A heterobimetallic zinc(II)/uranium(IV) complex with the Schiff base 2-amino-N,N′-bis(3-hydroxy-salicylidene)benzylamine

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Key indicators

Single-crystal X-ray study
$T = 100$ K
Mean σ(C–C) = 0.012 Å
R factor = 0.048
wR factor = 0.083
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, [μ-2-amino-N,N′-bis(3-hydroxysalicyl-idene)benzylamine(4−)]bis(pentane-2,4-dionato)(pyridine)-zinc(II)uranium(IV) tetrahydrofuran solvate, [UZn-$(C_{21}H_{14}N_2O_4)(C_5H_7O_2)_2(C_5H_5N)]\cdot C_4H_8O$, is a novel example of a dinuclear complex including one $3d$ and one $5f$ metal ions. The U atom is located in the O_4 site of the Schiff base ligand 2-amino-N,N′-bis(3-hydroxysalicyl-idene)benzylamine (L^1) and is further bound to two acetyl-acetonate groups, which gives an octacoordinated dodecahedral environment. The Zn atom is in the inner N_2O_2 site. Its bonding to an axial pyridine molecule results in a pentacoordinated square-pyramidal environment.

Comment

In the course of our investigation of the synthesis, crystal structure and magnetic properties of compartmental Schiff base complexes containing paramagnetic $3d$ (Cu[II]) and $5f$ (U[IV]) metal ions (Le Borgne *et al.*, 2000, 2002; Salmon *et al.*, 2003a), we have described the first strictly dinuclear complex in this family, [CuL^2(py)U(acac)$_2$]·1.5py, (II), where L^2 is N,N′-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanedi-amine (Salmon *et al.*, 2003b). Comparison of the magnetic properties of (II) with those of its Zn[II] analogue confirmed the antiferromagnetic nature of the Cu—U interaction in this case. We recently reported that treatment of [M(H$_2$L)] (M = Cu and Zn, and L is a salen-derived Schiff-base ligand with varying diimine bridge other than L^2) with one equivalent of U(acac)$_4$ in refluxing pyridine afforded directly the trinuclear compounds [{ML(py)$_x$}$_2$U], where x = 0 or 1, without it being possible to isolate the [ML(py)$_x$U(acac)$_2$] intermediates. However, we found that the latter could be observed by ^{1}H NMR spectroscopy when the reaction was carried out at room temperature. Thus, a mixture of the M_2U and MU complexes is formed from equimolar amounts of the mono-nuclear starting materials. Further work has shown that, in the pure heterotrimetallic compounds [{CuL(py)$_x$}$_2$U], where x = 0 or 1, the nature, ferro- or antiferromagnetic, of the Cu—U interaction is dependent on slight geometrical changes asso-ciated with the variation of the diimine chain length (Salmon *et al.*, 2005). In the case in which M = Zn and L^1 = N,N′-bis(3-hydroxysalicylidene)-2-amino-benzylamine, single crystals of [ZnL^1(py)U(acac)$_2$]·THF, (I), (THF is tetrahydrofuran) were obtained from the slurry at 353 K. The crystal structure of this compound, reported here, provides a novel example of a rare $3d/5f$ dinuclear complex with a Schiff base ligand.
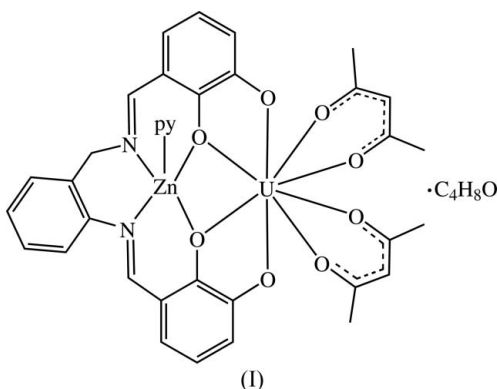
The asymmetric unit in (I) (Fig. 1) contains one complex and one THF solvent molecule. The overall structure is analogous to those of the CuU and ZnU complexes with ligand L^2 (Salmon *et al.*, 2003b), with the $3d$ metal and U

atoms in the inner N_2O_2 and outer O_4 sites of the Schiff base, respectively. The Zn atom in (I) is at mean distances of 2.066 (7) and 2.023 (5) Å from the Schiff base N and O atoms, respectively, and it is displaced by 0.513 (3) Å from the mean plane defined by these four atoms (r.m.s. deviation 0.19 Å). The Zn—N(pyridine) bond length (Table 1) is identical to the other two and the metal environment is slightly distorted square pyramidal. These values are in agreement with those in the ZnU complex with L^2 [$\langle$Zn—N(L^2)$\rangle$ = 2.079 (16)Å, $\langle$Zn—O$\rangle$ = 1.977 (6)Å and Zn—N(py) = 2.057 (10) Å]. The geometry around Zn is also nearly identical to that in the trinuclear complex [{ZnL^1(py)}$_2$U] (Salmon et al., 2005): the bond lengths and angles vary at most by ca 0.01 Å and 2°, respectively, and the displacement of Zn out of the N_2O_2 plane is 0.533 (15) Å in the latter compound.

Figure 1
A view of (I), with the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii. Displacement ellipsoids are drawn at the 50% probability level.

diimine bridge makes dihedral angles of 22.29 (13) and 34.79 (19)° with the terminal rings and it is further involved in a weak C—H···π interaction with the pyridine molecule (H36···Cg = 2.839 Å and C36—H36···Cg = 166°; Cg is the centroid of the C9-benzene ring).

