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Dioxouranium(VI) complexes with 2,6-acetylpyridinebenzoylhydrazones and -semicarbazones

C.C. Gatto [a], E. Schulz Lang [a], A. Jagst [b], U. Abram [b,*]

[a] *Departamento de Quimica, Universidade Federal de Santa Maria, 97.111 Santa Maria-RS, Brazil*
[b] *Freie Universität Berlin, Institute of Chemistry, Fabeckstr. 34-36, D-14195 Berlin, Germany*

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Abstract

Benzoylhydrazones and semicarbazones derived from 2,6-diacetylpyridine react with common dioxouranium(VI) compounds such as uranyl nitrate or $[NBu_4]_2[UO_2Cl_4]$ to form air-stable complexes. 2,6-Diacetylpyridinebis(benzoylhydrazone) (H_2L^1), 2,6-diacetylpyridinebis(N4-phenylsemicarbazone) (H_2L^2) and the asymmetric proligand 2,6-diacetylpyridine(benzoylhydrazone)-(N4-phenylsemicarbazone) (H_2L^3) give yellow products of the composition $[UO_2(L)]$. The neutral compounds contain doubly deprotonated ligands and possess uranium atoms with distorted pentagonal-bipyramidal coordination spheres. The equatorial coordination spheres of the metal atoms can be extended by the addition of a monodentate ligand such as pyridine or DMSO. The uranium atoms in the resulting complexes have hexagonal-bipyramidal coordination environments with the oxo ligands in axial positions.

X-ray diffraction studies on $[UO_2(L^1)(DMSO)]$, $[UO_2(L^2)]$, $[UO_2(L^2)(DMSO)]$ and $[UO_2(L^3)]$ show relatively short U–O bonds to the benzoylic oxygen atoms between 2.273(6) and 2.368(5) Å. This suggests a preference of these donor sites of the ligands over their imino and amine functionalities (U–N bond lengths: 2.502(7)–2.671(7) Å). The addition of a sixth ligand to the equatorial coordination sphere results in a lengthening of the metal–pyridine bonds.

Keywords: Uranium; Benzoylhydrazones; Semicarbazones; Actinides; Structure analysis

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1. Introduction

As a part of our systematic studies of the coordination chemistry of the early actinide elements, we recently published a report on the structural chemistry of thiosemicarbazonato complexes of uranium(VI) [1]. The formation of complexes with moderate stability was observed with acetylpyridine thiosemicarbazone. The presence of the pyridine nitrogen atom was mandatory for the formation of chelate complexes. This additional donor site is obviously essential to establish a bond between the relatively 'hard' metal ion UO_2^{2+} and 'soft' donor sites such as the thione sulfur atoms in thiosemicarbazones. More stable complexes are expected with 'harder' donor atoms such as oxygen, as are provided by semicarbazones or hydrazones. A number of studies have been undertaken with both ligand systems and the formation of chelates with various compositions has 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 of complexes with 2,6-diacetylpyridine-bis(2′-pyridyl)hydrazones [4], benzoylhydrazones [5]

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[*] Corresponding author. Tel.: +49 30 83854002; fax: +49 30 838542676.
E-mail address: abram@chemie.fu-berlin.de (U. Abram).

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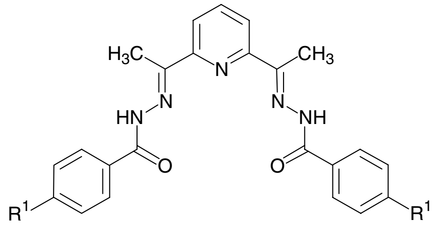
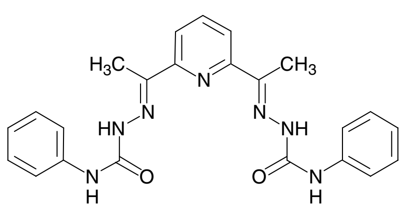
and semicarbazones [6] describe uranyl complexes having pentagonal bipyramidal or hexagonal bipyramidal coordination spheres. The reasons for the respective composition of the equatorial coordination spheres and the influence of substituents are not yet clear. In the present paper, we describe the reactions of uranyl nitrate and $[NBu_4]_2[UO_2Cl_4]$ with 2,6-diacetylpyridinebis(benzoylhydrazone) (H_2L^{1a}), 2,6-diacetylpyridinebis(N4-phenylsemicarbazone) (H_2L^2), and 2,6-diacetylpyridine(benzoylhydrazone)(N4-phenylsemicarbazone) (HL^3), and the solid state structures of the products. H_2L^3 represents a prototype of new of asymmetric ligands, which combine three donor functionalities (aromatic amine, benzoylhydrazone and semicarbazone) in one molecule.

