Uranyl(VI)–Acetylacetonate Coordination Compounds with Various N-Heterocyclic Ligands

Takeshi Kawasaki,[1] Tatsuru Nishimura,[1] and Takafumi Kitazawa*[1,2]

[1]Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi 274-8510

[2]Research Center for Materials with Integrated Properties, Toho University, Miyama, Funabashi 274-8510

Received June 8, 2010
E-mail: kitazawa@chem.sci.toho-u.ac.jp

Seven uranyl(VI) complexes, $[UO_2(acac)_2(L)]$ [L = 4-methylpyridine (**1**), 4-ethylpyridine (**2**), 2,4-dimethylpyridine (**3**), (−)-nicotine (**4**), and imidazole (**5**)], $[\{UO_2(acac)_2\}_2$-(4,4′-bipyridine)] (**6**), and $[(2,2'\text{-bipyridine})_2H][UO_2(acac)$-$(NO_3)_2]$ (**7**) have been synthesized and characterized crystallographically. The coordination geometry of U has a UNO_6 pentagonal-bipyramidal coordination in **1**–**6**, and a UO_8 hexagonal-bipyramidal coordination in **7**.

The actinide elements are analogous to the lanthanides and result from the filling of 5f orbitals, as the lanthanides result from the filling of 4f. The coordination chemistry of the actinides has potentially been linked to the reprocessing of nuclear fuels and treatment of actinide wastes in the backend chemistry for nuclear power plants which operate everyday. The fundamental investigation of the bonding and structure of uranium complexes provides important information on the field of backend chemistry. Various "actinyl(VI)" $An^{VI}O_2^{2+}$ complexes with β-diketonate have been reported.[1–3] Uranium β-diketonates with neutral donor ligands have been extensively studied due to their importance in the separation of uranium by solvent extraction. In particular, acetylacetonate is the simplest β-diketonate ligand and an important coordination compound of actinide.

Structural properties of $[AnO_2(acac)_2(py)]$ ($An = U^{VI}$ or Np^{VI}) have been reported.[2] $[AnO_2(acac)_2(py)]$ complexes exhibit pentagonal-bipyramidal geometry about the An^{VI} ion which are coordinated by the two actinyl(VI) oxygen atoms, the four oxygen atoms from the acac and the one nitrogen atom from the pyridine molecule. The ^{237}Np Mössbauer spectra of the $[NpO_2(acac)_2(py)]$ indicate that the electron donation of the N atom in the py might have a larger effect on the Np 5f orbital than electron donation of the oxygen atom in the acac.[2d] We report herein the synthesis and crystal structures of the uranyl(VI) acetylacetonate complexes $[UO_2(acac)_2(L)]$ (L = 4-Mepy: **1**, 4-Etpy: **2**, 2,4-dmpy: **3**, nic: **4**, and imH: **5**), $[\{UO_2(acac)_2\}_2(4,4'\text{-bpy})]$: **6**, and $[(bpy)_2H][UO_2(acac)$-$(NO_3)_2]$: **7** (4-Mepy: 4-methylpyridine, 4-Etpy: 4-ethylpyridine, 2,4-dmpy: 2,4-dimethylpyridine, nic: (−)-nicotine, and imH: imidazole). To our knowledge, in **1** and **2**, synthesis and spectroscopic study have already been reported[2a] but crystal data have not been reported. The remaining complexes are novel.

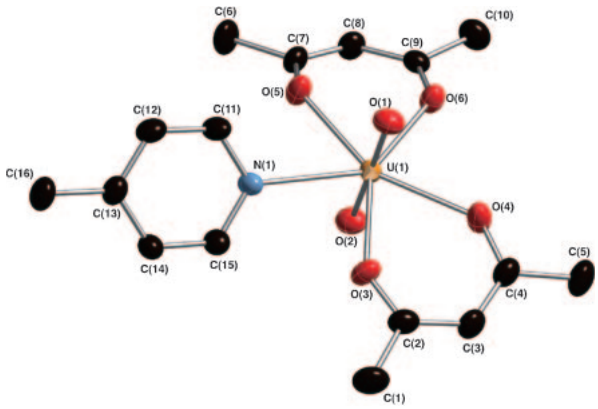

Figure 1. Molecular view of **1** with 30% thermal ellipsoids, Hydrogen atoms are omitted clarity.