Experimental

An NMR tube was charged with [Zn(H$_2$L)] (5.0 mg, 0.012 mmol) and U(acac)$_4$ (7.5 mg, 0.012 mmol) in C$_6$D$_5$N (0.4 ml). After 1 h at 293 K, the ^{1}H NMR spectrum of the brown–orange solution showed the signals of the trinuclear complex [{ZnL(py)$_x$}$_2$U] [δ (C$_6$D$_5$N, 293 K) −7.40 (4H, NCH$_2$), −0.07, 0.55, 1.21 and 1.38 (4 × 2H, aromatic of diimine chain), 3.20, 3.34, 5.30, 5.39, 14.32, 14.38, 23.79, 24.46 (8 × 2H, aromatic H and CH═N)] and other resonances attributed to the dinuclear complex [ZnL(py)$_x$U(acac)$_2$] [δ −19.73 (12H, acac), −10.70 (2H, acac), −7.06 (2H, NCH$_2$), −0.03, 0.67, 1.25 and 1.41 (4 × 1H, aromatic of diimine chain), 3.93 and 4.62 (2 × 1H, CH═N), 11.24, 12.62, 24.49, 25.55, 50.40 and 51.75 (6 × 1H, aromatic H). Prolonged heating at 353 K led to crystallization of the dinuclear compound (I).

The U atom is bound to the four O atoms of the Schiff base, with mean bond lengths of 2.257 (5) and 2.437 (5) Å for terminal and bridging donor O atoms, respectively, and is located at 0.014 (3) Å from the mean plane defined by these four atoms (r.m.s. deviation 0.065 Å). It is also bound to the four acetylacetonate O atoms, with a mean bond length of 2.375 (6) Å, in agreement with values previously determined (Salmon et al., 2003) and it is located in the plane defined by these four atoms (r.m.s. deviation 0.158 Å). The two mean O_4 planes around U make a dihedral angle of 87.63 (13)° and the environment of the metal is distorted dodecahedral (Kepert, 1982). The A and B sites of the dodecahedron correspond to the two sets of atoms O2/O3/O6/O7 and O1/O4/O5/O8, respectively. The ratio of the mean $\langle$U—A$\rangle$ to $\langle$U—B$\rangle$ bond lengths is 1.035, slightly lower than the value of 1.06 in the trinuclear complexes in which two nearly orthogonal Schiff bases encompass the U atom (Le Borgne et al., 2002; Salmon et al., 2003a). The M···U distance which, in the analogous CuU complexes, is of primary importance for the nature of the magnetic interaction (Salmon et al., 2005), is 3.7009 (8) Å in (I), nearly identical to that in the trinuclear [{ZnL^1(py)}$_2$U] complex, 3.705 (8) Å. In the corresponding dinuclear compound with the ligand L^2, containing a shorter diimine bridge, this distance decreases by about 0.04 Å.

The Schiff base ligand adopts the usual umbrella conformation, with a dihedral angle of 18.4 (3)° between the two terminal aromatic rings. The C9-containing benzene ring in the
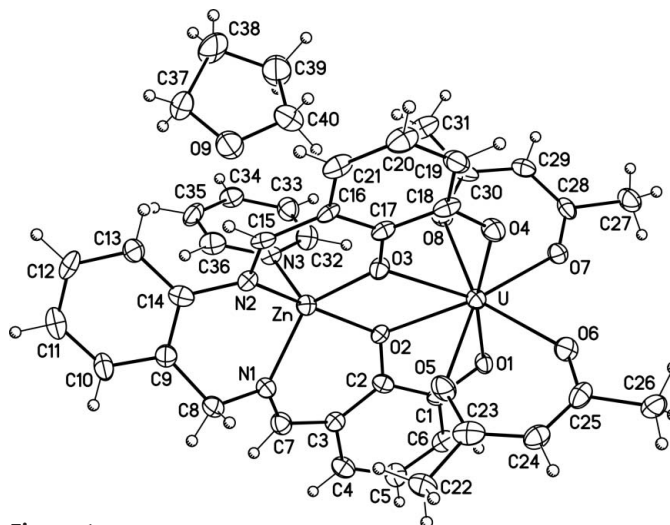
Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2)$	
$R[F^2 > 2\sigma(F^2)] = 0.048$		$\quad + 27.6914P]$	
$wR(F^2) = 0.083$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.03$		$(\Delta/\sigma)_{max} = 0.001$	
7103 reflections		$\Delta\rho_{max} = 0.60$ e Å^{-3}	
491 parameters		$\Delta\rho_{min} = -0.75$ e Å^{-3}	
H-atom parameters constrained			

Table 1
Selected geometric parameters (Å, °).

U—O1	2.258 (5)	U—O8	2.383 (5)
U—O2	2.415 (5)	Zn—O2	2.049 (5)
U—O3	2.459 (5)	Zn—O3	1.997 (5)
U—O4	2.255 (5)	Zn—N1	2.027 (6)
U—O5	2.385 (5)	Zn—N2	2.105 (7)
U—O6	2.364 (6)	Zn—N3	2.080 (7)
U—O7	2.368 (5)		
O1—U—O2	66.66 (18)	N1—Zn—N2	93.5 (3)
O2—U—O3	60.99 (17)	N2—Zn—O3	88.4 (2)
O3—U—O4	66.10 (17)	O2—Zn—O3	75.3 (2)
O4—U—O1	166.46 (19)	O2—Zn—N3	95.7 (2)
O5—U—O6	70.57 (19)	O3—Zn—N3	117.2 (2)
O6—U—O7	75.89 (19)	N1—Zn—N3	102.8 (3)
O7—U—O8	70.09 (19)	N2—Zn—N3	103.4 (3)
O8—U—O5	144.65 (19)	O3—Zn—N1	138.3 (2)
O2—Zn—N1	90.2 (2)	O2—Zn—N2	159.2 (2)

Three reflections with low θ values were omitted from the refinement. The H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH$_2$) or 0.96 Å (CH$_3$), U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C).

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