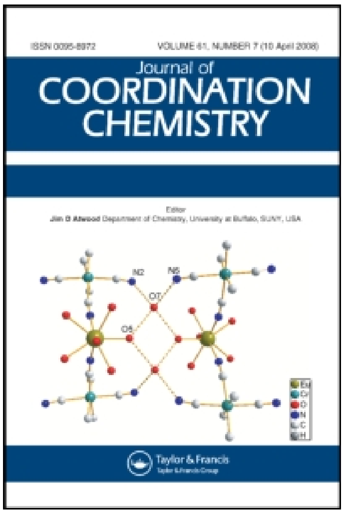

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Syntheses and structures of two new uranyl complexes $[UO_2(DPDPU)_2(NO_3)_2](C_6H_5CH_3)$ and $[UO_2(PMBP)_2(DPDPU)](CH_3C_6H_4CH_3)_{0.5}$

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Two new uranyl complexes $[UO_2(DPDPU)_2(NO_3)_2](C_6H_5CH_3)$ (**1**) and $[UO_2(PMBP)_2(DPDPU)](CH_3C_6H_4CH_3)_{0.5}$ (**2**), (DPDPU = *N*,*N*′-dipropyl-*N*,*N*′-diphenylurea, HPMBP = 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) were synthesized and characterized. The coordination geometry of the uranyl atom in **1** is distorted hexagonal bipyramidal, coordinated by two oxygen atoms of two DPDPU molecules and four oxygen atoms of two bidentate nitrate groups. The coordination geometry of the uranyl atom in **2** is distorted pentagonal bipyramidal, coordinated by one oxygen atom of one DPDPU molecule and four oxygen atoms of two chelating PMBP molecules.

Keywords: Crystal structure; Uranyl nitrate; Uranyl bis(β-diketonate); Substituted urea

1. Introduction

Tributyl phosphate (TBP) has been widely used as the extraction reagent in U–Th fuel to separate uranium from thorium. But dibutyl phosphate (DBP) and butyl phosphate (MBP), the radiolytic products of TBP, exhibit some coordination ability to fission elements, such as Zr and Nb. Substitutes for TBP have been studied for several decades [1–4]. We are interested in studying the behavior of new extractants and the crystal structures of the extracted compounds [5–11]. Substituted urea compounds are effective extractants [9–11]; 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 has been widely studied as extractant and chelating agent of metal ions [12, 13]. In this work, two new uranyl complexes $[UO_2(DPDPU)_2(NO_3)_2](C_6H_5CH_3)$ (**1**) and $[UO_2(PMBP)_2(DPDPU)]$ $(CH_3C_6H_4CH_3)_{0.5}$ (**2**), (DPDBU = *N*,*N*′-dipropyl-*N*,*N*′-diphenylurea, HPMBP

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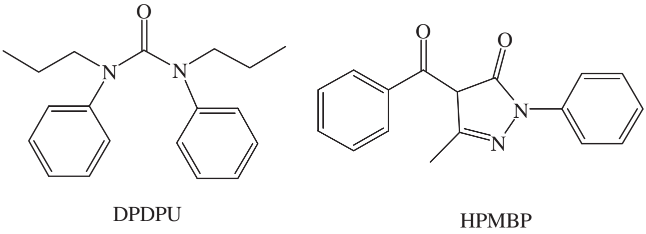

Scheme 1. Structures of the ligands.

= 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) were synthesized and characterized by using DPDPU and HPMBP (scheme 1).

2. Experimental

2.1. *Materials and physical measurements*

All reagents were analytical grade and used without further purification. $UO_2(PMBP)_2 \cdot 2H_2O$ was prepared according to the reported method [14]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region.

