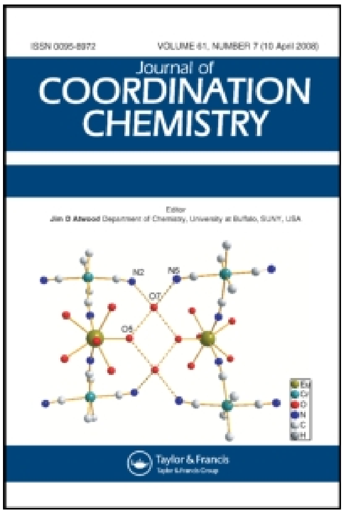

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Synthesis and structures of two uranyl β-diketonate complexes $[UO_2(DBM)_2(DEDPU)]$ and $[UO_2(PMBP)_2(DEDPU)]$

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Synthesis and structures of two uranyl *β*-diketonate complexes $[UO_2(DBM)_2(DEDPU)]$ and $[UO_2(PMBP)_2(DEDPU)]$

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Two new uranyl *β*-diketonate complexes $[UO_2(DBM)_2(DEDPU)]$ (**1**) and $[UO_2(PMBP)_2(DEDPU)](CH_3C_6H_5)_{0.5}$ (**2**), (HDBM = dibenzoylmethane, HPMBP = 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, DEDPU = *N*,*N*′-diethyl-*N*,*N*′-diphenylurea) were synthesized and characterized. The coordination geometries of the uranyl atoms in **1** and **2** are distorted pentagonal bipyramidal, coordinated by one oxygen atom of DBDPU molecule and four oxygen atoms of two chelating DBM molecules in **1** and PMBP molecules in **2**.

Keywords: Crystal structure; 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 di-butyl 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 sought for decades. Substituted sulphoxides [1–3] and amide [4–8] are effective extractants in solvent extraction separation of actinide ion from acid media. Raymond recently reviewed the rational design of sequestering agents for plutonium and other actinides [9]. Mathur recently reviewed actinide partitioning [10], emphasizing extraction performance of fully-optimized reagents, comparing the salient features of the various techniques and reagents for actinide recycling and presenting the separation and recovery of actinides from TRU wastes.

Dibenzoylmethane (HDBM) [11–13], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) [14–27] and other *β*-diketonates [22, 28, 29] have been widely studied as extractants and chelating agents of lanthanide [14–21], actinide [12, 13, 21, 22, 28, 29] and other metal ions [11, 12, 23–27]. The mixture of *β*-diketonates and other extractants

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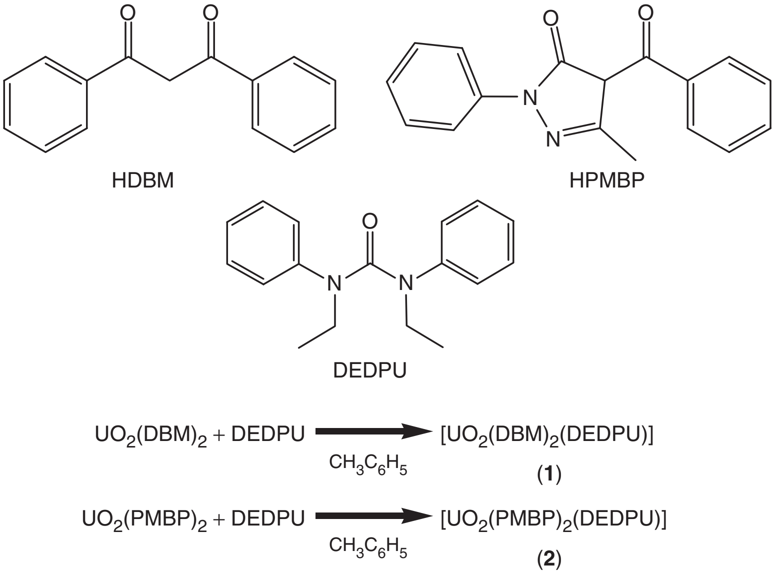
can enhance effective extraction of metal anions [11, 12, 17–22, 28, 29]. Dibenzoylmethane (HDBM) [30–36] and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) [14, 37–40] with uranyl [30–33, 37], lanthanide [14, 34, 38] and other metal complexes [35, 36, 39, 40] were characterized structurally. Previously, our laboratory studied the extraction of uranyl using substituted sulphoxides [3, 41, 42] and amides [43] and determined some crystal structures of uranyl complexes [44–46]. Recently we explored the extraction behavior [47–49] of substituted urea *N*,*N*′-diethyl-*N*,*N*′-diphenylurea (DEDPU), *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea (DMDPU) and tetrabutylurea and determined the crystal structures with uranylnitrate [47, 50]. To expand our work, we synthesized and characterized two new uranyl β-diketonate complexes $[UO_2(DBM)_2(DEDPU)]$ (**1**) and $[UO_2(PMBP)_2(DEDPU)](CH_3C_6H_5)_{0.5}$ (**2**), (HDBM = dibenzoylmethane, HPMBP = 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5, DEDPU = *N*,*N*′-diethyl-*N*,*N*′-diphenylurea).

