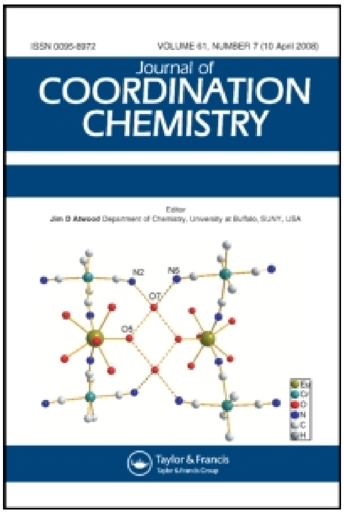

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Syntheses and structures of three disulfoxide uranyl complexes

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Three disulfoxide uranyl complexes $[UO_2(DBSOB)(NO_3)_2]_n$ (**1**), $[UO_2(DBM)_2]_2(DBSOB)$ (**2**), and $[UO_2(PMBP)_2]_2(DBSOB)$ (**3**) (DBSOB = 1,4-di(butylsulfinyl)butane, HDBM = dibenzoylmethane, HPMBP = 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) were synthesized and characterized. The $[UO_2(NO_3)_2]$ groups are connected by bridging disulfoxide ligands DBSOB to form a 1-D zigzag chain in **1**. Two $[UO_2(DBM)_2]$ or $[UO_2(PMBP)_2]$ groups are connected by a bridging DBSOB to form the dimeric structures of **2** or **3**, respectively. Complexes **1**, **2**, and **3** are the first structurally characterized disulfoxide–actinide compounds. Thermal stabilities of **1**, **2**, and **3** were investigated.

Keywords: Uranyl complex; Disulfoxide; β-Diketonate; Crystal structure; 1,4-Di(butylsulfinyl)butane

1. Introduction

Actinide coordination chemistry is important for the development of new technologies for the safe separation and the management of highly radioactive waste [1]. Various ligands such as phosphine oxide [2], diphosphine dioxides [3], and substituted urea compounds [4] have been widely explored for separation of minor actinides from highly active nuclear water solution. Extraction of actinide with sulfoxides has been studied [5] and a number of coordination compounds have been reported [6]. Mixture of β-diketonates and other extractants can enhance the effective extraction of metal anions [7]. Some dibenzoylmethane (HDBM) [8–11] and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) [12–14] uranyl complexes were characterized structurally.

We previously studied solvent extraction and separation properties of a variety of bifunctional disulfoxides with actinide [15]. However, there is no structural study on disulfoxide–actinide compounds. In view of the lack of structural reports on disulfoxide–actinide compounds, we felt that it was very important to study such complexes in order to establish the fundamental structural properties. In this study, we synthesized three disulfoxide–uranyl complexes $[UO_2(DBSOB)(NO_3)_2]_n$ (**1**),

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$[UO_2(DBM)_2]_2(DBSOB)$ (**2**), and $[UO_2(PMBP)_2]_2(DBSOB)$ (**3**) (DBSOB = 1,4-di(butylsulfinyl)butane, HDBM, HPMBP) (scheme 1), and the structures are determined.

2. Experimental

2.1. *General procedures*

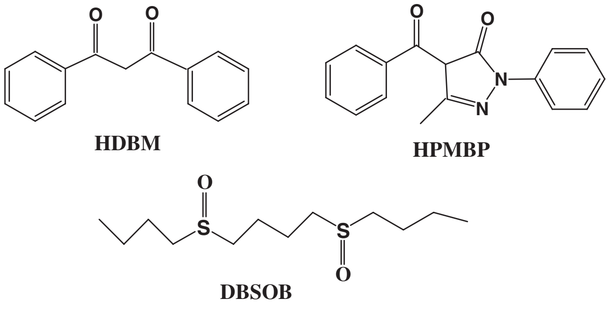
2.1.1. Materials and general methods. All reagents were of analytical grade and used without purification. DBSOB was synthesized according to literature method [15] and$UO_2(DBM)_2$ and $UO_2(PMBP)_2$ were prepared according to the literature method [16]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained as KBr pellets on a Nicolet 170SX FT-IR spectrophotometer from 4000 to 400 cm^{-1}. TGA analyses were measured on a Thermal Analyst 2100 TA Instrument and an SDT 2960 Simultaneous TGA–DTA Instrument in flowing dinitrogen at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of* $[UO_2(DBSOB)(NO_3)_2]_n$ *(1)*

