ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Solid State Chemistry 180 (2007) 2597–2602

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

In situ ligand synthesis with the UO_2^{2+} cation under hydrothermal conditions

Mark Frisch[a], Christopher L. Cahill[a,b,*]

[a]*Department of Chemistry, The George Washington University, Washington, DC, USA*
[b]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA*

Received 16 May 2007; received in revised form 18 June 2007; accepted 24 June 2007
Available online 21 July 2007

Abstract

A novel uranium (VI) coordination polymer, $(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2$ (**1**), has been prepared under the hydrothermal reaction of uranium nitrate hexahydrate and L-pyroglutamic acid. Compound **1** (monoclinic, $C2/c$, $a = 22.541(6)$ Å, $b = 5.7428(15)$ Å, $c = 15.815(4)$ Å, $\beta = 119.112(4)^\circ$, $Z = 4$, $R_1 = 0.0237$, $wR_2 = 0.0367$) consists of uranium pentagonal bipyramids linked via L-pyroglutamate and oxalate anions to form an overall two-dimensional (2D) structure. With the absence of oxalic acid within the starting materials, the oxalate anions are hypothesized to form *in situ* whereby decarboxylation of L-pyroglutamic acid occurs followed by coupling of CO_2 to form the oxalate linkages as observed in the crystal structure. Addition of copper (II) to this system appears to promote oxalate formation in that synthetic moolooite $(Cu(C_2O_4) \cdot nH_2O;\ 0 \leqslant n \leqslant 1)$ and a known uranyl oxalate $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2 \cdot H_2O]$, co-crystallize in significant quantity. Compound **1** exhibits the characteristic uranyl emission spectrum upon either direct uranyl excitation or ligand excitation, the latter of which shows an increase in relative intensity. This subsequent increase in the intensity indicates an energy transfer from the ligand to the uranyl cations thus illustrating an example of the antenna effect in the solid state.

Keywords: Hydrothermal synthesis; Uranium (VI) coordination polymers; Decarboxylation; Oxalate formation; Fluorescence

---

1. Introduction

Metal-organic frameworks (MOFs) and coordination polymers (CPs) are typically engineered by tethering metal ions through appropriate homo-, or heterofunctional organic linkers [1–3]. These materials have been synthesized by a variety of methods such as hydro(solvo)thermal, sol–gel and room temperature self-assembly. Each of these methods has resulted in a collection of compounds, however in comparison to the extensive assembly of transition metal-based MOFs and CPs [4–16], actinide-based materials have not been explored as comprehensively. That said, an interesting family of uranium (VI) CPs based upon the near-linear uranyl cation (UO_2^{2+}) continues to evolve [17–33]. The uranyl oxygen atoms tend to be terminal, therefore additional bonding to the uranium metal center occurs through the equatorial plane resulting in local geometries such as square-, pentagonal-, or hexagonal-bipyramids. These primary building units can further polymerize to form secondary building units such as dimers, tetramers, one-dimensional (1D) chains or 2D sheets.

From an applications point of view, uranium (VI)-containing MOFs and CPs are currently of interest for their potential in areas such as catalysis, ion exchange, gas storage, and optics [27–31]. Uranium CPs are also being investigated for their appealing luminescent properties [18,19,27,34–39]. Emission from the uranyl ion has been demonstrated to photooxidize organic molecules such as alcohols [40,41] and cellulose acetate [36]. More recently, Bharadwaj et al. [42] have illustrated cleavage of DNA using a 1,10-phenanthroline complex. An attractive feature of this luminescent behavior is the potential to tune emission through judicious choice of sensitizer ligands. This "antenna effect" [43,44] involves energy transfer from excited π molecular orbitals in conjugated ligands to the

---

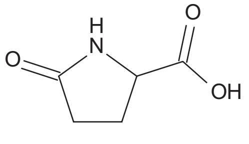
*Corresponding author. Department of Chemistry, The George Washington University, Washington, DC, USA. Fax: +1 202 994 5873.
E-mail address: cahill@gwu.edu (C.L. Cahill).

0022-4596/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.06.036

uranyl center. In addition to exploring intriguing luminescent behavior, the hydrothermal synthesis of uranium (VI) materials also advances our knowledge of uranium compounds and speciation in environmentally relevant settings such as the behavior of spent nuclear fuel under proposed geological repository conditions as well as the nuclear fuel cycle in general [45–50].