2.2. H_2L^3

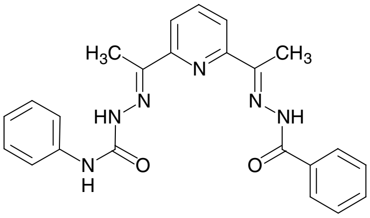
A suspension of HL^{3a} (340 mg, 1.2 mmol) and benzoylhydrazine (160 mg, 1.2 mmol) in 30 ml of iso-propanol was heated at reflux for 36 h. The hot reaction mixture was filtered and the bright-yellow precipitate was washed with 5 ml of ethanol. Yield: 0.33 g (66%). *Anal.* Calc. for $C_{23}H_{22}N_6O_2$: C, 66.7; H, 5.4; N, 20.3. Found: C, 66.5; H, 5.6; N, 19.9%. IR (ν_{max}/cm^{-1}): 3389, 3201 (NH), 1689, 1653 (C=O). ^{1}H NMR (400 MHz, dmso-d$_6$): δ (ppm): CH_3 2.42 (s, 3H,); 2.53 (s, 3H); phenyl 7.04–8.43 (m, 13H); NH 8.99 (s, 1H), 9.96 (s, 1H), 10.89 (s, 1H). FAB$^+$-MS: $m/z = 415$ (3%, $[M - H]^+$); 105 (12%, $[Ph{-}C{=}O]^+$).



H_2L^{1a}: $R^1 = H$ **H_2L^{1b}**: $R^1 = OMe$



H_2L^2



H_2L^3

2. Experimental

HL^1 and HL^2 were prepared by refluxing equimolar amounts of 2,6-diacetylpyridine (Aldrich) and benzoylhydrazine (ACROS) or 4-phenylsemicarbazide (ACROS) in ethanol and recrystallizing from ethanol/water [6,7]. $[NBu_4]_2[UO_2Cl_4]$ was prepared from uranyl nitrate, aqueous HCl and tetrabutylammonium chloride following a standard procedure. Infrared spectra have been recorded for KBr pellets on a Shimadzu FT IR spectrometer in the range between 4000 and 400 cm^{-1}.

2.1. *2,6-Diacetylpyridinemono(4N-phenylsemicarbazone),* HL^{3a}

2,6-Diacetylpyridine (1.63 g, 10.0 mmol) was dissolved in 50 ml of a hot 1:1 mixture of ethanol and water. A solution of 4-phenylsemicarbazide (1.51 g, 10.0 mmol) in 75 ml of water was slowly added to the reaction mixture. After heating at reflux for 1 h, the colourless precipitate was filtered off and washed with ethanol. Yield: 2.75 g (93%). *Anal.* Calc. for $C_{16}H_{16}N_4O_2$: C, 64.9; H, 5.4; N, 18.9. Found: C, 64.6; H, 5.5; N, 19.1%. IR (ν_{max}/cm^{-1}): 3375, 3194 (NH), 1697,1680 (C=O). ^{1}H NMR (400 MHz, dmso-d$_6$): δ (ppm): CH_3 2.20 (s, 3H), 2.67 (s, 3H); phenyl 7.03–8.65 (m, 8H); NH 9.01, 10.03 (s, 2H). FAB$^+$-MS: $m/z = 297$ ($[M - H]^+$); 204 (58%, $[M - NH - Ph]^+$).

2.3. $[UO_2(L^{1a})]$

HL^{1a} (440 mg, 1.1 mmol) was partially dissolved in 5 ml of methanol and added to a solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ (502 mg, 1 mmol) in 3 ml of methanol. A clear yellow solution was formed while heating the mixture at reflux, and a bright yellow powder began to precipitate after about 15 min. After an overall refluxing 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. Then, the precipitation of the solid is complete after 30 min. The solid is almost insoluble in alcohols. Yield: 633 mg (95%). *Anal.* Calc. for $C_{23}H_{19}N_5O_4U$: C, 41.4; H, 2.8; N, 10.5. Found: C, 41.2; H, 2.7; N, 10.5%. IR (ν_{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.

2.4. $[UO_2(L^{1a})(DMSO)]$

$[UO_2(L^{1a})]$ (333 mg, 0.5 mmol) was dissolved in about 1 ml of 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%). *Anal.* Calc. for $C_{25}H_{25}N_5O_5SU$: C, 41.2; H, 3.4; N, 9.6; S, 4.4. Found: C, 41.2; H, 3.3; N, 9.7; S, 4.5%. IR (ν_{max}/cm^{-1}): 1585 (C=N), 914 (O=U=O).