A 10 mL EtOH solution of DBSOB1.0 mmol was added to a 10 mL EtOH solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) with stirring. The resulting yellow precipitate was filtered and washed with EtOH. The yellow dry solid was then dissolved in 20 mL 1 : 1 (v/v) CH_3CN/CH_3NO_2. Yellow crystals of **1** (yield: 86%) were obtained after about 2 weeks. Anal. Calcd for $C_{12}H_{26}N_2O_{10}S_2U$ (**1**): C, 21.82; H, 3.97; N, 4.24%. Found: C, 21.68; H, 3.92; N, 4.19. IR data (cm^{-1}): 3456 w, 1597 m, 1535 vs, 1520 vs, 1474 s, 1366 vs, 1304 m, 1219 w, 1065 w, 1026 w, 972 w, 910 m, 826 w, 748 m, 718 w, 687 w, 602 w, 517 w, 478 w.

2.3. *Synthesis of* $[UO_2(DBM)_2]_2(DBSOB)$ *(2) and* $[UO_2(PMBP)_2]_2(DBSOB)$ *(3)*

A 10 mL toluene solution of DBSOB 0.5 mmol was added to a 15 mL toluene solution of $UO_2(DBM)_2$ (1.0 mmol) or $UO_2(PMBP)_2$ (1.0 mmol) (HDBM, HPMBP) with stirring. The solution was filtered and the filtrate stood on the desk at room



Scheme 1. The structures of the ligands.

temperature to give yellow crystals of **2** (yield: 92%) or orange crystals of **3** (yield: 83%) after about 2 weeks. Anal. Calcd for $C_{72}H_{70}O_{14}S_2U_2$ (**2**): C, 50.89; H, 4.15. Found: C, 50.75; H, 4.07. IR data (cm^{-1}) for **2**: 3464 m, 1605 s, 1574 s, 1528 m, 1474 s, 1427 m, 1381 m, 1157 w, 1057 w, 980 m, 918 m, 841 m, 763 m, 733 m, 617 w. Anal. Calcd for $C_{80}H_{78}O_{14}S_2U_2$ (**3**): C, 50.16; H, 4.10; N, 5.85%. Found: C, 50.03; H, 4.02; N, 5.76. IR data (cm^{-1}) for **3**: 3325 m, 1612 s, 1506 s, 1427 m, 1388 m, 1273 m, 1103 w, 1042 w, 1011 w, 964 m, 915 m, 787 m, 748 m, 694 w.

2.4. *X-ray crystallography*

Suitable single crystals of **1**, **2**, and **3** for X-ray crystallography were carefully selected under an optical microscope and glued to thin glass fibers. Diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected by the ω-scan technique. The structures were solved by direct methods and refined with full-matrix least-squares (*SHELXTL-97*) [17]. Positions of hydrogens were determined with theoretical calculation. The parameters of the crystal data collection and refinement of complexes **1–3** are given in table 1 and selected bond lengths and angles in table 2.

3. Results and discussion

3.1. *Syntheses and IR spectra*

Scheme 2 shows the synthesis of **1**, **2**, and **3**. $[UO_2(DBSOB)(NO_3)_2]_n$ (**1**) is synthesized by the reaction of $UO_2(NO_3)_2 \cdot 6H_2O$ and the disulfoxide ligand DBSOB in EtOH with

