

A bis(acetylacetonato)uranium(IV) complex of the Schiff base *N,N'*-bis(3-hydroxysalicylidene)- 2-methyl-1,2-propanediamine

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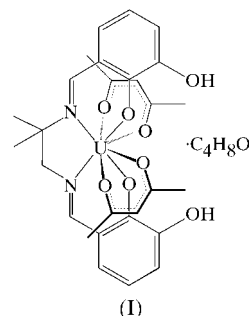
The title complex, bis(acetylacetonato- κ^2O,O')[*N,N'*-bis(3-hydroxy-2-oxidobenzaldimino)-2-methyl-1,2-propanediamine- κ^4N,O,O',N']uranium(IV) tetrahydrofuran solvate, $[U(C_{18}H_{18}N_2O_4)(C_5H_7O_2)_2] \cdot C_4H_8O$, is a rare example of a uranium(IV) complex with a compartmental Schiff base. The U atom is located in the N_2O_2 inner site of the hexadentate *N,N'*-bis(3-hydroxy-2-oxidobenzaldimino)-2-methyl-1,2-propanediamine group and is bound also to the two O atoms of both acetylacetonate moieties, which results in a dodecahedral coordination environment. Centrosymmetric dimers are formed through intermolecular hydrogen bonds that link the terminal uncoordinated hydroxy groups to one another and to the O atoms of the acetylacetonate ligands.

Comment

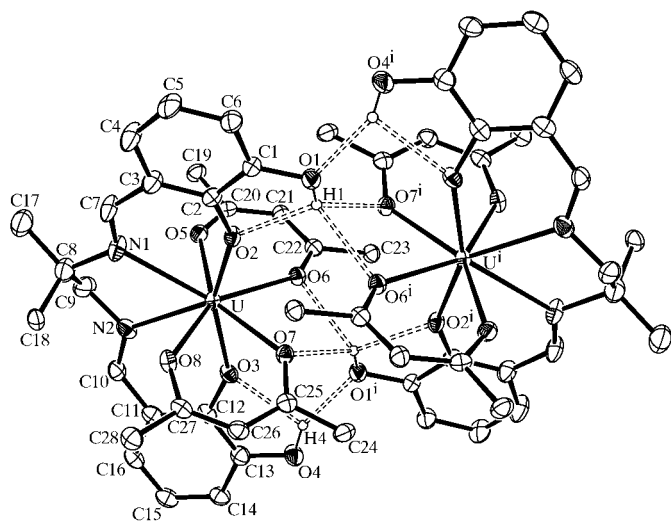
While crystal structure determinations of uranyl ion complexes of tetra- or pentadentate Schiff bases are quite common (Maurya & Maurya, 1995), those of their counterparts with U^{IV} are exceedingly rare, being limited to those of $[U(\text{salen})Cl_2(\text{thf})_2]$, where salen is *N,N'*-bis(salicylidene)-ethylenediamine and thf is tetrahydrofuran (Calderazzo *et al.*, 1976), and $[U(\text{methoxysalen})Cl_2(\text{py})_2]$, where methoxysalen is *N,N'*-bis(3-methoxysalicylidene)ethylenediamine (Le Borgne *et al.*, 2002). We have recently investigated the magnetic properties of heterobi- and heterotrimetallic 3d metal- U^{IV} complexes with hexadentate Schiff bases (Le Borgne *et al.*, 2002; Salmon, Thuéry, Rivière *et al.*, 2003). In the course of this study, we obtained crystals of the title complex, (I), formed between $U(\text{acac})_2$, where acac is acetylacetonate, and the potentially ditopic Schiff base ligand *N,N'*-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine, and determined its crystal structure.

The asymmetric unit in (I) (Fig. 1) contains one complex and one tetrahydrofuran solvent molecule. As in the two structures previously reported, the U atom is located in the

inner N_2O_2 coordination site, with mean U—O and U—N bond lengths (Table 1) of 2.22 (3) and 2.64 (4) Å, respectively, which can be compared with values of 2.15 (4) and 2.62 (4) Å in the salen complex, and 2.17 (2) and 2.62 (3) Å in the methoxysalen complex. The four donor atoms define a mean



