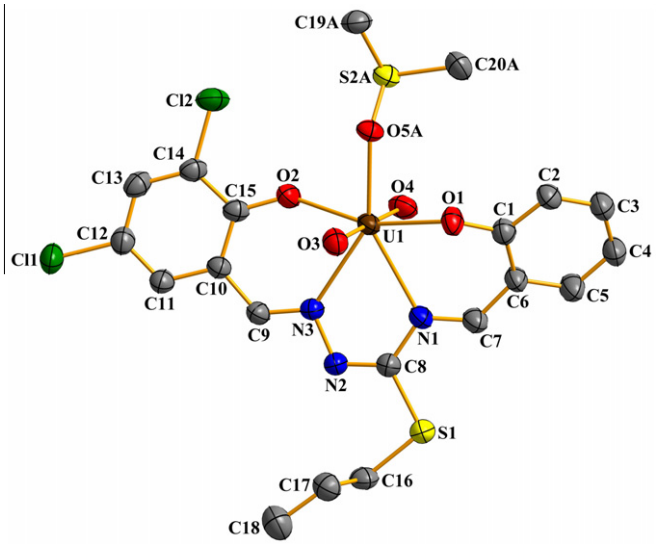

Fig. 2. The molecular structure of complex **1** shown with 30% probability displacement ellipsoids and illustrating the atom-numbering scheme. H atoms have been omitted for clarity and only the major part of disordered fragment is shown.

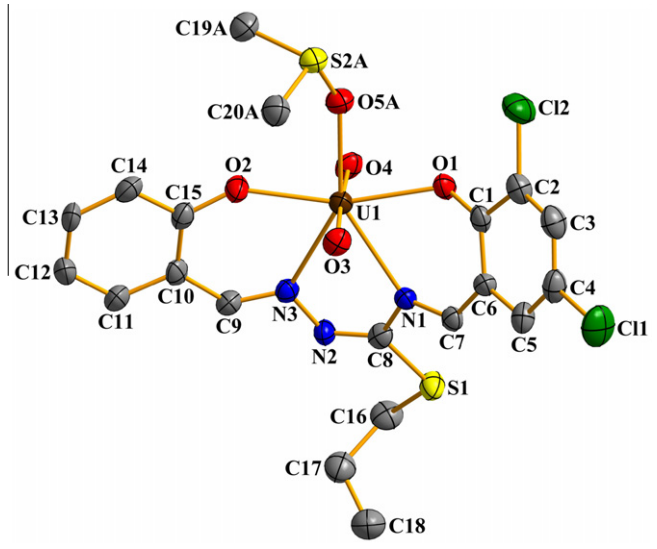

Fig. 3. The molecular structure of complex **2** shown with 30% probability displacement ellipsoids and illustrating the atom-numbering scheme. H atoms have been omitted for clarity and only the major part of disordered fragment is shown.

3.2. Structural studies of the uranyl complexes

The solid state structures of compounds **1** and **2** were verified by single crystal X-ray analysis. The perspective DIAMOND [66] views

Table 2
Selected geometrical parameters for complexes **1** and **2**.