Crystals suitable for X-ray diffraction were obtained directly from the reaction mixture.

2.5. [$UO_2(L^2)$]

The compound was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ or $[NBu_4]_2[UO_2Cl_4]$ and H_2L^2 following the procedure given for [$UO_2(L^{1a})$]. Yellow powder. Yield: 60%. *Anal.* Calc. for $C_{23}H_{21}N_7O_4U$: C, 39.6; H, 3.0; N, 14.1. Found: C, 40.0; H, 3.1; N, 14.0%. IR (ν_{max}/cm^{-1}): 1570 (C=N), 905 (O=U=O).

2.6. Attempts to prepare [$UO_2(L^2)(DMSO)$]

[$UO_2(L^2)$] (348 mg, 0.5 mmol) was dissolved in about 3 ml of hot DMSO. Orange-red crystals deposited upon diffusion of water into the DMSO solution. The crystals that deposit from such solutions have a composition of [$UO_2(L^2)$] · [$UO_2(L^2)(DMSO)$] · DMSO · H_2O and were suitable for X-ray diffraction. Yield: 176 mg (45%). *Anal.* Calc. for $C_{25}H_{25}N_5O_5SU$: C, 41.2; H, 3.4; N, 9.6; S, 4.4. Found: C, 41.2; H, 3.3; N, 9.7; S, 4.5%. IR (ν_{max}/cm^{-1}): 1572 (C=N), 908 (O=U=O).

2.7. [$UO_2(L^3)$]

The compound was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ or $[NBu_4]_2[UO_2Cl_4]$ and H_2L^3 following the procedure given for [$UO_2(L^{1a})$]. Yellow crystals suitable for X-ray diffraction deposited directly from the reaction mixture. Yield: 40%. *Anal.* Calc. for $C_{23}H_{20}N_6O_4U$: C, 40.5; H, 2.9; N, 12.3. Found: C, 40.1; H, 3.4; N, 11.7%. IR (ν_{max}/cm^{-1}): 1591, 1554 (C=N), 908 (O=U=O).

2.8. X-ray structure determinations

The X-ray diffraction data were collected on an automated single crystal diffractometer of the type CAD4 (Enraf-Nonius, Delft) with Mo Kα radiation. The structures were solved by direct methods using SHELXS-97 [8]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL-97 [9]. The positions of the hydrogen atoms were calculated for idealized 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 1. Additional information on the structure determinations have been deposited at the Cambridge Crystallographic Data Centre. See information for Authors, Issue No. 1.

3. Results and discussion

$UO_2(NO_3)_2 \cdot 6H_2O$ as well as $[NBu_4]_2[UO_2Cl_4]$ react with the benzoylhydrazone or semicarbazone ligands H_2L^1–HL^3 in boiling methanol under complete substitution of the equatorial coordination sphere of the metal. Under these conditions, complete deprotonation of both ligand types 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 organic ligands, as has been observed for related semicarbazones of lanthanides and chromium(III) [10], and other highly charged metal ions [6]. 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 depending 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}, H_2L^2 or H_2L^3 are heated with $UO_2(NO_3)_2 \cdot 6H_2O$ 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 (partially) NMR measurements showing that the products formed from the different uranium precursors were identical. The compounds are poorly soluble in common solvents and, thus, do not allow a detailed NMR analysis, and in coordinating solvents such as DMSO or pyridine a conversion of the complexes is observed.

The U=O double bonds show characteristic IR bands between 900 and 908 cm^{-1}. This value is in accord with the neutral uranyl complexes in [5b], whereas anionic derivatives absorb in the range between 920 and 950 cm^{-1}. The proton NMR spectra prove the absence of NH protons of the organic ligands. No evidence was found for the coordination of methanol or water. This allows the conclusion that complexes of the composition [$UO_2(L)$] have been formed, despite the fact that the crystal structure of [$UO_2(L^4)(H_2O)$] (H_2L^4 = bis(2,6-diacetylpyridinebis(semicarbazone))) has been reported in a previous paper [6]. No evidence could be found for anionic uranyl complexes with non-deprotonated or monodeprotonated ligands. This strongly suggests that the hydrazonato and semicarbazonato complexes of the present study possess the same coordination sphere as the uranyl complex with 2,6-diacetylpyridine bis(methoxybenzoylhydrazone), H_2L^{1b}, which

