

Separation of actinides and lanthanides: Synthesis and molecular structure of a new di- μ -phenoxo-bridged dinuclear bis(dioxouranium(VI)) complex

Ramu Kannappan^a, Duncan M. Tooke^b, Anthony L. Spek^b, Jan Reedijk^{a,*}

^a *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

^b *Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 20 July 2005; accepted 14 August 2005

Available online 27 September 2005

Abstract

The new phenoxo-bridged uranyl [(UO₂)₂L₂(thf)₂] [H₂L = N(2-oxo-phenyl)-3-methoxy salicylaldiminato (C₁₄H₁₁NO₃)] compound has been synthesized and characterized. The 3D structure of the free ligand is also reported. The complex crystallizes in the monoclinic space group *P*2₁/*c* with lattice parameters *a* = 19.5915(15) Å, *b* = 10.4096(9) Å, *c* = 17.5216(14) Å and β = 99.9960(7)° with *z* = 4. The compound consists of a dinuclear unit composed of two dioxouranium(VI) ions, bridged by two phenoxide oxygens. The coordination around each uranium atom can be regarded as approximately pentagonal bipyramidal. The two uranyl groups are separated by 3.9192(5) Å. The title complex is one of the few examples for bis-uranyl groups bridged by phenoxo ligands. These types of ligands are candidates for the sequestration of the uranium from nuclear waste and provide a good selectivity over competing lanthanide cations in solution. The ligand has been found to selectively bind to a representative actinide (UO₂²⁺) rather than to lanthanum (Ln³⁺), which is probably related to the larger ionic radii of Ln(III). So, the ligand is not suitable to clutch two lanthanide metals via the phenolate bridge (Ln–O_(phenol)–Ln). The spherical shape and the larger size of the Ln(III) ions apparently do not allow a fit within the bite angle of phenolate bridge.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Dinuclear uranium; Crystal structure; Phenoxo-bridge; THF as ligands

1. Introduction

The development of nuclear science and technology in particular to the peaceful uses of nuclear energy has been ongoing for a long period. The reduction of radioactive waste and further improvement of nuclear safety and reliable environment management system are the tasks that remain to be solved by exploring the wider application of nuclear technology [1]. Uranium is one of the elements that contribute to the long-term radiotoxicity of nuclear waste, and the mixture of lanthanides and actinides is a compli-

cated one, from which the actinides should be separated for recovery. Unfortunately, lanthanide/actinide separations are among the most difficult separations of all metal ions [2]. This difficulty is primarily related to the other identical oxidation states and the almost equal ionic radii of the involved metals [3]. Because of the safety requirements in nuclear waste disposals, lanthanide and actinide discrimination is an area of worldwide concern.

Phenoxo-bridged uranyl compounds are scarce in comparison to the d-block metals. In contrast, as far as we know, only few publications have been reported in which phenoxo-bridged uranium compounds are reported [4–7]. An example is the dioxouranium(VI) citrate species [8]. In the course of our studies on the synthesis and structure

* Corresponding author.

E-mail address: reedijk@chem.leidenuniv.nl (J. Reedijk).

of dioxo-uranium compound with the ligand N(2-oxyphenyl)-3-methoxy salicylaldiminato abbreviated H_2L , we obtained the crystals of $[(UO_2)_2L_2(thf)_2]$. Herein, we report the synthesis and characterization of this new bisphenoxo-bridged uranyl(VI) complex, together with its X-ray structure and solution NMR studies.