In complexes **1**–**6**, this moiety around the U atom is similar to the reported $[UO_2(acac)_2(py)]$: **8**.[2] The U atom exhibits a UNO_6 pentagonal-bipyramidal coordination geometry as show in Figures 1, S2a, S3a, S4a, S4b, S5a, and S6a. The two O atoms from the uranyl(VI) ion occupy the axial positions whereas four O atoms from the two chelating acac ligands and one N atom of the N-heterocyclic ligand form the equatorial plane. The O=U=O angle of the uranyl(VI) ion is almost linear. The equatorial plane of the U atom is nearly flat. For example, in **1**, the deviations of the four acac O atoms [O(3), O(4), O(5), and O(6)], one N(1) atom of 4-Mepy and one U(1) atom from the equatorial plane [O(3), O(4), O(5), O(6), and N(1)] are within 0.17 Å (details are listed in Table S3). The U–N bond lengths between the U atom and the N atom of the N-heterocyclic ring, O=U=O angles, and the dihedral angles between the N-heterocyclic ring and the equatorial plane of the U atom in $[UO_2(acac)_2(L)]$ (L = N-heterocyclic ligand) complexes **1**–**6** are listed in Table 1.

In complexes **1** and **2**, all bond lengths and angles around the U atom and dihedral angle between the pyridine ring of the ligand and equatorial plane of the U atom are close to **8**.[2d] However, **8** crystallized in the non-centrosymmetric space group, *Fdd*2, whereas **1** and **2** crystallized in the centrosymmetric space group $P\bar{1}$ (Figures S1 and S2b).

Complex **3** crystallized in the centrosymmetric space group $P2_1/n$ (Figure S3b). The values of the U(1)–N(1) bond length and the dihedral angle between the pyridine ring of the 2,4-dmpy ligand and equatorial plane of the U atom are larger than **8**. The differences of the U–N bond length and dihedral angle are caused by the van der Waals repulsion between the α-methyl [C(16)] of 2,4-dmpy and uranyl(VI) oxygen atom, and between C(16) and acac oxygen atom (Figure S3a).

Complex **4** crystallized in the non-centrosymmetric space group $P2_1$ (Figure S4c), and there are two crystallographically independent U sites [U(1): site-1 (Figure S4a) and U(2): site-2 (Figure S4b)] for the effect of the chiral carbon atoms [C(16) in the site-1 and C(36) in the site-2] of the nic ligands coordinated

Published on the web December 2, 2010; doi:10.1246/bcsj.20100159

Table 1. The U–N Bond Lengths between the U Atom and the N Atom of the N-Heterocyclic Ring, O=U=O Angles, and the Dihedral Angles between the N-Heterocyclic Ring and the Equatorial Plane of the U Atom in $[UO_2(acac)_2(L)]$ (L = N-Heterocyclic Ligand) Complexes

Complex	L	U–N/Å	O=U=O /°	Dihedral angle/°
1	4-Mepy	U(1)–N(1) 2.614(6)	179.2(2)	42.5
2	4-Etpy	U(1)–N(1) 2.605(3)	179.1(1)	43.1(2)
3	2,4-dmpy	U(1)–N(1) 2.648(9)	179.2(4)	69.4
4 site-1	nic	U(1)–N(1) 2.58(1)	178.5(4)	64.0(4)
4 site-2	nic	U(2)–N(3) 2.61(1)	177.4(4)	58.9(4)
5	imH	U(1)–N(1) 2.53(1)	178.7(5)	38.5(8)
6	4,4′-bpy	U(1)–N(1) 2.66(1)	179.3(4)	41.7
8[a)]	py	2.602(3)	178.3(2)	42

a) Our re-determination of $[UO_2(acac)_2(py)]$. A part of this result is described in the Ref. 2d.

to the U atoms. The N atoms of 1-methyl-2-pyrrolidyl in the nic [N(2) in the site-1 and N(4) in the site-2] are not coordinated to the U atoms. In site-1, the U(1)–N(1) bond length is slightly shorter than the U–N bond of **8**. In site-1 and site-2, the dihedral angles between the pyridine ring of the nic ligand and equatorial plane of the U atom are larger than **8**. These differences of dihedral angles might be caused because the molecules have been packed into the cell becoming more dense. In site-1, the larger dihedral angle leads to decrease of the van der Waals repulsion between the pyridine ring of the nic ligand and two acac oxygen atoms, therefore, the U(1)–N(1) bond length may be slightly short. On the other hand, although the dihedral angle in site-2 is larger than **8**, U(2)–N(3) bond length is similar to U–N bond length of **8**. The bond length might be caused by the repulsion between the lone pair of N(4) atom and lone pair of acac oxygen atom O(9).