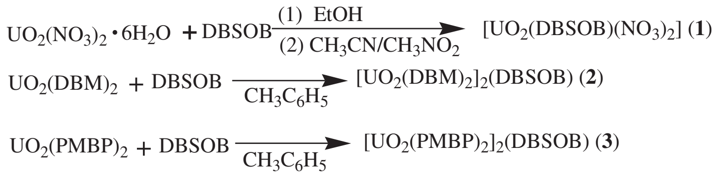
Table 1. Crystallographic data for **1–3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_{12}H_{26}N_2O_{10}S_2U$	$C_{72}H_{70}O_{14}S_2U_2$	$C_{80}H_{78}N_8O_{14}S_2U_2$
Formula weight	660.50	1699.46	1915.68
Temperature (K)	223(2)	223(2)	153(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	16.161(3)	9.6579(11)	15.697(3)
b	8.5138(13)	13.9355(11)	16.475(3)
c	16.893(3)	14.2905(9)	17.611(3)
α	90	62.539(7)	102.198(1)
β	114.057(3)	74.952(9)	103.415(2)
γ	90	84.245(11)	114.408(2)
Volume (Å^3), Z	2122.5(6), 4	1647.7(3), 1	3783.7(10), 2
Calculated density, ρ ($g\,cm^{-3}$)	2.067	1.713	1.681
Absorption coefficient, μ (mm^{-1})	7.893	5.037	4.400
$F(000)$	1264	830	1884
Reflections collected	9897	16,172	37,442
Independent reflections	1930 [R(int) = 0.0493]	5989 [R(int) = 0.0618]	[R(int) = 0.0548]
Parameters	124	415	965
Goodness-of-fit on F^2	1.036	1.083	1.088
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0276$, $wR_2 = 0.0667$	$R_1 = 0.0629$, $wR_2 = 0.1475$	$R_1 = 0.0705$, $wR_2 = 0.1792$

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
U(1)–O(1)	1.755(3)	U(1)–O(2)	2.531(3)
U(1)–O(3)	2.537(3)	U(1)–O(5)	2.376(3)
O(1)–U(1)–O(2)	89.76(13)	O(1)–U(1)–O(3)	90.18(13)
O(2)–U(1)–O(3)	50.08(9)	O(1)–U(1)–O(5)	89.65(13)
O(2)–U(1)–O(5)	64.05(9)	O(5)–U(1)–O(3)	114.13(10)
O(1)–U(1)–O(1A)	180.00(19)	O(2)–U(1)–O(2A)	180.0
O(3)–U(1)–O(3A)	180.0	O(5)–U(1)–O(5A)	180.00(4)
2			
U(1)–O(1)	1.759(7)	U(1)–O(2)	1.761(6)
U(1)–O(3)	2.330(6)	U(1)–O(4)	2.339(6)
U(1)–O(5)	2.367(7)	U(1)–O(6)	2.378(6)
U(1)–O(7)	2.395(6)		
O(1)–U(1)–O(2)	179.6(3)	O(1)–U(1)–O(3)	90.0(3)
O(1)–U(1)–O(4)	85.6(3)	O(1)–U(1)–O(5)	89.1(3)
O(1)–U(1)–O(6)	89.7(3)	O(1)–U(1)–O(7)	87.1(3)
O(2)–U(1)–O(3)	89.6(3)	O(2)–U(1)–O(4)	94.1(3)
O(2)–U(1)–O(5)	91.3(3)	O(2)–U(1)–O(6)	90.6(3)
O(2)–U(1)–O(7)	92.9(3)	O(3)–U(1)–O(4)	69.5(2)
O(3)–U(1)–O(5)	145.9(2)	O(3)–U(1)–O(6)	144.6(2)
O(3)–U(1)–O(7)	74.6(2)	O(4)–U(1)–O(5)	144.3(2)
O(4)–U(1)–O(6)	75.2(2)	O(4)–U(1)–O(7)	143.3(2)
O(5)–U(1)–O(6)	69.4(2)	O(5)–U(1)–O(7)	71.4(2)
O(6)–U(1)–O(7)	140.7(2)		
3			
U(1)–O(1)	1.754(8)	U(1)–O(2)	1.762(7)
U(1)–O(3)	2.372(7)	U(1)–O(4)	2.351(8)
U(1)–O(5)	2.337(8)	U(1)–O(6)	2.394(7)
U(1)–O(13A)	2.389(13)	U(1)–O(13B)	2.379(18)
U(2)–O(7)	1.760(7)	U(2)–O(8)	1.749(7)
U(2)–O(9)	2.331(7)	U(2)–O(10)	2.418(7)
U(2)–O(11)	2.340(7)	U(2)–O(12)	2.410(6)
U(2)–O(14)	2.386(8)		
O(1)–U(1)–O(2)	177.9(4)	O(1)–U(1)–O(3)	84.8(3)
O(1)–U(1)–O(4)	91.7(4)	O(1)–U(1)–O(5)	91.9(4)
O(1)–U(1)–O(6)	91.4(3)	O(1)–U(1)–O(13A)	83.9(5)
O(1)–U(1)–O(13B)	93.0(17)	O(2)–U(1)–O(3)	93.2(3)
O(2)–U(1)–O(4)	87.2(3)	O(2)–U(1)–O(5)	90.0(3)
O(2)–U(1)–O(6)	88.6(3)	O(2)–U(1)–O(13A)	97.3(5)
O(2)–U(1)–O(13B)	88.4(17)	O(3)–U(1)–O(4)	72.9(3)
O(3)–U(1)–O(5)	145.1(3)	O(3)–U(1)–O(6)	74.1(2)
O(3)–U(1)–O(13A)	141.2(6)	O(3)–U(1)–O(13B)	148.7(14)
O(4)–U(1)–O(5)	142.0(3)	O(4)–U(1)–O(6)	146.5(3)
O(4)–U(1)–O(13A)	70.4(6)	O(4)–U(1)–O(13B)	70.0(14)
O(5)–U(1)–O(6)	71.2(3)	O(5)–U(1)–O(13A)	72.4(6)
O(5)–U(1)–O(13B)	66.1(14)	O(6)–U(1)–O(13A)	143.1(6)
O(6)–U(1)–O(13B)	137.2(14)	O(7)–U(2)–O(8)	179.5(4)
O(7)–U(2)–O(9)	90.0(3)	O(7)–U(2)–O(10)	88.2(3)
O(7)–U(2)–O(11)	89.6(3)	O(7)–U(2)–O(12)	89.7(3)
O(7)–U(2)–O(14)	90.4(3)	O(8)–U(2)–O(9)	89.5(4)
O(8)–U(2)–O(10)	91.7(3)	O(8)–U(2)–O(11)	90.8(3)
O(8)–U(2)–O(12)	90.2(3)	O(8)–U(2)–O(14)	90.0(4)
O(9)–U(2)–O(10)	72.6(2)	O(9)–U(2)–O(11)	145.3(3)
O(9)–U(2)–O(12)	74.2(2)	O(9)–U(2)–O(14)	144.5(3)
O(10)–U(2)–O(11)	142.1(2)	O(10)–U(2)–O(12)	146.7(2)
O(10)–U(2)–O(14)	72.0(3)	O(11)–U(2)–O(12)	71.0(2)
O(11)–U(2)–O(14)	70.2(3)	O(12)–U(2)–O(14)	141.2(3)

