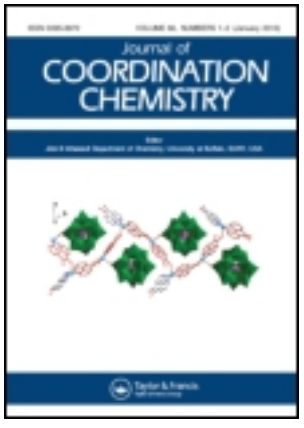

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Dioxouranium(VI) complexes with N_2O_2 chelating thiosemicarbazones [UO_2L(R-OH)]

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Dioxouranium(VI) complexes with N_2O_2 chelating thiosemicarbazones [UO_2L(R-OH)]

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Three alkylated thiosemicarbazones (**1–3**) substituted on sulfur were synthesized using 5-bromosalicylaldehyde as starting material. The template reactions of the S-alkyl-thiosemicarbazones in the presence of dioxouranium(VI) were investigated. Six dioxouranium(VI) (**1a–3b**) complexes were synthesized. Propyl or allyl alcohol used as second ligand completed the seventh coordination site of UO_2^{2+}. The synthesized thiosemicarbazones and template complexes were characterized by elemental analysis, UV–visible, FTIR, and ^{1}H NMR. The structure of the dioxouranium(VI) complex, [UO_2L(allylalcohol)], was studied by single-crystal diffraction. The uranium is seven-coordinate in a pentagonal-bipyramidal arrangement with two oxo groups occupying the apical positions.

Keywords: Template synthesis; Dioxouranium(VI); Thiosemicarbazones; X-ray diffraction

1. Introduction

Uranyl salts have catalytic activity [1] and uranyl ions adsorbed in mesoporous materials like MCM-41 and MCM-48 have catalytic properties in some reactions like selective oxidation of some alcohols to form the corresponding carbonyl compounds [2], oxidation of CO and adsorption/decomposition of CH_3OH [3]. In addition, some uranyl complexes exhibit catalytic activity as seen in the oxidation of alcohols to ketones [4] and acyl transfer reactions [5].

Uranyl compounds with Schiff bases contribute to clinical studies concerning prevention, diagnosis, and treatment of uranium or heavy metals poisoning and help to build further models for heavy metals damage inhibition [6]. Due to the fact that the uranyl ion is hazardous for both health and environmental issues, it is very important to extract and remove it from aqueous media. Uranium exists commonly in the uranyl form (UO_2^{2+}) in aqueous media and has high stability in natural environments [7]. In this context, many studies have been carried out to prevent its contamination into water using arene-based magnetite nano-particles [8], organic ligands, material modified organic ligands [9–11], and new functionalized polymer structures [12].

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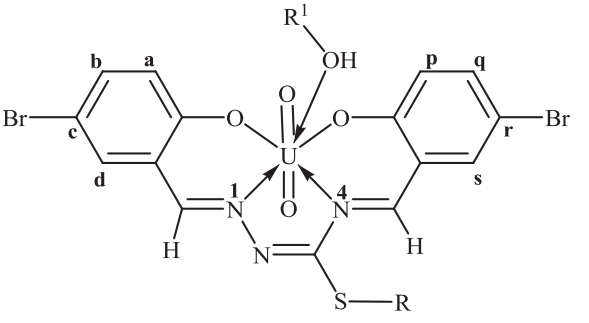

Figure 1. The complexes. **R/R[1]**: methyl/propyl (**1a**), methyl/allyl (**1b**), propyl/propyl (**2a**), propyl/allyl (**2b**), allyl/propyl (**3a**), allyl/allyl (**3b**).

However, new methods are being sought to detect and imprint uranyl ions. There is also need to develop new methods with high selectivity towards uranyl ions [13–15]. Thiosemicarbazide condenses to monocarbonyl compounds such as an aldehyde or ketone through the hydrazinic nitrogen. However, the amidic nitrogen does not give a condensation as mentioned above. This can be achieved with metal ions like uranyl cation which manipulates the donors to give a macrocyclic structure. In early studies, the solvated asymmetric uranyl complexes of thiosemicarbazone ligands containing H_2O, MeOH, EtOH, DMSO, and DMF as solvent have been reported [16, 17]. In our laboratory, we have previously synthesized the template complexes of uranyl with coordinated alcohols having long alkyl chains [18–20].

Herein, we present six dioxouranium(VI) complexes with bromo substituted salicylaldeyde thiosemicarbazones in the N_2O_2 coordination mode (figure 1). We obtained the dioxouranium(VI) complexes having allyl alcohol coordinated as seventh site to the UO_2^{2+} center. The compounds were characterized by elemental analysis, FTIR, and ^{1}H NMR spectroscopies. The structure of **2b** was determined by X-ray single-crystal diffraction.

2. Experimental

2.1. *Physical measurements*

The chemicals were reagent grade and used without purification. The elemental analyzes were determined on a Thermo-Finnigan Flash EA 1112 Series Elementary Analyzer. UV-visible spectra were obtained from ATI Unicam UV–vis Spectrometer UV2 Series. Infrared spectra were recorded on a Mattson 1000 FTIR spectrophotometer from 4000 to 400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz and Bruker Avance spectrometer (500 MHz) using deuterated chloroform and DMSO at 25 ± 2 °C. Magnetic measurements were carried out at room temperature by the Gouy technique with an MK I model device obtained from Sherwood Scientific. The molar conductivities of the compounds were measured in 3×10^{-5} M DMSO solution at 25 ± 1 °C using a digital WPA CMD 750 conductivity meter.

