

Separation of actinides and lanthanides: crystal and molecular structures of *N,N'*-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1, 2-phenylenediamine and its uranium complex

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Received 9 June 2004; accepted 16 July 2004

Available online 28 August 2004

Abstract

The preparation of the tetradentate dianionic ligand *N,N'*-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine [H_2L] is described, together with the corresponding uranium complex $[UO_2(L)CH_3OH]$. H_2L has been found to selectively bind to a representative actinide (UO_2^{2+}) rather than to lanthanum (La^{3+}) due to its cavity size. Both the free ligand and uranyl complex were characterized by elemental analysis, spectroscopic methods and single-crystal X-ray diffraction. The crystal structure of $[UO_2(L)CH_3OH]$ complex show that uranyl cation adopts a distorted pentagonal bipyramidal conformation, with two imine nitrogen atoms, two phenolic oxygen atoms and a methanol oxygen in the coordination sphere, together with two *trans* oxo groups. The oxo groups have a (O–U–O, 176.85(15)°) angle consistent with linear coordination and U–O bond lengths of 1.786(4) and 1.805(4) Å. The difference in the bond distances can be ascribed to the existence of a hydrogen bond between one uranyl oxygen and the O–H of a methanol of neighboring molecule. This complex has one of the highest solubilities in organic solvents of all uranium compounds, making it a potential candidate for applications in solvent extraction.

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Keywords: Uranium; Crystal structure; N, O donor ligands

1. Introduction

One of the critical tasks in the restoration and nuclear waste is the separation of radioactive waste for disposal and for long term storage. There has been great interest in the separation of actinides (Ac) and lanthanides (Ln) in solution to aid the safe management of nuclear waste

[1–3]. Many Schiff-base ligands have been designed and prepared with the aim of discriminating between Ln and Ac [4–7]. Tetradentate Schiff-base ligands are suitable for coordination to d-block transition metals due to their cavity size and planarity, but very few ligands have been found that chelate to f-block metals. One noticeable limitation in using these kinds of ligands lies in the fact that they are generally insoluble after binding to form a neutral complex [8]. The title complex is highly soluble in a range of solvents, which is likely due to the incorporation of *t*-butyl groups into the ligand.

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Our research is currently focused on the synthesis of related ligands and the formation of analogous Ln^{3+} and (UO_2^{2+}) coordination complexes.

In this paper, we explore the synthesis, spectroscopic characterization, crystal structures and hydrogen bonding interactions of the first of our ligands, *N,N'*-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine, and its corresponding uranyl complex. This ligand has a cavity for which preliminary modelling had shown that a Ln^{3+} ion would probably not bind in the chelating mode, whereas the uranyl groups would bind.

2. Experimental

2.1. Synthesis of *N,N'*-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine [H_2L]

3,5-di-*t*-Butylsalicylaldehyde (4.68 g, 0.02 mol, 2 equiv.) and 4,5-dimethyl-1,2-phenylenediamine (1.32 g, 0.01 mol, 1 equiv.) were refluxed overnight in methanol (50 ml). The solution was allowed to cool to room temperature, yielding a yellow precipitate, which was filtered off and washed with diethyl ether. This solid was dissolved in a $\text{CH}_3\text{OH}/\text{CHCl}_3$ mixture and a small quantity of activated charcoal was added. The solution was heated to reflux and filtered, and the yellow crystalline compound obtained by solvent evaporation. Yield: 2.84 g (47.8%); m.p. 135 °C. *Anal.* Calc. for $\text{C}_{38}\text{H}_{52}\text{N}_2\text{O}_2$: C, 80.19; H, 9.21; N, 4.46. Found: C, 77.47; H, 8.89; N, 4.22%. FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1615 $\nu(\text{C}=\text{N})$ and 1590 $\nu(\text{C}=\text{C})$. MS (m/z): 569. ^1H NMR (CDCl_3): δ 8.33 (s, 2H), 7.36 (m, 2H), 7.25 (m, 2H),

7.07 (m, 2H), 2.20 (s, 6H), 1.53 (s, 6H), 1.45 (s, 15H) and 1.31 (s, 15H).

