Dioxouranium Complexes with Acetylpyridine Benzoylhydrazones and Related Ligands

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Abstract. Acetylpyridine benzoylhydrazone and related ligands react with common dioxouranium(VI) compounds such as uranyl nitrate or $[NBu_4]_2[UO_2Cl_4]$ to form air-stable complexes. Reactions with 2,6-diacetylpyridinebis(benzoylhydrazone) (H₂L^{1a}) or 2,6-diacetylpyridinebis(salicylhydrazone) (H₂L^{1b}) give yellow products of the composition $[UO_2(L^1)]$. The neutral compounds contain doubly deprotonated ligands and possess a distorted pentagonalbipyramidal structure. The hydroxo groups of the salicylhydrazonato ligand do not contribute to the complexation of the metal. The equatorial coordination spheres of the complexes can be extended by the addition of a monodentate ligand such as pyridine or DMSO. The uranium atoms in the resulting deep-red complexes have hexagonal-bipyramidal coordination environments with the oxo ligands in axial positions.

The sterical strains inside the hexagonal plane can be reduced when two tridentate benzoylhydrazonato ligands are used instead of the pentadentate 2,6-diacetylpyridine derivatives. Acetylpyridine benzoylhydrazone (HL²) and bis(2-pyridyl)ketone benzoylhydrazone (HL³) deprotonate and form neutral, red [UO₂(L)₂] complexes. The equatorial coordination spheres of these complexes are puckered hexagons.

X-ray diffraction studies on $[UO_2(L^{1a})(pyridine)]$, $[UO_2(L^{1b})(DMSO)]$, $[UO_2(L^2)_2]$ and $[UO_2(L^3)_2]$ show relatively short U–O bonds to the benzoylic oxygen atoms between 2.328(6) and 2.389(8) Å. This suggests a preference of these donor sites of the ligands over their imino and amine functionalities (U–N bond lengths: 2.588(7)–2.701(6) Å).

Keywords: Uranium; Benzoylhydrazonato ligands, Actinides, Uranyl chelates; Structure analysis

Dioxouranium-Komplexe mit Acetylpyridinbenzoylhydrazon und verwandten Liganden

Inhaltsübersicht. Acetylpyridinbenzoylhydrazon und davon abgeleitete Liganden reagieren mit Uranylnitrat oder $[NBu_4]_2[UO_2Cl_4]$ unter Bildung luftstabiler Dioxouranium(VI)-Komplexe. Bei Reaktionen mit 2,6-Diacetylpyridinbis(benzoylhydrazon) (H₂L^{1a}) und 2,6-Diacetylpyridinbis(salicylhydrazon) (H₂L^{1b}) entstehen gelbe Pulver der Zusammensetzung [UO₂(L¹)]. Die Koordination des Uranatoms in den Neutralkomplexen mit doppelt deprotonierten organischen Liganden ist verzerrt pentagonal-bipyramidal. Die Hydroxosubstituenten des Salicylhydrazonato-Liganden [L^{1b}]^{2–} sind an der Komplexierung des Metallatoms nicht beteiligt.

Reaktionen von $[UO_2(L^1)]$ -Komplexen mit monodentaten Liganden wie Pyridin oder DMSO führen zur Aufweitung der äquatorialen Koordinationssphäre und zur Bildung von tiefroten, kristallinen Verbindungen mit einer verzerrten, hexagonal-bipyramidalen Koordination um die Uranatome. Die sterische Belastung der äquatorialen Koordinationsebene kann verringert werden, wenn anstelle der fünfzähnigen H_2L^1 -Liganden dreizähnige Benzoylhydrazonato-Liganden verwendet werden. 2-Acetylpyridinbenzoylhydrazon (HL²) und Bis(2-pyridyl)ketonbenzoylhydrazon (HL³) bilden unter einfacher Deprotonierung neutrale Komplexe der Zusammensetzung [UO₂(L)₂]. Die hexagonalen Grundflächen der gebildeten Bipyramiden sind in diesen Produkten deutlich gewellt.