plane, with an r.m.s. deviation of 0.100 Å, the U atom being 0.088 (3) Å from this plane. The U atom is further bound to the four O atoms of the acac groups, with a mean U—O bond length of 2.36 (2) Å, in agreement with the values in acac complexes of U^{IV} present in the Cambridge Structural Database (Allen, 2002), which are in the range 2.218–2.395 Å [mean value 2.32 (5) Å]. The four O atoms of the acac groups define a mean plane, with an r.m.s. deviation of 0.029 Å, that contains the U atom [distance from the plane = 0.004 (2) Å]. The dihedral angle between the N_2O_2 and O_4 mean planes is 89.8 (1)°. The O2—U—O3 and O5—U—O8 angles differ by about 10°, and the N1—U—N2 and O6—U—O7 angles by about 8°. These two sets of atoms thus define two nearly orthogonal trapezia with shapes that are only slightly different, the overall U-atom environment geometry being a slightly distorted dodecahedron (Kepert, 1982), in which the *A* and *B* sites correspond to N1, N2, O6 and O7, and to O2, O3, O5 and O8, respectively. The ratio of the mean $\langle U-A \rangle$ to $\langle U-B \rangle$ bond lengths is 1.095, a value almost identical to that in $[U(\text{methoxysalen})Cl_2(\text{py})_2]$ (1.08) and larger than the values in heterotrimetallic $[UM_2]$ complexes (where *M* is a transition metal ion) in which the U atom is bound to the four O atoms of each of two nearly perpendicular Schiff bases (1.06; Le Borgne *et al.*, 2002; Salmon, Thuéry, Rivière *et al.*, 2003). The angles around the U atom are identical within 1.5° to those in $[U(\text{salen})Cl_2(\text{thf})_2]$ and $[U(\text{methoxysalen})Cl_2(\text{py})_2]$ for the Schiff base donor atoms and differ slightly more for the other donor atoms. In particular, the O6—U—O7 angle is ~4–7° larger than its counterpart involving two thf O atoms or two pyridine N atoms, while the O5—U—O8 angle is ~1–2.5° smaller than its Cl—U—Cl counterparts. These differences are likely to be due to the replacement of four independent chlorine and thf or pyridine ligands in $[U(\text{salen})Cl_2(\text{thf})_2]$ and $[U(\text{methoxysalen})Cl_2(\text{py})_2]$ by two bidentate ligands in (I). Atoms O1 and O4 are both protonated, which results in intramolecular hydrogen bonds with the neighbouring phenoxide O atoms (O2 and O3) and in intermolecular hydrogen bonds linking O1 to the two proximal O atoms of the acac groups (O6ⁱ and O7ⁱ) and linking O4 to O1ⁱ [symmetry code: (i) 1 - x, -y, 1 - z; Table 2]. The latter bond appears to be stronger than the others (having a shorter H...O distance and


Figure 1

View of the centrosymmetric hydrogen-bonded dimer formed by the complex molecule in (I). Hydroxy H atoms are shown as small spheres of arbitrary radii, and hydrogen bonds are shown as dashed lines. Solvent molecules and non-hydroxy H atoms have been omitted. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $1 - x, -y, 1 - z$].

an O—H...O angle closer to 180°). The O1—H1 hydroxy group is thus involved in a trifurcated hydrogen bond, in which all three components are weak, and O4—H4 in a bifurcated bond, in which one component is stronger than the other. Two centrosymmetrically related molecules are thus held together by two strong and four weaker hydrogen bonds, resulting in a dimer of slightly offset complexes. Such dimerization of complexes with Schiff bases derived from 3-hydroxysalicylidene has been described previously (e.g. Salmon, Thuéry & Ephritikhine, 2003), but the originality of the structure of (I) is the multiplicity of hydrogen bonds linking the different ligands. In view of these intermolecular hydrogen bonds, each complex in the dimer can be seen as a second-sphere ligand for the U atom of the other. The Schiff base molecule adopts the usual umbrella conformation, with a dihedral angle of $20.8(2)^\circ$ between the two aromatic rings. A weak π — π stacking interaction is present between the C1—C6 ring and its counterpart in a neighbouring molecule [distance between centroids = 3.979 \AA , interplanar spacing = 3.451 \AA , centroid offset = 1.98 \AA and shortest interatomic contact = 3.506 \AA , which is slightly larger than twice the van der Waals radius of C (1.7 \AA); the rings are related by an inversion centre at $(0, 0, \frac{1}{2})$]. A loose C—H... π interaction is also seemingly present in the packing, between the H atom of the central C21 atom of an acac molecule and the centroid (Cg) of the C11—C16 ring of a neighbouring molecule [$\text{H} \cdots \text{Cg}^{\text{ii}} = 2.674 \text{ \AA}$ and $\text{C21—H21} \cdots \text{Cg}^{\text{ii}} = 169^\circ$; symmetry code: (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$].