2.2. Synthesis of $[\text{UO}_2(\text{L})\text{CH}_3\text{OH}]$

Uranyl nitrate (0.25 g, 0.0005 mol) was dissolved in the minimum amount of methanol and added to an equimolar solution of H_2L (0.284 g, 0.0005 mol) in methanol (50 ml). A red precipitate was formed, which was filtered and dried in vacuo. The crude product was recrystallized from chloroform to obtain the pure compound. Red single crystals for X-ray diffraction were grown in a $\text{CH}_3\text{OH}/\text{CHCl}_3$ mixture by solvent evaporation at room temperature over three days. Yield: 0.346 g (79%). *Anal.* Calc. for $\text{C}_{39}\text{H}_{54}\text{N}_2\text{O}_5\text{U}$: C, 53.91; H, 6.26; N, 3.22. Found: C, 53.11; H, 7.18; N, 4.04%. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1609 ($\text{C}=\text{N}$); 1533 ($\text{C}=\text{C}$) and 888 ($\text{O}=\text{U}=\text{O}$). UV/Vis ($\lambda_{\text{max}}/\text{nm}$): 398, 295.

2.3. Physical measurements

All the chemicals and solvents were of analytical grade and were used as received (Caution! *Uranyl nitrate is a weak radioactive salt and care should be taken in handling the compound*). C, H and N analyses were performed with a Perkin–Elmer 2400 series II analyzer. Infrared spectra ($4000\text{--}300\text{ cm}^{-1}$, resp. 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, using TMS as the internal standard. Diffuse reflectance spectra were obtained on a Perkin–

Table 1
Selected crystallographic data

	$[\text{H}_2\text{L}] \cdot \text{acetone}$	$[\text{UO}_2(\text{L})\text{CH}_3\text{OH}]$
Empirical formula	$\text{C}_{38}\text{H}_{52}\text{N}_2\text{O}_2 \cdot \text{C}_3\text{H}_6\text{O}$	$\text{C}_{39}\text{H}_{54}\text{N}_2\text{O}_5\text{U}$
Formula weight	626.89	868.87
Temperature (K)	150(2)	173(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.9077 (8)	13.637(3)
b (Å)	35.083(3)	29.118(6)
c (Å)	11.9115(1)	10.476(2)
β (°)	113.93(1)	112.26(3)
Volume (Å ³)	3784.5(5)	3849.8(14)
Z	4	4
D_{calc} (Mg/m ³)	1.100	1.499
Absorption coefficient (mm ⁻¹)	0.07	4.26
Measured reflections	48 657	34 578
Independent reflections	6647	8864
R_{int}	0.0635	0.0788
Reflections with $I > 2\sigma(I)$	4739	6008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.063$; $wR_2 = 0.174$	$R_1 = 0.044$; $wR_2 = 0.076$
R indices (all data)	$R_1 = 0.088$; $wR_2 = 0.191$	$R_1 = 0.088$; $wR_2 = 0.084$
Goodness-of-fit on F^2	1.06	1.02
Largest difference peak and hole (e Å ⁻³)	−0.30 and 0.47	−0.764 and 1.316

Elmer Lambda 900 spectrophotometer using MgO as a reference. Electrospray mass spectra (ESI-MS) in methanol were recorded on Thermo finnigan AQA apparatus.

2.4. Single crystal X-ray structures

2.4.1. $(H_2L) \cdot (acetone)$ and $[UO_2(L)CH_3OH]$

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 for each compound was collected, and integrated by the HKL2000 [11] and SORTAV [12] programs. No absorption correction was applied. The ligand 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. An empirical absorption correction was applied using the SADABS program [16] for the Uranyl complex. The structure was solved and refined using SHELXS-97 [17], SHELXL-97 [14] for structure solution and structure refinement, respectively. All non-hydrogen atoms were refined anisotropically. 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 new tetradentate ligand *N,N'*-bis(3,5-di-*t*-butylsalicylidene)-4,5-dimethyl-1,2-phenylenediamine was synthesized from a reaction of 4,5-dimethyl-1,2-phenylenediamine with 3,5-di-*t*-butylsalicylaldehyde, using the synthetic procedure described above. Schiff-base uranyl complexes are generally soluble only in donor solvents such as DMSO and DMF, whereas the title compound is highly soluble in ethanol, methanol, chloroform, dichloromethane and acetone. This good solubility may be due to the presence of tertiary butyl groups, which will improve the solubility of the complex in less strong donor or organic solvents [18]. The IR spectrum of the ligand shows the formation of a $\nu(C=N)$ peak [19] at 1615 cm^{-1} , which, together with the disappearance of the $\nu(C=O)$ peak is indicative of a Schiff-base condensation.