Parameter	1	2
Bond lengths (Å)		
U1–O1	2.273(4)	2.266(7)
U1–O2	2.249(5)	2.245(7)
U1–O3	1.766(5)	1.763(7)
U1–O4	1.746(5)	1.770(8)
U1–O5A	2.378(5)	2.375(9)
U1–O5B	2.381(6)	2.377(9)
U1–N1	2.556(5)	2.570(8)
U1–N3	2.567(5)	2.560(9)
Cl1–C12/C4	1.751(7)	1.740(12)
Cl2–C14/C2	1.732(6)	1.720(13)
S1–C8	1.766(7)	1.748(11)
S1–C16	1.802(7)	1.801(12)
S2A–O5A	1.542(6)	1.513(9)
S2B–O5B	1.541(6)	1.513(9)
S2A–C19A	1.75(2)	1.781(15)
S2A–C20A	1.79(2)	1.755(16)
S2B–C19B	1.75(2)	1.782(15)
S2B–C20B	1.79(2)	1.756(16)
O1–C1	1.312(8)	1.307(12)
O2–C15	1.301(8)	1.300(13)
N1–C7	1.295(9)	1.296(12)
N1–C8	1.400(8)	1.409(13)
N2–N3	1.412(7)	1.427(12)
N2–C8	1.273(8)	1.246(13)
N3–C9	1.301(8)	1.283(13)
C6–C7	1.418(9)	1.423(15)
C9–C10	1.437(9)	1.440(15)
Bond angles (°)		
O1–U1–O2	161.07(17)	161.3(3)
O1–U1–O3	88.9(2)	90.2(3)
O1–U1–O4	90.1(2)	87.4(3)
O1–U1–O5A	77.5(2)	79.5(4)
O1–U1–O5B	85.2(3)	78.5(5)
O2–U1–O3	94.4(2)	89.8(3)
O2–U1–O4	86.8(2)	93.2(3)
O2–U1–O5A	84.2(2)	81.9(4)
O2–U1–O5B	75.9(3)	82.8(5)
O3–U1–O4	178.8(2)	176.6(4)
O3–U1–O5A	85.3(2)	95.3(6)
O3–U1–O5B	99.9(3)	88.4(9)
O4–U1–O5A	95.2(2)	86.5(6)
O4–U1–O5B	80.7(3)	93.4(9)
O1–U1–N1	69.98(17)	68.3(3)
O2–U1–N3	69.43(16)	70.4(3)
O3–U1–N1	95.9(2)	82.7(3)
O3–U1–N3	81.43(19)	94.0(3)
O4–U1–N1	83.1(2)	94.2(3)
O4–U1–N3	98.66(19)	85.7(3)
N1–U1–N3	62.05(16)	61.2(3)
O5A–S2A–C19A	105.0(13)	104.9(8)
O5A–S2A–C20A	103.4(13)	105.6(7)
O5B–S2B–C19B	105.1(13)	104.9(8)
O5B–S2B–C20B	103.5(13)	105.4(7)
Torsion angles (°)		
S1–C8–N2–N3	179.6(4)	179.1(7)
S1–C8–N1–C7	22.4(9)	−30.7(12)
S1–C16–C17–C18	176.6(6)	−56.8(16)
N1–C8–N2–N3	1.0(10)	−3.8(15)
N1–C7–C6–C5	−170.5(8)	163.3(10)
N2–N3–C9–C10	−178.7(6)	178.4(9)
N2–C8–N1–C7	−159.0(7)	152.2(10)
N2–C8–S1–C16	−2.1(7)	5.9(11)
N3–C9–C10–C11	−176.1(6)	−171.8(11)
C6–C7–N1–C8	−174.0(7)	175.3(10)
C8–N2–N3–C9	−178.1(6)	−161.3(10)
C8–S1–C16–C17	−76.3(6)	−78.3(11)

of the complexes with the atomic numbering scheme are depicted in Figs. 2 and 3. Selected geometrical parameters are given in Table 2. Both complexes contain a dichloro-substituted N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazone ligand, which differ by the position of the two chlorine atoms, with an uranyl ion and one dimethylsulfoxide (DMSO) ligand. The crystallization characteristics of the two isomers are different, with complexes **1** and **2** crystallizing in the space groups $P2_1/c$ and *Pbca*, respectively. The DMSO ligand in both complexes is disordered over two positions, and in the following discussion, parameters related to the minor part of the disordered O atom of the DMSO ligand are quoted in square brackets.

The pentagonal-bipyramidal nature of the complexes is easily seen. Two imine nitrogen atoms and two phenolic oxygen atoms from the tetradentate thiosemicarbazone ligand (N1, N3, O1 and O2) and one oxygen atom (O5) from the dimethylsulfoxide ligand form a pentagon, while the axial sites are occupied by two oxo groups (O3 and O4). The oxo groups of the uranyl moiety lie *trans* to one another with a nearly linear O_{oxo}–U–O_{oxo} angle of 178.8(2)° for **1** and 176.6(4)° for **2**. The U=O distances, ranging from 1.746(5) to 1.770(8) Å, are almost the same in the two compounds, and are shorter than the equatorial U–O bond lengths, no doubt reflecting the multiple bond order. The bond distances of the uranyl moieties are in good agreement with the average value [1.77 Å] for comparable bonds found in the Cambridge Structural Database (CSD, Version 5.28) [67], which has been searched using the CONQUEST software (Version 3.6) [68], illustrating how the coordination environments surrounding the uranyl cations have very little effect on the apical bond lengths. The U–N_{imine} distances are typically found to be longer than the U–$O_{phenolic}$ distances, a behavior which can be explained by Pearson's hard and soft acid–base concept [69,70]. This concept agrees well with that which is observed in the two compounds studied, as nitrogen would be expected to be bonded less strongly to a hard acid such as (UO_2^{2+}), while oxygen has a relatively higher base strength towards uranium [71]. As expected, the U–$O_{phenolic}$ and the U–N_{imine} bond lengths are similar to those observed in previously reported dioxouranium(VI) complexes [53,72].