Experimental

For the synthesis of complex (I), tetrahydrofuran (15 ml) was condensed in a flask charged with *N,N'*-bis(3-hydroxysalicylidene)-2-

methyl-1,2-propanediamine (100 mg, 0.304 mmol) and $[\text{U}(\text{acac})_4]$ (193 mg, 0.304 mmol). The reaction mixture was stirred overnight at 353 K. Crystals of (I) were deposited from the orange solution (151 mg, 65%). ^1H NMR (200 MHz, 296 K in d_8 -tetrahydrofuran): δ -42.1 (2H, NCH₂), -28.4 (6H, Me), -16.23 (12H, acac), -8.86 (2H, acac), 17.05, 17.42, 19.51, 19.95, 21.32, 25.63, 25.46, 28.78 ($8 \times 1\text{H}$, aromatic H and CH=N). Analysis calculated for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_8\text{U}$ ($M_r = 762$): C 44.09, H 4.20, N 3.67%; found: C 44.32, H 4.48, N 3.81%.

Crystal data

$[\text{U}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)(\text{C}_5\text{H}_7\text{O}_2)_2] \cdot \text{C}_4\text{H}_8\text{O}$
 $M_r = 834.69$
 Monoclinic, $P2_1/c$
 $a = 11.9744(6) \text{ \AA}$
 $b = 15.7475(4) \text{ \AA}$
 $c = 16.7330(8) \text{ \AA}$
 $\beta = 91.249(2)^\circ$
 $V = 3154.5(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.758 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 21 373 reflections
 $\theta = 2.8\text{--}25.7^\circ$
 $\mu = 5.20 \text{ mm}^{-1}$
 $T = 100(2) \text{ K}$
 Platelet, translucent light brown
 $0.40 \times 0.20 \times 0.05 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans
 Absorption correction: refined from ΔF (DELABS in PLATON; Spek, 2003)
 $T_{\text{min}} = 0.326, T_{\text{max}} = 0.776$
 21 373 measured reflections
 5900 independent reflections
 4733 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 25.7^\circ$
 $h = -14 \rightarrow 12$
 $k = -18 \rightarrow 17$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.092$
 $S = 1.05$
 5900 reflections
 403 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 7.4599P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.56 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

U—N1	2.666 (6)	U—O5	2.358 (4)
U—N2	2.604 (5)	U—O6	2.354 (4)
U—O2	2.201 (4)	U—O7	2.388 (4)
U—O3	2.241 (4)	U—O8	2.342 (4)
O2—U—N1	70.99 (17)	O5—U—O6	70.51 (15)
N1—U—N2	64.78 (19)	O6—U—O7	72.81 (14)
N2—U—O3	68.54 (18)	O7—U—O8	71.33 (14)
O2—U—O3	155.58 (16)		

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{—H} \cdots A$	$D\text{—H}$	$\text{H} \cdots A$	$D \cdots A$	$D\text{—H} \cdots A$
O1—H1...O2	0.85	2.34	2.746 (6)	110
O4—H4...O1 ⁱ	0.90	1.94	2.747 (6)	148
O4—H4...O3	0.90	2.25	2.716 (7)	112
O1—H1...O6 ⁱ	0.85	2.27	2.806 (6)	121
O1—H1...O7 ⁱ	0.85	2.33	2.953 (6)	130

Symmetry code: (i) $1 - x, -y, 1 - z$.

The hydroxy H atoms in (I) were found from a difference Fourier map and were introduced as riding atoms, with U_{iso} values equal to $1.2U_{\text{eq}}$ of the parent atom. All other H atoms were introduced at calculated positions and treated as riding atoms, with C–H bond lengths of 0.93 (CH), 0.97 (CH₂) and 0.96 Å (CH₃), and U_{iso} values equal to 1.2 (CH and CH₂) or 1.5 (CH₃) times the U_{eq} value of the parent atom.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Bruker, 1999) and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1021). Services for accessing these data are described at the back of the journal.

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