Symmetry transformations used to generate equivalent atoms: (A) $-x+3/2$, $-y+1/2$, $-z+1$ for **1**.
Sulfoxide S and O are disordered with occupancy factors 0.70 for S(1A), 0.30 for S(1B), 0.70 for S(2A), 0.30 for S(2B), 0.70 for O(13A), and 0.30 for O(13B) for 3.

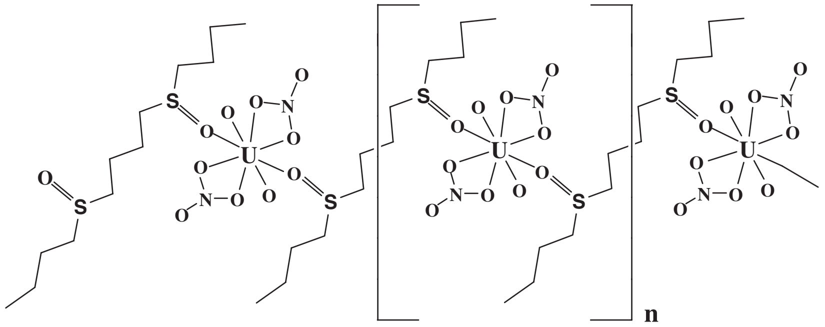


$$UO_2(NO_3)_2 \cdot 6H_2O + DBSOB \xrightarrow[(2)\ CH_3CN/CH_3NO_2]{(1)\ EtOH} [UO_2(DBSOB)(NO_3)_2]\ (\mathbf{1})$$