2.2. *Syntheses*

2.2.1. N^1–5-Bromosalicylidene-S-methyl-thiosemicarbazone (1). The N^1–5-Bromosalicylidene-S-alkyl(methyl/propyl/allyl)-thiosemicarbazones (figure 2) were synthesized by reaction of 5-bromosalicylaldehyde with S-alkyl-thiosemicarbazide according to method described in the literature [21].

The colors, m.p. (°C), yields (%), elemental analyzes, UV–vis (in $CHCl_3$, nm (log ε), FT-IR (KBr, cm^{-1}) and ^1H NMR ($CDCl_3$, 25 °C, ppm, i: isomerism, s: singlet, d: doublet, t: triplet) data of the thiosemicarbazones are given as follows:

(**1**): Light yellow, 190–191, 85. Found (Calcd) for $C_9H_{10}BrN_3OS$ (288.16 g/M) C, 37.56 (37.51); H, 3.66 (3.50); N, 14.11 (14.58); S, 10.98 (11.13)%. UV–vis: 241 (4.06), 298 (4.15), 312 (4.07), 343 (4.08), 360 (3.99). IR: υ(OH) 3476 s, $\upsilon_s(NH_2)$ 3284 s, $\upsilon_{as}(NH_2)$ s 3092, δ(N–H) 1638 s, υ(C=N) 1607 s, υ(C–O) 1158 s, υ(C–H) 2930, 2998. ^1H NMR: 11.57 s, 11.34 s (1H, i:1/2, ***OH***), 8.30 s (syn), 8.15 s (anti) (1H, i:2/1, ***CH***=*N*), 6.80 d (1H, j:8.30, ***a***), 7.24–7.30 m (2H, ***b***,***d***), 4.99 s, 4.75 s (2H, i:2/1, NH_2), 2.39 s, 2.41 s (3H, i:3/2, CH_3–).

(**2**): Light yellow, 138–139, 90. Found (Calcd) for $C_{11}H_{14}BrN_3OS$ (316.22 g/M) C, 42.01 (41.78); H, 4.89 (4.46); N, 13.33 (13.29); S, 10.65 (10.14)%. UV–vis: 242 (4.06), 300 (4.13), 312 (4.09), 344 (4.10), 360 (4.03). IR: υ(OH) 3480 s, $\upsilon_s(NH_2)$ 3280 s, $\upsilon_{as}(NH_2)$ s 3095, δ(N–H) 1632 s, υ(C=N) 1605 s, υ(C–O) 1150 s, υ(C–H) 2929, 2968. ^1H NMR: 11.55 s, 11.34 s (1H, i:1/2, ***OH***), 8.28 s (syn), 8.15 s (anti) (1H, i:2/1, ***CH***=*N*), 6.79 d (1H, j:8.30, ***a***), 7.25–7.30 m (2H, ***b***,***d***), 5.00 s (2H, NH_2), 2.99 t, 2.84 t (2H, i:2/1, j:7.32, *S*–CH_2–), 1.68 m (2H, –CH_2–), 0.96 t, 1.01 t (3H, i:1/2, j:7.32, CH_3–).

(**3**): Light yellow, 141–142, 85. Found (Calcd) for $C_{11}H_{12}BrN_3OS$ (314.20 g/M) C, 42.15 (42.05); H, 3.77 (3.85); N, 13.98 (13.37); S, 10.66 (10.21)%. UV–vis: 242 (4.15), 298 (4.21), 312 (4.15), 343 (4.13), 360 (4.00). IR: υ(OH) 3464 s, $\upsilon_s(NH_2)$ 3283 s, $\upsilon_{as}(NH_2)$ s 3079, δ(N–H) 1643 s, υ(C=N) 1601 s, υ(C–O) 1189 s, υ(C–H) 2952. ^1H NMR: 11.49 s, 11.29 s (1H, i:4/3, ***OH***), 8.29 s (syn), 8.14 s (anti) (1H, i:2/1, ***CH***=*N*), 6.79 d (1H, j:8.29, ***a***), 7.25–7.30 m (2H, ***b***,***d***), 5.00 s, 4.58 s (2H, NH_2), 3.56 d, 3.67 d (2H, j:6.83 J:6.34, *S*–CH_2–), 5.92 m (1H, –***CH***=), 5.31 d (1H, j:17.09, =CH_aH), 5.17 d (1H, j:9.77, =CHH_b).