Kristallstrukturanalysen von $[UO_2(L^{1a})(Pyridin)]$, $[UO_2(L^{1b})-(DMSO)]$, $[UO_2(L^2)_2]$ und $[UO_2(L^3)_2]$ zeigen relativ kurze Bindungen zwischen den Uranatomen und den Benzoylgruppierungen (2.328(6)-2.389(8) Å). Das legt eine bevorzugte Bindung an die Sauerstoffatome der Liganden nahe, während die Uran-Stickstoff-Bindungen deutlich länger sind (2.588(7)-2.701(6) Å).

Introduction

As a part of our systematic studies of the coordination chemistry of the early actinide elements, we recently pub-

* Prof. Dr. Ulrich Abram Freie Universität Berlin Institut für Chemie Fabeckstraße 34–36 D-14195 Berlin Email: abram@chemie.fu-berlin.de lished a report on the structural chemistry of thiosemicarbazonato complexes of uranium(VI) [1]. The formation of complexes with medium stability was observed with acetylpyridine thiosemicarbazone in which the pyridine nitrogen atom provides an additional donor site to the metal atoms. More stable complexes are expected with 'harder' donor atoms such as oxygen, as is provided by semicarbazones or hydrazones. A number of studies have been undertaken with both ligand systems and the formation of chelates with various compositions have been suggested on the basis of spectroscopic data [2]. Some of the compounds have been proposed for the spectrophotometric determination of metal ions including UO_2^{2+} [3], but less is known about the composition of the coordination environment of the metal. First structural reports performed with 2,6-diacetylpyridinebis(2'-pyridyl)hydrazones [4] and benzoylhydrazones [5] describe uranyl complexes having pentagonal bipyramidal or hexagonal-bipyramidal coordination spheres at the uranium atoms. The reasons for the respective composition of the equatorial coordination spheres and the influence of substituents are not yet clear. In the present paper, we describe the reactions of uranyl nitrate and [NBu₄]₂[UO₂Cl₄] with 2,6-diacetylpyridinebis(benzoylhydrazone) (H_2L^{1a}), 2,6-diacetylpyridinebis(salicylhydrazone) (H₂L^{1b}), 2-acetylpyridine benzoylhydrazone (HL²) and bis(2-pyridyl)ketone benzoylhydrazone (HL³), Scheme 1, and the solid state structures of the products.



Scheme 1

Results and Discussion

 $UO_2(NO_3)_2 \cdot 6H_2O$ as well as $[Bu_4N]_2[UO_2Cl_4]$ react with the benzoylhydrazone or salicylhydrazone ligands H₂L¹-HL³ in boiling methanol under complete substitution of the equatorial coordination sphere of the metal atom. Under these conditions, complete deprotonation of the ligands is observed independent of the uranium precursor used, and neutral dioxouranium complexes are formed. No evidence has been found for the formation of complexes with non-deprotonated or semi-deprotonated (H₂L¹) hydrazone ligands as has been observed for related semicarbazones of chromium(III) [6] and other highly charged metal ions including the uranyl ion [7]. A complicated coordination pattern has also been described for products obtained from reactions of uranyl salts and 2,6-diacetylpyridine bis(p-methoxybenzoylhydrazone), where different structures have been assigned on the basis of spectroscopic

data in dependence on the solvents and the uranium starting materials used [5b]. The only compound in this report which has been characterized by X-ray crystallography, however, is a neutral dioxouranium(VI) complex with a doubly deprotonated organic ligand in which the uranium atom is seven-coordinate.