2. Experimental

2.1. Synthesis of N(2-oxyphenyl)-3-methoxy salicylaldiminato (H_2L)

2-(Aminomethyl) pyridine (2.16 g, 20 mmol) dissolved in ethanol (5 mL) was added to the stirred ethanol solution of O-vanillin (3.04 g, 20 mmol). The reaction mixture was stirred overnight. The solvent was removed by rotavaporation. The final red residue was saturated with diethyl ether to obtain a red solid, which was recrystallized by hot methanol. Yield: 62.8 % (3.33 g), m.p. (104 °C), IR: 1625 cm^{-1} (C=N), 1H NMR (in CD_3OD): 8.63 (s, 1H, imine -H), 8.53 (m, 1H, Py), 7.87 (m, 1H, Py), 7.51 (m, 1H, Py), 7.36 (m, 1H, Py), 7.02 (m, 2H, Ar), 6.83 (m, 1H, Ar), 3.85 (s, 2H, Benzylic), 3.31 (s, 3H, OCH_3): Mass: theoretical: 242.3 (obs.: 243.4). Elemental analysis: Calc. For $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.01; H, 5.94; N, 11.62%.

2.2. Synthesis of $[(UO_2)_2L_2(thf)_2]$

A methanol solution of uranyl nitrate (0.25 g, 0.5 mmol, 10 mL) was added to a warm solution of ligand (0.24 g, 1.0 mmol, 30 mL) in $CHCl_3$ with 3 equiv. of KOH. The resultant red solution was kept for stirring overnight. The solution was filtered and the filtrate kept for slow evaporation after a week, a precipitate was obtained, which was recrystallized with hot $CH_3OH:CHCl_3$ mixture. X-ray quality crystals were obtained from THF after 4 days. Yield 0.482 g (41%). Anal. Calc. for $C_{36}H_{38}N_2O_{12}U_2$: C, 37.05; H, 3.28; N, 2.40. Found: C, 39.93; H, 2.93; N, 3.20%. IR (ν_{max}/cm^{-1}): 1610 (C=N); 1469 (C=C) and 900 (O=U=O).

2.3. Physical measurements

All the chemicals and solvents were of analytical grade and used as such without prior purification. (*Caution.* Uranyl nitrate is a weak radioactive salt and care should be taken in handling the compound). Infrared spectra (4000–300 cm^{-1} , respectively, 4 cm^{-1}) were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. 1H NMR spectra were recorded on a Bruker 300 DPX MHz spectrometer in $CDCl_3$ solution for ligand and the uranyl complex was recorded in CD_3OD , using TMS as the internal standard. C, H and N analyses were performed with a Perkin–Elmer 2400 series II analyzer. Electrospray mass spectra (ESI–MS) in methanol were recorded on a Thermo Finnigan AQA apparatus.

2.4. Single crystal X-ray structures

The X-ray data were collected with a Nonius Kappa-CCD diffractometer using graphite-monochromatized $Mo K\alpha$ radiation. An initial unit cell determination was performed using the Nonius Collect software suite [9] and the DIRAX [10] indexing program. A complete dataset was collected, and integrated by the HKL2000 [11] and SORTAV [12] programs. No absorption correction was applied, given the small size of the crystal. The structure was solved using the SHELXS-86 program [13], and refined with SHELXL-97 [14]. The program PLATON [15] was used for space group determination, validation and the preparation of diagrams. Hydrogen atoms were placed at idealized positions and allowed to ride on the connecting atom. Selected crystal data are given in Table 1.

3. Results and discussion

3.1. Ligand and metal coordination

The tridentate ligand of N(2-oxyphenyl)-3-methoxy salicylaldiminato (H_2L) was successfully synthesized by the reaction of 2-(aminomethyl) pyridine with O-vanillin in ethanol. The methanolic solution of uranyl nitrate was reacted with the chloroform solution of ligand and the new bisphenoxo-bridged diuranyl complex was obtained in high yield. Crystals of $[(UO_2)_2L_2(thf)_2]$ suitable for X-ray studies were grown in THF solvents within 4 days and the structure was determined.