The uranyl complex $[UO_2(L)CH_3OH]$ was prepared using the method described above. The IR spectrum shows subtle differences in comparison to the free ligand, with peaks at 1609 cm^{-1} $\nu(C=N)$ and 1533 cm^{-1} $\nu(C=C)$. A new peak was observed at 888 cm^{-1} due to $\nu(O=U=O)$, which indicates the presence of a linear, symmetric dioxouranium(VI) group [20]. The ligand field spectrum of the complex in the solid state

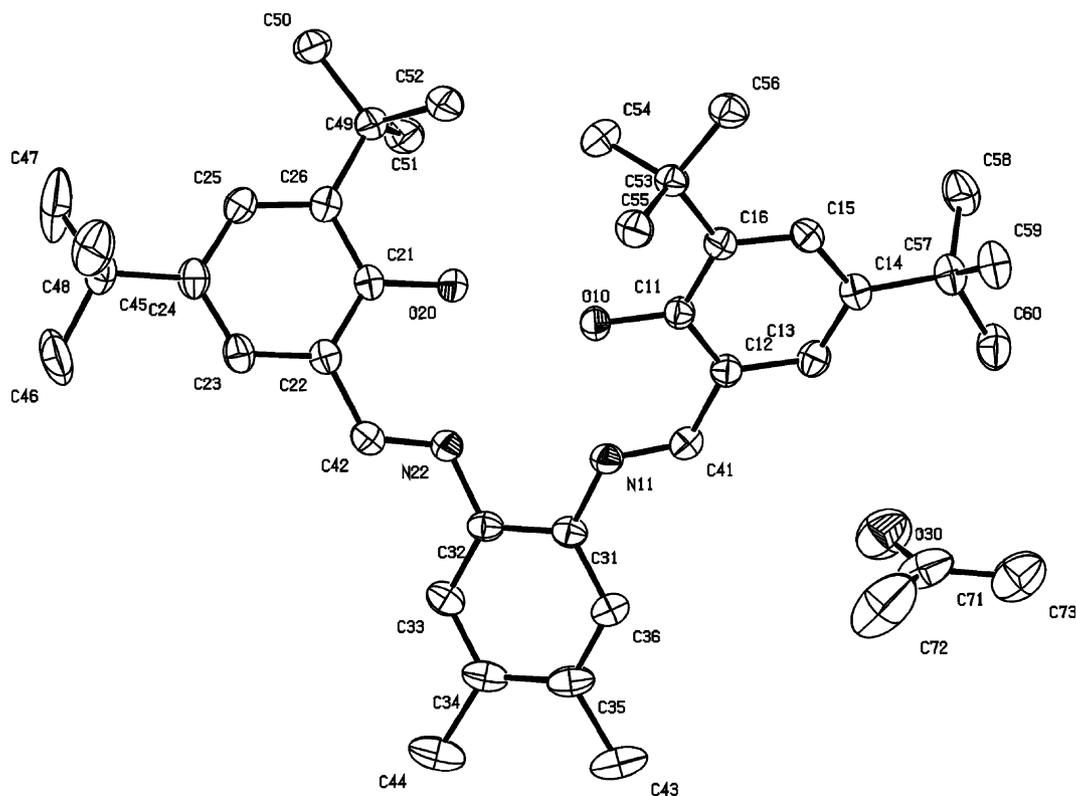


Fig. 1. Crystal structure of ligand (H_2L) and acetone, with hydrogen atoms omitted for clarity and displacement ellipsoids drawn at the 50% probability level.