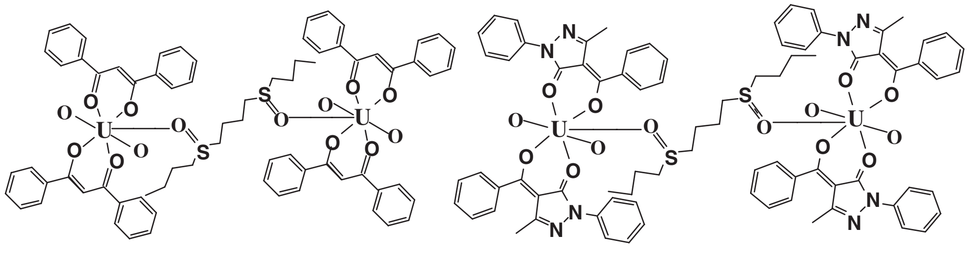
$$UO_2(DBM)_2 + DBSOB \xrightarrow[CH_3C_6H_5]{} [UO_2(DBM)_2]_2(DBSOB)\ (\mathbf{2})$$

$$UO_2(PMBP)_2 + DBSOB \xrightarrow[CH_3C_6H_5]{} [UO_2(PMBP)_2]_2(DBSOB)\ (\mathbf{3})$$

Scheme 2. The syntheses of complexes **1**, **2**, and **3**.



The one-dimensional chain of **1**.



The disulfoxide dimeric **2**. The disulfoxide dimeric **3**.

Scheme 3. The structures of **1–3**.

recrystallization from CH_3CN/CH_3NO_2. $[UO_2(DBM)_2]_2(DBSOB)$ (**2**) and $[UO_2(PMBP)_2]_2(DBSOB)$ (**3**) were obtained by reactions of DBSOB with $UO_2(DBM)_2$ or $UO_2(PMBP)_2$ in toluene.

IR absorption bands of the asymmetric stretch (ν_{asym}) of UO_2^{2+} are at $910\,cm^{-1}$ for **1**, $918\,cm^{-1}$ for **2**, and $915\,cm^{-1}$ for **3**. The S=O absorption bands of DBSOB are $972\,cm^{-1}$ for **1**, $980\,cm^{-1}$ for **2**, and $964\,cm^{-1}$ for **3**, lower than for free DBSOB, indicating coordination of sulfoxide oxygen to the uranyl [8–10, 13–15]. The bidentate chelating nitrate of **1** shows absorptions at 1597, 1535, 1520, 1474, 1366, and $1304\,cm^{-1}$. The carbonyl absorption bands of β-diketonates are 1605 and $1574\,cm^{-1}$ for DBM of **2** and 1612 and $1506\,cm^{-1}$ for PMBP of **3**, respectively [8–10, 13–15].

3.2. *The structures*

Scheme 3 shows the structures of **1–3**. X-ray diffraction analysis shows that $[UO_2(DBSOB)(NO_3)_2]_n$ (**1**) is a 1-D chain. Each U(VI) is situated at the center of

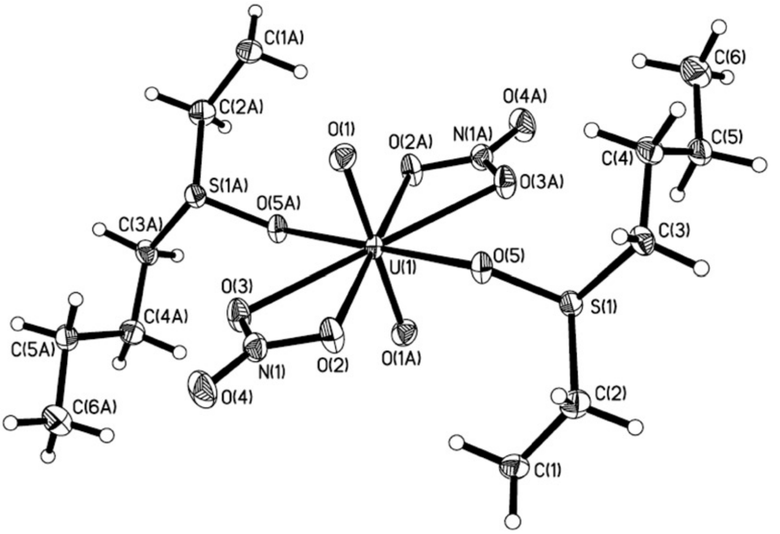


Figure 1. The coordination environment of U(VI) in **1** with 30% thermal ellipsoids.