Table 1
X-ray structure data collection and refinement parameters

	$[UO_2(L^{1a})(DMSO)]$	$[UO_2(L^2)] \cdot [UO_2(L^2)(DMSO)] \cdot DMSO \cdot H_2O$	$[UO_2(L^3)]$
Formula	$C_{25}H_{25}N_5O_5SU$	$C_{50}H_{54}N_{14}O_{11}S_2U_2$	$C_{23}H_{20}N_6O_4U$
M (g mol^{-1})	745.60	1567.25	682.48
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a	18.130(3)	8.284(1)	8.141(2)
b	17.514(1)	15.283(2)	10.985(2)
c	8.221(3)	23.700(3)	29.120(2)
α	90	75.52(1)	90
β	90	88.92(1)	93.71(9)
γ	90	78.30(1)	90
V (Å^3)	2610.5(6)	2843.1(7)	2598.7(8)
Z	4	2	4
D_c (g cm^{-3})	1.897	1.831	1.744
Linear absorption coefficient (mm^{-1})	6.343	5.832	6.284
Absorption correction	Ψ scans	Ψ scans	DELABS [13]
T_{min}/T_{max}	0.1339/0.4831	0.7094/0.9783	0.230/0.391
Measured reflections	6963	14998	3849
Independent reflections/R_{int}	2928/0.055	12389/0.033	3048/0.049
Refined parameters	178	716	307
$R_1(F)/wR_2(F^2)$ $(I > 2\sigma(I))$[a]	0.0459/0.0976	0.0459/0.0922	0.0677/0.1535
Goodness-of-fit	1.162	0.997	1.034
CCDC Deposit Nos.	230958	230959	230960

[a] $R_1 = |F_o - F_c|/|F_o|; wR_2 = [W(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.

shows a distorted pentagonal-bipyramidal coordination sphere of the metal atom [b]. 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 2), which suggests the possibility of the extension of the coordination number of the uranium atom by the addition of an appropriate monodentate ligand. This has been tested by heating the $[UO_2(L)]$ complexes in a strongly coordinating solvent such as DMSO. The yellow solids slowly dissolve in these solvents and the colour changes. Whereas a dark red solution was obtained with $[UO_2(L^{1a})]$, an orange-red colour was obtained with $[UO_2(L^2)]$. This behaviour suggests different reaction patterns for the hydrazonato and semicarbazonato complexes.

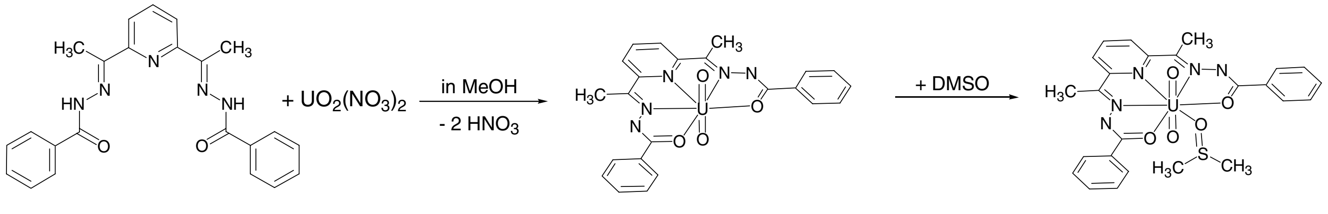
A reaction sequence according to Scheme 1 can be derived for HL^{1a}. It results in the formation of a neutral $[UO_2(L^{1a})(DMSO)]$ complex, which can be isolated in crystalline form by the addition of a small amount of water to the DMSO solution and slow cooling. The U=O stretching vibration is slightly shifted to higher frequencies. 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 $[UO_2(L^{1a})(DMSO)]$ have been studied by X-ray crystallography, showing that the complex possesses an eight-coordinate uranium atom. An ellipsoid representation of the molecular structure is shown in Fig. 1. Selected bond lengths and angles are summarized in Table 2. The coordination environment of the uranium atom can be described as a slightly distorted hexagonal bipyramid. Whereas the five donor atoms of the hydrazonato ligand and the uranium atom are almost perfectly coplanar (mean deviations from the mean least-square plane: 0.0816 Å, r.m.s. 0.0670), O30 deviated from this plane by 0.619(9) Å. The phenyl groups of the ligands are coplanar with the equatorial coordination sphere within 5°. The *X*–*U*–*Y* angles (*X* and *Y* are neighbouring equatorial donor atoms) range between 59.7(2)° and 61.6(1)°. The extension of the coordination number of the uranium atom causes lengthening of the uranium–nitrogen bonds to the chelating ligand as can be seen from a comparison with the corresponding data in the seven-coordinate complex $[UO_2(L^{1b})]$ [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 ligand, which is doubly deprotonated in both compounds. Whereas the double bond between C7 and N2 is almost localized, a delocalization of the electron density of the C17–O18 double bond can be concluded. This results in a significant shortening of the C17–N3 bond as a consequence of complex formation and can best be described by the bonding scheme represented in **I**, irrespective of the coordination number of the uranium atoms and the ligand type, and has also been found in the semicarbazonato complexes $[UO_2(L^2)]$ and $[UO_2(L^2)(DMSO)]$.