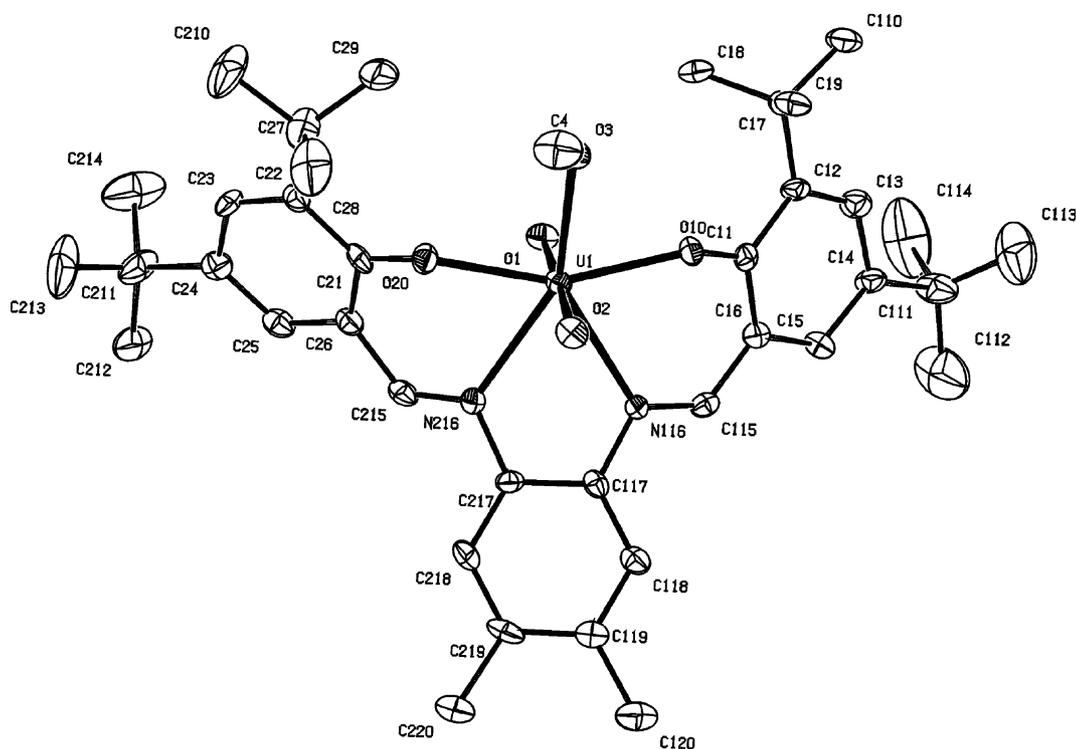


Fig. 2. Crystal structure of $[\text{UO}_2(\text{L})\text{CH}_3\text{OH}]$ with hydrogen atoms omitted for clarity and displacement ellipsoids drawn at the 50% probability level.

shows absorptions around 398 nm with a shoulder of 295 nm, assigned to the charge transfer (phenolato-O–U) and $\pi-\pi^*$ of ligand. As expected, the proton NMR spectrum of the complex shows the imine proton shifted downfield from 8.33 to 8.86 ppm. The aromatic as well as methyl protons were found to be unaltered.

We tried to prepare lanthanide complexes by using the above method with a 1:1 mole ratio of the ligand and metal salt in methanol solvent. At the final stage after evaporation, we observed the formation of crystals of the ligand and metal salt separately. The ligand crystal was obtained with one acetone molecule. We also change the reaction conditions with different temperatures and times, and periods of 3, 6 h and overnight reflux were used. These repeated attempts to prepare 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, which may be due to a mismatch of its ionic size (radii, La^{3+} : 1.02 Å for 8 coordination; U^{6+} : 0.80 Å for 6–8 coordination) with the cavity of the ligand.