2. Experimental

2.1. *Materials and physical measurements*

All reagents were of analytical grade and used without further purification. $UO_2(DBM)_2 \cdot 2H_2O$ and $UO_2(PMBP)_2 \cdot 2H_2O$ were prepared according to reported methods [51]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were obtained as KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. Scheme 1 shows the structures of the ligands and the synthesis of **1** and **2**.



Scheme 1. The structures of the ligands and the synthesis reaction of the complexes **1** and **2**.

2.2. *Synthesis of [$UO_2(DBM)_2(DEDPU)$] (1)*

A solution of DEDPU (0.064 g, 0.2 mmol) in 10 mL toluene was added to a solution of $UO_2(DBM)_2 \cdot 2H_2O$ (0.150 g, 0.2 mmol) in 10 mL toluene and stirred for 20 min. The mixture was filtered and the filtrate was allowed to stand under the desk at room temperature. The orange-yellow crystals of **1** were obtained after two weeks. Yield: 81%. Found: C, 57.24; H, 4.26; N, 2.78. Calcd for $C_{47}H_{42}N_2O_7U$ (**1**): C, 57.32; H, 4.30; N, 2.84%. Main IR absorption bands (KBr, cm^{-1}): 1590s, 1544s, 1520s, 1474s, 1451m, 1373s, 1304m, 1258w, 1227w, 1189w, 1134w, 1065w, 1027w, 911m, 756m, 717m, 695m, 610w, 517m and 448w cm^{-1}.

2.3. *Synthesis of [$UO_2(PMBP)_2(DEDPU)$] ($CH_3C_6H_5$)$_{0.5}$ (2)*

A solution of DEDPU (0.064 g, 0.2 mmol) in 10 mL toluene was added to a solution of $UO_2(PMBP)_2 \cdot 2H_2O$ (0.172 g, 0.2 mmol) in 10 mL toluene, stirred for 20 min and the mixture was filtered. Orange crystals of **2** were obtained after one week. Yield: 76%. Found: C, 57.28; H, 4.26; N, 7.43. Calcd for $C_{54.50}H_{50}N_6O_7U$ (**2**): C, 57.47; H, 4.42; N, 7.38%. Main IR absorption bands (KBr, cm^{-1}): 3431m, 3060w, 2970w, 1598s, 1563s, 1472s, 1427s, 1375m, 1250w, 1157m, 1073w, 1025w, 918s, 834w, 759m, 695m, 656w, 613w, 543w, 508w, 461w and 409w cm^{-1}.

2.4. *Crystal structure determination*

The single crystals of **1** and **2** with approximate dimensions $0.30 \times 0.20 \times 0.12$ and $0.45 \times 0.42 \times 0.13\ mm^3$ 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) [52]. 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 918 cm^{-1} in **1** and **2** is assigned to the asymmetric stretching bands (ν_{asym}) of UO_2^{2+}. The C=O absorption bands of DBM and DEDPU in **1** are 1590 and 1544 cm^{-1}, respectively [30–32]. The C=O absorption bands of PMBP and DEDPU in **2** are 1598 and 1563 cm^{-1}, respectively [53].