For an ideal pentagonal-bipyramidal complex, each of the five angles subtended at the equatorial plane should be 72°. The angles around the U atoms defined by adjacent donor atoms in the equatorial plane are not equivalent and lie in the range 62.05(16)–85.2(3)° for **1** and 61.2(3)–82.8(5)° for **2**. It should be pointed out here that for an ideal pentagonal array of donor atoms, a cyclic ligand with identical donor atoms and bond lengths is required. As can be seen from the angles, the coordination polyhedra around

Table 3
Hydrogen bonding geometries for complexes **1** and **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
1				
C17–H17B···N2	0.97	2.59	3.150(10)	117
C7–H7···S1	0.93	2.44	2.913(7)	112
2				
C7–H7···S1	0.93	2.55	2.956(11)	107

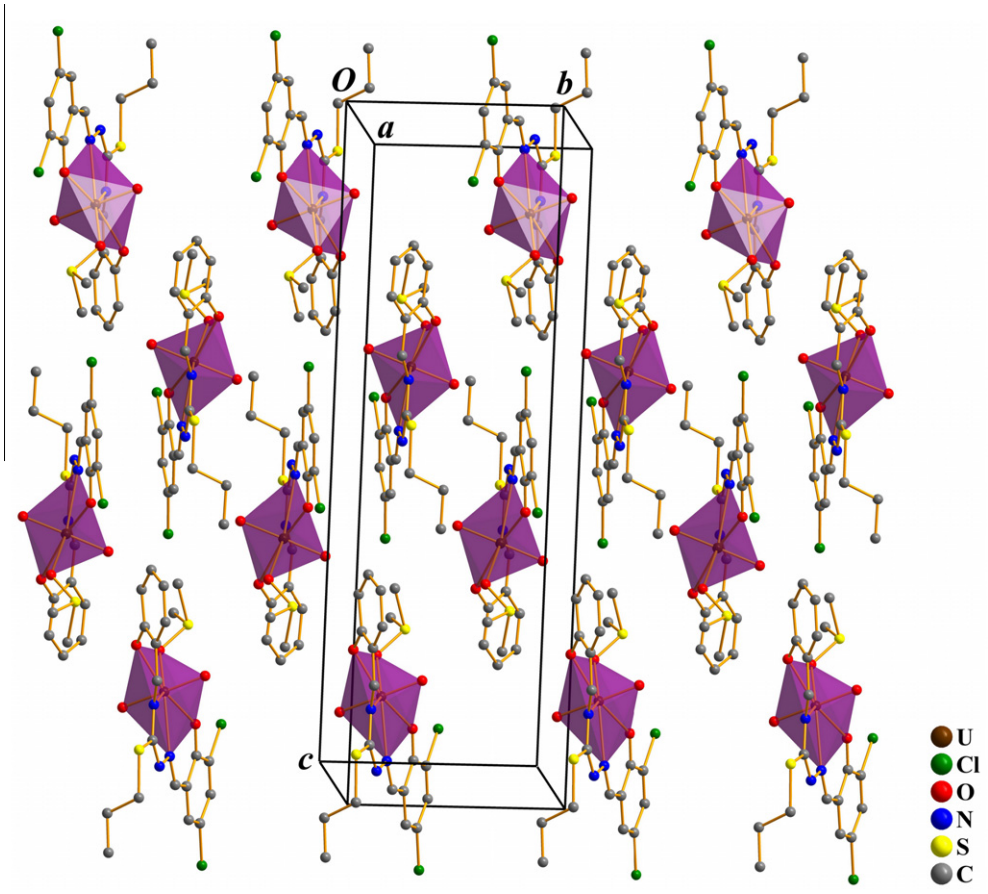

Fig. 4. Polyhedral representation of a partial cell packing diagram for complex **1**. For the sake of clarity, H atoms and the minor part of disordered fragment have been omitted.