3.2. Crystal structures

The crystal structures of (H_2L) and $[\text{UO}_2(\text{L})\text{CH}_3\text{OH}]$ are depicted in Figs. 1 and 2, with selected crystal data in

Table 2
Selected bond lengths (Å) and angles (°) for complex $[\text{UO}_2(\text{L})\text{CH}_3\text{OH}]$

Bond lengths	
U(1)–O(1)	1.786(4)
U(1)–O(2)	1.805(4)
U(1)–O(10)	2.228(3)
U(1)–O(20)	2.240(3)
U(1)–N(216)	2.521(4)
U(1)–O(3)	2.530(4)
U(1)–N(116)	2.590(4)
Bond angles	
O(1)–U(1)–O(2)	176.85(15)
O(1)–U(1)–O(10)	86.33(14)
O(2)–U(2)–O(10)	95.65(14)
O(1)–U(1)–O(20)	86.89(14)
O(2)–U(1)–O(20)	92.18(14)
O(10)–U(1)–O(20)	157.14(13)
O(1)–U(1)–N(216)	86.51(15)
O(2)–U(1)–N(216)	90.34(15)
O(10)–U(1)–N(216)	131.56(13)
O(20)–U(1)–N(216)	69.65(13)
O(1)–U(1)–O(3)	99.98(14)
O(2)–U(1)–O(3)	82.86(14)
O(10)–U(1)–O(3)	77.89(12)
O(20)–U(1)–O(3)	81.83(12)
N(216)–U(1)–O(3)	150.42(12)
O(1)–U(1)–N(116)	93.16(14)
O(2)–U(1)–N(116)	85.25(15)
O(10)–U(1)–N(116)	69.79(13)
O(20)–U(1)–N(116)	132.43(13)
N(216)–U(1)–N(116)	62.88(13)
O(3)–U(1)–N(116)	144.16(12)

Table 1 and selected bond distances and angles given in Table 2.

The molecular structure of the H₂L ligand crystallized with one acetone molecule is shown in Fig. 1, which shows that in the uncoordinated ligand, the molecule is distinctly non-planar. In order to accommodate the two central O–H groups the 3,5-di-*t*-butylsalicylidene groups are displaced to opposite sides of the 4,5-dimethyl-1,2-phenylenediamine ring plane, with dihedral angles of 34.97(11)° between the C(31)–C(36) plane and C(11)–(C16) plane, and –37.39(11)° between the C(31)–C(36) plane and C(21)–(C26) plane (Fig. 1, Supplementary material).

The tetradentate dianionic ligand binds equatorially to the dioxouranium(VI) group leading to a seven-coordinated center with a distorted pentagonal bipyramidal

coordination geometry. The uranium oxide coordination sphere contains two imine nitrogen atoms, two phenol oxygen atoms and a third oxygen atom from the methanol molecule. The oxo groups of the uranyl moiety lie *trans* to one another with a nearly linear O–U–O angle of 176.85(15)° and U–O bond length of 1.786(4) Å for U–O(1) and 1.805(4) Å for U–O(2). The lengthening of the U–O(2) bond length can be ascribed to the existence of a hydrogen bond, D–H···A length of 2.831(6) Å, between O(2) and the O–H group of the methanol molecule.

The uranium atom, N(116), N(216), and O(20) all lie approximately in a plane, with a maximum deviation from the mean squares plane of 0.0383(3) Å for U(1). O(10) is displaced significantly out of the plane by 0.390(4) Å. The U–N(116), U–N(216), U(1)–O(10) and