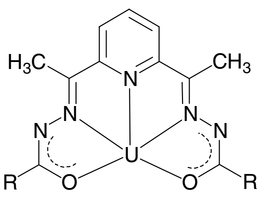
Table 2
Selected bond lengths (Å) and angles (°) in $[UO_2(L^{1a})(DMSO)]$, $[UO_2(L^{1b})]$[a], $[UO_2(L^2)(DMSO)]$ and $[UO_2(L^2)]$

	$[UO_2(L^{1a})(DMSO)]$	$[UO_2(L^{1b})]$[a]	$[UO_2(L^2)(DMSO)]$	$[UO_2(L^2)]$
U–O10/O11	1.771(7)	1.77	1.752(5)	1.748(6)
U–O20/O12	1.764(6)	1.77	1.763(5)	1.762(6)
U–O18/O58	2.359(5)	2.32	2.360(5)	2.341(5)
U–O28/O68	[b]	2.30	2.368(5)	2.273(6)
U–N2/N42	2.617(5)	2.47	2.559(6)	2.505(7)
U–N4/N44	[b]	2.49	2.583(6)	2.503(7)
U–N1/N41	2.671(7)	2.52	2.610(6)	2.502(7)
U–O30	2.542(6)		2.673(6)	
O18/O58–C17/C57	1.265(8)	1.26	1.278(8)	1.27(1)
O28/O68–C27/C67	[b]	1.30	1.259(9)	1.29(1)
C17/C57–N3/N43	1.306(9)	1.33	1.313(9)	1.33(1)
C27/C67–N5/N45	[b]	1.30	1.34(1)	1.32(1)
N3/N43–N2/N42	1.380(8)	1.41	1.373(8)	1.381(9)
N4/N44–N5/N45	[b]	1.40	1.385(8)	1.38(1)
N2/N42–C7/C47	1.303(8)	1.31	1.290(9)	1.29(1)
N4/N44–C9/C49		1.31	1.278(9)	1.28(1)
C7/C47–C6/C46	1.44(1)	1.50	1.45(1)	1.46(1)
C9/C49–C2/C42	[b]	1.48	1.47(1)	1.48(1)
O18/O58–U–N2/N42	59.7(2)	63.5	61.5(2)	63.6(2)
O28/O68–U–N4/N44	59.7(2)[b]	63.3	61.3(2)	63.6(2)
N2/N42–U–N1/N41	59.9(1)	63.3	61.6(2)	63.8(2)
N4/N44–U–N1/N41	59.9(1)[b]	63.3	61.1(2)	63.5(2)
O18/–U–O30	61.6(1)		61.7(2)	
O18–U–O18′/O28				
O58–U–O68	120.6(2)	106.8	113.7(2)	105.5(2)
N1···N2/N41···N42	2.64	2.62	2.65	2.64
N1···N4/N41···N44	2.64[b]	2.63	2.64	2.64
N2···O18/N21···O58	2.49	2.52	2.52	2.56
N4···O28/N44···O68	2.49[b]	2.52	2.53	2.52

[a] Values taken from [5b] and adopted to the atomic labelling schemes given in Figs. 1 and 2.
[b] Symmetry related.



Scheme 1.



I

R = Ph, NHPh

$[UO_2(L^2)]$ and $[UO_2(L^2)(DMSO)]$ co-crystallize as large orange-red plates when $[UO_2(L^2)]$ is recrystallized from hot DMSO. The presence of two complexes with different coordination environments around uranium in the same crystals is somewhat surprising in light of the fact that the extension of the coordination number proceeds readily at $[UO_2(L^1)]$ and that additional solvent molecules (H_2O and DMSO) are present. The structures of the complex molecules are illustrated in Fig. 2. The sulfur atom of the DMSO ligand in $[UO_2(L^2)(DMSO)]$ is disordered over two positions. The overall bonding pattern in $[UO_2(L^2)(DMSO)]$ is similar to that in $[UO_2(L^{1a})(DMSO)]$ and $[UO_2(L^4)(H_2O)]$, with the uranium atom in an almost regular hexagonal-bipyramidal coordination environment. The pentadentate semicarbazonato ligands are almost