Similar complexes are obtained when the ligands H_2L^{1a} or H_2L^{1b} are heated with $UO_2(NO_3)_2 \cdot 6 H_2O$ or $[NBu_4]_2$ - $[UO_2Cl_4]$ in boiling methanol. The reaction is faster when a supporting base such as triethylamine is added, but this is not mandatory. Yellow precipitates are formed upon cooling, which have been isolated and characterized by elemental analysis, IR and NMR measurements showing that the products formed from the different uranium precursors were identical. The U=O double bonds show characteristic IR bands between 900 and 905 cm⁻¹. This value is in accord with the neutral uranyl complexes in ref. [5b], whereas anionic derivatives absorb in the range between 920 and 950 cm⁻¹. The proton NMR spectra prove the absence of the NH protons of the organic ligands, whereas an OH signal for the complex with ligand $[L^{1b}]^{2-}$ was observed at 12.9 ppm. This is in the same position as in H_2L^{1b} , which suggests that the hydroxylic group of the salicylhydrazone does not contribute to the coordination of the metal atom. No evidence was found for the coordination of methanol or water. This allows the conclusion that complexes of the composition $[UO_2L^1]$ have been formed. These complexes possess the same coordination sphere at the metal atoms as the uranyl complex with 2,6-diacetylpyridine bis(methoxybenzoylhydrazone), which shows distorted pentagonal-bipyramidal coordination of the metal atom [5b]. No evidence could be found for anionic uranyl complexes with non-deprotonated or monodeprotonated ligands. The bond angles between neighbouring atoms inside the equatorial coordination sphere are approximately 63° (4 times) and 107° (between the oxygen atoms of the benzoyl groups) [5b] (see also Table 1 and Fig. 4), which suggests the possibility of the extension of the coordination number by the addition of an appropriate monodentate ligand. This has been proven by heating the $[UO_2(L^1)]$ complexes in coordinating solvents such as DMSO, pyridine or THF. The yellow solids slowly dissolve in these solvents and the colour changes to red. A reaction sequence resulting in the formation of neutral $[UO_2(L^1)(solvent)]$ complexes can be derived (see Scheme 2). The products can be isolated in crystalline form by the slow evaporation of the solvents (THF and pyridine) or addition of a small amount of water and slow cooling (DMSO). The U=O stretching vibrations are shifted to



Scheme 2



Figure 1 Ellipsoid presentation [13] of $[UO_2(L^{1a})(pyridine)]$. Thermal ellipsoids represent 50 per cent probability.

Table 1 Selected bond lengths /Å and angles/° in $[UO_2(L^{1a})-(pyridine)]$, $[UO_2(L^{1b})(DMSO)]$ and $[UO_2(L^{1c})]$.

	[UO ₂ (L) ^{1a} (pyridine)]	$[\mathrm{UO}_2(\mathrm{L})^{1\mathrm{b}}(\mathrm{DMSO})]$	$[UO_2(L)^{1c}]^{a)}$
U-010	1.774(2)	1.77(1)	1.77
U-O20	-	1.777(9)	1.77
U-018	2.356(3)	2.389(8)	2.32/2.30 ^{b)}
U-N2	2.630(3)	2.613(9)	2.47/2.49 ^{b)}
U-N1	2.685(8)	2.65(1)	2.52
U-N21/O30	2.68(1)	2.527(9)	_
O18-C17	1.280(5)	1.28(1)	1.26/1.30 ^{b)}
C17-N3	1.293(5)	1.32(1)	1.33/1.30 ^{b)}
N3-N2	1.398(5)	1.38(1)	1.41/1.40 ^{b)}
N2-C7	1.284(4)	1.31(1)	1.31/1.31 ^{b)}
C7-C6	1.455(6)	1.45(1)	1.50/1.48 ^{b)}
C7-C8	1.502(6)	1.49(1)	1.50/1.51 ^{b)}
O18-U-N2	60.07(9)	60.3(3)	63.5/63.3 ^{b)}
N2-U-N1	59.34(7)	59.8(2)	63.3/63.3 ^{b)}
O18-U-N21/O30	61.39(7)	61.8(2)	_
O18-U-O18'	122.8(1)c)	119.2(4)d)	106.8
N1…N2	2.631(5)	2.62/2.63	
N2…O18	2.507(4)	2.52/2.52	

^{a)} Values taken from ref. [5b] and adopted to the atomic labelling schemes given in Figures 1 and 2. ^{b)} Two values since there is no intramolecular symmetry in this complex. ^{c)} Symmetry operation: 1-x, -y, z. ^{d)} Symmetry operation: x, -0.5-y, z.

higher frequencies compared with the values in the $[UO_2(L^1)]$ complexes and occur between 914 and 920 cm⁻¹. Similar changes in the position of the uranyl bands in dependence on the coordination number of the metal atom have been observed previously [5b].

