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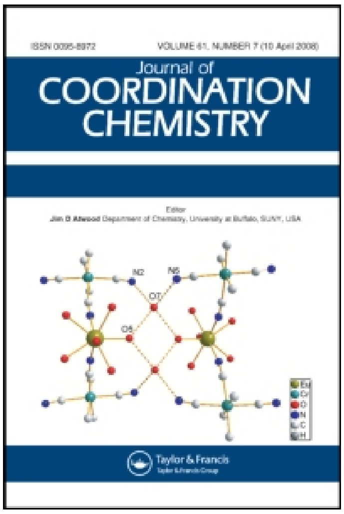

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Hydrothermal syntheses and crystal structures of new uranyl complexes: UO_2(<i>p</i> -$C_7H_4O_2Br)_2(H_2O)$ and UO_2(<i>m</i> -$C_7H_4O_2Br)_2$

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Hydrothermal syntheses and crystal structures of new uranyl complexes: $UO_2(p\text{-}C_7H_4O_2Br)_2(H_2O)$ and $UO_2(m\text{-}C_7H_4O_2Br)_2$

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Two uranyl complexes, $UO_2(p\text{-}C_7H_4O_2Br)_2(H_2O)$ and $UO_2(m\text{-}C_7H_4O_2Br)_2$, are synthesized by hydrothermal method and their structures determined by single-crystal X-ray diffraction. $UO_2(p\text{-}C_7H_4O_2Br)_2(H_2O)$: $R = 0.0606$, monoclinic, space group $P2(1)/c$, with $a = 19.8400(12)$ Å, $b = 8.8081(5)$ Å, $c = 10.0914(6)$ Å, $\alpha = 90°$, $\beta = 92.687(2)°$, $\gamma = 90°$, $Z = 4$, has a chair configuration with two UO_2^{2+} cations. $UO_2(m\text{-}C_7H_4O_2Br)_2$: $R = 0.0333$, monoclinic, space group $P2(1)/c$, with $a = 5.1084(7)$ Å, $b = 17.642(3)$ Å, $c = 9.0716(13)$ Å, $\alpha = 90°$, $\beta = 94.063(2)°$, $\gamma = 90(2)°$, $Z = 2$, forms a 1D chain with the ligand (*m*-bromobenzoic acid) taking the bridging mode.

Keywords: Humic acid; Uranium complex; Hydrothermal reaction; Crystal structure

1. Introduction

Renewal of interest in the chemistry of compounds containing uranyl ion reflects its considerable compositional range, chemical and structural diversity with various dimensionalities, properties and potential applications in nuclear industry, ion-exchange and catalysis [1–10].

The uranyl ion can also model the migration of radionuclides in the environment because the most important mechanism is the complexation of radionuclides by carboxylate groups of natural humic acids from water [11]. Humic acid contains a variety of functional groups (–COOH, –OH, $-NH_2$, etc.) which can form stable chelate complexes with uranyl ion (UO_2^{2+}) [12]. Speciation and structural information of the UO_2^{2+} -humate complexes are important to a mechanism describing uranium transport underground. Under geological condition, humic substances are coordinated with UO_2^{2+} and the soluble complex moves with the groundwater. When the complex meets a reducing barrier formed by H_2, CH_4, H_2S etc., UO_2^{2+} is reduced to UO_2 and deposited as mineral.

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In order to gain better understanding of the intrinsic interactions between uranyl ion and humic substances, some organic acids as model compounds were chosen to react with uranium(VI). In the present study, we report the synthesis of two new uranyl bromobenzoic acid complexes by hydrothermal synthesis. The crystal structures of two uranyl complexes are reported.

2. Experimental

All chemicals were used as purchased without further purification. Distilled and millipore filtered water with a resistance of 18.2 MΩ was used in all reactions. CAUTION: Uranyl oxynitrate is radioactive and standard precautions for handling radioactive substances should be followed.

2.1. *Syntheses of the complexes*

2.1.1. $UO_2(C_7H_4O_2Br)_2(H_2O)$ (1). A mixture of uranium oxynitrate hexahydrate 0.1259 g (0.25 mmol), *p*-bromobenzoic acid 0.1009 g (0.5 mmol) and 0.0155 g (0.3 mmol) potassium hydroxide in deionized water (10 mL) was prepared in a 23 mL (pH = 4.5) Teflon-lined Parr bomb and then heated statically at 180°C for 7 days, followed by slow cooling at 10°C h^{-1} to room temperature. Bright yellow crystals were filtered, washed with water and dried in air. Yield: 0.0833 g, 48.6%. Anal. Calcd for **1**: C, 24.45; H, 1.46. Found: C, 24.14; H, 1.88.