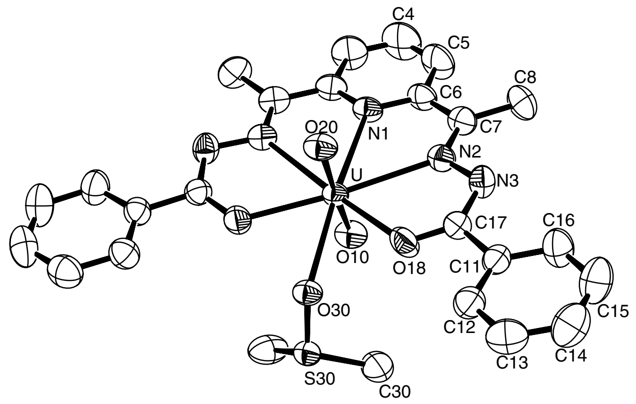


Fig. 1. Ellipsoid presentation [14] of $[UO_2(L^{1a})(DMSO)]$. Thermal ellipsoids represent 50% probability.

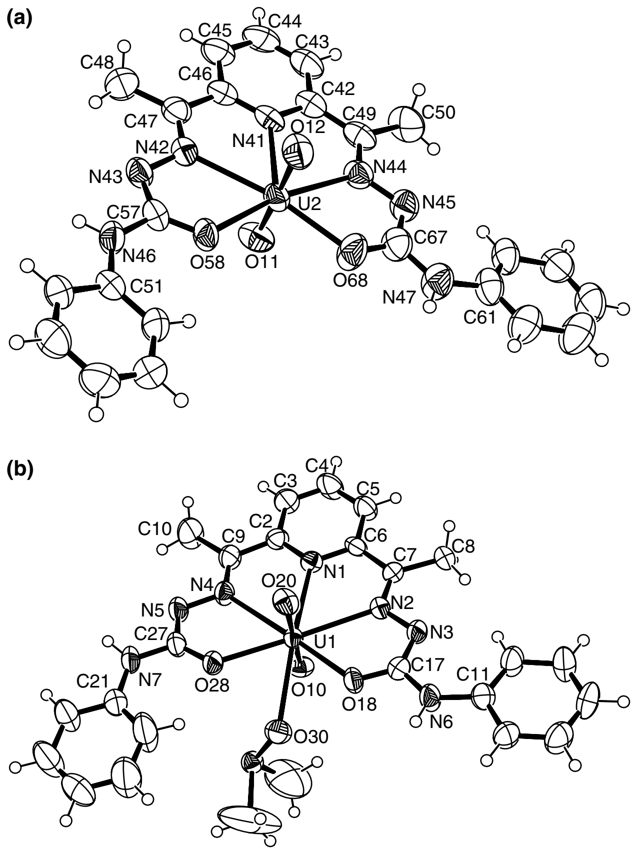
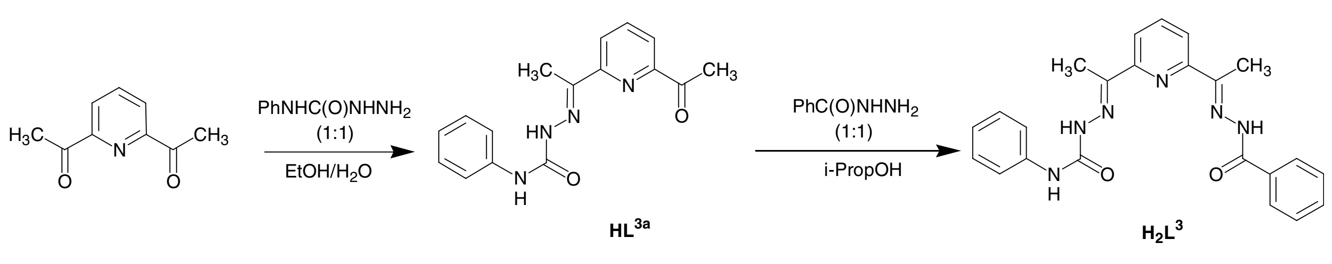


Fig. 2. Ellipsoid presentations [14] of (a) $[UO_2(L^2)]$ and (b) $[UO_2(L^2)(DMSO)]$. Thermal ellipsoids represent 50% probability.