Single crystals of $[UO_2(L^{1a})(pyridine)]$ and $[UO_2(L^{1b})(DMSO)]$ have been studied by X-ray crystallography, showing that the complexes possess eight-coordinate uranium atoms. An ellipsoid representation of the molecular structure of $[UO_2(L^{1a})(pyridine)]$ is shown in Figure 1. Selected bond lengths and angles are summarised in Table 1. The coordination environment of the uranium atom can be described as an almost perfect hexagonal bipyramid with a planar equatorial coordination sphere (maximum deviation from a mean least-square plane formed by the atoms U, N21, O18, N2, N1 N2' and O18': 0.201(3) Å for O18 and O18', r.m.s. 0.1455). The X-U-Y angles (X and Y are neighbouring equatorial donor atoms) range from 59.34 to 61.39°. The torsion angle between the pyridine ring and the hexagonal plane is $61.4(1)^{\circ}$, which minimises steric hindrance between the pyridine ligand and the benzoylhydrazonato arms of the pentadentate ligand and the two oxo oxygen atoms. The extension of the coordination number of uranium causes lengthening of the U-N bonds to the chelating ligand as can be seen from a comparison with the corresponding data in the seven-coordinate complex $[UO_2(L^{1c})]$ [5b]. Selected bond lengths and angles of this compound are included in Table 1; the atomic numbering has been adopted to fit the labelling scheme applied in the present paper. No significant change can be derived for the bonding situation inside the hydrazonato ligands, which are doubly deprotonated in all complexes described in this paper. Whereas the double bond between C7 and N2 is almost localised, a delocalisation of the electron density of the C17-O18 double bond can be concluded, which results in a significant shortening of the C17-N3 bond as a consequence of complex formation. This situation can best be described by the bonding scheme represented in I, irrespective of the coordination number of the uranium atom. It has also been found in $[UO_2(L^{1b})(DMSO)]$, which has been prepared by heating of $[UO_2(L^{1b})]$ in DMSO.



Scheme 3

[UO₂(L^{1b})(DMSO)] crystallizes as large red blocks, and the results of an X-ray structure analysis confirm the spectroscopic conclusion that the hydroxylic group of the salicylhydrazone is not involved in the coordination of the metal atom. The structure of the complex is illustrated in Figure 2. The OH substituents of the salicylic groups are disordered. The occupation of the two positions is about 0.8/0.2 with a preference of the position on C16 (Figure 2) which allows intramolecular hydrogen bonds to O18 and O30. The overall bonding pattern in $[UO_2(L^{1b})(DMSO)]$ is similar to that in [UO₂(L^{1a})(pyridine)], with the uranium atom in an almost regular hexagonal-bipyramidal coordination environment. Only small deviations from planarity can be found for the hexagonal plane (maximum deviation: 0.170(4) A for O30, r.m.s. 0.1459), and the bond angles are very close to 60°. The corresponding values and selected bond lengths are listed in Table 1. It is interesting to note that the increase in coordination number and the observed lengthening of the uranium-nitrogen bonds are not related to an increase of the bite angles of the binding sites, which



Figure 2 Ellipsoid presentation [13] of $[UO_2(L^{1b})(DMSO)]$. Thermal ellipsoids represent 50 per cent probability.

can be estimated by the intramolecular distances between the donor atoms N1 and N2 or N2 and O18. The corresponding values are also listed in Table 1.

