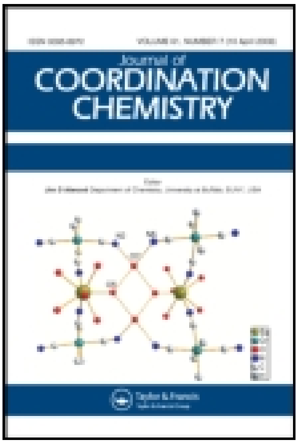
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:21
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, spectroscopy, and electrochemistry of a uranium complex

Juan Wang [a] [b], Fulan He [b], Xiaoyu Wang [a], Lihong Tian [b] & Ziying Li [c]

[a] Institute of Applied Chemistry, Jiangxi Academy of Sciences, Nanchang 330029, P.R. China

[b] College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P.R. China

[c] Beijing Research Institute of Uranium Geology, Beijing 100029, P.R. China

Published online: 05 Jul 2011.

To cite this article: Juan Wang, Fulan He, Xiaoyu Wang, Lihong Tian & Ziying Li (2011) Synthesis, crystal structure, spectroscopy, and electrochemistry of a uranium complex, Journal of Coordination Chemistry, 64:13, 2312-2320, DOI: 10.1080/00958972.2011.594509

To link to this article: http://dx.doi.org/10.1080/00958972.2011.594509

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 64, No. 13, 10 July 2011, 2312–2320

Taylor & Francis
Taylor & Francis Group

Synthesis, crystal structure, spectroscopy, and electrochemistry of a uranium complex

JUAN WANG*†‡, FULAN HE‡, XIAOYU WANG†, LIHONG TIAN‡ and ZIYING LI§

†Institute of Applied Chemistry, Jiangxi Academy of Sciences,
Nanchang 330029, P.R. China
‡College of Chemistry and Chemical Engineering, Hubei University,
Wuhan 430062, P.R. China
§Beijing Research Institute of Uranium Geology, Beijing 100029, P.R. China

(*Received 31 May 2010; in final form 9 May 2011*)

A uranium coordination compound with pyridine-2,6-dicarboxylic acid in deionized water has been synthesized and characterized by IR, UV, XPS, and X-ray single-crystal diffraction. The crystal belongs to the monoclinic system, space group $C2/c$ with $a = 1.8427(4)$ nm, $b = 0.6886(16)$ nm, $c = 1.5442(4)$ nm, $\alpha = 90^\circ$, $\beta = 94.082(2)^\circ$, $\gamma = 90^\circ$, $Z = 4$, and $V = 1.9544(8)$ nm^3. The structure shows an eight-coordinate uranium forming a hexagonal bi-pyramidal 3-D geometry with pyridine-2,6-dicarboxylate as building units. Fluorescent studies show several strong emissions. Cyclic voltammetric measurement of the compound reveals that uranium(VI) is reduced irreversibly at $E_{1/2} = 927$ mV with $\Delta E_p = 77$ mV, $E_{1/2} = -289$ mV with $\Delta E_p = 113$ mV. The electron transfer number (n) involved in reduction processes could be calculated to be approximately two and one, which corresponded to the unusual U(VI)/U(IV) and U(IV)/U(III) couples.

Keywords: Uranium complex; Crystal structure; Spectroscopy; Electrochemistry

1. Introduction

Although the chemistry of the 5f elements is under development [1–5], the number of coordination compounds of actinides is much less than that of transition metals and lanthanides. Among the actinides the chemistry of uranium has been more explored [6, 7], with a number of complexes of uranium in different oxidation states (III, IV, V, and VI) reported.