The IR spectra [16,17] of the complex show subtle differences in comparison to the free ligand with peaks at

Table 1
Crystallographic data of ligand (H_2L) and its complex $[(UO_2)_2L_2(thf)_2]$

Compound	H_2L	$[(UO_2)_2L_2(thf)_2]$
Empirical formula	$C_{14}H_{13}NO_3$	$C_{36}H_{38}N_2O_{12}U_2$
Formula weight	243.25	116.74
Temperature (K)	150	150
Crystal system	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.9786(14)	19.5915(10)
b (Å)	12.628(5)	10.4096(10)
c (Å)	20.085(3)	17.5216(10)
β (°)	90	99.9960(10)
V (Å ³)	2277.3(10)	3519.1(4)
Z	8	4
$F(000)$	1024	2192
Calculated density (Mg/m^3)	1.419	2.202
Absorption coefficient (mm^{-1})	0.101	9.260
Crystal size (mm)	$0.09 \times 0.15 \times 0.20$	$0.09 \times 0.15 \times 0.20$
Measured reflections	17956	48072
Independent reflections	2491	6917
R_{int}	0.061	0.098
Reflections with $I > 2\sigma(I)$	1644	5166
Final R indices [$I > 2\sigma(I)$]	$R = 0.0482$, $wR_2 = 0.1174$	$R = 0.0354$, $wR_2 = 0.0698$
Goodness-of-fit on F^2	1.02	1.02
Largest difference peak and hole ($e \text{ \AA}^{-3}$)	−0.23 and 0.23	−1.36 and 1.53

1610 cm^{-1} $\nu_{(\text{C}=\text{N})}$ and for the free ligand $\nu_{(\text{C}=\text{N})}$ peak at 1615 cm^{-1} . The absorption band of a similar Schiff base ligand with a copper and a rhenium complex shows the $\nu_{(\text{C}=\text{N})}$ at 1639 cm^{-1} [18,19]. A new peak was also observed at 900 cm^{-1} (O–U–O), which indicates the presence of a linear symmetric dioxouranium(VI) group [20]. The uranyl complex ^1H NMR spectrum shows peaks at 3.78 (t, α THF) and 1.84 ppm (s, β THF) for free THF compared to 4.06 (s, α THF), 3.96 (m, β THF) and 1.92 (m, β THF) for coordinated to UO_2^{2+} . The above observation suggests that the labile THF molecules are partially displaced by the stronger Lewis base CD_3OD in solution.

Attempts to synthesize lanthanide complexes by using the above method with a 2:1 mole ratio of the ligand and metal salts in range of solvents, such as methanol, ethanol, and a mixture of chloroform and methanol, have remained without success. Contrary to our anticipation, only the free ligand was crystallized under these conditions. We also changed the reaction conditions by using different temperatures and times and periods of 3, 6 and even overnight reflux. These repeated attempts to synthesis lanthanide complexes starting from LnCl_3 , $\text{La}(\text{NO}_3)_3$, $\text{Pr}(\text{NO}_3)_3$, GdCl_3 and $\text{Gd}(\text{NO}_3)_3$ with the same ligand were also unsuccessful; the large ionic size (radii, La^{3+} : 1.02 Å for eight-coordination; U^{6+} : 0.80 Å for 6–8 coordination) is likely to be the origin. Unlike uranium coordination, this ligand is not suitable to seize two lanthanide metals via a similar phenolate bridge ($\text{Ln}-\text{O}_{(\text{phenol})}-\text{Ln}$). Experiments in which uranyl and Ln(III) were used in comparable amounts only resulted in the uranyl complexes.

3.2. X-ray crystal structures

The molecular structure of the new N(2-oxyphenyl)-3-methoxy salicylaldiminato ligand and its uranium complex and the hydrogen-bonded network structure of the ligand are depicted in Figs. 1–4; selected crystallographic data are listed in Table 1 and selected bond distances and bond angles given in Table 2.

The uncoordinated ligand is noticeably non-planar and its molecular packing diagram shows a hydrogen-bonded zig-zag infinite chain network. Among the two phenolic OH groups, methoxy group substituted phenolic OH is ionized and the other one is neutral in the reaction medium. Fig. 2 clearly shows that the imine hydrogen ($\text{H}-\text{N}=\text{C}$) is involved in intramolecular hydrogen bonding ($\text{H12}-\text{O2}$: 1.888, $\text{H12}-\text{O1}$: 2.345). The phenolic OH of the aminophenol is involved in intermolecular hydrogen bonding with the O of the methoxy group and with a deprotonated oxygen of a neighbouring unit. This one-dimensional network is depicted in Fig. 2.