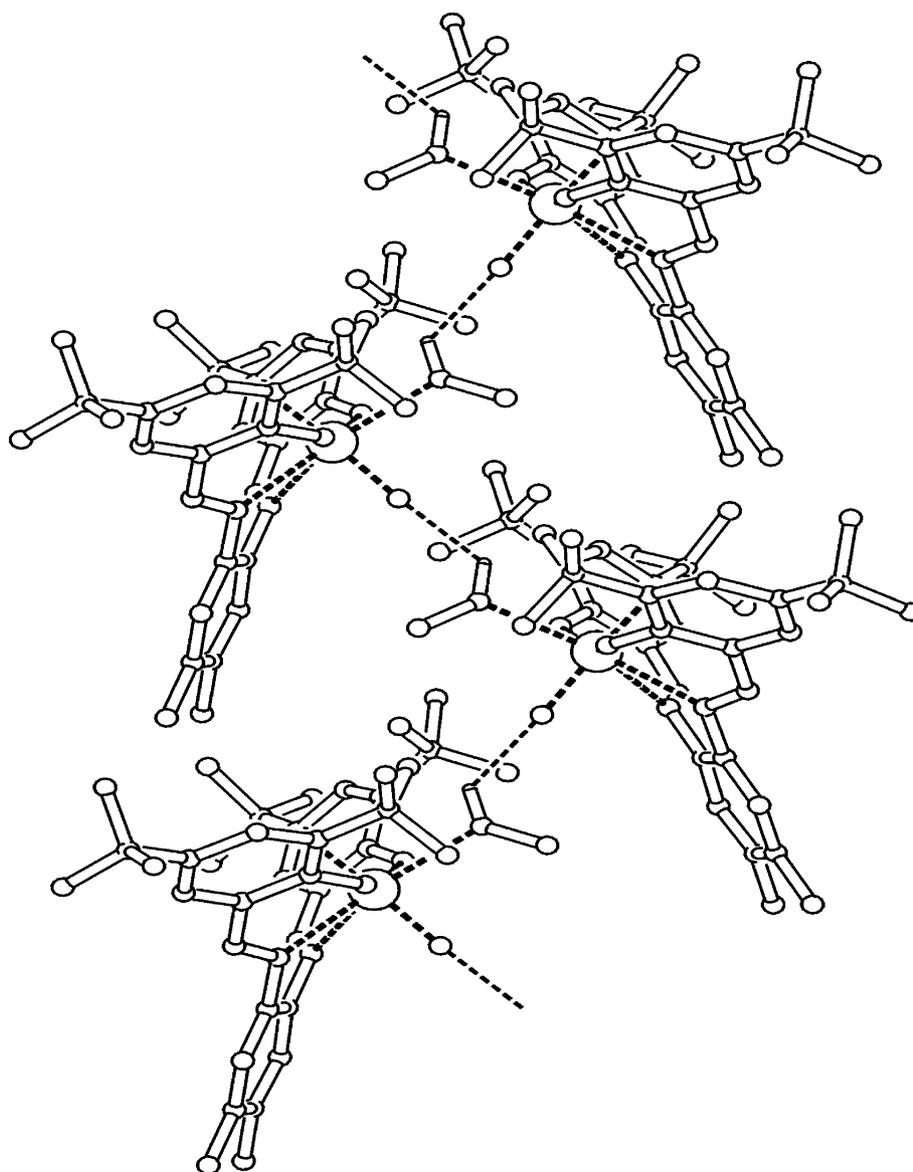


Fig. 3. Molecular packing of [UO₂(L)CH₃OH] complex showing hydrogen bonded zigzag infinite chain.

U(1)–O(20) bond distances, of 2.590(4), 2.521(4), 2.228(3) and 2.240(3) Å, respectively, are in good agreement with those reported previously [8,21–23]. U–N distances are typically found to be longer than U–O distances, a behavior which can be explained by Pearson's hard and soft acid–base concept [24,25]. This concept agrees well with what is observed in the title compound, as nitrogen would be expected to be bonded less strongly to a hard acid such as (UO₂²⁺), while oxygen has relatively higher base strength towards uranium. The methanol oxygen atom, O(3), also lies outside the main U–N–N–O plane, though on the other side to O(10), with a deviation of –0.334(4) Å. The U–O(3) bond length is 2.530(4) Å, which is comparable with related complexes in the literature [25].

The ligand is not planar, but, in contrast to the uncoordinated structure, the two 3,5-di-*t*-butylsalicylidene groups are now on the same side of the 4,5-dimethyl-1,2-phenylenediamine ring, which gives the complex a distinctive “book” appearance when viewed from the side (Fig. 2, Supplementary material). Evidently, in the five-membered ring (C117, C217, N116, N216 and U1), the small bite angle (62.88°), may enhance the planarity of chelating mode to non-binding with lanthanides.

Due to the hydrogen-bonding between the methanol molecule and O(2) the structure forms an infinite polymer with a distinctive ‘zigzag’ motif (Fig. 3). No π – π stacking is present, due to the unfavorable orientations of the aromatic rings in the structure.