Complex **5** crystallized in the centrosymmetric space group $P2_1/c$ (Figure S5b). The values of the U(1)–N(1) bond length and the dihedral angle between the imidazole ring and equatorial plane of the U atom are smaller than **8**. The N(2) atom of the NH moiety in the imH ligand of **5** (Figure S5a) is connected with O(4) and O(6) atoms of the acac by intermolecular hydrogen bonds [N(2)···O(4) = 3.00(2) Å and N(2)···O(6) = 3.07(2) Å]. This results in a 1-D chain aggregate of **5** along the *c* axis (Figure S5b).

Complex **6** crystallized in the centrosymmetric space group $P2_1/n$ (Figure S6b). A 4,4′-bpy ligand bridges two U atoms in the $[UO_2(acac)_2]$ fragments, defining the binuclear U^{VI} complex $[\{UO_2(acac)_2\}_2(4,4'\text{-bpy})]$ (Figure S6a). The midpoint of C(13)–C(13)′ bond is located on an inversion center. The U(1)–N(1) bond length is the longest length between the uranium and nitrogen atoms of the pyridine ring in the $[UO_2(acac)_2(L)]$ moiety in this work. Up to the present investigation, the bond lengths between the U and N atoms of the 4,4′-bpy ligand in uranyl(VI)–4,4′-bpy complexes are varied irrespective of whether 4,4′-bpy ligands are mono- or bidentate.[4] Therefore, the cause of the long U(1)–N(1) bond length in **6** could not be concluded clearly.

In the $[UO_2(acac)_2(L)]$ complexes in this work, **1**–**6**, the dihedral angles between the N-heterocyclic ring of the ligand and equatorial plane of the U atom are neither vertical nor parallel. Most other $[UO_2(acac)_2(L)]$ complexes[2,3] are also similar. On the other hand, to our knowledge, the dihedral angles of the majority of the non acetylacetonate complexes are nearly vertical.[4,5] This indicates interaction between acac oxygen atoms and α-hydrogen atoms of the N-heterocyclic ring.

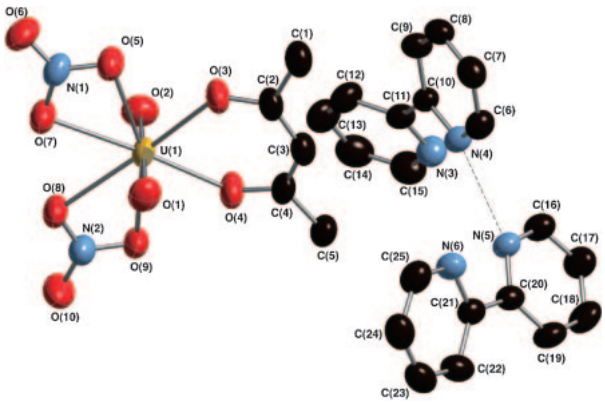

Figure 2. Molecular view of $[UO_2(acac)(NO_3)_2]^-$ ion and $[(bpy)_2H]^+$ ion in **7** with 50% thermal ellipsoids, Hydrogen atoms are omitted clarity.

Table 2. Selected Bond Lengths and Angles of **7**

	Bond length/Å	Bond angle/°
U=O	U(1)–O(1) 1.759(2)	O(1)–U(1)–O(2) 178.0(1)
	U(1)–O(2) 1.748(2)	O(3)–U(1)–O(4) 71.02(8)
$U–O_{acac}$	U(1)–O(3) 2.341(2)	O(3)–U(1)–O(5) 65.08(7)
	U(1)–O(4) 2.339(2)	O(4)–U(1)–O(9) 65.38(8)
$U–O_{nitrate}$	U(1)–O(5) 2.544(2)	O(5)–U(1)–O(7) 49.58(7)
	U(1)–O(7) 2.541(2)	O(7)–U(1)–O(8) 59.86(7)
	U(1)–O(8) 2.561(2)	O(8)–U(1)–O(9) 49.39(7)
	U(1)–O(9) 2.529(2)	