2.2.2. Synthesis of N^1,N^4-di-(5-bromosalicylidene)-S-propylthiosemicarbazidato dioxouranium(VI) allyl alcohol (2b). About 110 mg $UO_2(CH_3COO)_2{\cdot}2H_2O$ (0.26 mM) was dissolved in 10 mL allyl alcohol, and to this solution 0.34 mL triethylorthoformate

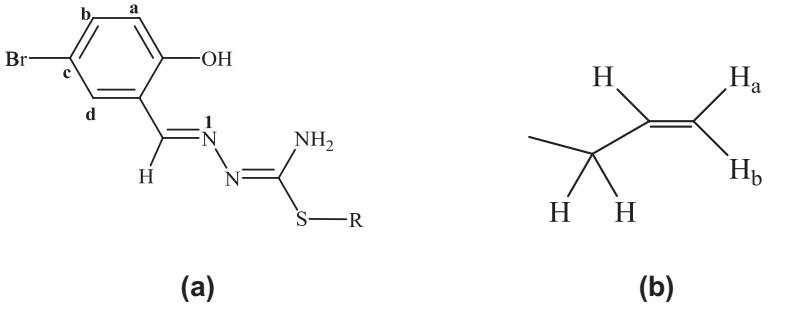

Figure 2. (a) S-Alkylthiosemicarbazones, R: methyl (**1**), propyl (**2**), allyl (**3**); (b) the protons of allyl group.

(2.34 mM) was added. The mixture was then allowed to stand at room temperature for about 10 h. The next day, solution of 82 mg 5-bromosalicylidene-S-propylthiosemicarbazone (0.26 mM) and 52 mg 5-bromosalicylaldehyde (0.26 mM) in 10 mL allyl alcohol was added dropwise to the metal solution with vigorous stirring. The resulting red reaction mixture yielded a bright red precipitate in two weeks. The product was collected by filtration and washed twice by 2 mL of cold allyl alcohol. The precipitates were dried at room temperature.

Dioxouranium(VI) complexes (**1a**, **1b**, **2a**, **2b**, **3a** and **3b**) were synthesized in a similar manner (figures 1 and 3).

The colors, m.p. (°C), yields (%), μ_{eff} (B.M.), elemental analysis, UV–vis (in $CHCl_3$, nm (log ε), FTIR (KBr, cm^{-1}) and ^1H NMR ($CDCl_3$, 25 °C, ppm, i: isomerism, s: singlet, d: doublet, t: triplet) data of the dioxouranium complexes are:

(**1a**): Red, 281–283, 45, 0.11. Found (Calcd) for $C_{19}H_{19}Br_2N_3O_5SU$ (799.27 g/M) C, 28.88 (28.55); H, 2.56 (2.40); N, 5.33 (5.26); S, 4.13 (4.01)%. UV–vis: 262 (4.51), 309 (4.33), 417 (4.01). IR: υ(OH) 3469, υ(C=N) 1592, 1576, υ(C–O) 1184, υ(C–H) 2976, $\upsilon_s(UO_2)$ 907, $\upsilon_{as}(UO_2)$ 885. ^1H NMR: 9.62 s (1H, *CH*=*N*), 9.54 s (1H, *CH*=*N*), 8.15 d (1H, j:1.95, ***d***), 7.95 d (1H, j:1.95, ***s***), 7.84 dd (1H, j:1.95, j:8.78, ***b***), 7.70 dd (1H, j:2.44, j:8.78, ***q***), 7.02 d (1H, j:8.78, ***a***), 6.92 d (1H, j:8.78, ***p***), S-*methyl*; 2.81 s (3H, *S*–*CH*$_3$), *propyl alcohol*; 4.31 s (1H, O***H***), 3.32 q (2H, O–C***H***$_2$–), 1.40 m (2H, –C***H***$_2$–), 0.82 t (3H, j:7.81, j:7.32, –*CH*$_3$).

(**1b**): Red, >250 (decomp.), 40, 0.11. Found (Calcd) for $C_{19}H_{17}Br_2N_3O_5SU$ (797.24 g/M) C, 29.51 (28.62); H, 2.33 (2.15); N, 5.00 (5.27); S, 4.45 (4.02)%. UV–vis: 260 (4.46), 309 (4.30), 417 (3.99). IR: υ(OH) 3446, υ(C=N) 1592, 1576, υ(C–O) 1184, υ(C–H) 2930, $\upsilon_s(UO_2)$ 912, $\upsilon_{as}(UO_2)$ 877. ^1H NMR: 9.62 s (1H, *CH*=*N*), 9.54 s (1H, *CH*=*N*), 8.14 d (1H, j:2.44, ***d***), 7.95 d (1H, j:1.95, ***s***), 7.84 dd (1H, j:2.44, j:8.79, ***b***), 7.70 dd (1H, j:2.44, j:8.78, ***q***), 7.02 d (1H, j:8.79, ***a***), 6.92 d (1H, j:8.78, ***p***), S-*methyl*; 2.81 s (3H, –C***H***$_3$), *allyl alcohol*; 4.68 t (1H, j:5.37, –O***H***), 5.89 m (1H, –C***H***=), 5.17 d (1H, j:17.57, –C***H***$_a$H=), 5.01 d (1H, j:10.02, –CH***H***$_b$=), 3.92 t (2H, j:5.37, O–*CH*$_2$–).