symmetry (figure 1) as a distorted hexagonal bipyramid. The equatorial plane is defined by two oxygens [U(1)–O(5) 2.376(3) Å] from S=O of two symmetry-related DBSOB ligands and four oxygens [U(1)–O(2) 2.531(3) Å], [U(1)–O(3) 2.537(3) Å] from two symmetry-related bidentate nitrates, with the mean deviation of 0.0015 Å from the plane. The U–O (DBSOB) bond lengths [2.376(3) Å] are much shorter than that of the U–O (nitrate) [2.531(3) to 2.537(3) Å]. The axial positions are occupied by two oxygens [U(1)–O(1) 1.755(3) Å] of two symmetry-related oxygen ligands. The distorted hexagonal bipyramidal coordination geometry of **1** is typical of uranyl nitrate complexes, such as $[UO_2(H_2O)_2(NO_3)_2]$ [18], $[UO_2(C_4H_4O)_2(NO_3)_2]$ (C_4H_4O = tetrahydrofuran) [19], $UO_2[(C_4H_9)_3PO]_2(NO_3)_2$ [20], and $[UO_2(DPDPU)_2(NO_3)_2](C_6H_5CH_3)$ (DPDPU = *N*,*N*′-dipropyl-*N*,*N*′-diphenylurea) [14].

Each DBSOB shows bis-monodentate coordination to two U(VI). The $[UO_2(NO_3)_2]$ groups are connected by bridging DBSOB to form a 1-D zigzag chain with U ⋯ U distance of 9.133(2) Å (figure 2). To the best of our knowledge, $[UO_2(DBSOB)(NO_3)_2]_n$ (**1**) is the first structurally characterized disulfoxide–actinide compound.

$UO_2(DBM)_2]_2(DBSOB)$ (**2**) and $[UO_2(PMBP)_2]_2(DBSOB)$ (**3**) are dimeric uranyl complexes. The complex **2** has a center of symmetry located at the center of butyl group between two S=O groups. There is one independent U(VI) in **2**, but there are two independent U(VI)'s in **3**. Figures 3 and 4 show the molecular structure of **2** and **3**, respectively. The sulfoxide S are disordered with occupancy factors 0.70 for S(1A) and 0.30 for S(1B) of **2**; sulfoxide S and O are disordered with occupancy factors 0.70 for S(1A), 0.30 for S(1B), 0.70 for S(2A), 0.30 for S(2B), 0.70 for O(13A), and 0.30 for O(13B) for **3**. The coordination geometry of U(VI) of **2** and **3** are distorted pentagonal bipyramids, similar to β-diketonates (DBM, PMBP) and other extractant mixed-ligand uranyl complexes $[UO_2(DBM)_2(camphor)]$ [8], $[\{UO_2(DBM)_2\}_2(C_6H_5NHCO)_2CH_2] \cdot CHCl_3$ [9], $[UO_2(DBM)_2(DPPMO)]$, and $[\{UO_2(DBM)_2\}_2(DPPMO)]$ (DPPMO = bis(diphenylphosphino)methane dioxide) [10], $[UO_2(DBM)_2(TPPO)]$ (TPPO =

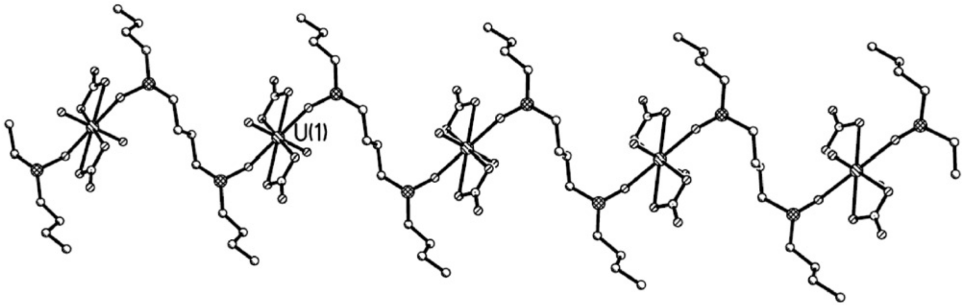


Figure 2. A 1-D chain of **1**.