Complex **7** is composed of $[UO_2(acac)(NO_3)_2]^-$ ions and $[(bpy)_2H]^+$ ions as shown in Figure 2. The U atom exhibits UO_8 hexagonal-bipyramidal coordination geometry. The two O atoms from the uranyl(VI) ion occupy the U atom axial positions whereas two O atoms [O(3) and O(4)] from the one chelating acac ion and four O atoms [O(5), O(7), O(8), and O(9)] from the two chelating nitrate ions form the equatorial plane. Selected bond lengths and angles in **7** are listed in Table 2. The O=U=O [O(1)–U(1)–O(2)] angle of the uranyl(VI) ion is almost linear. Deviations of the two acac O atoms, four nitrate O atoms and one U atom of the equatorial plane [O(3), O(4), O(5), O(7), O(8), and O(9)] are within 0.11 Å (details are listed in Table S3). The $U–O_{nitrate}$ bond lengths are longer than $U–O_{acac}$ bonds. The structure of $[UO_2(acac)(NO_3)_2]^-$ ion of **7** is an isostructure with $[(2,4,6\text{-trimpy})H][UO_2(acac)(NO_3)_2]$[1a] (2,4,6-trimpy: 2,4,6-trimethylpyridine). The N atoms of the bpy molecule are not coordinated to the U atom and one N atom seems connected with the one N atom of the another bpy molecule through a proton by a hydrogen bond [N(3)···N(5) = 2.844(3) Å]. $[UO_2(acac)_2(bpy)]$ was not formed in this synthesis. This might be because the bpy is too large to approach the U atom enclosed by the acac anions.

In conclusion, we synthesized and characterized crystallographically the complexes **1** and **2**, and new complexes **3**, **4**, **5**,

6, and **7**. These complexes were prepared by the same method except differences of solvent. In $[UO_2(acac)_2(L)]$ complexes, **1**–**6**, these moieties around the U atom are similar to **8**.[2] The U atom has a UNO_6 pentagonal-bipyramidal coordination environment. On the other hand, in complex **7**, this moiety around the U atom is similar to $[(2,4,6\text{-trimpy})H][UO_2(acac)(NO_3)_2]$.[1a] The U atom has a UO_8 hexagonal-bipyramidal coordination geometry. The common features of both are that the O=U=O angle is linear, and that the equatorial plane of the U atom is flat. This is a prevailing climate[1–5] in uranyl(VI) complexes with a few exceptions.[4a,6] The bond lengths around the U atom including previous reports[1–6] tend to be U=O < U–O_{acac} < U–$O_{chelating\text{-}nitrate}$ < U–N. In the analogous neptunium compounds of **1**–**6**, it would be also interesting to investigate changes of the ^{237}Np Mössbauer spectra induced by the influence of chirality, hydrogen bonds between the N-heterocyclic ligand and acac, bridge between two U atoms, etc, being associated with ^{237}Np Mössbauer parameters of $[NpO_2(acac)_2(py)]$.

Experimental

Synthesis. **1**, **3**, and **6** were prepared and crystallized by reaction of a methanol mixture, and the remaining complexes were prepared and crystallized by reaction of an acetonitrile mixture. To a 10 mL solution containing 1.0 mmol $UO_2(NO_3)_2 \cdot 6H_2O$ was added 3.0 mmol acetylacetone (Hacac) and 3.0 mmol N-heterocyclic compound in 5 mL of solvent. After the solvent evaporated slowly at room temperature for a few days, crystals were obtained.

Structure Determination. Crystal structures of **1**, **3**, and **6** were determined using a Rigaku AFC5S diffractometer with monochromeated Mo Kα radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods with *Crystal Structure* software.[7] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated geometrically.

Crystal structures of **2**, **4**, **5**, and **7** were determined using a BRUKER APEX SMART CCD area-detector diffractometer with monochromeated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal of complex **5** was unstable in air, therefore, a single crystal of **5** was coated with resin for the collection of X-ray diffraction intensity data. The diffraction data of **2**, **4**, **5**, and **7** were treated using *SMART*[8] and *SAINT*[9] software, and absorption correction was performed using *SADABS*.[10] The structures were solved by direct methods with *SHELXTL*.[11] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated geometrically. The crystal data of **1**–**7** and selected bond lengths and angles in $[UO_2(acac)_2(L)]$ type complexes **1**–**6** are listed in Table S1 and Table S2 (see Supporting Information), respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-793245–793251 for compounds **1**–**7**, respectively. Copies of the 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, U.K.; Fax: +44 1223 336033: e-mail: deposit@ccdc.cam.ac.uk).