2.2. *Synthesis of [$UO_2(DPDPU)_2(NO_3)_2](C_6H_5CH_3)$ (1)*

A 10 mL solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.201 g, 0.2 mmol) in 3 M HNO_3 was extracted by *N*,*N*′-dipropyl-*N*,*N*′-diphenylurea (DPDPU) (0.149 g, 0.5 mmol) dissolved in 20 mL toluene at room temperature until the organic phase was saturated. The organic phase was separated and filtered. The filtrate was allowed to stand in the dark at room temperature. Yellow crystals suitable for X-ray diffraction analysis were obtained one week later. Found: C, 49.76; H, 4.96; N, 8.16. Calcd for $C_{45}H_{56}N_6O_{10}U$ (**1**): C, 50.09; H, 5.23; N, 7.79%. Main IR absorption bands (KBr, cm^{-1}): 1548vs, 1484vs, 1432s, 1382s, 1269s, 1144w, 1074w, 1025m, 930m, 743m, 696m, 568w and 463m cm^{-1}.

2.3. *Synthesis of [$UO_2(PMBP)_2(DPDPU)](CH_3C_6H_4CH_3)_{0.5}$ (2)*

A solution of DPDPU (0.070 g, 0.2 mmol) in 10 mL 1,4-dimethylbenzene was added to a solution of $UO_2(PMBP)_2 \cdot 2H_2O$ (0.172 g, 0.2 mmol) in 10 mL 1,4-dimethylbenzene and stirred for 20 min. The mixture was filtered and the filtrate was allowed to stand in the dark at room temperature. Orange crystals were obtained after two weeks. Found: C, 58.17; H, 4.65; N, 7.08. Calcd for $C_{57}H_{55}N_6O_7U$ (**1**): C, 58.31; H, 4.72; N, 7.16%. Main IR absorption bands (KBr, cm^{-1}): 1598s, 1562vs, 1471vs, 1425s, 1379m, 1296w, 1234w, 1155m, 1058vs, 949w, 919m, 833m, 833w, 756m, 694m, 656w, 609m, 472s and 417s cm^{-1}.

Table 1. Crystallographic data for **1** and **2**.

Empirical formula	$C_{45}H_{56}N_6O_{10}U$	$C_{57}H_{55}N_6O_7U$
Formula weight	1078.99	1174.10
Temperature (K)	193(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.692(2)	10.3280(8)
b (Å)	9.735(2)	13.2320(11)
c (Å)	13.398(3)	19.9762(15)
	73.394(15)	71.895(5)
β (°)	74.767(17)	83.801(7)
	88.32(2)	83.357(7)
V (Å^3)	1167.4(4)	2569.9(4)
Z	1	2
$F(000)$	540	1174
ρ (g cm^{-3})	1.535	1.517
μ (mm^{-1})	3.537	3.217
Crystal size (mm^3)	0.30 × 0.20 × 0.12	0.45 × 0.42 × 0.13
θ range for data collection (°)	3.01–25.33	3.01–25.35
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-14 \le l \le 16$	$-12 \le h \le 11$, $-15 \le k \le 15$, $-24 \le l \le 24$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	4238 [R(int) = 0.0478]	9336 [R(int) = 0.0293]
Parameter	305	641
Goodness of fit S	1.011	1.042
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0365, 0.0704	0.0292, 0.0684
R_1 and wR_2 indices (all data)	0.0381, 0.0715	0.0327, 0.0703
Largest diff. peak and hole (e Å^{-3})	0.913 and −2.241	1.639 and −1.210

2.4. *Crystal structure determination*

The single crystals of **1** and **2** with approximate dimensions 0.30 × 0.20 × 0.12 and 0.45 × 0.42 × 0.13 mm^3 were selected for lattice parameter determination and collection of intensity data using 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 technique (SHELXTL-97) [15]. The positions of hydrogen atoms were determined with theoretical calculation except that the hydrogen atoms of the disordered toluene were not located. The parameters of the crystal data collection and refinement of **1** and **2** are given in table 1. Selected bond lengths and bond angles of **1** and **2** are shown in table 2.