2.1.2. $UO_2(C_7H_4O_2Br)_2$ (2). A mixture of uranium oxynitrate hexahydrate 0.1259 g (0.25 mmol), *m*-bromobenzoic acid 0.1051 g (0.5 mmol) and 0.0155 g (0.3 mmol) potassium hydroxide in deionized water (10 mL) was prepared in a 23 mL (pH = 4.5) Teflon-lined Parr bomb and then heated statically at 180°C for 7 days, followed by slow cooling at 10°C h^{-1} to room temperature. Bright yellow crystals were filtered, washed with water and dried in air. Yield: 0.0637 g, 38.0%. Anal. Calcd for **2**: C, 25.10; H, 1.20. Found: C, 25.26; H, 1.31.

2.2. *X-ray crystallographic analysis*

Data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiaton ($\lambda = 0.71073$ Å). Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed tube and a monocapillary collimator. SMART was used for preliminary determination of the cell constants and data collection control. The determination of integral intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integration algorithm. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix least-squares method on F^2. The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Selected data collection parameters and crystallographic characteristics are provided in table 1. Additional details can be found in Supporting Information.

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3. Results and discussion

3.1. *Description of the crystal structures*

3.1.1. Crystal structure of 1. Compound **1** contains a dinuclear unit (figure 1). Both of the two uranium atoms are seven-coordinate in a pentagonal bipyramidal structure, including uranyl ion, four carboxylate oxygens and a water. The U–O distance in the

Table 1. Crystal data and structure refinement for $UO_2(p\text{-}C_7H_4O_2Br)_2(H_2O)$ and $UO_2(m\text{-}C_7H_4O_2Br)_2$.

Complex	**1**	**2**
Chemical formula	$C_{14}H_{10}Br_2O_7U$	$C_{14}H_8Br_2O_6U$
M (g mol^{-1})	687.98	670.00
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions (Å, °)		
a	19.8400(12)	5.1084(7)
b	8.8081(5)	17.642(3)
c	10.0914(6)	9.0716(13)
α	90	90
β	92.687(2)	94.063(2)
V (Å^3)	1761.56(18)	815.5(2)
Z	4	2
D_{Calcd} (g cm^{-3})	2.587	1.694
μ (mm^{-1})	2.587	1.694
$F(000)$	1240	383
θ range	2.06–28.37	2.31–25.10
T (K)	273(2)	273(2)
Number of data collected	12466	4059
Number of unique data	4386	1438
Number of parameters	218	107
R_1^a	0.0606	0.0333
wR_2^b	0.0804	0.0603
Independent reflections (R_{int})	4386	1438
	0.0529	0.0344
Goodness-of-fit on F^2	1.137	1.338
Final R indices	$R_1=0.0382$, $wR_2=0.0750$	$R_1=0.0255$, $wR_2=0.0588$
R indices (all data)	$R_1=0.0606$, $wR_2=0.0804$	$R_1=0.0333$, $wR_2=0.0603$
Largest diff. in peak and hole (e Å^{-3})	1.621 and −1.837	1.349 and −1.379

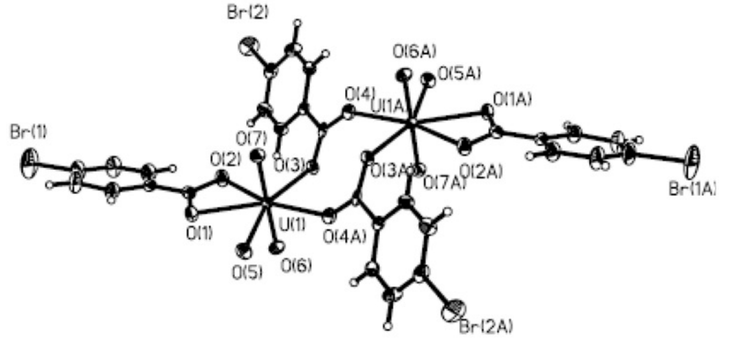

Figure 1. The crystal structure for **1**, ellipsoids are drawn at the 30% probability level.

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uranyl groups (O6, O7, etc.) ranges from 1.758 to 1.765 Å, mean value 1.761 Å, a little shorter than reference distance reported [13, 14]. The U–O distances in the equatorial plane (O1, O2, O3, O4, O5, etc.) are quite different and lie in a range between 2.313 and 2.470 Å with average 2.384 Å, well in agreement with the values in a similar complex [15]. The five donor atoms define a plane with mean deviation of 0.0538 Å, the uranium atom being 0.0227 Å out of the plane (table 2).