Contrary to our expectations, the uranium compound exists as a dinuclear species (Figs. 3 and 4). The molecule has a centre of symmetry and each uranium is coordinated in approximately pentagonal bipyramidal geometry by six oxygen atoms and one nitrogen atom. The uranium ions are bridged by two phenoxo ligands. Two tetrahydrofuran

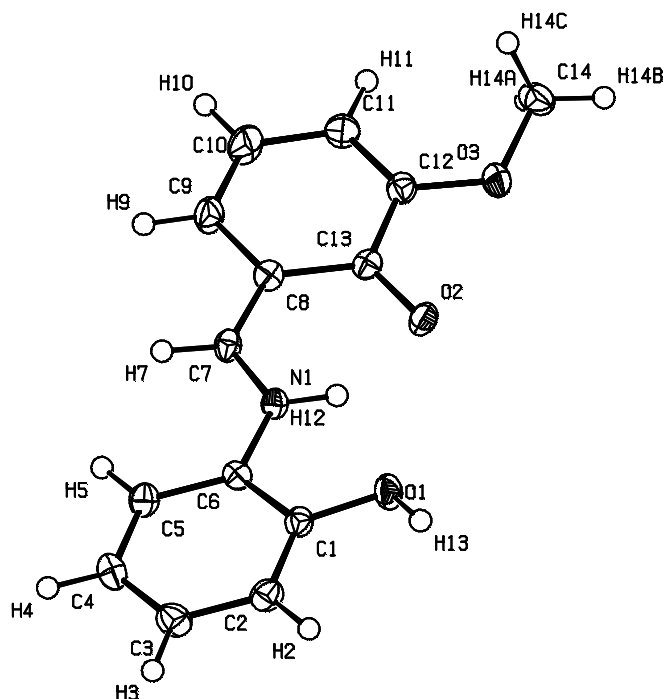


Fig. 1. Molecular structure and labelling scheme for the free ligand N(2-oxyphenyl)-3-methoxy salicylaldiminato. Thermal ellipsoids are drawn at the 50% probability level.

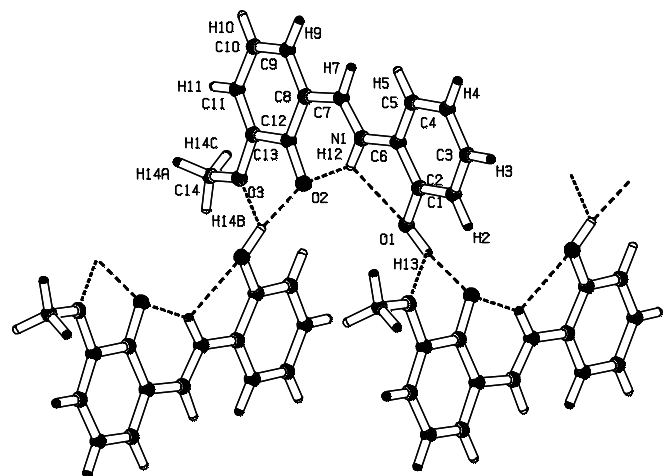


Fig. 2. Drawing of the molecular packing of the ligand along the *a*-axis. Dashed lines indicate intra- and intermolecular H bonds.

ligands are coordinated to each uranium in a non-adjacent *trans* fashion [21]. The coordination is completed by an imine nitrogen and a terminal phenoxide (not bridging). The oxo groups of the uranyl moiety lie *trans* to one another with a near linear O=U=O bond angles of 177.33(18)° for O(7)–U(1)–O(8) and 179.31(18)° for O(9)–U(2)–O(10) (Table 2). The U(1)–O(oxo) distances, at 1.776(4) and 1.769(4) Å, and the U(2)–O(oxo) distances, at 1.769(4) and 1.772(4) Å, are identical within experimental error, and are consistent with the U–O bond lengths found in seven-coordinate uranyl complexes in the literature [22–25]. The U–O (phenoxide terminal) bond lengths