(**2a**): Red, >250 (decomp.), 40, 0.10. Found (Calcd) for $C_{21}H_{23}Br_2N_3O_5SU$ (827.32 g/M) C, 30.31 (30.49); H, 2.93 (2.80); N, 5.33 (5.08); S, 4.00 (3.88)%. UV–vis: 260 (4.49), 309

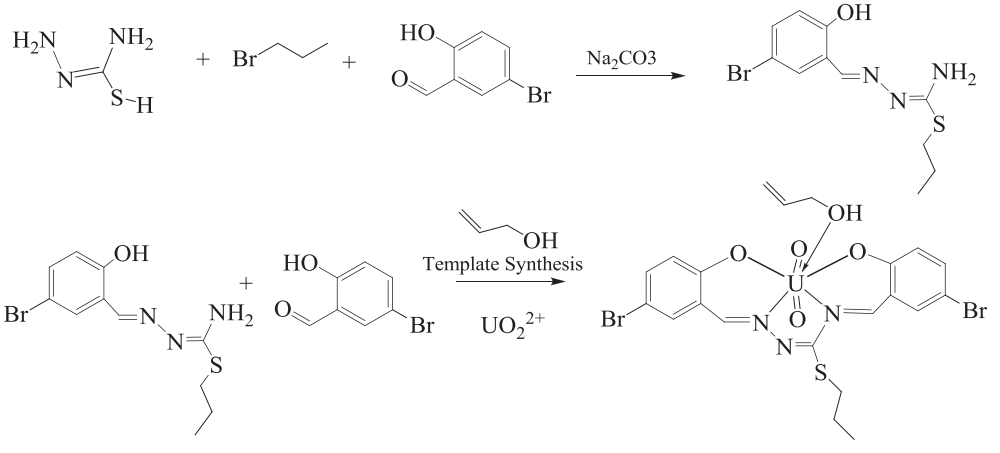

Figure 3. The formation of the dioxouranium(VI) complexes.

(4.31), 415 (4.00). IR: υ(OH) 3434, υ(C=N) 1597, 1574, υ(C–O) 1189, υ(C–H) 2964, $\upsilon_s(UO_2)$ 915, $\upsilon_{as}(UO_2)$ 869. ^{1}H NMR: 9.64 s (1H, *CH=N*), 9.53 s (1H, *CH=N*), 8.16 d (1H, j:2.93, ***d***), 7.97 d (1H, j:2.93, ***s***), 7.83 dd (1H, j:2.93, j:8.78, ***b***), 7.70 dd (1H, j:2.44, j:8.78, ***q***), 7.02 d (1H, j:8.79, ***a***), 6.92 d (1H, j:8.79, ***p***), S-*propyl*; 3.38 t (2H, j:7.32, j:6.84, S–C***H***$_2$–), 1.87 m (2H, –C***H***$_2$–), 1.09 t (3H, j:7.32, –***CH***$_3$). *Propyl alcohol*; 4.31 t (1H, j:4.88, j:5.37, –O***H***), 3.42 m (2H, O–C***H***$_2$–), 1.87 m (2H, –C***H***$_2$–), 1.05 t (3H, j:6.83, j:7.32, ***CH***$_3$–).

(**2b**): Red, 243–345, 45, 0.13. Found (Calcd) for $C_{21}H_{21}Br_2N_3O_5SU$ (825.31 g/M) C, 30.13 (30.56); H, 2.50 (2.56); N, 5.64 (5.09); S, 4.25 (3.89).%. UV–vis: 260 (4.49), 310 (4.23), 416 (3.90). IR: υ(OH) 3453, υ(C=N) 1601, 1574, υ(C–O) 1189, υ(C–H) 2929, $\upsilon_s(UO_2)$ 915, $\upsilon_{as}(UO_2)$ 877. ^{1}H NMR: 9.64 s (1H, *CH=N*), 9.53 s (1H, *CH=N*), 8.16 d (1H, j:2.93, ***d***), 7.97 d (1H, j:2.93, ***s***), 7.84 dd (1H, j:2.44, j:8.79, ***b***), 7.70 dd (1H, j:2.44, j:8.78, ***q***), 7.01 d (1H, j:8.79, ***a***), 6.92 d (1H, j:8.79, ***p***), S-*propyl*; 3.38 t (2H, j:6.83, j:7.32, S–C***H***$_2$–), 1.86 m (2H, –C***H***$_2$–), 1.09 t (3H, j:7.32, –***CH***$_3$). *Allyl alcohol*; 4.69 t (1H, j:5.37, –O***H***), 5.90 m (1H, –C***H***=), 5.17 d (1H, j:15.12, –C***H***$_a$H=), 5.00 d (1H, j:10.25, –CH***H***$_b$=), 3.93 t (2H, j:4.88, O–***CH***$_2$–).