Due to the variable oxidation states of uranium, electrochemical studies [8–12] of uranium complexes are valuable to understand the influence of ligand environment on the relative stability of the U(III), U(IV), U(V), and U(VI) species in solution. Almost all complexes of uranium(VI) are of uranyl cation UO_2^{2+} [13]. Herein, we have synthesized a U(VI) compound. A new uranium(VI) complex with pdc (pdc = pyridine-2,6-dicarboxylate) is described in this article. The planar pyridine-2,6-dicarboxylic acid

---

*Corresponding author. Email: wangjuan_hd@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.594509

has previously been used as a ligand for UO_2^{2+}. Two tridentate ligands encompass one uranyl ion bound to nitrogen and one oxygen from each acid group [14, 15], which is also the case with the related ligand pyridine-2,6-bis(monothiocarboxylic) acid [16]. We decided to investigate the uranyl complexes formed with pdc. In this article, the crystal structure, spectroscopy, and electrochemistry behavior of the obtained compound are studied.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were from commercial sources and deionized water used as solvent without purification. Elemental analyses were carried out on an Italy Elemental Analyzer EO1106 elemental analyzer. Fluorescence data were collected on an Edinburgh FL-FS920 TCSPC system. Thermal gravimetric analysis (TGA) was tested under nitrogen with a heating rate of $10^{\circ}C\,min^{-1}$ using a Perkin-Elmer TGA-7 Thermal Analysis system. Cyclic voltammograms were obtained on a model CHI660C electrochemical analyzer (CH Instruments, Austin, TX, USA) controlled by a personal computer at room temperature.

2.2. *Synthesis of the complex*

UO_2 (0.1351 g, 0.5 mmol) was put in a beaker with 8 mL of concentrated hydrochloric acid. To the yellow solution, pyridine-2,6-dicarboxylic acid was added. The mixture was then transferred to a flask and refluxed for 7 h at 70°C. When the solution cooled to room temperature, green crystals were collected after 2 weeks. Anal. Calcd for $C_{14}H_7N_2O_{10}U \cdot 4H_2O$ (%): C, 24.96; H, 1.04; N, 4.16. Found (%): C, 24.75; H, 1.21; N, 4.18.

2.3. *Single-crystal structure determination*

A single crystal with dimensions of 0.22 mm × 0.24 mm × 0.28 mm was selected for data collection on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) by using an ω scan mode ($4.4 < 2\theta < 48.0$) at 291(2) K. A total of 5059 reflections were collected and 1911 were independent ($R_{int} = 0.035$), of which 1520 reflections with $I > 2\sigma(I)$ were considered as observed. Correction for Lp factors was applied. The structure was solved by direct methods with SHELXS [17] and refined using full-matrix least-squares on F^2 with SHELXL [18]. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and structural determination for the title compound is listed in table 1. Selected bond lengths and angles are provided in tables 2 and 3.

Table 1. Data collection and processing parameters for the complex.

Compound	$UO(H_2O)(pdc)_2 \cdot 4H_2O$
Formula weight	673.31
Temperature	291(2) K
Wavelength	0.071073 nm
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (nm, °)	
a	1.8427(4)
b	0.6886(16)
c	1.5442(4)
α	90
β	94.082(2)
γ	90
Volume (nm^3), Z	1.9544(8), 4
Calculated density, D_c ($g\,cm^{-3}$)	2.288
Absorption coefficient (mm^{-1})	8.38
$F(000)$	1268
Crystal size (mm^3)	$0.22 \times 0.24 \times 0.28$
θ range for data collection	2.2–24.0
Index ranges	$-22 \le h \le 21$; $-8 \le k \le 8$; $-9 \le l \le 18$
Reflections collected/unique (R_{int})	5059/1911(0.035)
Goodness-of-fit on F^2	0.98
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0327$; $wR_2 = 0.0733$
Largest diffraction peak and hole ($e\,Å^{-3}$)	1.72 and −1.50

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$; $w^{-1} = [s^2(F_o)^2 + (0.04\,P)^2 + 0.88\,P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond distances (nm) and angles (°) for the compound.