3. Results and discussion

The IR absorption band at 930 cm^{-1} in **1** is assigned to the asymmetric stretching band (ν_{asym}) of UO_2^{2+}. The absorption bands at 1484, 1269, 1025 and 743 cm^{-1} are attributed to NO_3^- [16, 17]. The C=O absorption band of free DPDPU ligand is at 1656 cm^{-1} but changes to 1548 cm^{-1} for complex **1**. The asymmetric stretching band (ν_{asym}) of UO_2^{2+} of **2** is at 919 cm^{-1}. The C=O absorption band of free HPMBP at 1640 cm^{-1} changes to 1598 cm^{-1} for complex **2** [12]. The absorption at 1562 cm^{-1} is attributed to the C=O

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

1			
U(1)–O(2)	1.762(3)	U(1)–O(1)	2.361(3)
U(1)–O(3)	2.515(3)	U(1)–O(4)	2.518(3)
O(1)–U(1)–O(3)	64.94(10)	O(3)–U(1)–O(4)	50.59(10)
O(1)–U(1)–O(4A)	64.66(10)	O(2)–U(1)–O(1)	89.29(12)
O(2)–U(1)–O(3)	90.71(12)	O(2)–U(1)–O(4)	87.16(12)
2			
U(1)–O(1)	1.771(2)	U(1)–O(2)	1.772(2)
U(1)–O(3)	2.342(2)	U(1)–O(4)	2.396(2)
U(1)–O(5)	2.367(2)	U(1)–O(6)	2.410(2)
U(1)–O(7)	2.378(2)		
O(1)–U(1)–O(2)	179.42(11)	O(3)–U(1)–O(4)	71.25(8)
O(4)–U(1)–O(5)	72.68(8)	O(5)–U(1)–O(6)	71.72(8)
O(6)–U(1)–O(7)	71.30(8)	O(7)–U(1)–O(3)	73.67(8)
O(1)–U(1)–O(3)	92.70(10)	O(1)–U(1)–O(4)	86.89(10)
O(1)–U(1)–O(5)	94.06(10)	O(1)–U(1)–O(6)	89.29(10)
O(1)–U(1)–O(7)	89.98(10)	O(2)–U(1)–O(3)	87.89(10)
O(2)–U(1)–O(4)	93.32(10)	O(2)–U(1)–O(5)	85.49(10)
O(2)–U(1)–O(6)	90.22(10)	O(2)–U(1)–O(7)	90.16(10)

Symmetry code: A $-x+2$, $-y$, $-z+2$.

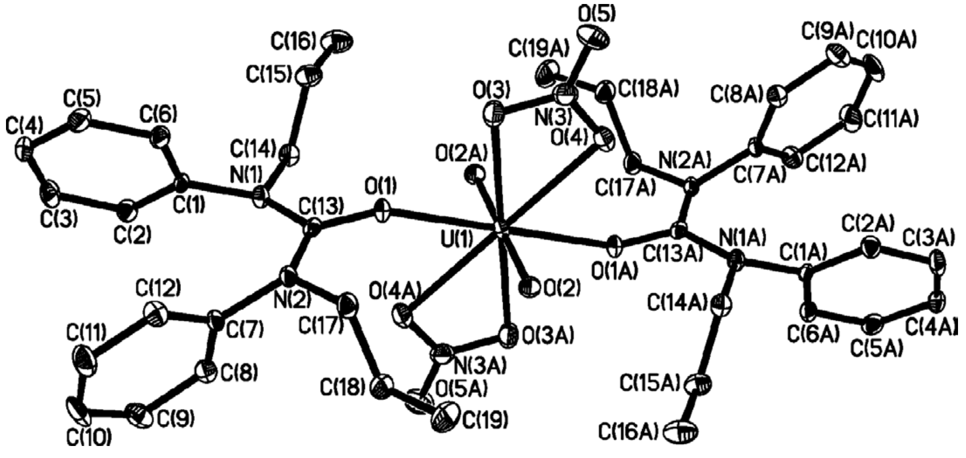

Figure 1. Local coordination of U(VI) in **1** with 30% thermal ellipsoids.

absorption of the coordinated DPDPU ligand. These results are confirmed by the X-ray crystal structures of complexes **1** and **2**.