(**3a**): Red, 240–242, 35, 0.13. Found (Calcd) for $C_{21}H_{21}Br_2N_3O_5SU$ (825.31 g/M) C, 30.30 (30.56); H, 2.81 (2.56); N, 5.15 (5.09); S, 4.01 (3.89)%. UV–vis: 259 (4.50), 310 (4.30), 418 (4.10). IR: υ(OH) 3441, υ(C=N) 1597, 1578, υ(C–O) 1189, υ(C–H) 2975, $\upsilon_s(UO_2)$ 908, $\upsilon_{as}(UO_2)$ 869. ^{1}H NMR: 9.67 s (1H, *CH=N*), 9.58 s (1H, *CH=N*), 8.17 d (1H, j:2.93, ***d***), 7.98 d (1H, j:2.44, ***s***), 7.85 dd (1H, j:2.44, j:8.78, ***b***), 7.73 dd (1H, j:2.44, j:8.78, ***q***), 7.03 d (1H, j:8.78, ***a***), 6.94 d (1H, j:8.78, ***p***), S-*allyl*; 6.13 m (1H, –C***H***=), 5.53 d (1H, j:15.63, –C***H***$_a$H=), 5.26 d (1H, j:9.28, –CH***H***$_b$=), 4.10 d (2H, j:6.83, S–***CH***$_2$–). *Propyl alcohol*; 4.32 t (1H, j:5.37, j:4.88, –O***H***), 3.42 m (2H, O–C***H***$_2$–), 1.88 m (2H, –C***H***$_2$–), 1.05 t (3H, j:6.83, j:7.32, ***CH***$_3$–).

(**3b**): Red, >250 (decomp.), 40, 0.10. Found (Calcd) for $C_{21}H_{19}Br_2N_3O_5SU$ (823.29 g/M) C, 30.55 (30.64); H, 2.50 (2.33); N, 5.55 (5.10); S, 4.09 (3.89)%. UV–vis: 259 (4.56), 310 (4.37), 418 (4.05). IR: υ(OH) 3445, υ(C=N) 1593, 1574, υ(C–O) 1185, υ(C–H) 2975, $\upsilon_s(UO_2)$ 912, $\upsilon_{as}(UO_2)$ 877. ^{1}H NMR: 9.63 s (1H, *CH=N*), 9.57 s (1H, *CH=N*), 8.16 d (1H, j:2.44, ***d***), 7.97 d (1H, j:2.44, ***s***), 7.84 dd (1H, j:2.44, j:8.78, ***b***), 7.71 dd (1H, j:2.44, j:8.78, ***q***), 7.02 d (1H, j:8.79, ***a***), 6.93 d (1H, j:8.79, ***p***), S-*allyl*; 6.12 m (1H, –C***H***=), 5.52 d (1H, j:17.08, –C***H***$_a$H=), 5.25 d (1H, j:10.25, –CH***H***$_b$=), 4.08 d (2H, j:6.83, S–***CH***$_2$–). *Allyl alcohol*; 4.69 t (1H, j:5.37, –O***H***), 5.90 m (1H, –C***H***=), 5.18 d (1H, j:17.56, –C***H***$_a$H=), 5.01 d (1H, j:10.24, –CH***H***$_b$=), 3.92 t (2H, j:5.37, j:4.88, O–***CH***$_2$–).

2.3. *X-ray analysis*

The single-crystal X-ray data were collected on a Rigaku RAXIS-RAPID diffractometer at 293 K. Graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) and the ω-scan technique were used. The structure was solved by direct methods using SHELXS-97 [22] and refined through full-matrix least-squares using SHELXL-97 [23], implemented in the WINGX [24] program suite. All hydrogens were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.82, 0.93, 0.96, and 0.97 Å for OH, CH plus terminal CH_2, CH_3, and CH_2 groups, respectively. The displacement parameters of the hydrogens were fixed at $U_{iso}(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl H and OH) of their parent atoms. In the

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

CCDC deposition no.	815247
Color/shape	Red/block
Chemical formula	$[UO_2(C_{18}H_{15}Br_2N_3O_2S)(C_3H_6O)]$
Formula weight	825.32
Temperature (K)	293
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a, b, c (Å)	14.2368(5), 9.3705(2), 23.4239(9)
α, β, γ (°)	90, 125.865(2), 90
Volume (Å^3)	2532.41(16)
Z	4
D_{Calcd} (g cm^{-3})	2.165
μ (mm^{-1})	9.684
Absorption correction	Multi-scan
T_{min}, T_{max}	0.085, 0.379
F(000)	1544
Crystal size (mm^3)	0.40 × 0.20 × 0.10
Diffractometer/measurement method	Rigaku RAXIS-RAPID/ω scan
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 11$, $-26 \le l \le 27$
θ Range for data collection (°)	$2.42 \le \theta \le 25.00$
Reflections collected	46,721
Independent/observed reflections	4442/4394
R_{int}	0.0622
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4442/141/345
Goodness-of-fit on F^2	1.306
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0579$, $wR_2 = 0.1283$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.1295$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	1.982, −1.293

complex, the *S*-propyl and 2-propenol moieties show positional disorder and the refined site-occupancy factors of the disordered parts, viz. (C17A-C18A/C17B-C18B) and (C19A-C20A-C21A/C19B-C20B-C21B), are 0.79(2)/0.21(2)% and 0.653(17)/0.347(17)%, respectively. The disordered atoms were refined using the following restraints: SIMU, DELU, and SADI [23]. Data collection: PROCESS-AUTO [25], cell refinement: PROCESS-AUTO, data reduction: CRYSTALSTRUCTURE [26]. Details of the data collection conditions and the parameters of the refinement process are given in table 1. The general-purpose crystallographic tool PLATON [27] was used for the structure analysis and presentation of the results.

