

## An ion pair uniting a gadolinium(III)–Schiff base complex and uranyl tetrachloride

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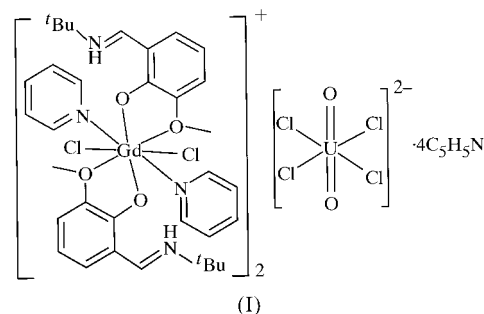
The Schiff base *N*-(*tert*-butyl)-3-methoxysalicylalimine (*LH*) forms a complex with gadolinium(III) chloride,  $[\text{GdCl}_2(\text{LH})_2(\text{C}_5\text{H}_5\text{N})_2]^+$ , in which the two O atoms of each ligand are coordinated (the phenolic O atom being deprotonated) and the imine N atom is protonated and involved in a hydrogen bond with the phenoxide group. This complex crystallizes as an ion pair with uranyl tetrachloride, *i.e.* bis{bis[2-(*tert*-butyliminiomethyl)-6-methoxyphenolato-*O,O'*]dichlorobis(pyridine-*N*)gadolinium(III)} tetrachlorodioxouranium(VI) tetrapyridine solvate  $[\text{GdCl}_2(\text{C}_{12}\text{H}_{17}\text{NO}_2)_2(\text{C}_5\text{H}_5\text{N})_2]_2[\text{UCl}_4\text{O}_2] \cdot 4\text{C}_5\text{H}_5\text{N}$ . The U atom of the  $\text{UCl}_4\text{O}_2$  anion lies on an inversion centre.

### Comment

In the course of our studies on the synthesis, structure and magnetic properties of heterobimetallic complexes containing uranium, we have prepared, by reaction of  $\text{L}_2\text{UCl}_2$  with  $\text{GdCl}_3$  [*LH* is *N*-(*tert*-butyl)-3-methoxysalicylalimine], the U–Gd compound  $\text{L}_2\text{UGdCl}_5$ , in which the metal ions are associated with two Schiff base molecules *L*. Attempted crystallization of this compound from pyridine afforded crystals of a new complex, (I), in which uranium is found in the form of a dissociated uranyl ion; this certainly results from the presence of adventitious traces of water in the solvent used. This is the first report of the crystal structure of a complex involving the Schiff base *L*.

The asymmetric unit in (I) is composed of one gadolinium(III) complex, half a uranyl tetrachloride moiety (with the U atom located on a symmetry centre), a non-bonding pyridine molecule and two half pyridine molecules (disordered around symmetry centres). The uranyl-containing group presents usual features (see Table 1), with a mean U–Cl bond length of 2.67 (2) Å and a nearly perfect square-planar equatorial environment. The gadolinium ion is surrounded by two Schiff base molecules, each of them bound through a phenoxide and an ether O atom, with mean Gd–O distances

of 2.300 (3) and 2.62 (2) Å, respectively, two chloride ions, with a mean Gd–Cl distance of 2.68 (1) Å, and two pyridine molecules, with a mean Gd–N distance of 2.615 (8) Å. This complex molecule possesses a pseudo (non-crystallographic) binary axis. The gadolinium ion is thus eight-coordinate, with two bidentate and four monodentate ligands. The coordination polyhedron geometry is closer to that of a very distorted