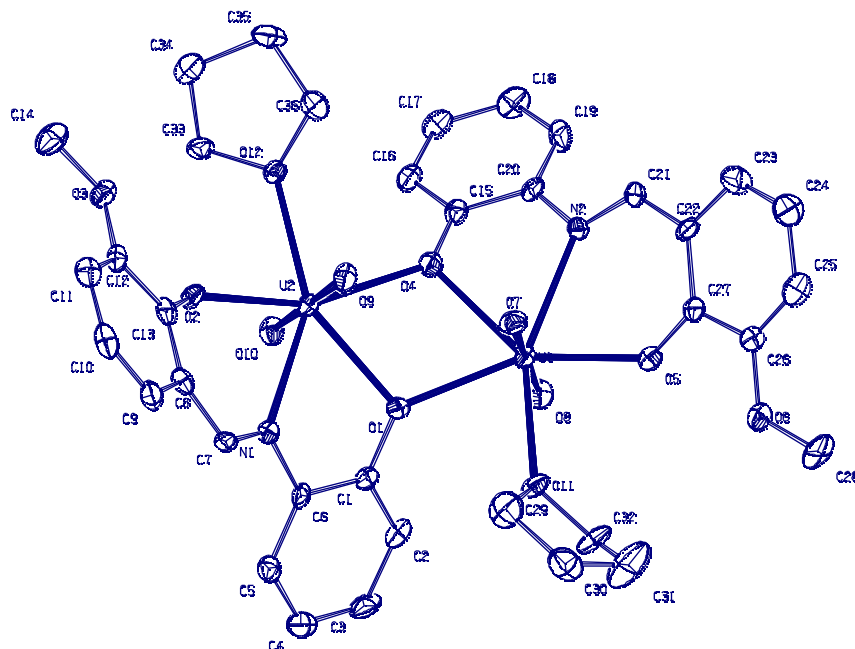


Fig. 3. Molecular structure and labelling scheme for $[(\text{UO}_2)_2\text{L}_2(\text{thf})_2]$. Thermal ellipsoids are drawn at the 50% probability level.

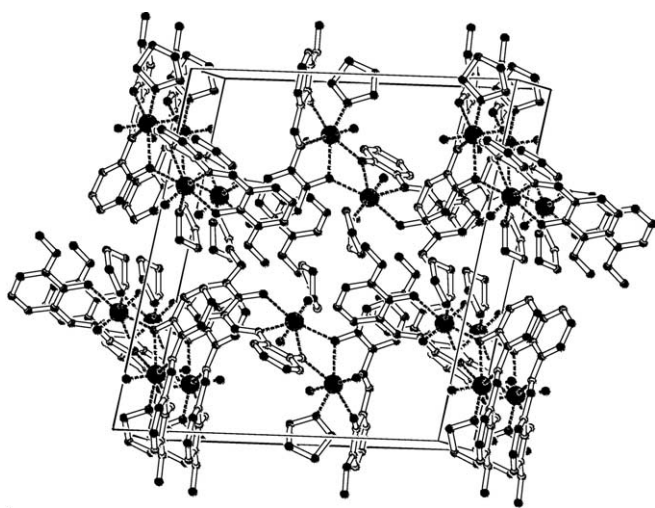


Fig. 4. Packing diagram of $[(\text{UO}_2)_2\text{L}_2(\text{thf})_2]$, viewed along the b -axis. The hydrogen atoms are omitted for clarity.

[2.224(4) and 2.214(4) Å] also show good agreement with literature values [21,22]. The U–(μ -O) bond distances [U(1)–O(1) 2.402(4) Å, U(1)–O(4) 2.429(4) Å, U(2)–O(1) 2.391(4) Å and U(2)–O(4) 2.454(4) Å] and U–(μ -O)–C bond angles [U(1)–O(4)–C(15) 115.3(3)°, U(1)–O(1)–C(1) 135.6(4)°, U(2)–O(4)–C(15) 137.6(4)° and U(2)–O(1)–C(1) 114.6(3)°] are asymmetric, due to the restriction in bonding imposed by the length of the C–N bridge in the ligand. The U–O(THF) bond distances [U(1)–O(11) 2.431(4) Å, U(2)–O(12) 2.428(4) Å] are similar to those found in the literature [21].