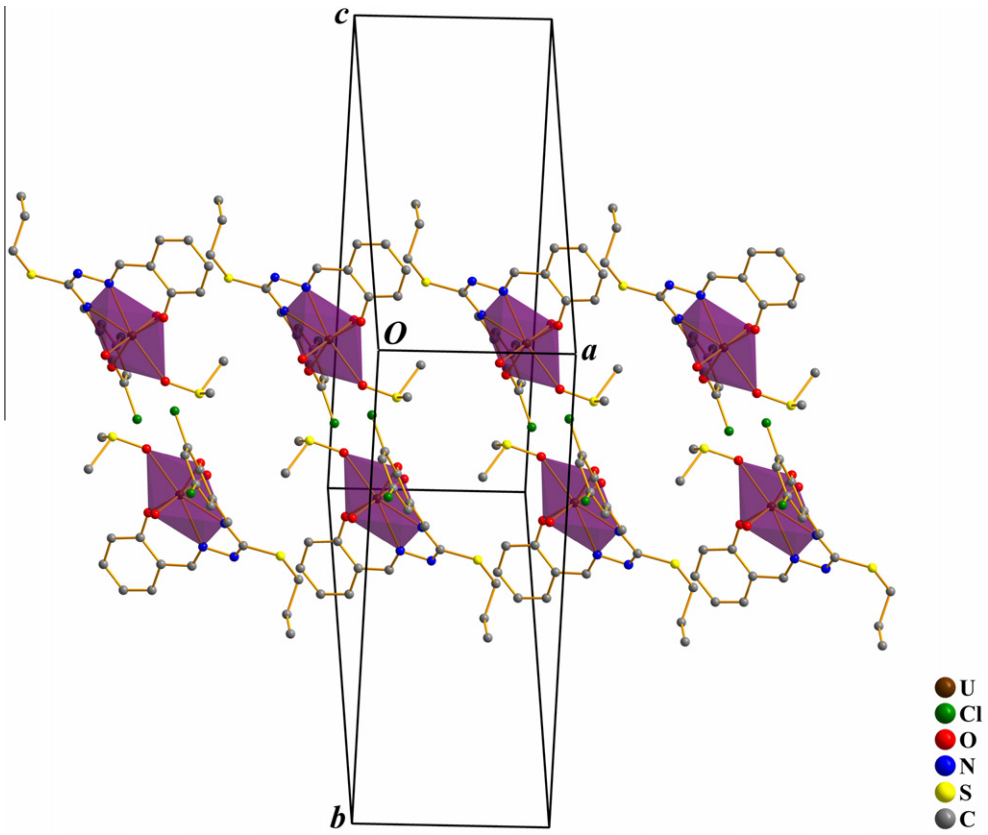

Fig. 5. Polyhedral representation of a partial cell packing diagram for complex **2**. For the sake of clarity, H atoms and the minor part of disordered fragment have been omitted.

the U atoms can be visualized as being distorted, with O_{oxo}–U–O,N angles in the range 80.7(3)–99.9(3)° for **1** and 82.7(3)–95.3(6)° for **2**. The distortion from an ideal pentagonal-bipyramid geometry is due to the asymmetric nature of the bonded tetradentate Schiff base ligand. The angle between the MN_2O_3 plane and the plane including the metal and the two axial O atoms is 87.79(13)° [87.97(15)°] for **1** and 89.66(17)° [88.62(16)°] for **2**.

In the title complexes, the pentagon plane defined by the five equatorial donor atoms is not planar, with root mean square (r.m.s.) deviations of 0.232 and 0.148 Å [0.222 and 0.144 Å] for **1** and **2**, respectively, and the atom U1 being displaced by −0.035(2) Å [0.090(3) Å] for **1** and by −0.026(5) Å [0.032(7) Å] for **2**. The dihedral angles between the pentagon plane and the benzene and chlorophenyl ring planes are 39.91(18)° and 25.15(10)° [43.10(17)° and 21.03(12)°] for **1**, and 14.37(18)° and 49.77(22)° [13.17(17)° and 50.76(21)°] for **2**, respectively, and that between the last two planes is 40.14(16)° and 63.93(19)° for **1** and **2**, respectively, indicating a non-planar disposition of the tetradentate thiosemicarbazone ligand. It is clear from these results that the distortion in **2** is more than that in **1**, and this is also supported by the conformations of the chelate rings. In both complexes, the six-membered chelate rings exhibit a half-chair conformation. However, although the five-membered chelate ring in **1** is planar, proving some electron delocalization in the thiosemicarbazide group, it has an envelope conformation in **2**. The relative orientations of the DMSO and *S*-propyl groups in the title complexes are somewhat different, presumably due to different crystal packing.

In complex **1**, there are two intramolecular interactions of the type C–H···N and C–H···S, forming six- and five-membered rings, respectively (Table 3). However, there is only one intramolecular interaction of the type C–H···S, forming a five-membered ring, in the molecular structure of complex **2**. In the crystal structure of both complexes, no intermolecular hydrogen bonding is observed. The crystal packing of the complexes (Figs. 4 and 5) is achieved by van der Waals forces.

4. Conclusions

In the present paper, we report the synthesis, spectroscopic data and crystal structures of two dioxouranium(VI) complexes containing a dichloro-substituted N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazone ligand and one dimethylsulfoxide (DMSO) ligand, and structural differences between these two dioxouranium(VI) complexes. N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazidato ligands, $\mathbf{L_I}$ and $\mathbf{L_{II}}$, are bonded to the uranium atom through an ONNO donor set. By a template condensation, strong coordination bonds are formed between the uranium centre and the donor atoms of the thiosemicarbazidato ligand, such that even the chemical shifts of the *S*-propyl protons, which are away from the coordinated atoms, are significantly changed, shifting to a lower field. Some physical properties, such as melting point and molar conductance, of the characterized isomeric complexes **1** and **2** are slightly different. The two isomeric complexes crystallize in different space groups and have a distorted pentagonal-bipyramidal geometry. These distortions can be attributed to the asymmetric nature of the bonded tetradentate Schiff base ligand. It is seen that the relative orientations of the DMSO and *S*-propyl groups in the complexes are affected by crystal packing.

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Appendix A. Supplementary data

CCDC 779460 and 779461 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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