X-ray diffraction analysis shows that **1** consists of neutral [$UO_2(DBM)_2(DEDPU)$] (figure 1) and **2** contains coordinated uranyl [$UO_2(PMBP)_2(DEDPU)$] and disordered toluene molecule (figure 3). The cell packing structures of **1** and **2** are shown in figures 4 and 5 respectively. The uranium atoms in **1** and **2** are both surrounded by seven oxygen atoms in a distorted pentagonal bipyramid. Four oxygen atoms [U(1)–O(1)

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

Empirical formula	$C_{47}H_{42}N_2O_7U$	$C_{54.50}H_{50}N_6O_7U$
Formula weight	984.86	1139.04
Temperature (K)	173(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	13.0284(7)	10.2660(10)
b (Å)	17.4893(9)	13.3960(11)
c (Å)	18.2553(10)	18.5124(17)
α (°)	90	77.788(5)
β (°)	98.0000(10)	78.387(5)
γ (°)	90	84.348(6)
V (Å^3)	4119.1(4)	2433.2(4)
Z	4	2
$F(000)$	1944	1134
ρ (g cm^{-3})	1.588	1.555
μ (mm^{-1})	3.994	3.395
Crystal size (mm^3)	0.40 × 0.35 × 0.25	0.45 × 0.15 × 0.07
θ range for data collection (°)	3.15–27.48	3.01–25.68
Index ranges	$-16 \le h \le 14$, $-22 \le k \le 22$, $-20 \le l \le 23$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 22$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	4677 [$R_{\mathrm{int}} = 0.0284$]	9207 [$R_{\mathrm{int}} = 0.0357$]
Parameter	260	607
Goodness of fit S	1.100	1.049
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0218, 0.0512	0.0350, 0.0752
R_1 and wR_2 indices (all data)	0.0238, 0.0521	0.0410, 0.0790
Largest diff. peak and hole (e Å^{-3})	0.949 and −0.784	1.646 and −1.148

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

1			
U(1)–O(1)	2.3545(18)	U(1)–O(2)	2.3596(16)
U(1)–O(3)	2.369(3)	U(1)–O(4)	1.7739(19)
O(1)–U(1)–O(2)	70.66(6)	O(2)–U(1)–O(3)	142.89(4)
O(1)–U(1)–O(3)	72.60(4)	O(1)–U(1)–O(1A)	145.19(8)
O(2)–U(1)–O(2A)	74.21(8)	O(4)–U(1)–O(4A)	179.80(10)
O(4)–U(1)–O(1)	91.90(8)	O(4)–U(1)–O(2)	86.34(7)
O(4)–U(1)–O(3)	89.90(5)		
2			
U(1)–O(1)	1.772(3)	U(1)–O(2)	1.757(3)
U(1)–O(3)	2.400(3)	U(1)–O(4)	2.350(3)
U(1)–O(5)	2.419(3)	U(1)–O(6)	2.335(3)
U(1)–O(7)	2.359(3)		
O(4)–U(1)–O(3)	72.10(10)	O(4)–U(1)–O(5)	71.15(9)
O(6)–U(1)–O(5)	72.13(9)	O(6)–U(1)–O(7)	73.56(10)
O(3)–U(1)–O(5)	142.72(10)	O(6)–U(1)–O(3)	145.13(10)
O(7)–U(1)–O(3)	71.77(10)	O(6)–U(1)–O(4)	142.29(10)
O(4)–U(1)–O(7)	143.84(10)	O(7)–U(1)–O(5)	144.86(9)
O(2)–U(1)–O(1)	179.46(14)	O(1)–U(1)–O(3)	89.48(13)
O(1)–U(1)–O(4)	92.63(13)	O(1)–U(1)–O(5)	86.16(12)
O(1)–U(1)–O(6)	93.22(12)	O(1)–U(1)–O(7)	88.39(12)
O(2)–U(1)–O(3)	90.02(13)	O(2)–U(1)–O(4)	87.02(13)
O(2)–U(1)–O(5)	94.12(12)	O(2)–U(1)–O(6)	87.31(13)
O(2)–U(1)–O(7)	91.65(12)		

Symmetry code: A: $-x+1$, y, $-z+1/2$ for **1**.