MOFs and CPs have been assembled by a variety of techniques, however, *in situ* ligand synthesis is an alternative synthetic route that has been demonstrated here in the production of compound **1**. *In situ* ligand synthesis is a new approach to the crystal engineering of extended compounds and has recently seen more attention as the frequency with which 'surprise' ligands are appearing in hybrid materials. Researchers are eager to comprehend *in situ* ligand synthesis in order to exploit this synthetic pathway for the production of novel CPs. Some advantages of *in situ* ligand synthesis are illustrated by Zhang [51]: producing ligands from an organic precursor eliminates the need to synthesize ligands directly, it provides a slow formation process for the ligands thereby allowing for the growth of sufficiently large single crystals for structure determination, and finally these processes may be environmentally friendly. This complementary approach to crystal engineering has yielded numerous examples of *in situ* ligand syntheses ranging from acylation, hydroxylation, carbon–carbon bond formation, alkylation, and hydrolysis [51–58]. According to the Zhang review, hydrothermal decarboxylation was first detected in 2003 by Lu and co-workers [59] when they observed the formation of 1,4-biphencarboxyl from 1,2,4-benzenetricarboxylic acid in the presence of copper (II) acetate. Decarboxylation specifically within actinide and lanthanide systems (although rare) has been observed recently [31,60–65].

Using the various synthetic pathways described above to create novel materials, our interests lie in the synthesis of uranium (VI) CPs including both homo- and heterometallic compounds. The choice of L-pyroglutamic acid (Scheme 1) as an organic linker will help promote heterometallic compounds by taking advantage of the distinct hard and soft functional groups within this linker. Furthermore, we can theorize the different coordination modes of the metal centers to L-pyroglutamic acid by utilizing hard/soft acid/base (HSAB) distinctions [66,67]. A harder metal such as uranium will tend to bind to a harder functional group such as a carboxylic acid while a softer metal center will bind to a softer functional group, in this case the nitrogen of the pyrrolidine ring within L-pyroglutamic acid. This approach has been successful in the past while utilizing 3,5-pyrazoledicarboxylic acid as the linker to produce a bimetallic uranium–copper coordination polymer [18]. Herein, however, a novel uranium (VI) compound was synthesized, $(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2$ (**1**), that contains metal centers polymerized through both L-pyroglutamate and oxalate linkages. The oxalate anions are believed to be the result of an *in situ* decarboxylation of L-pyroglutamic acid followed by coupling to form the anions as observed in the final structure.



Scheme 1. L-Pyroglutamic acid, $C_5H_7NO_3$.

2. Experimental

2.1. Synthesis

Caution: The uranium (VI) nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, used in this study contains depleted uranium yet standard precautions for handling radioactive substances should be followed.

The $UO_2(NO_3)_2 \cdot 6H_2O$ was purchased from Strem Chemicals while L-pyroglutamic acid was purchased from Fisher Scientific. Each reagent was used without further purification. Crystals of **1** were obtained from a hydrothermal reaction mixture that contained 251 mg (0.5 mmol) uranium (VI) nitrate hexahydrate, 66 mg (0.5 mmol) L-pyroglutamic acid and 1.36 g deionized H_2O (77 mmol). These reagents were combined in a 23 mL Teflon-lined stainless steel reaction vessel (initial $pH = 1.23$) and heated to 120 °C for 3 days. The reaction mixture was then allowed to cool to room temperature. The yellow mother liquor (final $pH = 1.13$) was extracted and the remaining yellow crystals were subsequently washed with both distilled water and ethanol and allowed to air dry at room temperature (17 mg, 3.8% yield based upon the uranium).

2.2. Instrumentation

The crystal structure of compound **1** was determined via single crystal X-ray diffraction and the crystallographic data are summarized in Table 1. A yellow crystal of **1** was mounted on a glass fiber using epoxy gel. Intensity data were collected on a Bruker SMART diffractometer equipped with an APEX II CCD detector. Data processing

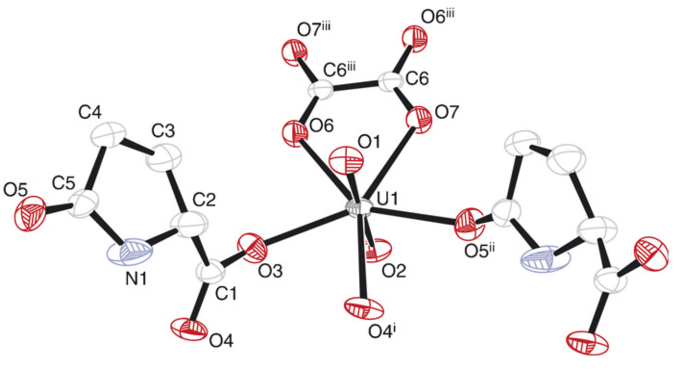


Fig. 1. ORTEP of compound **1**. Ellipsoids are shown at the 50% level and the hydrogen atoms are omitted for clarity. Symmetry equivalents: (i) $-x, y, -z+1/2$; (ii) $x, -y, z+1/2$; (iii) $-x+1/2, -y+1/2, -z$.