More distortions from an ideal hexagonal bipyramid are found in the structures of the complexes $[UO_2(L^2)_2]$ and $[UO_2(L^3)_2]$, which also possess coordination number 8 at the uranium atoms. The compounds are formed during reactions of uranyl nitrate or [NBu₄]₂[UO₂Cl₄] with an excess of the ligands in boiling methanol. They precipitate as orange-red solids directly from the reaction mixtures and recrystallisation from hot methanol or CHCl₃/methanol mixtures results in red crystals. The IR spectra show the expected v(UO₂) bands at 912 cm⁻¹ ([UO₂(L²)₂]) and 911 cm⁻¹ ([UO₂(L³)₂]). The absences of NH bands indicates deprotonation of the hydrazones; the coordination of the benzoyl group is strongly suggested by the shift of the corresponding v(C=O) bands to lower frequencies. A shift of the band at 990 cm^{-1} in the spectra of the proligands, which can be assigned to the breathing motion of the pyridine ring, to higher frequencies indicates the coordination of the pyridyl groups and, thus, a tridentate, monoanionic bonding scheme is expected for both of these hydrazones, irrespective of the possible binding mode of HL³ as a bidentate, neutral bipyridine analogue, which has been observed recently for a rhenium(I) tricarbonyl complex [8].

The coordination environments of the uranium atoms in the molecular structures of $[UO_2(L^2)_2]$ (Fig. 3) and $[UO_2(L^3)_2]$ (Fig. 4) are similar and can best be described as a strongly distorted hexagonal bipyramid. Selected bond lengths and angles of both complexes are summarized in Table 2. For $[UO_2(L^2)_2]$, the atomic labelling scheme of $[UO_2(L^3)_2]$ has been applied, with the exception that the second $[L^2]^-$ ligand is symmetry-generated in $[UO_2(L^2)_2]$ since the atoms O10, U and O20 are situated on a 2-fold crystallographic axis. The U-N bond lengths in both complexes are in the same range as has been found in $[UO_2(L^1)-$ (solvent)] complexes with 8-coordinate uranium atoms and are accordingly longer than the values in $[UO_2(L^{1c})]$. This is another indication that the observed bond lengthening is due to steric overcrowding of the equatorial coordination spheres in the compounds with coordination number 8 at the metal atoms.



Figure 3 Ellipsoid presentation [13] of $[UO_2(L^2)_2]$. Thermal ellipsoids represent 50 per cent probability.



Figure 4 Ellipsoid presentation [13] of $[UO_2(L^3)_2]$. Thermal ellipsoids represent 50 per cent probability.

The six equatorial atoms in $[UO_2(L^2)_2]$ and $[UO_2(L^3)_2]$ form puckered hexagons in which the five-membered chelate rings are almost planar and angles between 13° and 18° are established between them. This allows for the minimisation of steric interaction. Figure 5 shows a comparison of the coordination spheres of $[UO_2(L^{1c})]$, $[UO_2(L^{1a})-(pyridine)]$ and $[UO_2(L^3)_2]$ containing uranium atoms with the coordination numbers seven and eight. Particularly the side views indicate that the sterical hindrance inside the equatorial coordination sphere is reduced by the coordination of two tridentate ligands rather than a 5+1 coordination as is established in $[UO_2(L^{1a})(pyridine)]$ or $[UO_2(L^{1b})(DMSO)]$. The views along the uranyl units, however, show almost regular hexagons for the equatorial coordination spheres of both structural types.

The present study shows that acetylpyridine benzoylhydrazones and related ligands are well suited for the formation of stable complexes with dioxouranium(VI) units. All hydrazone units of the ligands are deprotonated in the

Table 2 Selected bond lengths/Å and angles/° in $[UO_2(L^2)_2]$ and $[UO_2(L^3)_2]$.

	$[UO_2(L^2)_2]$	$[UO_2(L^3)_2]$
U-010	1.725(9)	1.771(6)
U-O20	1.727(9)	1.756(6)
U-018	2.371(6)	2.328(6)
U-N2	2.612(7)	2.610(7)
U-N1	2.701(6)	2.635(7)
U-N31	$2.701(6)^{a}$	2.670(7)
U-N4	$2.612(7)^{a}$	2.588(7)
U-058	2.371(6)	2.355(6)
C7-N2	1.30(1)	1.28(1)
N2-N3	1.377(9)	1.376(9)
C17-O18	1.28(1)	1.29(1)
C37-N4	$1.30(1)^{a}$	1.31(1)
N4-N5	$1.377(9)^{a}$	1.385(9)
C51-O58	1.28(1) ^{a)}	1.27(1)
O18-U-N2	60.0(2)	59.9(2)
N2-U-N1	59.5(2)	59.1(2)
N1-U-O18'/O58	65.3(2) ^{b)}	64.8(2)
O58-U-N4	$60.0(2)^{a}$	61.0(2)
N4-U-N31	59.5(2) ^{a)}	59.4(2)
O18-U-N1'/N31	65.3(2) ^a	67.1(2)
O10-U-O20	180	177.3(3)