2.3545(18) Å, U(1)–O(2) 2.3596(16) Å] of two symmetry-related DBM ligands in **1** and one oxygen [U(1)–O(3) 2.369(3) Å] of one DEDPU form a planar pentagon. The axial positions are occupied by two oxygen atom ligands [U(1)–O(4) 1.7739(19) Å]. The four oxygen atoms [U(1)–O(3) 2.400(3) Å, U(1)–O(4) 2.350(3) Å, U(1)–O(5) 2.419(3) Å, U(1)–O(6) 2.335(3) Å] of two independent PMBP ligands in **2** and one

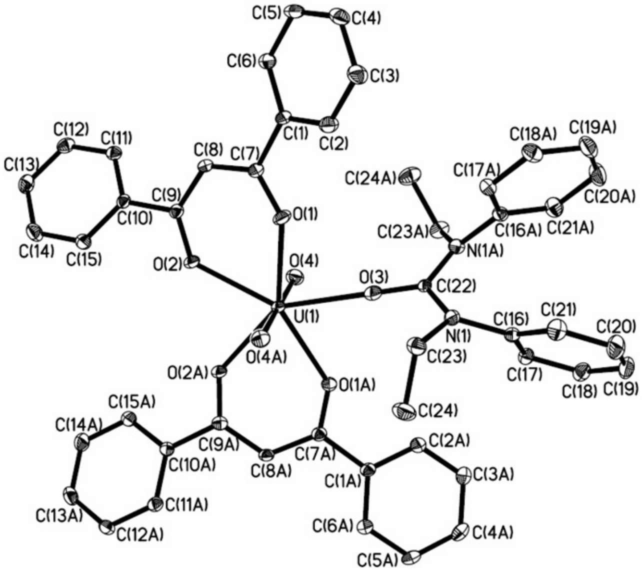


Figure 1. Local coordination of U(VI) in **1** with 30% thermal ellipsoids.

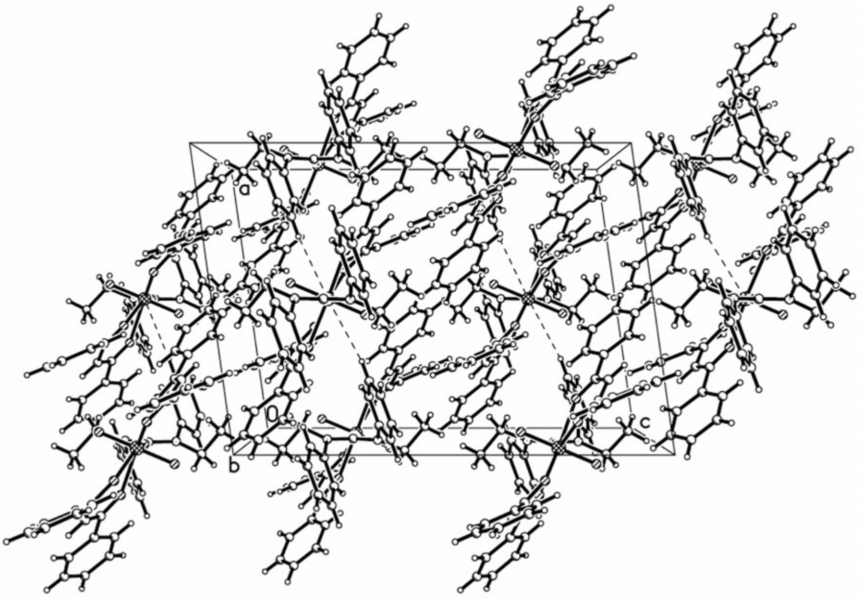


Figure 2. The cell packing structure of **1**.