Table 1
Crystallographic data for compound **1**, $(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2$

Formula weight (g/mol)	884.30
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	22.541(6)
b (Å)	5.7428(15)
c (Å)	15.815(4)
α (deg)	90
β (deg)	119.112(4)
γ (deg)	90
Volume (Å^3)	1788.6(8)
Z	4
D_c (Mg/m^3)	3.284
Absorption coefficient (mm^{-1})	18.168
Absorption correction	Semi-empirical
F(000)	1568
Crystal size (mm)	$0.12 \times 0.04 \times 0.02$
Theta range for data collection	2.07–26.43
Index ranges	$-28 \leqslant h \leqslant 28$, $-5 \leqslant k \leqslant 7$, $-19 \leqslant l \leqslant 19$
Reflections collected	13,566
R_{int} (independent reflections)	0.0498 (1840)
Goodness-of-fit on F^2	1.040
R^a $[I > 2\sigma(I)]$	0.0237
$wR_2{}^a$	0.0367

$^a R = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

was performed using SAINT [68]. The structure was solved using direct methods while the refinement was carried out using SHELXL-97 [69] within the WINGX software suite [70]. Powder X-ray diffraction data were collected on a Rigaku MiniFlex II Desktop X-ray Diffractometer (Cu-$K\alpha$, 3–60°, 0.05° step, 1.0 s step^{-1}) and manipulated utilizing the JADE software package [71]. UV–Vis investigations were performed on a Shimadzu UV-2401PC UV–Vis recording spectrophotometer. Fluorescent studies were conducted on a Shimadzu RF-5301 PC spectrofluorophotometer (ligand excitation wavelength: 270 nm; uranyl excitation wavelength: 365 nm [72]; emission wavelength: 400–600 nm; slit width: 3.0 nm (excitation) and 3.0 nm (emission); sensitivity: high with a UV-39 filter.

3. Results and discussion

The structure of compound **1** (Fig. 1) was found to consist of central hexavalent uranium metal centers bound to two axial oxygen atoms, O1 and O2, at an average distance of *ca.* 1.757 Å forming an angle of 178.4(2)°. The uranium is further bound to two L-pyroglutamate anions through a carboxylate oxygen atom, O3 and O4, at a distance of 2.349(4) and 2.401(4) Å, respectively. A third acid unit is bound through O5 from the γ-lactam at a distance of 2.345(4) Å from the uranium. An oxalate anion is additionally bound to the uranium in a bidentate fashion through O6 and O7 at distances of 2.422(4) and 2.441(4) Å, respectively, to form the pentagonal bipyramidal geometry of the uranium (VI). Furthermore, each oxalate anion bridges two uranium metal centers to form $[(UO_2)_2(O_6)(C_2O_4)]$ dimers (Fig. 2). These dimers are additionally linked through the O3–C1–O4 carboxylate group to form "zigzag" chains as can be viewed down the [001] direction which ultimately form a 3D structure through the bonding of the γ-lactam (O5) and the uranium metal centers (Fig. 3).

The intriguing feature of this compound is the presence of the oxalate linker in the final product despite the fact there was no oxalic acid in the starting materials. In the past, a few possible explanations have been proposed for the formation of oxalate anions. For example, it has been suggested that these linkages could result from the reductive coupling of ambient CO_2(g) [73–77]. If this was occurring in the L-pyroglutamic acid system, the theoretical yield (assuming CO_2(g) was the limiting reagent) would be