U1–O1	0.2502(4)	U1–O1w	0.2337(6)
U1–O3	0.2503(4)	U1–O5	0.1762(5)
U1–N1	0.2618(5)	O1–C1	0.1257(8)
O2–C1	0.1281(7)	O3–C7	0.1202(9)
O4–C7	0.1255(7)	N1–C6	0.1387(8)
N1–C2	0.1387(9)	C1–C2	0.1355(9)
C6–C7	0.1470(9)	O1–U1–O1w	86.73(9)
O1–U1–O3	120.92(14)	O1–U1–O5	93.27(9)
O1–U1–N1	61.36(15)	O1w–U1–O3	100.01(8)
O1w–U1–O5	180.00(2)	O1w–U1–N1	92.69(9)
O3–U1–O5	79.99(8)	O3–U1–N1	59.74(16)
O5–U1–N1	87.31(9)	U1–O1–C1	124.4(3)
U1–O3–C7	128.0(4)	U1–O1w–H1	123.00(2)
U1–N1–C6	122.0(4)	C2–N1–C6	120.3(5)
U1–N1–C2	117.2(4)	O2–C1–C2	126.8(6)
O1–C1–C2	120.5(5)	O3–C7–C6	120.2(5)
O4–C7–C6	109.4(6)	C3–C7–O4	128.3(6)
N1–C6–C7	109.2(5)	N1–C6–C5	120.3(5)
N1–C2–C3	118.4(7)	N1–C2–C1	116.4(5)

3. Results and discussion

3.1. *Description of the crystal structure*

As shown in figure 1, the structure reveals that pyridine-2,6-dicarboxylate binds bidentate to uranium by two oxygens of two monodentate carboxylates and one

Table 3. Hydrogen bond distances (nm) and angles (°) for the compound.

D–H···A	D–H	H···A	D···A	D–H···A
O1W–H1···O5^{i}	0.0850	0.2420	0.2787	106.00
O2W–H2x···O3^{ii}	0.0850	0.2430	0.2811	108.00
O3W–H3X···O2^{iii}	0.0850	0.1560	0.2159	125.00
O3W–H3Y···O4^{iv}	0.0850	0.2000	0.2662	135.00

Symmetry codes: $^{(i)}$ x, $y-1$, z; $^{(ii)}$ $x+1/2$, $y-1/2$, z; $^{(iii)}$ $x+1$, $-y+1$, $z-1/2$; $^{(iv)}$ $-x+1$, $y-1$, $-z+1/2$.

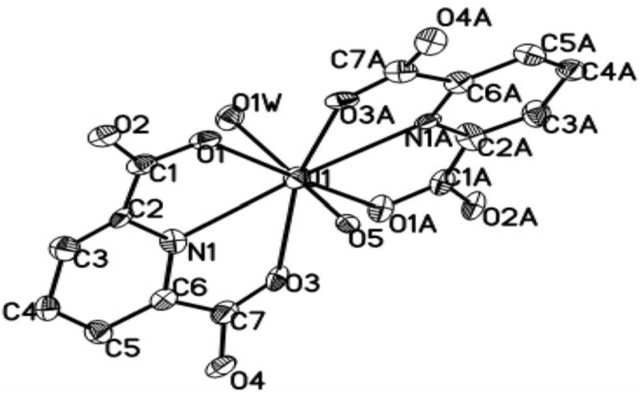


Figure 1. The molecular structure of the uranium complex with displacement ellipsoids drawn at the 50% probability level. Atoms labeled with the suffix A are related by the symmetry operator ($-x$, y, $1/2-z$).