3. Results and discussion

3.1. *Chemistry*

The reaction of 5-bromosalicylidene-S-alkylthiosemicarbazones and 5-bromosalicylaldehyde in the presence of dioxouranium(VI) acetate yielded stable red complexes. The magnetic susceptibility measurements indicated that all complexes were diamagnetic. In DMSO, the complexes behaved as non-electrolytes. The complexes were soluble in common organic solvents such as alcohols, chloroform, DMSO, dimethyl formamide (DMF), acetone, and insoluble in water. All compounds were fully characterized by spectroscopic methods such as elemental analysis, infrared, ^{1}H NMR, and UV–vis. In addition, the structure of **2b** was

determined by X-ray crystallography. These results indicate that thiosemicarbazones are dianionic coordinating to uranium through two phenols and two nitrogens. Solvent having oxygen donor occupies the 7th coordination site of uranium. The coordination geometry around uranium atom was distorted pentagonal bipyramidal.

3.2. *Spectral analysis*

In IR spectra of **1–3**, the stretching bands assigned to phenolic ν(OH), ν_a(NH), ν_s(NH), and the intra-planar bending band assigned to $\delta(NH_2)$ at 3464–3480, 3079–3095, 3280–3284, and 1632–1643 cm^{-1}, respectively, were not present in spectra of complexes. Thus, the phenolic hydroxy lost a proton and coordinates to uranium; disappearance of bands of NH_2 indicates condensation of the aldehyde to form a new imine C=N. The stretching vibrations of C=N of the ligands at 1607 cm^{-1} (1), 1605 cm^{-1} (2), and 1601 cm^{-1} (3) shifted to lower wavenumbers as a result of complex formation and the new imine bands were clear. The characteristic bands of UO_2(VI) were also present at 869–885 cm^{-1} as asymmetric $\upsilon_{as}(UO_2)$ and 907–915 cm^{-1} symmetric $\upsilon_a(UO_2)$ in spectra of complexes.

UV–vis spectra of the ligands and complexes were obtained in solutions of 3×10^{-5} M $CHCl_3$. The ligands and their dioxouranium(IV) complexes show similar UV–vis spectra in relation to the number of absorptions and the values of the extinction coefficient. The similar feature of these spectra is the presence of five absorptions in ligand spectra and three bands in complex spectra. The intense higher energy bands from 242 to 260 nm can be attributed to intra-ligand $\pi \rightarrow \pi^*$ transitions. The transitions in the 240 nm region of salicylidine thiosemicarbazone correspond to $\pi \rightarrow \pi^*$ transitions, where π^* is the unoccupied π molecular orbital. The absorption band at 310 nm in the ligand and complex spectra may be associated with charge transfer and $n \rightarrow \pi^*$ transitions. The $\pi \rightarrow \pi^*$ absorptions of the complexes are comprised of overlapping bands. Intense bands at 417 nm are also attributed to charge transfer transitions.

In ^{1}H NMR spectra of ligands, two singlets at 8.14–8.30 ppm belong to syn-anti isomerism of the imine (CH=N) proton [21]. This isomerism is not seen in spectra of the complex because of hindered rotation of the $C=N^1$ and $C=N^4$ double bonds. The imine protons of the metal chelates were between 9.53 and 9.67 as two sharp singlets downfield with respect to free thiosemicarbazones. As a result of the template reaction, protons of the phenolic hydroxyl and amine disappeared in ^{1}H NMR spectra of the dioxouranium(VI) chelates. These data show that phenolic oxygen loses a proton and a new imine formed by condensation of the free NH_2 with aldehyde. This ligand system coordinates to uranium through two phenolic oxygens and two imine nitrogens. Signals attributed to protons of alcohol (propyl or allyl alcohol) in the spectra of the complexes suggest coordination to uranium. The proton of the –OH group on coordinated alcohol gives a triplet due to the CH_2 in the α position. The protons of coordinated allyl alcohol were observed downfield by 0.2–0.3 ppm compared to those of the allyl bound to sulfur (figure 2[b]) for 3b.

3.3. *Crystal structure of 2b*

The solid-state structure of **2b** was verified by single-crystal X-ray analysis. The ORTEP-3 [28] view of the complex with the atom numbering scheme is depicted in figure 4 and selected geometric parameters are given in table 2. The complex is composed of a dibromo-substituted N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazone with a dioxouranium