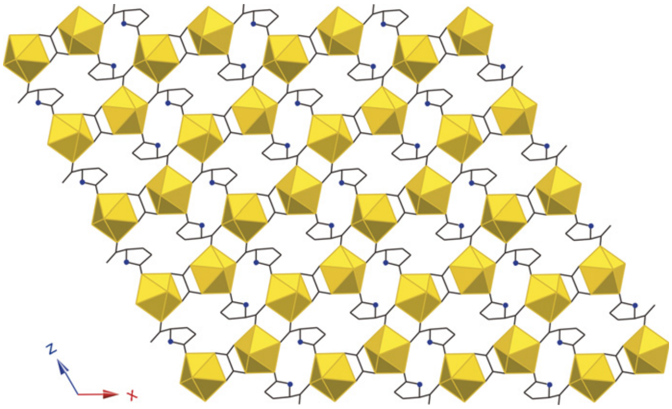


Fig. 2. A view of compound **1** down the [010] direction. The polyhedra are the uranium pentagonal bipyramids whereas the black lines are the organic linkers. The spheres are the nitrogen atoms from the L-pyroglutamate anions. The hydrogen atoms have been omitted for clarity.

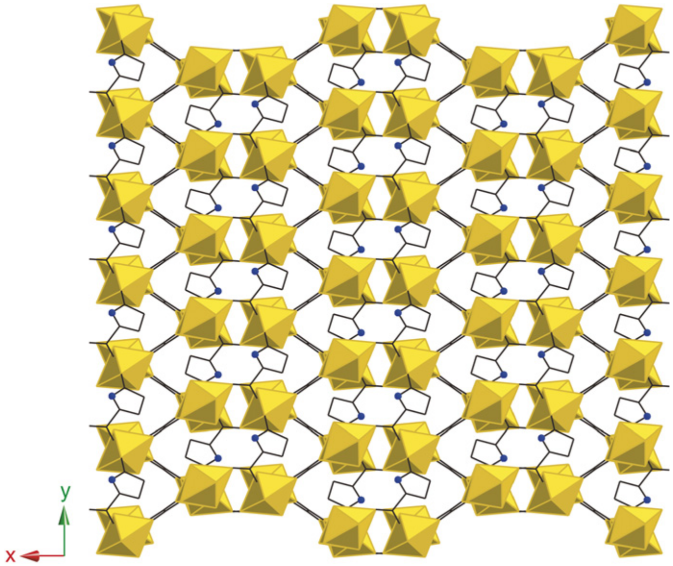


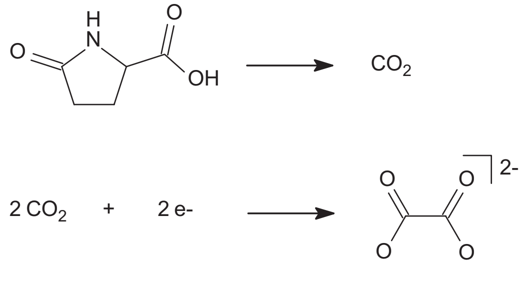
Fig. 3. Compound **1** as viewed down the [001] direction.

0.013 mg. The actual yield was 17 mg indicating that the oxalate could not have resulted from ambient CO_2(g). An alternative rationale is the degradation/oxidation of the starting organic [78] to an oxalate linkage or an oxalate precursor as demonstrated when L-ascorbic acid undergoes oxidative degradation to form dehydroascorbic acid which further decomposes to produce oxalic acid [79–82]. A third and more plausible explanation for this system is decarboxylation of the starting materials [61,83–86]. Under hydrothermal conditions within this system, the oxalate linkages could be formed via a two-step process by which decarboxylation of the organic (L-pyroglutamic acid) is followed by subsequent coupling to produce the oxalate linkages as seen in the final structure of **1** (Scheme 2).

Compound **1** $[(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2]$ contains the starting organic (L-pyroglutamic acid) in the final product along with the oxalate anion presumably produced from decarboxylation as previously hypothesized. In an effort to understand what factors play a role in influencing the decarboxylation process, a series of hydrothermal reactions were performed whereby the reaction conditions and the molar ratios of the starting materials were altered. Through this series of reactions, it was found that the decarboxylation process which produced compound **1** was influenced by the reaction time wherein increased times generated higher yields (3.8% for 3 days vs. 27.4% for 7 days). When the time was reduced to 1 day (keeping the temperature constant at 120 °C) the reaction yielded only yellow solution. Altering the molar ratio of the L-pyroglutamic acid (while keeping the reaction conditions unaltered) also affected the formation of **1**. When the amount of L-pyroglutamic acid was decreased to a third, the reaction produced a yellow solution, however, when the starting organic was only diminished by a half the reaction still yielded the oxalate containing compound **1**. If the L-pyroglutamic acid to uranium ratio was increased to either 3:1 or 5:1, a dark orange powder resulted which consisted of $(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2$ (**1**) as verified by powder X-ray diffraction.