We thank Prof. Masuo Takeda and Prof. Masashi Takahashi of Toho University and Dr. Masakatsu Saeki and Dr. Masami Nakada of JAERI (Present name: JAEA) for helpful discussion and preparation of the uranium complexes.

Supporting Information

The crystal data of **1**–**7**, selected bond lengths and angles in $[UO_2(acac)_2(L)]$ complexes **1**–**6**, and deviations from equatorial plane of **1**–**7** are listed in Table S1, Table S2, and Table S3, respectively. The packing view of **1** is shown in Figure S1, molecular and packing views of **2**–**6** are shown in Figures S2–S6, and packing view of **7** is shown in Figure S7, respectively. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 a) N. W. Alcock, D. J. Flanders, *Acta Crystallogr., Sect. C* **1987**, *43*, 1480. b) S. Kannan, S. S. Raj, H.-K. Fun, *Polyhedron* **2001**, *20*, 2145. c) A. A. Tahir, M. Hamid, M. Mazhar, M. Zeller, A. D. Hunter, *Acta Crystallogr., Sect. E* **2006**, *62*, m1780. d) J. Huuskonen, K. Raatikainen, K. Rissanen, *Acta Crystallogr., Sect. E* **2007**, *63*, m413. e) K. Takao, Y. Ikeda, *Acta Crystallogr., Sect. E* **2008**, *64*, m219. f) T. Kawasaki, T. Kitazawa, *Acta Crystallogr., Sect. E* **2008**, *64*, m673. g) G. V. Sidorenko, M. S. Grigor'ev, V. V. Gurzhiy, D. N. Suglobov, I. G. Tananaev, *Radiochemistry* **2009**, *51*, 345.

2 a) J. M. Haigh, D. A. Thornton, *J. Mol. Struct.* **1971**, *8*, 351. b) N. W. Alcock, D. J. Flanders, D. Brown, *J. Chem. Soc., Dalton Trans.* **1984**, 679. c) N. W. Alcock, D. J. Flanders, M. Pennington, D. Brown, *Acta Crystallogr., Sect. C* **1987**, *43*, 1476. d) T. Kawasaki, T. Kitazawa, T. Nishimura, M. Nakada, M. Saeki, *Hyperfine Interact.* **2006**, *166*, 417.

3 T. Kawasaki, T. Kitazawa, *Acta Crystallogr., Sect. E* **2008**, *64*, m788.

4 a) L. A. Borkowski, C. L. Cahill, *Cryst. Growth Des.* **2006**, *6*, 2248. b) P. Thuéry, *Acta Crystallogr., Sect. C* **2007**, *63*, m54.

5 a) J. C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, *Eur. J. Inorg. Chem.* **2000**, 1969. b) J. C. Berthet, M. Nierlich, M. Ephritikhine, *Chem. Commun.* **2004**, 870.

6 a) N. W. Alcock, D. J. Flanders, D. Brown, *J. Chem. Soc., Dalton Trans.* **1985**, 1001. b) J. C. Berthet, M. Nierlich, M. Ephritikhine, *Dalton Trans.* **2004**, 2814. c) I. A. Charushnikova, C. D. Auwer, *Russ. J. Coord. Chem.* **2004**, *30*, 511. d) I. A. Charushnikova, C. D. Auwer, *Russ. J. Coord. Chem.* **2007**, *33*, 53.

7 *Crystal Structure for the Crystal Structure Analysis Package*, Rigaku and Rigaku/MSC, **2002**.

8 *SMART Software for the CCD Detector System*, Bruker AXS Inc., Madison, WI, **2001**.

9 *SAINT Software for the CCD Detector System*, Bruker AXS Inc., Madison, WI, **2001**.

10 G. M. Sheldrick, *SADABS Program for Empirical Absorption Correction for Area Detector Data*, University of Göttingen, Göttingen, Germany, **1996**.

11 G. M. Sheldrick, *SHELXTL Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen, Germany, **1997**.