^{a)} Symmetry-related bond lengths or angles due to an intramolecular 2-fold axis. ^{b)} Symmetry operation: 1-x, y, 0.5-z. ^{d)} Symmetry operation: x, -0.5-y, z.



Figure 5 Representation [14] of the coordination spheres of a) $[UO_2(L^{1c})]$ [5b], b) $[UO_2(L^{1a})(pyridine)]$ and c) $[UO_2(L^{2})_2]$ in top and side views with respect to the O–U–O axis showing the distortions of the equatorial coordination spheres of the complexes in dependence on the chelating ligands.

uranium complexes studied in this paper. This is in contrast to the behaviour in some lanthanide complexes, where only partial deprotonation of the NH groups was observed [9]. The ready extension of a pentagonal equatorial coordination sphere in the complexes of the type $[UO_2(L^1)]$ indicates a higher stability of the products with coordination number 8 at the uranium atoms, despite the resulting steric strains due to the relatively rigid pentadentate ligands, which obviously cannot fully be compensated for by distortions of the coordination sphere.

Experimental

HL^{1a}, HL^{1b}, HL² and HL³ were prepared by refluxing equivalent amounts of 2,6-diacetylpyridine (ALDRICH), 2-acetylpyridine (ALDRICH) or di(2-pyridine)ketone (ACROS) with equivalent amounts of benzoylhydrazine (ACROS) or salicylhydrazine (ACROS) in ethanol and recrystallized from ethanol/water [8,10]. [NBu₄]₂[UO₂Cl₄] was prepared following a standard procedure from uranyl nitrate, aqueous HCl and tetrabutylammonium chloride. Infrared spectra were recorded for KBr pellets on a Shimadzu FT IR spectrometer between 4000 and 400 cm⁻¹.

 $[UO_2(L^{1a})]$. HL^{1a} (440 mg, 1.1 mmol) was partially dissolved in about 5 ml methanol and added to a solution of UO₂(NO₃)₂ · 6 H₂O (502 mg, 1 mmol) in 3 ml methanol. After heating the mixture to reflux, a clear yellow solution was formed, from which a bright yellow powder began to precipitate after about 15 min. After an overall reflux time of 2 h, the mixture was cooled to room temperature and the yellow solid was filtered off.

The reaction rate can be increased by the addition of two drops of triethylamine. In this case, the precipitation of the solid is complete after 30 min. The solid is almost insoluble in alcohols. Yield: 633 mg (95%). Elemental analysis, Found: C, 41.2; H, 2.7; N, 10.5%; Calcd. for $C_{23}H_{19}N_5O_4U$: C, 41.4; H, 2.8; N, 10.5%. IR (v_{max}/cm^{-1}): 1590 (C=N), 900 (O=U=O).

The same procedure can be applied when the reaction is performed with $[NBu_4]_2[UO_2Cl_4]$ instead of uranyl nitrate.

 $[UO_2(L^{1b})]$. The complex was prepared following the procedure given above for $[UO_2(L^{1a})]$ starting from $UO_2(NO_3)_2 \cdot 6 H_2O$ (502 mg, 1 mmol) and HL^{1b} (517 mg, 1.2 mmol). Yellow, sparingly soluble solid. Yield: 629 mg (90%). Elemental analysis, Found: C, 39.2; H, 2.7; N, 10.3%; Calcd. for $C_{23}H_{19}N_5O_6U$: C, 39.5; H, 2.7; N, 10.0%. IR (v_{max}/cm^{-1}): 3209 (OH), 1591 (C=N), 902 (O=U=O).