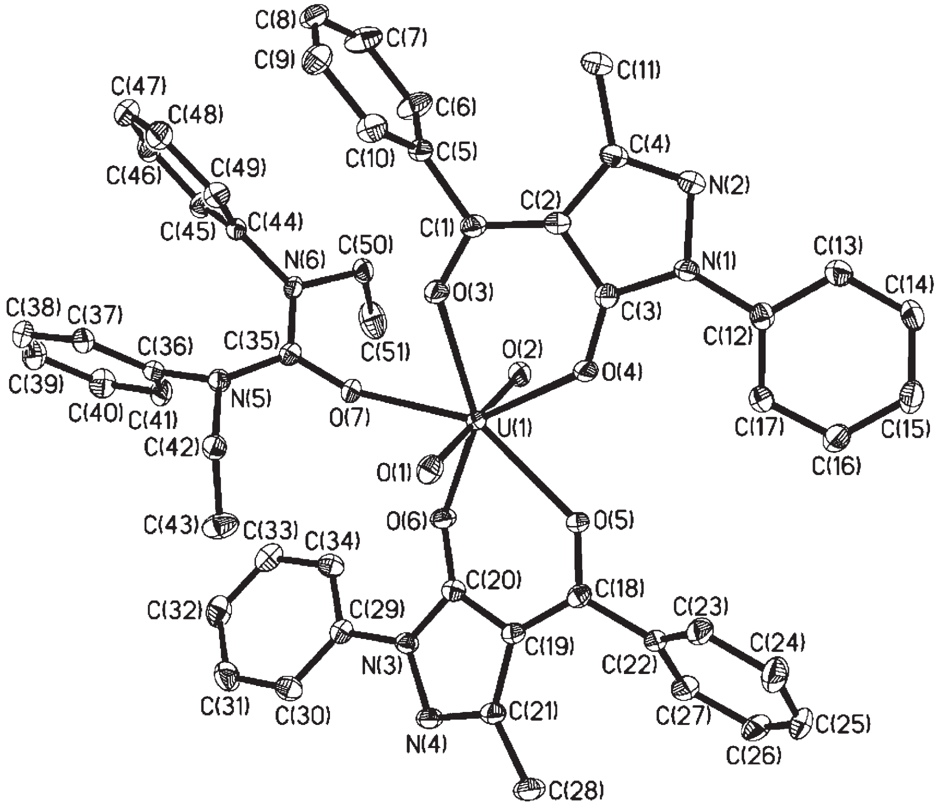


Figure 3. Local coordination of U(VI) in **2** with 30% thermal ellipsoids.

oxygen [U(1)–O(7) 2.359(3) Å] of one DEDPU form a planar pentagon and these oxygen atoms are coplanar to with the mean deviation of 0.0992 Å from the plane. The axial positions are occupied by two oxygen atom ligands [U(1)–O(1) 1.772(3) Å, U(1)–O(2) 1.757(3) Å].

This coordination geometries in **1** and **2** are similar to those in [UO$_2$(DBM)$_2$(camphor)] [30], [{UO$_2$(DBM)$_2$}$_2${(C$_6$H$_5$NHCO)$_2$CH$_2$}] [31], [UO$_2$(DBM)$_2$(DPPMO)] and [{UO$_2$(DBM)$_2$}$_2$(DPPMO)] (HDBM = dibenzoylmethane, DPPMO = *bis*(diphenylphosphino)methane dioxide) [32], [UO$_2$(DBM)$_2$ (Ph$_3$PO)] (Ph$_3$PO = triphenylphosphine oxide) [33], [UO$_2$(PMBP)$_2$(DMSO)] (DMSO = dimethylsulfoxide) [37]. The observed average bond lengths for U–O (uranyl) (1.7739(19) Å for **1** and 1.764(3) Å for **2**) agree well with reported values. The observed bond length for U–O (DBM) for **1** is 2.3570(18) Å, similar to reported values [30–33]. The observed bond length for U–O (PMBP) for **2** is 2.376(3) Å, compared to the value 2.367(7) Å in [UO$_2$(PMBP)$_2$(DMSO)] [37]. The U–O (DEDPU) bond lengths are 2.369(3) and 2.359(3) Å in **1** and **2**, respectively.