nitrogen donor. The compound crystallizes in a monoclinic system, space group *C2/c*. The asymmetric unit contains half of the independent molecule, with U(1) on a twofold rotation axis at special position 0.0000 0.73014(4) 0.2500. The central uranium was eight coordinate by four oxygens from carboxylate, two nitrogens, one water, and a uranyl oxygen forming a hexagonal bi-pyramidal geometry. Two ligands locate unsymmetrically in the equatorial positions. Water and oxygen occupy axial positions. The two pdc molecules in every unit are distorted, presenting a splayed shape. The U1–O1(pdc) and U1–O3(pdc) bond distances were the same. U1–N1 of 0.2618(5) nm was larger than the mean U–O (carboxylate) bond length. C6, C7, O3, U1, N1 were in one plane and C1, C2, O1, U1, N1 were in another plane, forming pentabasic rings. The C6–C7–O3, C7–O3–U1, O3–U1–N1, U1–N1–C6, and N1–C6–C7 angles were 120.5(5)°, 128.0(4)°, 59.74(16)°, 122.0(4)°, and 109.2(5)°, respectively, showing a 539.14(34)° value, in agreement with a rule that the interior angle of pentabasic ring equals 540°. Furthermore, the two pentabasic rings were not coplanar, defining a dihedral angle of 14.44°. The O4–C7–C6 angle was the same as the angle of N1–C6–C7. We concluded that the line of O4, C7, C6 and N1, C6, C7 were parallel.

Note that O3 connected O2W, O2W connected O4 formed one chain *via* hydrogen bonds. Additionally, O2W and O3W from two different waters connected O4 from the ligand, forming an irregular triangle *via* hydrogen bonds, as shown in figure 2. The chains then are stacked into a 3-D structure by offset face-to-face $\pi\cdots\pi$ stacking interactions (figure 3). The shortest distance between the offset face-to-face aromatic

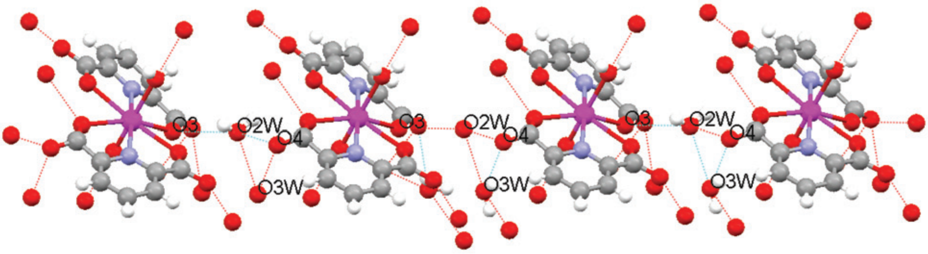


Figure 2. A chain structure *via* hydrogen bonds in the complex.

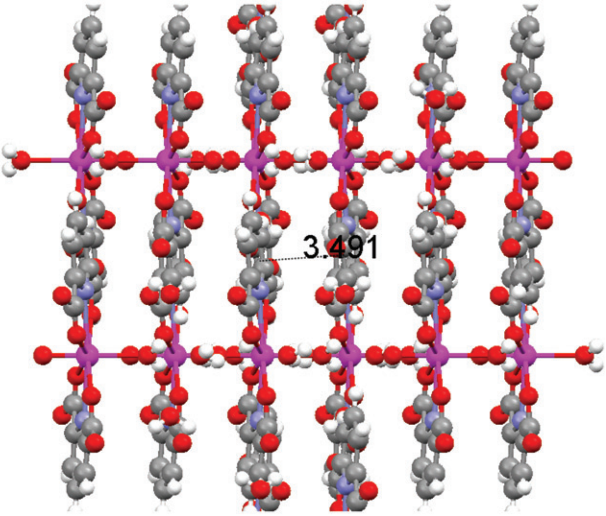


Figure 3. The distance between the offset, pyridine rings of neighboring pyridine-2,6-dicarboxylic acid molecules.

rings of neighboring pdc is 3.491 Å. The extensive $\pi \cdots \pi$ stacking and hydrogen-bonding interactions increase the stability of the structure.