The same procedure can be applied when the reaction is performed with $[NBu_4]_2[UO_2Cl_4]$ instead of uranyl nitrate.

 $[UO_2(L^{1a})(DMSO)]$. [UO₂(L^{1a})] (333 mg, 0.5 mmol) was dissolved in about 1 ml hot DMSO. Large red blocks deposited upon slow cooling of the solvent. More product could be obtained by diffusion of water into the DMSO solution. Yield: 224 mg (60%). Elemental analysis, Found: C, 41.2; H, 3.3; N, 9.7; S, 4.5%; Calcd. for C₂₅H₂₅N₅O₅SU: C, 41.2; H, 3.4; N, 9.6; S, 4.4%. IR (v_{max}/cm^{-1}): 1585 (C=N), 914 (O=U=O).

 $[UO_2(L^{1a})(pyridine)]$. The compound was prepared from $[UO_2(L^{1a})]$ and pyridine following the procedure given for $[UO_2(L^{1a})(DMSO)]$. Yield: 60%. Elemental analysis, Found: C, 45.0; H, 3.0; N, 11.0%; Calcd. for $C_{28}H_{24}N_6O_4U$: C, 45.0; H, 3.2; N, 11.3%. IR (v_{max}/cm^{-1}): 1587 (C=N), 912 (O=U=O). Single crystals suitable for X-ray diffraction were obtained directly from the reaction mixture.

 $[UO_2(L^{1a})(THF)]$. The compound was prepared from $[UO_2(L^{1a})]$ and THF following the procedure given for $[UO_2(L^{1a})(DMSO)]$. The large red crystals immediately decompose after removal from the solvent. This is most probably due to the loss of solvent incorporated in the crystal lattice. Elemental analysis was performed with the remaining red powder after drying in vacuum and confirmed the presence of coordinated THF. Yield: 80%. Elemental analysis, Found: C, 43.8; H, 3.6; N, 9.4%; Calcd. for $C_{27}H_{27}N_5O_5U$: C, 43.8; H, 3.7; N, 9.5%. IR (v_{max}/cm^{-1}): 1594 (C=N), 917 (O=U=O).

 $[UO_2(L^{1b})(DMSO)]$. The compound was prepared from $[UO_2(L^{1b})]$ and DMSO following the procedure given for

Table 3	X-ray structure	data	collection	and	refinement	parameters
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	[UO ₂ (L ^{1a})(pyridine)]	[UO ₂ (L ^{1b})(DMSO)]	$[UO_2(L^2)_2]$	$[UO_2(L^3)_2]$
Formula	C ₂₈ H ₂₄ N ₆ O ₄ U	C25H25N5O7SU	$C_{28}H_{24}N_6O_4U$	C ₃₆ H ₂₆ N ₈ O ₄ U
$M /g mol^{-1}$	746.56	777.60	746.56	872.68
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	Fdd2	Pnma	Pbcn	$P2_1/n$
Unit cell a	11.191(2)	17.979(2)	14.641(2)	11.863(1)
b	19.620(3)	17.716(1)	7.834(1)	15.127(2)
с	24.248(3)	8.300(1)	23.163(3)	18.780(2)
β				100.72(2)
V /Å ³	53234(1)	2642(5)	2656.7(6)	3311.3(6)
Z	8	4	4	4
$D_c/g \text{ cm}^{-3}$	1.863	1.955	1.866	1.751
Measuring device and temperature /°C	SMART CCD / -100	CAD4 / 20	CAD4 / 20	CAD4 / 20
Linear absorption coefficient /mm ⁻¹	6.144	6.276	6.156	4.955
Absorption correction	SADABS	Psi Scans	Psi Scans	Psi Scans
T _{min} / T _{max}	0.4601 / 0.5088	0.7583 / 0.9750	0.6754 / 0.8621	0.2419 / 0.6371
Measured reflections	16098	3148	7990	8449
Independent reflections / R _{int}	4004 / 0.035	2970 / 0.072	3517 / 0.1076	7201 / 0.0628
Refined parameters	179	197	178	442
R1 (F) $/wR2$ (F ²) (I > 2 σ (I)) ^{a)}	0.0208 / 0.0464	0.0626 / 0.0906	0.0495 / 0.1047	0.0526 / 0.0951
GooF	0.972	0.973	0.966	0.978
Deposit No.	CCDC 229649	CCDC 229650	CCDC 229651	CCDC 229652