Four *p*-bromobenzoic acids have two coordination modes. Two ligands are bidentate chelating, while the other two ligands are bidentate bridging. Two uranium atoms are connected into a dinuclear unit by bridging *p*-bromobenzoic acids. A view down the diagonal of the *ac* plane reveals a chair configuration with bridging ligands as chair surface and chelating ligands as chair foot and backrest. The coordinated water forms hydrogen bonds with carboxylic and uranyl oxygens. The O–O (O5–O1, O5–O6, O5–O7) distances are 2.800 to 2.958 Å. Adjacent units are linked to form a two-dimensional porous sheet structure via hydrogen bonds along the *bc* plane (figure 2).

3.1.2. Crystal structure of 2.

Compound **2** contains a mononuclear unit (figure 3). The U(VI) is six-coordinate octahedral, including two uranyl oxygens and four carboxyl oxygens, forming a coordination polymer (figure 4). The bond lengths of U(1)–O(1) and U(1)–O(1A) are 2.311(4) Å. The O(1)–U(1)–O(1A) and

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

U(1)–O(1)	2.421(4)	U(1)–O(7)	1.758(4)	C(2)–C(3)	1.385(10)
U(1)–O(2)	2.400(5)	Br(1)–C(5)	1.880(7)	C(2)–C(7)	1.394(10)
U(1)–O(3)	2.313(4)	Br(2)–C(12)	1.899(7)	C(3)–C(4)	1.385(10)
U(1)–O(4)#1	2.341(5)	C(1)–O(1)	1.265(8)	C(4)–C(5)	1.380(12)
U(1)–O(5)	2.470(4)	C(1)–O(2)	1.290(8)	C(5)–C(6)	1.353(12)
U(1)–O(6)	1.765(4)	C(1)–C(2)	1.456(9)	C(6)–C(7)	1.361(10)
O(7)–U(1)–O(6)	179.07(19)	O(3)–U(1)–O(2)	78.69(15)		
O(7)–U(1)–O(3)	90.14(18)	O(2)–U(1)–O(1)	54.21(15)		
O(6)–U(1)–O(3)	88.95(18)	O(4)$^{\#1}$–U(1)–O(5)	74.13(15)		
O(3)–U(1)–O(4)#1	83.01(15)	O(1)–U(1)–O(5)	70.15(15)		

#1 = $-x+2, -y+2, -z+2$.

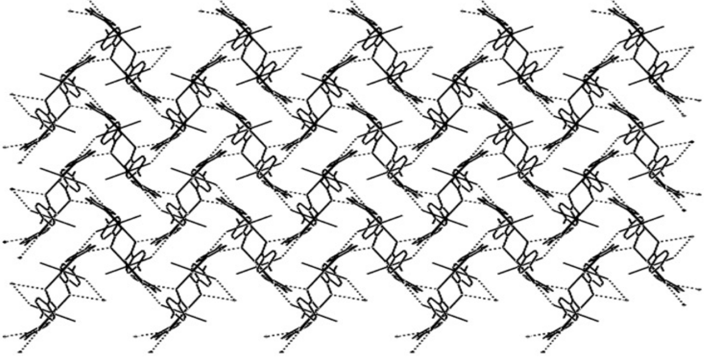

Figure 2. A view of the 2D porous sheet structure along the *bc* plane for **1**.

O(2)–U(1)–O(2A) bond angles are 179.999°(1) and 179.998°(1). The U(1)–O(2), U(1)–O(2A) distances are 1.755 Å, and the U(1)–O(3), U(1)–O(3A) distances are 2.290 Å (table 3). U(1) and four carboxyl oxygen atoms (O1, O1A, O3, O3A) from four *m*-bromobenzoic acid molecules are in the equatorial plane, and the line of O2–U1–O2A plumbs this equatorial plane. The *m*-bromobenzoic acid takes the mode of bridging, linking the uranyl ion to a 1D chain. The coordination of carboxyl is similar to that reported in the literature [13, 16].

Complex **2** forms a three-dimensional structure by van der waals forces between bromine and oxygen (figure 5).

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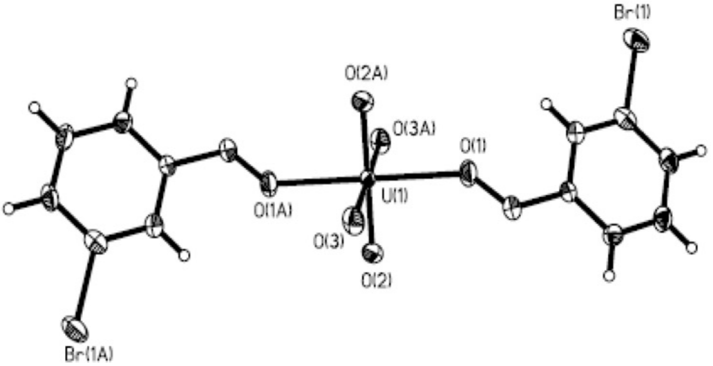

Figure 3. The crystal structure for **2**, ellipsoids are drawn at the 30% probability level.