3.2. *IR spectrum*

The IR spectrum of the complex exhibits a strong absorption at 3519 $\mathrm{cm^{-1}}$ due to the stretching vibration of O–H, indicating that the complex contains water [19]. The peak at 928 $\mathrm{cm^{-1}}$ can be assigned to the stretching vibration of $\mathrm{UO_2^{2+}}$. From two groups of the observed absorption bands at 1645 and 1597 $\mathrm{cm^{-1}}$, 1446 and 1397 $\mathrm{cm^{-1}}$, we can conclude that they are asymmetric and symmetric modes of vibration of the dicarboxylates. If $\Delta\nu$ $(\nu_{\mathrm{as}} - \nu_{\mathrm{s}}) > 200\,\mathrm{cm^{-1}}$, the carboxylate group is monodentate coordinated, otherwise is bidentate [20]. This article indicates that carboxylate is monodentate coordinated with uranium, consistent with the crystal structure.

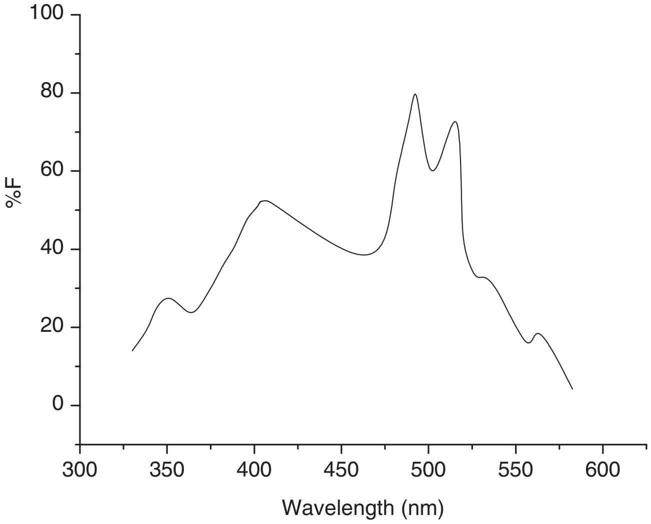


Figure 4. Emission spectrum of the complex in the liquid state.

3.3. *Fluorescence spectrum*

The emission spectrum of the complex in water is shown in figure 4. The excitation of free ligand and complex in water were both 310 nm. Emission peaks of ligand were 352 and 413 nm. Emission peaks of the complex were 352, 413, 493, and 534 nm. The complex showed similar peak positions at 352 and 413 nm, caused by intraligand fluorescence emissions, but presented two new peaks compared with the free ligand. The complex showed stronger intensity, indicating that the bridging interaction increased rigidity of the ligand, and the loss of energy decreased [21, 22]. For the emission bands at 493 and 534 nm, we conclude environmental influence of the metal ion with the ligand [23].

3.4. *Electrochemical behavior of* $[UO(H_2O)(pdc)_2]\cdot 4H_2O$

Cyclic voltammetric measurement of the complex was carried out in deionized water at 25°C under nitrogen using glassy carbon as the working electrode, a platinum(Pt) wire counter electrode and saturated calomel reference electrode at a scan rate of $100\,\mathrm{mV\,s^{-1}}$.

As shown in figure 5, two couples of reduction and oxidation were recorded. In the range $-1.0 \sim 1.5$ V, one cathodic response at 0.901 V and, in the return sweep, one anodic peak at 0.978 V were observed. The other couple of reduction and oxidation appeared at -0.339 and -0.226 V, and $E_{1/2}$ values were -0.289 and 0.927 V. Because the value of ΔE_p is not equal to 59 mV, we conclude that the transition was irreversible. For an irreversible system, $|E_p - E_{1/2}| = 47.7/\alpha n$ [24], α of totally irreversible electrode process was generally assumed to be 0.5 [25]. Thus, the electron transfer number (n) involved in the reduction processes could be calculated to be