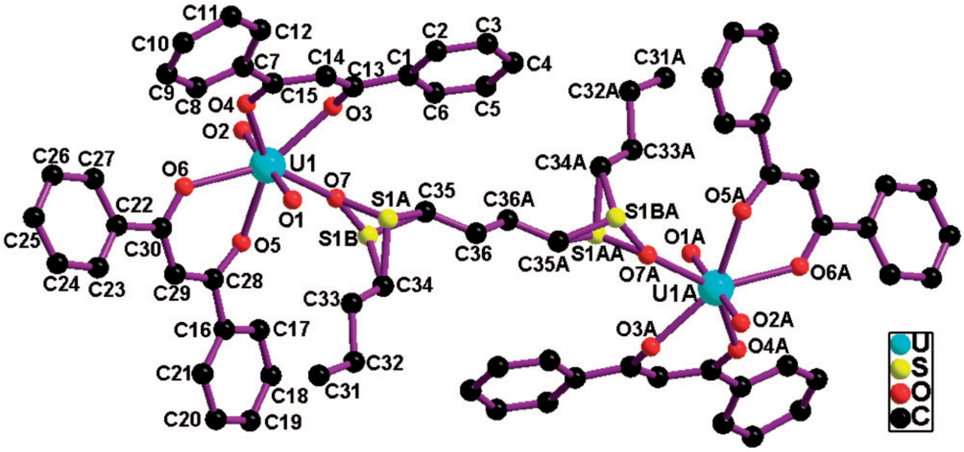


Figure 3. The molecular structure of **2**.

triphenylphosphine oxide) [11], $[UO_2(DBM)_2(DEDPU)]$ (*N*,*N*′-diethyl-*N*,*N*′-diphenylurea) [13], $[UO_2(PMBP)_2(C_2H_6SO)]$ (C_2H_6SO = dimethyl sulfoxide) [12], and $[UO_2(PMBP)_2(DEDPU)]$ [13], and $[UO_2(PMBP)_2(DPDPU)](CH_3C_6H_4CH_3)_{0.5}$ (DPDPU) [14].

The equatorial plane is defined by one oxygen [U(1)–O(7) 2.395(6) Å for **2**; U(1)–O(13A) 2.389(13) Å, U(1)–O(13B) 2.379(18) Å, U(2)–O(14) 2.385(8) Å for **3**] from the S=O of DBSOB, and four oxygens [U(1)–O(3) 2.330(6) Å, U(1)–O(4) 2.339(6) Å, U(1)–O(5) 2.367(7) Å, U(1)–O(6) 2.378(6) Å for **2**] from two DBM ligands, and four oxygens [U(1)–O(3) 2.372(7) Å, U(1)–O(4) 2.351(8) Å, U(1)–O(5) 2.337(8) Å, U(1)–O(6) 2.394(7) Å, U(2)–O(9) 2.331(7) Å, U(2)–O(10) 2.418(7) Å, U(2)–O(11) 2.340(7) Å, U(2)–O(12) 2.410(6) Å for **3**] from two PMBP ligands. Axial positions are occupied by two oxygens [U(1)–O(1) 1.759(7) Å, U(1)–O(2) 1.761(6) Å for **2**; U(1)–O(1) 1.754(8) Å, U(1)–O(2) 1.762(7) Å, U(2)–O(7) 1.760(7) Å, U(2)–O(8) 1.749(7) Å for **3**] of two ligands. The U–O bond lengths are in the normal range [8–14]. Two $[UO_2(DBM)_2]$ or $[UO_2(PMBP)_2]$ groups are connected by bridging DBSOB to form dimeric structures $[UO_2(DBM)_2]_2(DBSOB)$ (**2**) and $[UO_2(PMBP)_2]_2(DBSOB)$ (**3**).