Uranium is known to exist in solution as the uranyl dication, in which the atoms are arranged in a linear fashion with the uranium at the centre. The uranyl cation

Table 2
Selected bond lengths (Å) and bond angles (°) for the complex $[(\text{UO}_2)_2\text{L}_2(\text{thf})_2]$

Bond lengths (Å)	
U(1)–O(1)	2.402(4)
U(1)–O(4)	2.429(4)
U(1)–O(5)	2.224(4)
U(1)–O(7)	1.776(4)
U(1)–O(8)	1.769(4)
U(1)–O(11)	2.431(4)
U(1)–N(2)	2.498(5)
U(2)–O(1)	2.391(4)
U(2)–O(2)	2.214(4)
U(2)–O(4)	2.454(4)
U(2)–O(9)	1.769(4)
U(2)–O(10)	1.772(4)
U(2)–O(12)	2.428(4)
U(2)–N(1)	2.528(5)
Bond angles (°)	
O(1)–U(1)–O(4)	66.76 (13)
O(7)–U(1)–O(8)	177.33(18)
O(1)–U(2)–O(4)	66.54(13)
O(9)–U(2)–O(10)	179.31(18)
U(1)–O(1)–U(2)	109.73(15)
U(1)–O(4)–U(2)	106.79(19)
O(2)–U(2)–N(1)	69.38(17)
O(5)–U(1)–N(2)	71.10(16)
O(1)–U(1)–O(5)	156.53(14)
O(4)–U(2)–O(12)	82.16(13)
O(1)–U(1)–O(4)	66.76 (13)
O(7)–U(1)–O(8)	177.33(18)
O(1)–U(2)–O(4)	66.54(13)
O(9)–U(2)–O(10)	179.31(18)
U(1)–O(1)–U(2)	109.73(15)
U(1)–O(4)–U(2)	106.79(19)
O(2)–U(2)–N(1)	69.38(17)
O(5)–U(1)–N(2)	71.10(16)
O(1)–U(1)–O(5)	156.53(14)

favours ligands with coordinate through oxygen and nitrogen atoms, and the above oxyphenyl ligands act as chelating ligands forming the complex. In the case of uranyl cation, the most stable ligands contain 5–6 co-ordinating donor sites to generate a chelate ring around the uranium centre. In the present case, the ligands with solvent (THF) will lead to the sequestration of the uranium and we believe that this will help to achieve a high selectivity over competing cations in solution.

4. Concluding remarks

In summary, we have prepared the new ligand N(2-oxyphenyl)-3-methoxy salicylaldiminato (H_2L) and its di- μ -phenoxo-bridged diuranyl(VI) complex and for both compounds detailed crystallographic studies have been presented. It appears that this salicylaldiminato ligand is suitable for uranium (UO_2^{2+}), but does not bind to lanthanides (La, Pr, Eu and Gd). Uranium exists in aqueous solution as the uranyl cation (UO_2^{2+}), where the atoms are arranged in a linear fashion with the uranium at the centre. The above oxyphenyl ligand is free and flexible to accommodate two uranyl moieties via two phenolate bridges. Apparently, the spherical shape and larger size of the Ln(III) ions do not allow to generate such a phenolate bridge.

We are presently involved in attempts to synthesize related uranyl compounds with only oxygen-donor ligands; and with competition studies from lanthanides and uranyl to improve the separation of uranium species in waste liquids from the nuclear fuel cycle.

5. Supplementary material

Crystallographic data for the free ligand and the uranyl complex are available upon request from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033; www: <http://www.ccdc.cam.ac.uk> or by e-mail from: deposit@ccdc.cam.ac.uk. Please quote the deposition numbers in all correspondences (CCDC Nos. 278628 and 245201, respectively).