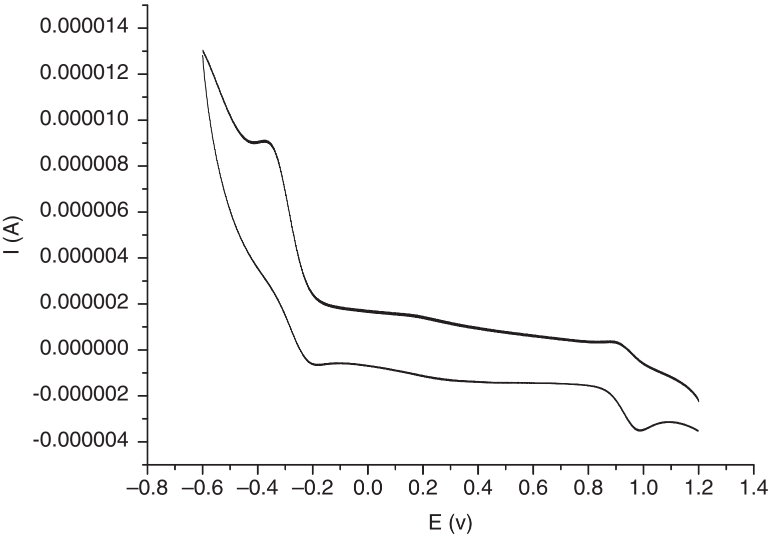


Figure 5. Cyclic voltammogram of the complex in water; scan rate: $100\,\mathrm{mV\,s^{-1}}$; working electrode: glassy carbon disk.

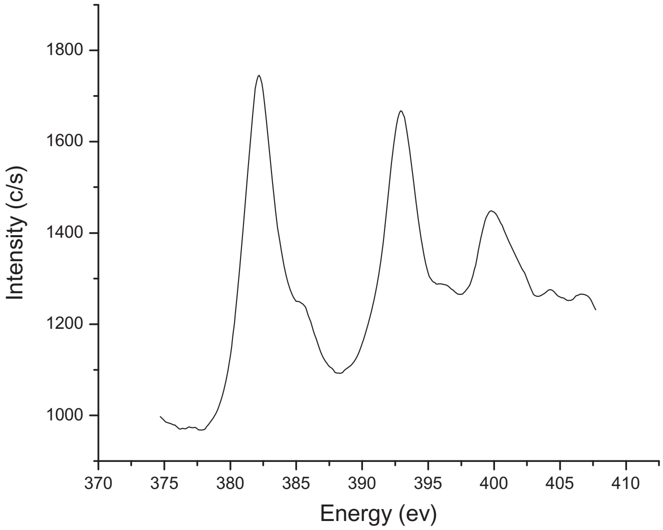


Figure 6. Deconvolution of $U4f_{7/2}$ photoelectron peaks.

two and one, respectively, which correspond to the unusual U(VI)/U(IV) and U(IV)/U(III) couples.

3.5. *XPS analysis*

The binding energies for U(VI) in the $U_{4f\ 7/2}$ peak are between 382.0 and 382.3 eV with an average value of 382.1 eV [26]. The observed binding energy 382.0 eV agrees with the previous reported value of 381.8 eV for U(VI) in metaschoepite [27] (figure 6).

4. Conclusions

A new uranium(VI) compound, $[UO(H_2O)(pdc)_2]\cdot 4H_2O$, has been synthesized and characterized. The compound presented a 3-D framework built up by O–H $\cdots$ O weak hydrogen-bonding interactions and $\pi \cdots \pi$ stacking. Spectroscopy and electrochemistry of the obtained compound are studied.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with Cambridge Crystallographic Data Center as supplementary publication No.755865. Copies of the data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the Natural Science Foundation of Jiangxi province (2010GZH0054) and Hubei province. We thank the Beijing Research Institute of Uranium Geology for financial support (A0120060596-06).