In an effort to produce a heterometallic compound, L-pyroglutamic acid was combined with copper (II) and uranium (VI) under hydrothermal conditions (120 °C, 3 days). Rather than producing a U–Cu–pyroglutamate as intended, an interesting observation was noted whereby a known uranium-oxalate $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2 \cdot H_2O]$ [87] was synthesized along with a green secondary phase identified via powder X-ray diffraction (PDF# 21-0297) to be a hydrated copper oxalate, moolooite $(Cu(C_2O_4) \cdot nH_2O;\ 0 \leqslant n \leqslant 1)$ [88,89]. The Abraham et al. compound, however was originally produced from the direct assembly of uranium (VI) nitrate and oxalic acid (along with potassium nitrate) under hydrothermal conditions. While L-pyroglutamic acid was the starting organic in this system, the linker was not observed in either of these aforementioned crystalline products which is in contrast to the formation of **1**. Compound **1** contains hexavalent uranium metal centers linked through both oxalate and L-pyroglutamate anions. The L-pyroglutamate linkers are subsequently absent with the addition of copper (II) in the reaction conditions leaving oxalate anions as the only organic linker observed in both moolooite and $(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2 \cdot H_2O$. Copper (II) has been present in other systems where decarboxylation was observed indicating that copper (II) may mediate or play a promotional role in this decarboxylation process. For example, other decarboxylation processes promoted by copper (II) ions have recently been reported [59,84,90–92]. Another transition metal, molybdenum (VI), has also been theorized to promote the decarboxylation of the starting organics malonic or malic acid (along with potassium hydroxide) to produce the oxalate containing $K_2[MoO(O_2)_2(C_2O_4)]$ [93] or using either tartaric or ascorbic acid (in addition to ammonium vanadate) as the starting organics to yield $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ [94].

Along with interesting structural features, **1** also contains attractive photophysical properties that can be recognized through luminescent investigations. The luminescence of hexavalent uranium in both the solution and solid state has been known for over 150 years and is recognized to result from vibronic transitions of the molecular $[O{=}U{=}O]^{2+}$ structure [95]. As such, compound **1** has been shown to exhibit photoluminescence emission in the solid state at room temperature (Fig. 4). When the uranyl ion is excited directly at 365 nm [72] the emission spectrum reflects the symmetrical vibration of the U=O bond to produce the characteristic vibronic structure of the UO_2^{2+} moiety [34–38,95,96]. The average



Scheme 2. A schematic illustrating the proposed pathway for the oxalate formation in compound **1**.

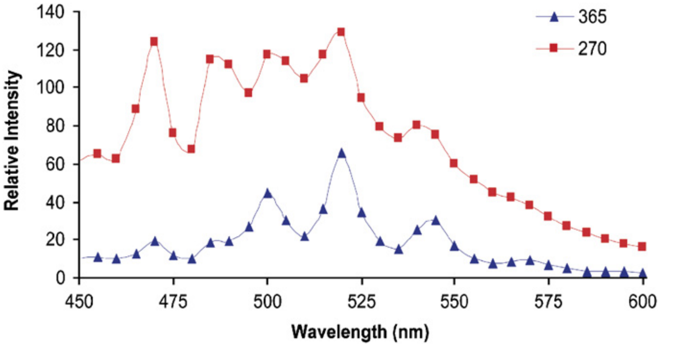


Fig. 4. Emission spectra for compound **1** at different excitation wavelengths: ligand (270 nm) and uranyl (365 nm).

vibronic splitting energy determined for the transitions is $\nu_s = 836 \pm 37\,\text{cm}^{-1}$ which agrees with the literature value of $\nu_s = 860\,\text{cm}^{-1}$ [95]. Compound **1** was alternatively excited at the ligand excitation wavelength of 270 nm also resulting in the uranyl emission from *ca.* 450 to 600 nm. The increased intensity of uranyl emission (compared to emission resulting from excitation at 365 nm) resulting from the ligand excitation suggests that there is an energy transfer from the ligand to the uranium metal centers, exemplifying indirect sensitization in the solid state.