perfectly planar in both complexes. There are maximum deviations from the mean least-squares planes which include all atoms of the L_2^{2-} ligands, with the exception of the phenylrings of the semicarbazone units, of 0.18 Å (r.m.s.: 0.0747) in $[UO_2(L^2)]$ and 0.081 Å (r.m.s.: 0.0351) in $[UO_2(L^2)(DMSO)]$. The phenyl rings are slightly twisted against these planes with angles between 2.1° and 11.8°. The oxygen atom of the DMSO ligand in $[UO_2(L^2)(DMSO)]$ has a distance of 1.26 Å to the plane formed by the donor atoms of the pentadentate ligand. It is interesting to note that the increase of the 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 can be estimated by the intramolecular distances between the donor atoms of the five-membered chelate rings. The corresponding values are also listed in Table 2. A lengthening of the U–N1 bond by 0.18 Å is the result of the coordination of a DMSO ligand to $[UO_2(L^2)]$, despite the fact that the resulting long U–O30 bond length of 2.673(6) Å reflects an only weak interaction (cf. uranium–DMSO bond lengths of 2.542(6) Å in $[UO_2(L^{1a})(DMSO)]$ or a mean value of 2.38 Å in $[UO_2(DMSO)_5][ClO_4]_2$ [11]).

The U–N bond lengths are longer in the eight-coordinate $[UO_2(L)(solvent)]$ complexes irrespective of the semicarbazonato or benzoylhydrazonato side arms. 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 eight.

The proligand H_2L^3 contains one benzoylhydrazone and one semicarbazone side arm and allows the coordination of metal atoms in an asymmetric manner. The synthesis of H_2L^3 succeeded by a stepwise condensation of 2,6-diacetylpyridine with N4-phenylsemicarbazide and benzoylhydrazine according to Scheme 2. This sequence is mandatory, since the reaction of 2,6-diacetylpyridine with semicarbazide always yields significant amounts of the bis-condensation product irrespective of the amounts of reactants applied. The general route of Scheme 2 can also be applied for the synthesis of other asymmetric ligands carrying Schiff base or thiosemicarbazone side arms. It gives approach to 'tailor-made' ligand systems in terms of 'hard' and 'soft'



Scheme 2.

donor atoms and/or their protonation/deprotonation behaviour.

Uranyl nitrate and $[NBu_4]_2[UO_2Cl_4]$ react with H_2L^3 in methanol to yield a yellow complex of the composition $[UO_2(L^3)]$. Expectedly, both side arms of the ligand are deprotonated and a neutral dioxouranium compound is formed. The U=O frequency is found at 908 cm^{-1}. The molecular structure of this compound, which is the first example of a mixed benzoylhydrazone/semicarbazone complex, is shown in Fig. 3. Selected bond lengths and angles are summarized in Table 3. The bonding situation inside the chelate rings is similar to those in the symmetric benzoylhydrazone and semicarbazone complexes. As has been observed previously, the U–N bond lengths are shorter in the seven-coordinate complexes compared with their analogues with coordination number eight, and almost localized C–N double bonds between the hydrazine nitrogen atoms and their neighbours can be stated. The O18–U–O28 angle of 109.9(6)° is larger than the corresponding value in $[UO_2(L^2)]$ and should allow the extension of the coordination sphere without introduction of disproportional steric strain. This has been proven by heating $[UO_2(L^3)]$ in DMSO, which results in the formation of a deep red solution and the formation of the DMSO adduct is suggested with respect to the similar behaviour of $[UO_2(L^1)]$ and partially $[UO_2(L^2)]$. The red crystals, however, decompose rapidly when they are removed from the solvent to give an yellow-orange powder, the analysis of which did not give satisfactory evidence for an intact DMSO adduct. A mixed composition of the material containing $[UO_2(L^3)]$ and $[UO_2(L^3)(DMSO)]$ is strongly suggested, but we were not yet able to grow single crystals suitable for an X-ray structure analysis.

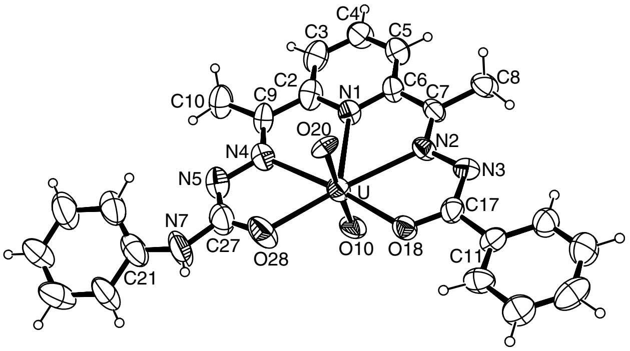


Fig. 3. Ellipsoid presentation [14] of $[UO_2(L^3)]$. Thermal ellipsoids represent 50% probability.