References

[1] J. Xu, K.N. Raymond. *Inorg. Chem.*, **38**, 308 (1999).
[2] A.E.V. Gorden, J. Xu, K.N. Raymond, P. Durbin. *Chem. Rev.*, **103**, 4207 (2003).
[3] M. Sawicki, J.-M. Siaugue, C. Jacopin, C. Moulin, T. Bailly, R. Burgada, S. Meunier, P. Baret, J.-L. Pierre, F. Taran. *Chem. Eur. J.*, **11**, 3689 (2005).
[4] P.D. Beer, G.D. Brindley, D.O. Fox, A. Grieve, M.I. Ogden, F. Szemes, M.G.B. Drew. *J. Chem. Soc., Dalton Trans.*, 3101 (2002).
[5] S.D. Conradson, D. Manara, F. Wastin, D.L. Clark, G.H. Lander, L.A. Morales, J. Rebizant, V.V. Rondinella. *Inorg. Chem.*, **43**, 6922 (2004).
[6] I.K.S. Gambarotta, L. Thompson, P.J. Hay, G.P.A. Yap. *Organometallics*, **20**, 5440 (2001).
[7] J. Sopo, H. Sviili, A. Valkonen, R. Sillanpaa. *Polyhedron*, **25**, 1223 (2006).
[8] K. Mizuoka, S.-Y. Kim, M. Hasegawa, T. Hoshi, G. Uchiyama, Y. Ikeda. *Inorg. Chem.*, **42**, 1031 (2003).
[9] J.L. Kiplinger, K.D. John, D.E. Morris, B.L. Scott, C.J. Burns. *Organometallics*, **21**, 4306 (2002).
[10] E.J. Schelter, J.M. Veauthier, J.D. Thompson, B.L. Scott, K.D. John, D.E. Morris, J.L. Kiplinger. *J. Am. Chem. Soc.*, **128**, 2198 (2006).
[11] J.L. Kiplinger, D.E. Morris, B.L. Scott, C.J. Burns. *Organometallics*, **21**, 3073 (2002).
[12] K. Mizuoka, S. Tsushima, M. Hasegawa, T. Hoshi, Y. Ikeda. *Inorg. Chem.*, **44**, 6211 (2005).
[13] P.C. Burns. *Can. Mineral.*, **43**, 1839 (2005).
[14] G. Marangoni, S. Degetto, R. Graziani, G. Bombieri, E. Forsellini. *J. Inorg. Nucl. Chem.*, **36**, 1787 (1974).
[15] A. Cousson, J. Proust, E.N. Rizkalla. *Acta Cryst.*, **C47**, 2065 (1991).
[16] M.P. Neu, M.T. Johnson, J.H. Matonic, B.L. Scott. *Acta Cryst.*, **C57**, 240 (2001).
[17] G.M. Sheldrick. *SHELXS, Program for the Solution of Crystal Structure*, University of Gottingen, Gottingen, Germany (2000).
[18] G.M. Sheldrick. *SHELXS, Program for the Refinement of Crystal Structure*, University of Gottingen, Gottingen, Germany (2000).

[19] S. Lis. *Alloys Compd*., **88**, 300 (2000).

[20] G.B. Deacon, R. Phillips. *J. Coord. Chem. Rev*., **23**, 227 (1980).

[21] L.Y. Zhang, G.F. Liu, S.L. Zheng, B.H. Ye, X.M. Zhang, X.M. Chen. *Eur. J. Inorg. Chem*., 2965 (2003).

[22] R.X. Yuan, R.G. Xiong, Y.L. Xie, X.Z. You, S.M. Peng, G.H. Lee. *Inorg. Chem. Commun*., **4**, 384 (2001).

[23] Z.Y. Fu, X.T. Wu, J.C. Dai, S.M. Hu, W.X. Du, H.H. Zhang, R.Q. Sun. *Eur. J. Inorg. Chem*., 2730 (2002).

[24] A.J. Bard, L.R. Faulkner. *Electrochemical Methods: Fundamentals and Applications*, 2nd Edn, Wiley, New York (2001).

[25] E. Laviron. *J. Electroanal. Chem*., **52**, 355 (1974).

[26] M. Schindler, F.C. Hawthorne, M.S. Freund, P.C. Burns. *Geochimica et Cosmochimica Acta*, **73**, 2471 (2009).

[27] R.A. Schueneman, A.I. Khaskelis, D. Eastwood, W.J. van Ooij, L.W. Burggraf. *J. Nucl. Mater*., **323**, 8 (2003).