4. Conclusions

A novel uranium oxalate, $(UO_2)_2(C_2O_4)(C_5H_6NO_3)_2$, was produced under hydrothermal conditions. This compound contains uranium metal centers linked through both L-pyroglutamates and oxalate anions. With the lack of oxalic acid present within the starting materials, the oxalate anions were formed *in situ* whereby decarboxylation of the starting material (L-pyroglutamic acid in this case) occurs followed by subsequent coupling of CO_2 to form the oxalate linkages as observed in the final crystal structure. Compound **1** has also been shown to exhibit the characteristic uranyl emission spectrum upon either direct uranyl excitation or ligand excitation. An increase in the intensity upon ligand excitation indicates an energy transfer to the uranyl cations thus providing an example of the antenna effect in the solid state.

5. Supplementary material

Crystallographic data (excluding structure factors) for compound **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 647512. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was supported by (1) The National Science Foundation (DMR-0348982 and DMR-0419754) and (2) the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, U.S. Department of Energy, under Grant DE-FG02-05ER15736 at GWU.

References

[1] C. Janiak, Dalton Trans. (2003) 2781–2804.
[2] G. Ferey, Chem. Mater. 13 (2001) 3084–3098.
[3] S.L. James, Chem. Soc. Rev. 32 (2003) 276–288.
[4] R. Nandini Devi, J. Zubieta, Inorg. Chim. Acta 343 (2003) 313–316.
[5] M.I. Khan, E. Yohannes, R.C. Nome, S. Ayesh, V.O. Golub, C.J. O'Connor, R.J. Doedens, Chem. Mater. 16 (2004) 5273–5279.
[6] M.I. Khan, E. Yohannes, S. Ayesh, R.J. Doedens, J. Mol. Struct. 656 (2003) 45–53.
[7] H. Li, M. Eddaoudi, M. O'Keeffe, M. Yaghi, Nature 402 (1999) 276–279.
[8] S. Kitagawa, K. Uemura, Chem. Soc. Rev. 34 (2005) 109–119.
[9] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319–330.
[10] J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239–8247.
[11] M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 369–378.
[12] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466–1496.
[13] T. Duren, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, Langmuir 20 (2004) 2683–2689.
[14] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi Omar, Science 295 (2002) 469–472.
[15] R. Horikoshi, T. Mochida, Chem. Rev. 250 (2006) 2595–2609.
[16] C. Livage, C. Egger, G. Ferey, Chem. Mater. 13 (2001) 410–414.
[17] C.L. Cahill, D.T. de Lill, M. Frisch, Cryst. Eng. Commun. 9 (2007) 15–26.
[18] M. Frisch, C.L. Cahill, Dalton Trans. (2006) 4679–4690.
[19] M. Frisch, C.L. Cahill, Dalton Trans. (2005) 1518–1523.
[20] J.-Y. Kim, A.J. Norquist, D. O'Hare, Chem. Mater. 15 (2003) 1970–1975.
[21] J.-Y. Kim, A.J. Norquist, D. O'Hare, Dalton Trans. (2003) 2813–2814.
[22] B. Masci, P. Thuery, Polyhedron 24 (2005) 229–237.
[23] P. Thuery, Chem. Commun. (2006) 853–855.
[24] L.A. Borkowski, C.L. Cahill, Acta Crystallogr. Sect. E. 60 (2004) m198–m200.
[25] J. Leciejewicz, N.W. Alcock, T.J. Kemp, Struct. Bond. 82 (1995) 43–84.
[26] P.C. Burns, Can. Mineral. 43 (2005) 1839–1894.
[27] Y.-R. Xie, H. Zhao, X.-S. Wang, Z.-R. Qu, R.-G. Xiong, X. Xue, Z. Xue, X.-Z. You, Eur. J. Inorg. Chem. (2003) 3712–3715.
[28] Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, J.-S. Chen, Chem.-Eur. J. 11 (2005) 2642–2650.
[29] Z.-T. Yu, G.-H. Li, Y.-S. Jiang, J.-J. Xu, J.-S. Chen, Dalton Trans. (2003) 4219–4220.
[30] Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, G.-D. Li, J.-S. Chen, Chem. Commun. (2004) 1814–1815.
[31] W. Chen, H.-M. Yuan, J.-Y. Wang, Z.-Y. Liu, J.-J. Xu, M. Yang, J.-S. Chen, J. Am. Chem. Soc. 125 (2003) 9266–9267.
[32] M. Ephritikhine, Dalton Trans. (2006) 2501–2516.
[33] C.-M. Wang, C.-H. Liao, H.-M. Kao, K.-H. Lii, Inorg. Chem. 44 (2005) 6294–6298.
[34] G. Geipel, A. Brachmann, V. Brendler, G. Bernhard, H. Nitsche, Radiochim. Acta 75 (1996) 199–204.
[35] S.J. Formosinho, H.D. Burrows, M. da Graca Miguel, M.E.D.G. Azenha, I.M. Saraiva, A.C.D.N. Ribeiro, I.V. Khudyakov, R.G. Gasanov, M. Bolte, M. Sarakha, Photochem. Photobiol. Sci. 2 (2003) 569–575.
[36] S.M. Fonseca, H.D. Burrows, M.G. Miguel, M. Sarakha, M. Bolte, Photochem. Photobiol. Sci. 3 (2004) 317–321.
[37] H.D. Burrows, M. da Graca Miguel, Adv. Colloid Interface Sci. 89–90 (2001) 485–496.
[38] G. Meinrath, Y. Kato, T. Kimura, Z. Yoshida, Radiochim. Acta 82 (1998) 115–120.
[39] Y.-Z. Zheng, M.-L. Tong, X.-M. Chen, Eur. J. Inorg. Chem. (2005) 4109–4117.
[40] S.L. Suib, A. Kostapapas, D. Psaras, J. Am. Chem. Soc. 106 (1984) 1614–1620.
[41] S.L. Suib, K.A. Carrado, Inorg. Chem. 24 (1985) 863–867.
[42] S. Das, C. Madhavaiah, S. Verma, P.K. Bharadwaj, Inorg. Chim. Acta 359 (2006) 548–552.
[43] J-C.G. Bunzli, C. Piguet, Chem. Rev. 102 (2002) 1897–1928.
[44] N. Sabbatini, M. Guardigli, J.M. Lehn, Coord. Chem. Rev. 123 (1993) 201–228.
[45] R.C. Ewing, Can. Mineral. 39 (2001) 697–715.