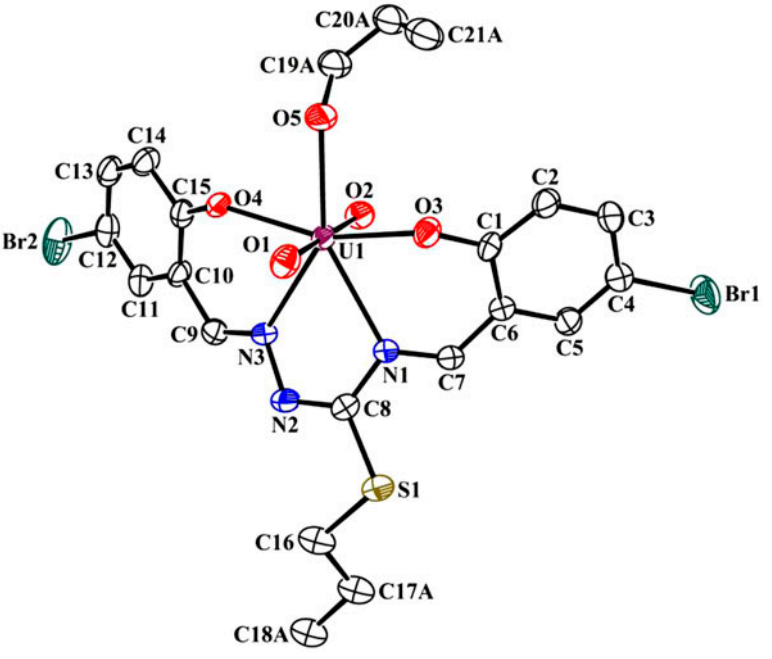

Figure 4. The molecular structure of **2b** with atom labeling shown with 30% probability displacement ellipsoids. Hydrogens have been omitted for clarity and only the major parts of disordered fragments are drawn.

(VI) and one allyl alcohol and crystallizes in the space group $P2_1/c$ with one molecule per asymmetric unit.

The uranium is seven-coordinate in a pentagonal-bipyramidal arrangement with two oxo groups (O1 and O2) occupying the apical positions. The equatorial plane consists of two imine nitrogens and two phenolic oxygens from the tetradentate thiosemicarbazone (N1, N3, O3, and O4) and one hydroxy oxygen (O5) from 2-propenol. The oxo groups of the uranyl moiety lie *trans* to one another with a nearly linear O_{oxo}–U–O_{oxo} angle of 179.8(4)°. The U=O distances, 1.760(8) and 1.768(7) Å, are shorter than the equatorial U–O bond lengths, reflecting the multiple bond order. The bond distances of the uranyl moieties are in agreement with the average value (1.77 Å) for comparable bonds found in the Cambridge Structural Database (CSD, Version 5.31 plus update of August 2010) [29], which has been searched using CONQUEST software (Version 1.12) [30], illustrating how the coordination environment surrounding the uranyl cation has very little effect on the apical bond lengths. U–N_{imine} distances are typically longer than the U–$O_{phenolic}$ distances, explained by Pearson's hard and soft acid–base concept [31, 32]. This concept agrees well with what is observed in the compound studied, as nitrogen would be expected to be bonded less strongly to a hard acid such as (UO_2^{2+}), while oxygen has relatively higher base strength towards uranium [33]. As expected, the U–$O_{phenolic}$ and the U–N_{imine} bond lengths are similar to those observed in previously reported dioxouranium(VI) complexes [16, 34]. However the U–$O_{alcohol}$ bond length [2.411(8) Å] is longer than those [2.368(3) Å], [2.352(3) Å], and [2.31(1), 2.35(2), 2.31(1), and 2.32(2) Å] in $[UO_2(L^1)(MeO)(MeOH)]_2$, $[UO_2(APTSC)(MeOH)(MeO)]_2$, and $[UO_2(L^1)(OH)]_2$, respectively [34, 35].

Table 2. Selected geometric parameters for **2b**.

Parameter		Parameter	
Bond lengths (Å)			
U1–O1	1.760(8)	O3–C1	1.315(12)
U1–O2	1.768(7)	O4–C15	1.338(12)
U1–O3	2.257(7)	O5–C19A	1.421(16)
U1–O4	2.291(7)	O5–C19B	1.421(16)
U1–O5	2.411(8)	N1–C7	1.281(13)
U1–N1	2.559(8)	N1–C8	1.411(14)
U1–N3	2.555(8)	N2–C8	1.280(14)
Br1–C4	1.897(12)	N2–N3	1.403(12)
Br2–C12	1.903(12)	N3–C9	1.301(13)
S1–C8	1.741(11)	C6–C7	1.430(14)
S1–C16	1.819(16)	C9–C10	1.454(14)
Bond angles (°)			
O1–U1–O2	179.8(4)	O4–U1–O5	77.4(3)
O1–U1–O3	87.8(3)	O1–U1–N1	92.7(3)
O1–U1–O4	87.5(3)	O1–U1–N3	90.8(3)
O1–U1–O5	91.1(3)	O2–U1–N1	87.1(3)
O2–U1–O3	92.1(3)	O2–U1–N3	89.0(3)
O2–U1–O4	92.6(3)	O3–U1–N1	69.8(3)
O2–U1–O5	89.1(3)	O4–U1–N3	69.8(2)
O3–U1–O4	158.5(3)	N1–U1–N3	61.6(3)
O3–U1–O5	81.7(3)		
Torsion angles (°)			
S1–C8–N2–N3	177.1(8)	N2–N3–C9–C10	178.5(10)
S1–C8–N1–C7	31.4(14)	N2–C8–N1–C7	−152.6(12)
S1–C16–C17A–C18A	177.3(16)	N2–C8–S1–C16	13.1(13)
S1–C16–C17B–C18B	119(4)	N3–C9–C10–C11	166.1(11)
O5–C19A–C20A–C21A	7(3)	C8–N2–N3–C9	161.8(11)
O5–C19B–C20B–C21B	110(4)	C6–C7–N1–C8	−177.8(11)
N1–C8–N2–N3	1.2(17)	C8–S1–C16–C17A	135.8(13)
N1–C7–C6–C5	−168.4(11)	C8–S1–C16–C17B	104(2)