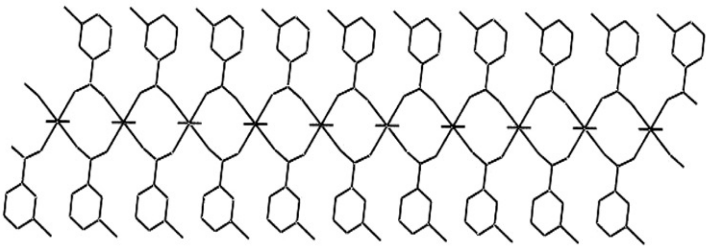

Figure 4. 1D chain of **2**.

Table 3. Selected bond lengths (Å) and angles (°) of **2**.

U(1)–O(1)	2.311(4)	U(1)–O(1)#1	2.311(4)	C(2)–C(3)	1.392(7)
U(1)–O(2)	1.754(4)	Br(1)–C(4)	1.896(6)	C(3)–C(4)	1.363(8)
U(1)–O(2)#1	1.754(4)	C(1)–O(1)	1.253(6)	C(1)–C(6)	1.384(6)
U(1)–O(3)	2.290(4)	C(1)#2–O(3)	1.259(6)	C(4)–C(5)	1.383(8)
U(1)–O(3)#1	2.289(3)	C(1)–C(2)	1.490(7)	C(5)–C(6)	1.380(8)
O(2)–U(1)–O(2)#1	179.998(3)	O(1)#1–U(1)–O(1)	179.999(1)		
O(2)–U(1)–O(3)#1	89.97(18)	O(2)#1–U(1)–O(1)#1	91.51(18)		
O(2)#1–U(1)–O(3)#1	90.03(18)	O(3)#1–U(1)–O(1)#1	92.20(14)		
O(3)#1–U(1)–O(3)	180.0(2)	O(2)–U(1)–O(1)	91.51(18)		

$\#1 = -x, -y+1, -z+1$.

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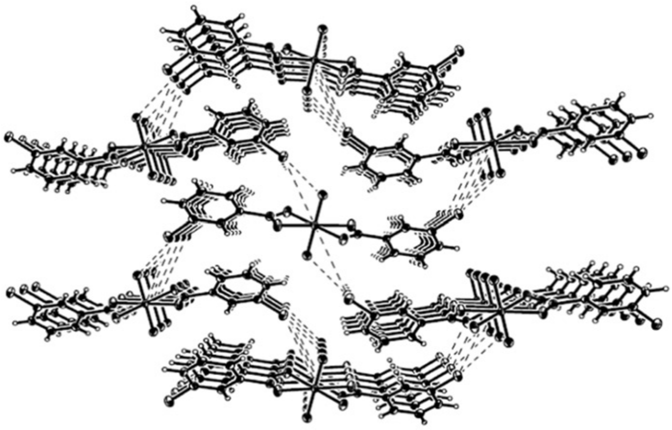

Figure 5. A view of the space filling model along the *a*-axis for **2**.

3.2. *IR spectra*

The IR spectrum of **1** has ν_{as}–COO$^-$ at 1588 cm^{-1}, ν_{as}C=C at 1487 cm^{-1} and 1536 cm^{-1}, absorption of δAr–H at 853 cm^{-1} and 771 cm^{-1}, and νC–Br is at 687 cm^{-1}. The IR spectrum of **2** has ν_{as}–COO$^-$ at 1590 cm^{-1}, ν_{as}C=C at 1463 cm^{-1} and 1619 cm^{-1}, δAr–H at 817 cm^{-1} and 749 cm^{-1}, and νC–Br at 646 cm^{-1}. For **1** and **2**, there are strong absorptions at 1590 cm^{-1} assigned to the –COO$^-$ asymmetric stretching vibration, indicating formation of the carboxylate complexes [17, 18].

4. Conclusion

Two uranyl complexes are synthesized via hydrothermal treatment of uranium oxynitrate with *p*-bromobenzoic acid and *m*-bromobenzoic acid. Complex **1** forms a 2D porous sheet by intermolecular hydrogen bonds. Complex **2** forms a 1D chain coordination polymer. The results indicate that organic acids can easily coordinate to uranyl ion at pH = 4–8. This means that uranyl ion could easily react with humic acid underground and migrates by complexation in the process of uranium mineralization.

Supplementary data

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-600949 and 661706). These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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