[46] D.L. Clark, S.D. Conradson, R.J. Donohoe, D.W. Keogh, D.E. Morris, P.D. Palmer, R.D. Rogers, C.D. Tait, Inorg. Chem. 38 (1999) 1456–1466.
[47] J.J. Lenhart, S.E. Cabaniss, P. MacCarthy, B.D. Honeyman, Radiochim. Acta 88 (2000) 345–353.
[48] L. Rao, J. Jiang, P. Zanonato, P. Di Bernardo, A. Bismondo, A.Y. Garnov, Radiochim. Acta 90 (2002) 581–588.
[49] D.A. Palmer, C. Nguyen-Trung, J. Sol. Chem. 24 (1995) 1281–1291.
[50] E.L. Shock, D.C. Sassani, H. Betz, Geochim. Cosmochim. Acta 61 (1997) 4245–4266.
[51] X.-M. Zhang, Coord. Chem. Rev. 249 (2005) 1201–1219.
[52] O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 2705–2712.
[53] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511–522.
[54] O.R. Evans, R.-G. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem. Int. Ed. 38 (1999) 536–538.
[55] J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin, Y.-H. Wen, J. Am. Chem. Soc. 126 (2004) 7796–7797.
[56] X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, K.-F. Li, Y.-X. Tong, X.-M. Chen, Chem.-Eur. J. 8 (2002) 3187–3194.
[57] X.-M. Zhang, M.-L. Tong, X.-M. Chen, Angew. Chem. Int. Ed. 41 (2002) 1029–1031.
[58] X.-M. Chen, M.-L. Tong, Acc. Chem. Res. 40 (2007) 162–170.
[59] Y. Yan, C.-D. Wu, C.-Z. Lu, Z. Anorg. Allg. Chem. 629 (2003) 1991–1995.
[60] Y.-S. Jiang, Z.-T. Yu, Z.-L. Liao, G.-H. Li, J.-S. Chen, Polyhedron 25 (2006) 1359–1366.
[61] Z.-B. Han, X.-N. Cheng, X.-F. Li, X.-M. Chen, Z. Anorg. Allg. Chem. 631 (2005) 937–942.
[62] Z.B. Han, Y.K. He, Acta Crystallogr. Sect. E 62 (2006) m2374–m2376.
[63] Y.-Q. Sun, J. Zhang, G.-Y. Yang, Chem. Commun. (2006) 1947–1949.
[64] L.-Z. Zhang, W. Gu, B. Li, X. Liu, D.-Z. Liao, Inorg. Chem. 46 (2007) 622–624.
[65] B. Li, W. Gu, L.-Z. Zhang, J. Qu, Z.-P. Ma, X. Liu, D.-Z. Liao, Inorg. Chem. 45 (2006) 10425–10427.
[66] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533–3539.
[67] R.G. Pearson, Coord. Chem. Rev. 100 (1990) 403–425.
[68] SAINT, V 5.053. Area-Detector Integration Software, Seimens Industrial Automation, Inc., Madison, WI, 1998.
[69] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis (Release 97–2), University of Gottingen, Germany, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[70] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.
[71] JADE, V6.1, Materials Data Inc., Livermore, CA, 2002.