For an ideal pentagonal-bipyramidal complex, each of the five angles subtended at the equatorial plane should be 72°. The angles around the U atom defined by adjacent donors in the equatorial plane are not equivalent and lie in the range 61.6(3)–81.7(3)°, indicating a fairly regular pentagon. It should be pointed out here that for an ideal pentagonal array of donors, a cyclic ligand with identical donor atoms and bond lengths is required. As can be seen from the angles, the coordination polyhedron around U can be visualized as being distorted, with O_{oxo}–U–O,N angles of 87.1(3)–92.7(3). The distortion from ideal pentagonal-bipyramid geometry is probably due to the asymmetric nature of the tetradentate Schiff base. The angle between the MN_2O_3 plane and the plane including the metal and the two axial O atoms is 89.41(20)°.

The pentagon defined by the five equatorial donors is planar with a r.m.s. deviation of 0.0743 Å. The dihedral angles between the pentagon plane and the bromophenyl ring planes are 35.25(35) and 23.93(39)°, and that between the two bromophenyl ring planes is 57.48(34)°, indicating a non-planar disposition of the tetradentate thiosemicarbazone. In addition, the five-member chelate ring adopts an envelope conformation, while the six-member chelate rings exhibit a half-chair conformation.

In the molecular structure of the complex, there are three intramolecular interactions, C–H···O, C–H···N, and C–H···S, forming five-membered rings with graph-set desciptor *S* (5) [36]. In the crystal structure, the molecules are packed in columns running along the *b* axis. There are no intermolecular interactions between the complex molecules in each

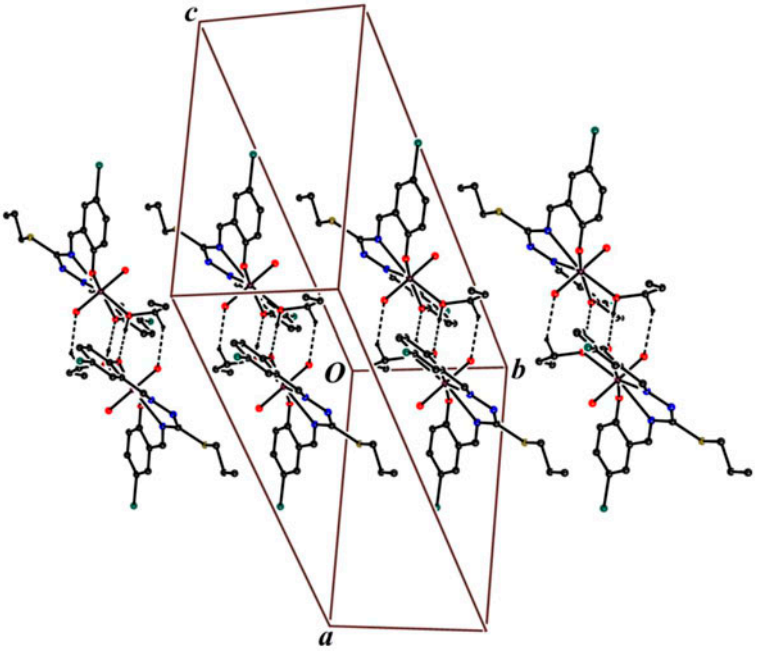

Figure 5. The molecular packing of **2b** showing the centrosymmetric $R_2^2(8)$ and $R_2^2(10)$ dimers.

Table 3. Hydrogen bonding geometry for **2b**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C7–H7···S1	0.93	2.49	2.938(11)	110
C16–H16B···N2	0.97	2.39	2.870(17)	110
C21A–H21A···O5	0.93	2.09	2.56(2)	110
O5–H5O···O4^{i}	0.82	1.84	2.658(11)	176
C19A–H19B···O1^{i}	0.97	2.34	3.191(18)	146

Symmetry code: $^{i}1 - x, -y, 1 - z$.

column. However, inversion-related columns are connected to each other by two intermolecular interactions, O–H···O and C–H···O, forming centrosymmetric $R_2^2(8)$ and $R_2^2(10)$ dimers [36], respectively (figure 5). The detailed geometry of the intra- and intermolecular interactions is given in table 3. There are no other significant interactions in the crystal structure of the complex.

4. Conclusion

In this study, six new dioxouranium(VI) complexes having coordinated alcohol to the UO_2^{2+} center were synthesized and characterized. We obtained the dioxouranium(VI) complexes having allyl alcohol as an unsaturated alcohol for the first time. The structure of **2b** was determined by X-ray crystallography. The complex is composed of a

dibromo-substituted N^1,N^4-diarylidene-*S*-propyl-thiosemicarbazone with uranyl ion and one allyl alcohol that crystallizes in space group $P2_1/c$ with one molecule per asymmetric unit. In this newly synthesized compound, uranium is seven-coordinate in a pentagonal-bipyramidal arrangement.

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Supplementary material

CCDC 815247 contains the supplementary crystallographic data for the structure reported in this article. 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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