When [UO$_2$(DBM)$_2$(DEDPU)] (**1**) and [UO$_2$(PMBP)$_2$(DEDPU)](CH$_3$C$_6$H$_5$)$_{0.5}$ (**2**) are compared with [UO$_2$(DEDPU)$_2$(NO$_3$)$_2$] [47], two larger DBM and PMBP ligands in **1** and **2** instead of two nitrate ions in [UO$_2$(DEDPU)$_2$(NO$_3$)$_2$] resulted in the uranyl in **1** and **2** only able to coordinate one DPDPU while the uranyl in

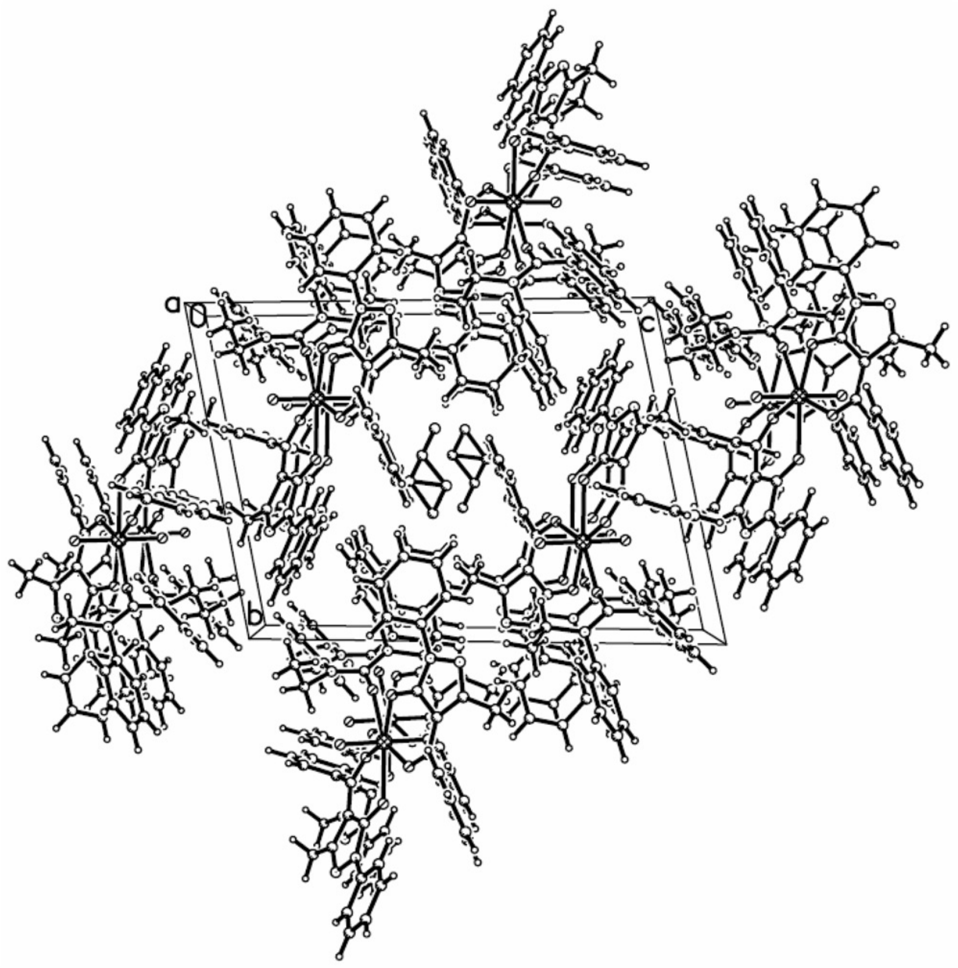


Figure 4. The cell packing structure of **2**.

$[UO_2(DEDPU)_2(NO_3)_2]$ can coordinate two DPDPU ligands due to steric constraints of two DBM in **1** and PMBP molecules in **2**. The coordination geometries of the U(VI) atoms are the distorted hexagonal bipyramid in $[UO_2(DEDPU)_2(NO_3)_2]$ [47] and a distorted pentagonal bipyramid in **1** and **2**.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (Email: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference numbers for **1** and **2** are 620317 and 620318, respectively.

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