[72] P.M. Almond, C.E. Talley, A.C. Bean, S.M. Peper, T.E. Albrecht-Schmitt, J. Solid State Chem. 154 (2000) 635–641.
[73] D.M.Y. Barrett Adams, I.A. Kahwa, J.T. Mague, New J. Chem. 22 (1998) 919–921.
[74] L.J. Farrugia, S. Lopinski, P.A. Lovatt, R.D. Peacock, Inorg. Chem. 40 (2001) 558–559.
[75] D.A. Morgenstern, R.E. Wittrig, P.E. Fanwick, C.P. Kubiak, J. Am. Chem. Soc. 115 (1993) 6470–6471.
[76] R.T. Stibrany, H.J. Schugar, J.A. Potenza, Acta Crystallogr. Sect. E 61 (2005) m1904–m1906.
[77] W.-K. Wong, L.-L. Zhang, F. Xue, T.C.W. Mak, Dalton (2000) 2245–2246.
[78] O.R. Evans, W. Lin, Cryst. Growth Des. 1 (2001) 9–11.
[79] R.W. Herbert, E.L. Hirst, E.G.V. Percival, R.J.W. Reynolds, F. Smith, J. Chem. Soc. (1933) 1270–1290.
[80] C. Unaleroglu, B. Zumreoglu-Karan, Y. Zencir, T. Hokelek, Polyhedron 16 (1997) 2155–2161.
[81] A.M. Thomas, G.C. Mandal, S.K. Tiwary, R.K. Rath, A.R. Chakravarty, Dalton (2000) 1395–1396.
[82] P. Orioli, B. Bruni, M. Di Vaira, L. Messori, F. Piccioli, Inorg. Chem. 41 (2002) 4312–4314.
[83] A.J. Belsky, P.G. Maiella, T.B. Brill, J. Phys. Chem. A 103 (1999) 4253–4260.
[84] M.V. Yigit, Y. Wang, B. Moulton, J.C. MacDonald, Cryst. Growth Des. 6 (2006) 829–832.
[85] L. Hegedues, H.-D. Foersterling, M. Wittmann, Z. Noszticzius, J. Phys. Chem. A 104 (2000) 9914–9920.
[86] X. Li, R. Cao, D. Sun, Q. Shi, W. Bi, M. Hong, Inorg. Chem. Commun. 6 (2003) 815–818.
[87] L. Duvieubourg, G. Nowogrocki, F. Abraham, S. Grandjean, J. Solid State Chem. 178 (2005) 3437–3444.
[88] R.M. Clarke, I.R. Williams, Mineral. Mag. 50 (1986) 295–298.
[89] F.C. Hawthorne, J. Jambor, K.W. Bladh, E.A.J. Burke, J.D. Grice, D. Phillips, A.C. Roberts, R.A. Schedler, J.E. Shigley, Am. Mineral. 72 (1987) 1023–1028.
[90] X.-M. Zhang, R.-Q. Fang, Inorg. Chem. 44 (2005) 3955–3959.
[91] Y.-Z. Zheng, M.-L. Tong, X.-M. Chen, New J. Chem. 28 (2004) 1412–1415.
[92] W. Yang, C. Lu, H. Zhuang, J. Chem. Soc. Dalton Trans. (2002) 2879–2884.
[93] C. Djordjevic, K.J. Covert, E. Sinn, Inorg. Chim. Acta 101 (1985) L37–L39.
[94] M. Cindric, N. Strukan, V. Vrdoljak, M. Devcic, B. Kamenar, J. Coord. Chem. 55 (2002) 705–710.
[95] E. Rabinowitch, R.L. Belford, Spectroscopy and Photochemistry of Uranyl Compounds, New York, 1964.
[96] A. Brachmann, G. Geipel, G. Bernhard, H. Nitsche, Radiochim. Acta 90 (2002) 147–153.