^{a)} R1 = $|F_o - F_c|/|F_o|$; wR2 = $[w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

 $\label{eq:cl_a} \begin{array}{l} [UO_2(L^{1a})(DMSO)]. \mbox{ Yield: 60\%. Elemental analysis, Found: C, } \\ 38.5; \mbox{ H, 3.2; N, 8.8; S, 4.4\%; Calcd. for $C_{25}H_{25}N_5O_7SU: C, 38.6; $H, 3.2; N, 9.0; S, 4.1\%. IR $(v_{max}/cm^{-1}): 3053$ (OH), 1591$ (C=N), 914 (O=U=O). \\ \end{array}$

Single crystals for the X-ray structure analysis were obtained by slow diffusion of water into a DMSO solution of the complex.

 $[UO_2(L^{1b})(pyridine)]$. The compound was prepared from $[UO_2(L^{1b})]$ and pyridine following the procedure given for $[UO_2(L^{1a})(pyridine)]$. Yield: 85%. Elemental analysis, Found: C, 43.2; H, 3.0; N, 12.1%; Calcd. for $C_{28}H_{24}N_6O_6U$: C, 43.2; H, 3.1; N, 12.3%. IR (v_{max}/cm^{-1}): 3005 (OH), 1588 (C=N), 915 (O=U=O).

 $[UO_2(L^2)^2]$. HL² (526 mg, 2.2 mmol) was dissolved in about 10 ml methanol and added to a solution of UO₂(NO₃)₂ · 6 H₂O (502 mg, 1 mmol) in 5 ml methanol. The mixture was heated at reflux for 1 h. During this period the solution turned red. A red, crystalline solid precipitated after reducing the volume to about 5 ml and cooling to room temperature. Addition of a few drops of triethylamine increased the rate of the reaction, but did not influence the overall yield of the product. The red solid was filtered off, washed with a small amount of cold methanol and dried in vacuum. Yield: 595 mg (80%). Elemental analysis, Found: C, 45.2; H, 3.3; N, 11.6%; Calcd. for C₂₈H₂₄N₆O₄U: C, 45.0; H, 3.2; N, 11.3%. IR (v_{max}/cm⁻¹): 1575 (C=N), 912 (O=U=O).

The same procedure can be applied when the reaction is performed with $[NBu_4]_2[UO_2Cl_4]$ instead of uranyl nitrate.

Single crystals suitable for X-ray diffraction were obtained from hot methanol.

 $[UO_2(L^3)_2]$. The compound was prepared as reported for $[UO_2(L^2)_2]$ starting from HL³ (665 mg, 2.2 mmol) and $UO_2(NO_3)_2 \cdot 6 H_2O$ (502 mg, 1 mmol). Red blocks were deposited directly from the reaction mixture. Yield: 785 mg (90%). Elemental analysis, Found: C, 49.8; H, 3.3; N, 12.8%; Calcd. for $C_{36}H_{26}N_8O_4U$: C, 49.5; H, 3.0; N, 12.8%. IR (v_{max}/cm^{-1}): 1574 (C=N), 911 (O=U=O).

Single crystals suitable for X-ray diffraction were obtained from a CHCl₃/methanol mixture.

X-Ray structure determinations

The X-ray diffraction data were collected on an automated single crystal diffractometer of the type CAD4 (Enraf-Nonius, Delft) or a BRUKER SMART CCD with Mo Ka radiation. The structures were solved by direct methods using SHELXS-97 [11]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97 [12]. The positions of the hydrogen atoms were calculated for idealised positions and treated with the 'riding model' option of SHELXL-97. Crystal data and more details of the data collections and refinements are contained in Table 3. Additional information on the structure determinations have been deposited at the Cambridge Crystallographic Data Centre. See information for Authors, Issue No. 1.

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