X-ray diffraction analysis shows that **1** contains coordinated uranyl [UO_2(DPDPU)$_2$(NO_3)$_2$] and a disordered toluene molecule. Figure 1 shows the local coordination of the U(VI) atom in **1**. Each U(VI) atom is situated at the center of symmetry. The coordination geometry of the U(VI) atom is distorted hexagonal bipyramidal. The equatorial plane is defined by two oxygen atoms [U(1)–O(1) 2.361(3) Å] from the carbonyl groups of two symmetry-related DPDPU ligands, and four oxygen atoms [U(1)–O(3) = 2.515(3) Å], [U(1)–O(4) = 2.518(3) Å] from two symmetry-related bidentate nitrate groups, with the mean deviation of 0.0506 Å from the plane. The U–O (DPDPU) bond lengths [2.361(3) Å] are much shorter than the U–O (nitrate) bond lengths [2.515(3) to 2.518(3) Å].

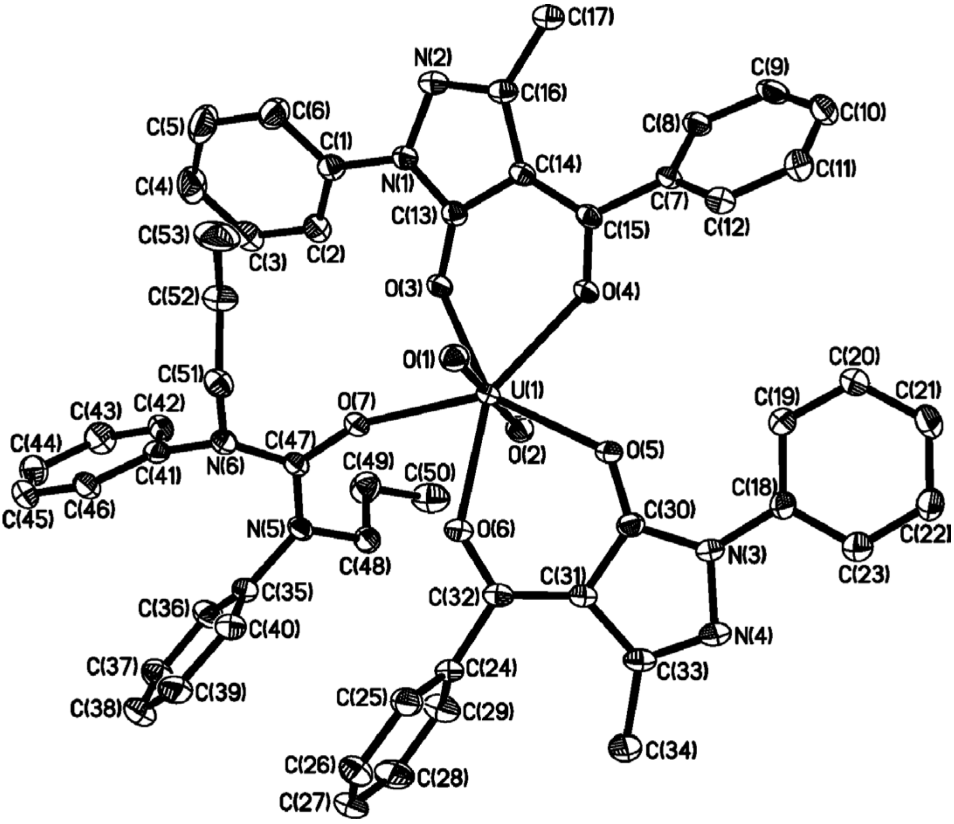

Figure 2. Local coordination of U(VI) in **2** with 30% thermal ellipsoids.