4. Conclusions

In this paper, we have described the successful synthesis of a ligand that is suitable for coordination to the actinide (UO₂²⁺), but not to lanthanides (La, Pr, Eu and Gd). Uranium exists as the uranyl cation (UO₂²⁺) in aqueous solution, where the oxo groups of the uranyl moiety lie *trans* to one another with an angle that is close to linear with the uranium as the center. This linear arrangement appears to help the uranyl cation enter into the cavity of the ligand frame like a “pen” into the “cap”. The uranium center is seven coordinate with a distorted pentagonal bipyramidal geometry. The lengthening of one U=O distance can be ascribed to the presence of a hydrogen bond between the oxygen and the O–H of a neighboring methanol molecule. Hydrogen bonding will lead to the sequestration of the uranium to achieve the high selectivity over competing cations in solution.

Apparently the spherical shape and the large size of the Ln(III) ions do not match with the ligand cavity, whereas the smaller size of U(VI) and the ellipsoid of the (UO₂²⁺) fit better. This principle is now further developed for a potential use in the separation of uranium and lanthanum.

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. Lies Bouwman for fruitful discussion. We thank Dr. W. Verboom (Twente university) for valuable discussion. Thanks are due to Meenal Godbole and Nilesh Mehendale for rendering their assistance.

Appendix A. Supplementary material

Complementary data for the ligand and 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 number in all correspondence (CCDC 243295, CCDC 243296). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2004.07.004](https://doi.org/10.1016/j.poly.2004.07.004).

References

- [1] L.F. Rao, A.Y. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo, *Inorg. Chem.* 42 (2003) 3685.
- [2] C. Den Auwer, R. Drot, E. Simoni, S.D. Conradson, M. Gailhanou, J.M. de Leon, *New J. Chem.* 27 (2003) 648.
- [3] O. Terra, N. Clavier, N. Dacheux, R. Podor, *New J. Chem.* 27 (2003) 957.
- [4] L. Salmon, P. Thuery, M. Ephritikhine, *Polyhedron* 23 (2004) 623.
- [5] D.J. Evans, P.C. Junk, M.K. Smith, *Polyhedron* 21 (2002) 2421.
- [6] M. Vidali, P.A. Vigato, U. Casellato, E. Tondello, O. Traverso, *J. Inorg. Nucl. Chem.* 37 (1975) 1715.
- [7] U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, R. Graziani, *J. Chem. Soc., Dalton Trans.* (1990) 1533.
- [8] M.S. Hill, P.R. Wei, D.A. Atwood, *Polyhedron* 17 (1998) 811.
- [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. 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] G.M. Sheldrick, *SADABS Program for Empirical Absorption Correction*, Bruker AXS.
- [17] G.M. Sheldrick, *SHELXS-97, Program for Crystal Structure Determination*, University of Gottingen, Germany, 1997.
- [18] S. Sitran, D. Fregona, U. Casellato, P.A. Vigato, R. Graziani, G. Faraglia, *Inorg. Chim. Acta* 132 (1987) 279.
- [19] G. Das, R. Shukla, S. Mandal, R. Singh, P.K. Bhadrwaj, J. van Hall, K.H. Whitmire, *Inorg. Chem.* 36 (1997) 323.
- [20] D.E. Fenton, P.A. Vigato, U. Casellato, R. Graziani, M. Vidali, *Inorg. Chim. Acta* 51 (1981) 195.
- [21] G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali, P.A. Vigato, *J. Chem. Soc., Chem. Commun.* (1971) 1330.

- [22] G. Bandoli, D.A. Clemente, M. Vidali, P.A. Vigato, *J. Chem. Soc., Chem. Commun.* (1972) 344.
- [23] M.N. Akhtar, E.D. McKenzie, R.E. Paine, A.J. Smith, *J. Inorg. Nucl. Chem.* 5 (1969) 673.
- [24] E.O. Schlempe, *Inorg. Chem.* 6 (1967) 2012.
- [25] G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali, P.A. Vigato, *J. Chem. Soc., Dalton Trans.* (1973) 2331.