Acknowledgements

This research has been financially supported by the Netherlands Technology Research Foundation (STW)

applied science division of The Netherlands Organisation for Scientific Research. We thank Dr. W. Verboom (Twente University), Dr. Elisabeth Bouwman, Dr. Ronald Hage (Unilever) and Mrs. Meenal D. Godbole for valuable assistance and discussions.

References

- [1] S.D. Conradson, D. Manara, F. Wastin, D.L. Clark, G.H. Lander, L.A. Morales, J. Rebizant, V.V. Rondinella, *Inorg. Chem.* 43 (2004) 6922.
- [2] E.N. Rizkalla, G.R. Choppin, *Handbook on the Physics and Chemistry of Rare Earths*, vol. 18, Elsevier, Amsterdam, 1994.
- [3] K.L. Nash, *Solv. Extract. Ion Exc.* 11 (1993) 729.
- [4] P.B. Duval, C.J. Burns, D.L. Clark, D.E. Morris, B.L. Scott, J.D. Thompson, E.L. Werkema, L. Jia, R.A. Andersen, *Angew. Chem.* 40 (2001) 3358.
- [5] A.J. Zozulin, D.C. Moody, R.R. Ryan, *Inorg. Chem.* 21 (1982) 3083.
- [6] L. Salmon, P. Thuery, M. Ephritikhine, *Polyhedron* 22 (2003) 2683.
- [7] U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, R. Graziani, *J. Chem. Soc., Dalton Trans.* (1990) 1533.
- [8] E. Vasca, G. Palladino, C. Manfredi, C. Fontanella, C. Sadun, R. Caminiti, *Eur. J. Inorg. Chem.* (2004) 2739.
- [9] B.V. Nonius, *Software Suite*, Delft University, Delft, 2004.
- [10] A.J.M. Duisenberg, *J. Appl. Crystallogr.* 25 (1992) 92.
- [11] Z. Otwinowski, W. Minor, *Macromolecular Crystallography*, vol. 276, Academic Press, London, 1992.
- [12] R.H. Blessing, *Acta Crystallogr., Sect. A* 51 (1995) 33.
- [13] G.M. Sheldrick, *Program for Crystal Structure refinement*, University of Gottingen, Germany, 1986.
- [14] G.M. Sheldrick, *Program for Crystal Structure refinement*, University of Gottingen, Germany, 1997.
- [15] A.L. Spek, *J. Appl. Crystallogr.* 36 (2003) 7.
- [16] D.E. Fenton, P.A. Vigato, U. Casellato, R. Graziani, M. Vidali, *Inorg. Chim. Acta* 51 (1981) 195.
- [17] X.L. Hu, Y.Z. Li, Q.H. Luo, *Polyhedron* 23 (2004) 49.
- [18] C. Bolzati, M. Porchia, G. Bandoli, A. Boschi, E. Malago, L. Uccelli, *Inorg. Chim. Acta* 315 (2001) 205.
- [19] W. Zhang, S. Liu, C. Ma, D. Jiang, *Polyhedron* 17 (1998) 3835.
- [20] S. Sitran, D. Fregona, U. Casellato, P.A. Vigato, R. Graziani, G. Faraglia, *Inorg. Chim. Acta* 132 (1987) 279.
- [21] M.P. Wilkerson, C.J. Burns, D.E. Morris, R.T. Paine, B.L. Scott, *Inorg. Chem.* 41 (2002) 3110.
- [22] D.M. Barnhart, C.J. Burns, N.N. Sauer, J.G. Watkin, *Inorg. Chem.* 34 (1995) 4079.
- [23] P. Charpin, M. Lance, M. Nierlich, D. Vigner, C. Baudin, *Acta Crystallogr., Sect. C* 43 (1987) 1832.
- [24] R.D. Rogers, L.M. Green, M.M. Benning, *Lanthanide Actinide Res.* 1 (1986) 185.
- [25] R. Kannappan, S. Tanase, D.M. Tooke, A.L. Spek, J. Reedijk, *Polyhedron* 23 (2004) 2285.