Fig. 4 shows a comparison of the coordination spheres of $[UO_2(L^{1a})(DMSO)]$, $[UO_2(L^2)]$ $[UO_2(L^2)(DMSO)]$ and $[UO_2(L^3)]$ containing uranium with the coordination numbers seven and eight. Particularly, the side views indicate the steric hindrance inside the equatorial coordination spheres of the metal atoms. The views along the uranyl units, however, show almost regular hexagons for the equatorial coordination spheres of $[UO_2(L^{1a})(DMSO)]$ and $[UO_2(L^2)(DMSO)]$, and the space between the oxygen donor atoms of the complexes with coordination number seven.

The present study shows that acetylpyridine benzoylhydrazones and semicarbazones are well suited to form stable complexes with dioxouranium(VI) units. All hydrazone and semicarbazone units of the ligands are deprotonated in the uranium complexes studied in this paper. This is in contrast to the behaviour in some lanthanide complexes where no or only partial deprotonation of the NH groups was observed [12]. The successful synthesis of the asymmetric ligand H_2L^3 and its uranium complex may provide a valuable tool for developing ligand systems, which can perfectly fit the coordination requirements of lanthanide and actinide ions.

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

U–O10	1.726(1)	C17–N3	1.31(2)
U–O20	1.70(2)	N2-N3	1.39(2)
U–O18	2.30(1)	N2–C7	1.28(2)
U–O28	2.33(1)	C7–C6	1.44(3)
U–N1	2.54(2)	C27–O28	1.36(2)
U–N2	2.53(2)	C27–N5	1.25(3)
U–N4	2.55(2)	N4–N5	1.43(2)
C17–O18	1.32(2)	C27–N7	1.36(3)
N1–U–N2	61.2(5)	N2–U–O18	62.7(5)
N1–U–N4	62.4(6)	N4–U–O28	63.7(6)
O18–U–28	109.9(6)		
N1···N2	2.58	N2···O18	2.52
N1···N4	2.64	N4···O28	2.59

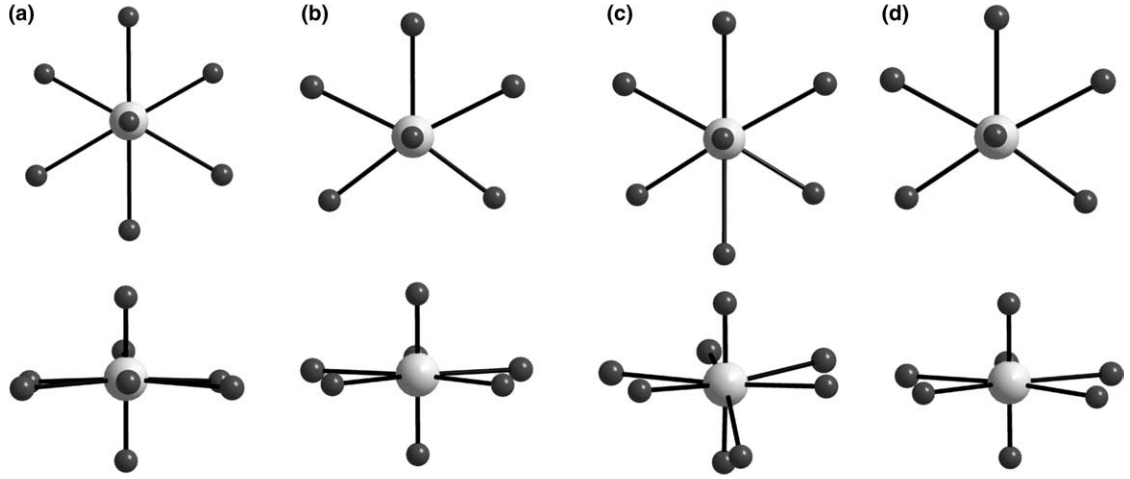


Fig. 4. Representation [15] of the coordination spheres of (a) $[UO_2(L^{1a})(DMSO)]$, (b) $[UO_2(L^2)]$, (c) $[UO_2(L^2)(DMSO)]$ and (d) $[UO_2(L^3)]$ in top and side views with respect to the O–U–O axis illustrating the distortions of the equatorial coordination spheres of the complexes in dependence on the chelating ligands and the coordination number of the metal atoms.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2004.07.011.

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