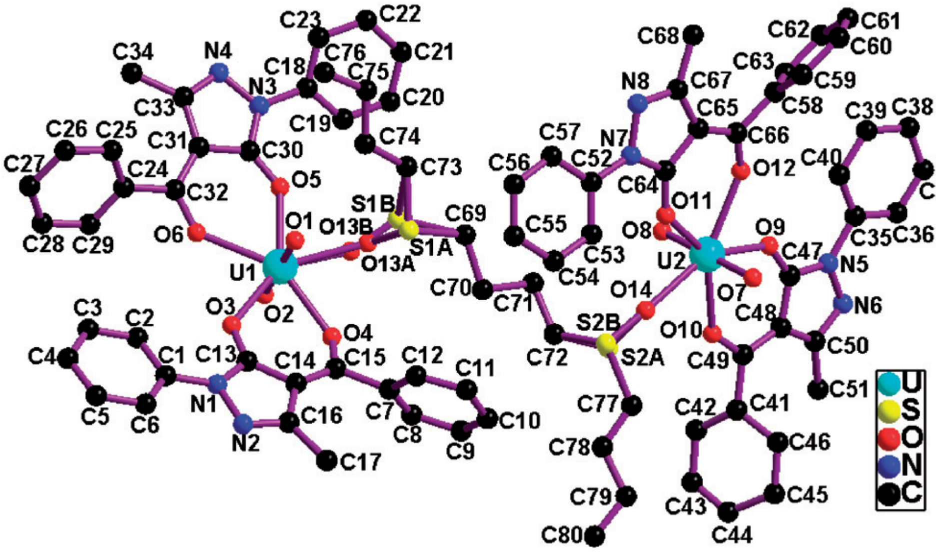


Figure 4. The molecular structure of **3**.

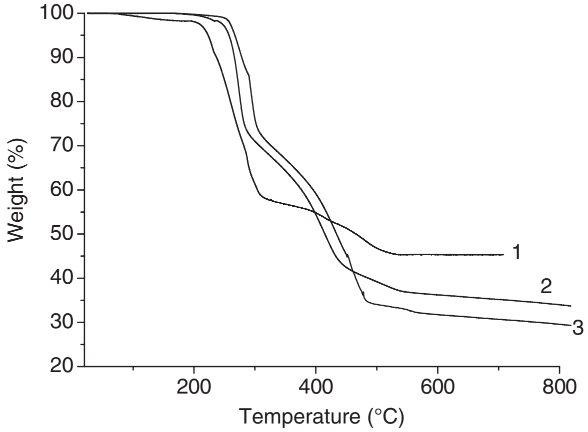


Figure 5. TG curves of **1**, **2**, and **3**.

3.3. *Thermal stability*

Thermal stabilities of **1**–**3** were investigated (figure 5). Weight of **1** is slowly lost from 70°C to 206°C (observed 2.22%) and rapidly lost from 206°C to 310°C (observed 39.06%). These are attributed to decomposition of DBSOB ligand (Calcd 40.35%). Then, NO_3^- decomposes from 206°C to approximately 520°C (observed 12.95%). The residue may be UO_3 (observed 45.32%; Calcd 43.30%) upon heating to 708°C for **1**. Complex **2** begins decomposition from 170°C to 240°C (observed 1.83%); rapid decomposition occurs from 240°C to 440°C (observed 54.49%) and then slow decomposition from 440°C to 800°C (observed 9.68%). The residue may be UO_3

(observed 34.00%; Calcd 33.66%) upon heating to 800°C for **2**. The weight of **3** is slowly lost from 170°C to 255°C (observed 1.51%), then rapidly from 255°C to 480°C (observed 63.07%) and continuously slowly from 480°C to 800°C (observed 5.86%). The residue may be UO_3 (observed 29.56%; Calcd 29.86%) upon heating to 800°C for **3**.

4. Conclusion

Three disulfoxide uranyl complexes $[UO_2(DBSOB)(NO_3)_2]_n$, $[UO_2(DBM)_2]_2(DBSOB)$, and $[UO_2(PMBP)_2]_2(DBSOB)$ were synthesized and characterized. The coordination geometry of the U(VI) atom in **1** is a distorted hexagonal bipyramid, typical for uranyl nitrate complexes [14, 18–20]. In **1**, the $[UO_2(NO_3)_2]$ groups are connected by bridging disulfoxide ligands DBSOB to form a 1-D zigzag chain. The coordination geometry of U(VI) in **2** and **3** are distorted pentagonal bipyramids, similar to β-diketonates (DBM, PMBP) and other extractant mixed-ligand uranyl complexes [8–14]. A bridging disulfoxide ligand DBSOB connects two $[UO_2(DBM)_2]$ or $[UO_2(PMBP)_2]$ groups to form the dimeric structures **2** and **3**. Thermal stabilities of **1**–**3** were investigated. Structures of sulfoxide–uranyl complexes are all mononuclear [5, 6]. Complexes **1**, **2**, and **3** are the first structurally characterized disulfoxide–actinide compounds.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, with CCDC reference nos 747670, 762995, and 762996.

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