The axial positions are occupied by two oxygen atoms [U(1)–O(2) = 1.762(3) Å] of two symmetry-related oxygen ligands. This coordination geometry is the typical of uranyl nitrate complexes and the same as found in $UO_2(NO_3)_2 \cdot 6H_2O$ [18], $[UO_2(NO_3)_2(C_{11}H_{22}N_2O)_2]$ [5], $UO_2(NO_3)_2[CH_2(CH_2)_2CONC_8H_{17}]_2$ [6], $UO_2(NO_3)_2[PhN(C_2H_5)C(O)(C_2H_5)NPh]_2$ [9], $UO_2(NO_3)_2[PhN(CH_3)C(O)(CH_3)NPh]_2$ [10]. The average bond lengths for U–O (uranyl) [1.762(3) Å], U–O (DPDPU) [2.361(3) Å] and U–O (nitrate) [2.517(3) Å] agree well with the literature complexes [5, 6, 9, 10].

X-ray diffraction analysis shows that **2** contains coordinated uranyl $[UO_2(PMBP)_2(DPDPU)]$ and 1,4-dimethylbenzene (Figure 2). The uranium atom in **2** is surrounded by seven oxygen atoms in a distorted pentagonal bipyramidal geometry. The four oxygen atoms [U(1)–O(3) = 2.342(2) Å, U(1)–O(4) = 2.396(2) Å, U(1)–O(5) = 2.367(2) Å, U(1)–O(6) = 2.410(2) Å] of two PMBP ligands and one oxygen [U(1)–O(7) = 2.378(2) Å] of DPDPU form a planar pentagon and these oxygen atoms are coplanar with mean deviation of 0.0811 Å from the plane. The axial positions are occupied by two oxygen atom ligands [U(1)–O(1) = 1.771(2) Å, U(1)–O(2) = 1.772(2) Å]. This coordination geometry is similar to those in $[UO_2(PMBP)_2(DMSO)]$ (DMSO = dimethylsulfoxide) [19], $[UO_2(DBM)_2(DPPMO)]$ and $[\{UO_2(DBM)_2\}_2(DPPMO)]$ (HDBM = dibenzoylmethane, DPPMO = bis(diphenylphosphino)methane dioxide) [20]. The observed bond lengths of U–O (PMBP) are in the range of 2.342(2) to 2.410(2) Å in **1**, compared to the values [from 2.325(7) to 2.403(6) Å] in [$UO_2(PMBP)_2(DMSO)$] [19]. The average U–O (PMBP) bond lengths are 2.379(2) Å in **1** and 2.367(7) Å in [$UO_2(PMBP)_2(DMSO)$]. The bond length of U–O (DPDPU) in **1** is 2.378(2) Å, similar to the value of U–O (DMSO) (2.378(7) Å) in [$UO_2(PMBP)_2(DMSO)$]. The U–O average bond lengths in the axial positions are 1.772(2) Å in **1** and 1.750(8) Å in [$UO_2(PMBP)_2(DMSO)$], much shorter than the U–O average bond lengths in the plane [2.379(2) Å in **1** and 2.369(7) Å in [$UO_2(PMBP)_2(DMSO)$]] [19].

When [$UO_2(PMBP)_2(DPDPU)$]($CH_3C_6H_4CH_3$)$_{0.5}$ (**2**) is compared with [$UO_2(DPDPU)_2(NO_3)_2$]($C_6H_5CH_3$) (**1**), the two larger PMBP ligand molecules in **2** instead of two nitrate ions in **1** resulted in the uranyl in **2** only coordinated by one DPDPU ligand molecule while the uranyl in **1** is coordinated by two DPDPU molecules. The coordination geometry of the U(VI) atom is a distorted hexagonal bipyramid in **1** and a distorted pentagonal bipyramid geometry in **2**.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference numbers are 286404 and 286405.

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