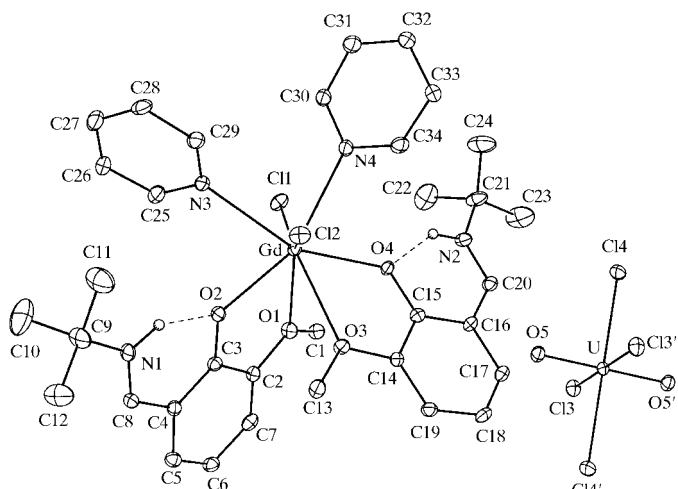


cube than to the most frequently observed square antiprismatic geometry (Kepert, 1982). The plane containing the gadolinium cation and the two Cl atoms is nearly perpendicular to that containing Gd and the N atoms of the pyridine molecules, with a dihedral angle of 89.52 (9)° between them, whereas the dihedral angle between the plane containing Gd, O1 and O3 and that containing Gd, O2 and O4 is 79.89 (9)°. Considering the whole coordination sphere, the five atoms Gd, N3, N4, O2 and O4 are roughly coplanar, with a maximum deviation of 0.177 (5) Å, but the five atoms Gd, Cl1, Cl2, O1 and O3 present a stronger departure from planarity, with maximum deviations of 0.417 (4) and –0.479 (4) Å for O1 and O3, respectively. The dihedral angle between these two five-atom mean planes is 84.68 (5)°, which confirms the distorted cube geometry of the coordination environment (the small ‘bite’ of the Schiff base ligand does not enable a closer approach to the cube geometry). The two Schiff base molecules are planar (maximum deviations from the mean plane are 0.0181 and 0.0633 Å with the methyl and *tert*-butyl groups omitted) and the dihedral angle between them is 54.29 (8)°. The bulky  $\text{NH}^+\text{C}(\text{CH}_3)_3$  groups are directed away from one another.

The uranyl moiety provides one negative charge per gadolinium complex. The electroneutrality results from the Schiff base molecules being formally neutral, since the charge on the phenoxide O atom is compensated for by that on the protonated N atom. The Schiff base ligand can thus be viewed as a zwitterionic species. Strong hydrogen bonds are present between the protonated N and phenoxide O atoms (see Table 2), resulting in an unprecedented arrangement of a Schiff base coordinated to a metallic cation. The non-bonding pyridine molecules occupy intermolecular voids in the crystal packing and present some distant contacts with the Schiff base molecules (as short as 3.33 Å), most likely indicating feeble interactions.

A search of the April 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993) found only one other crystal structure of a molecular compound containing both actinide and lanthanide ions. This compound is also an

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**Figure 1**

The title molecule with the atom-numbering scheme. H atoms have been omitted for clarity, except for those involved in hydrogen bonds, which are drawn as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Non-bonding pyridine molecules have been omitted. Displacement ellipsoids are drawn at the 20% probability level. [Symmetry code: (i)  $-x, -y, -z$ .]

ion-pair assemblage, with separated propionate complexes of uranyl and lanthanum(III) ions (Rojas *et al.*, 1990).

## Experimental

### Crystal data

$[\text{GdCl}_2(\text{C}_{12}\text{H}_{17}\text{NO}_2)_2(\text{C}_5\text{H}_5\text{N})_2]^{2-}$   
 $[\text{UCl}_4\text{O}_2] \cdot 4\text{C}_5\text{H}_5\text{N}$   
 $M_r = 2329.99$   
 Triclinic,  $P\bar{1}$   
 $a = 11.1331(5) \text{ \AA}$   
 $b = 11.8704(6) \text{ \AA}$   
 $c = 18.8044(7) \text{ \AA}$   
 $\alpha = 92.239(3)^\circ$   
 $\beta = 101.526(3)^\circ$   
 $\gamma = 91.353(3)^\circ$   
 $V = 2431.86(19) \text{ \AA}^3$

$Z = 1$   
 $D_x = 1.591 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 16 824 reflections  
 $\theta = 2.86\text{--}25.68^\circ$   
 $\mu = 3.288 \text{ mm}^{-1}$   
 $T = 100(2) \text{ K}$   
 Platelet, translucent dark orange  
 $0.18 \times 0.15 \times 0.10 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans  
 Absorption correction: empirical (PLATON; Spek, 2000)  
 $T_{\min} = 0.545, T_{\max} = 0.720$   
 16 824 measured reflections  
 8501 independent reflections

6568 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$   
 $\theta_{\text{max}} = 25.68^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -14 \rightarrow 14$   
 $l = -22 \rightarrow 22$   
 Intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.099$   
 $S = 1.019$   
 8501 reflections  
 547 parameters

H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.99 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$

The H atoms bound to N atoms were found in the Fourier difference map and were introduced as riding atoms with a displacement parameter equal to 1.2 times that of the parent atom. Two pyridine molecules were found disordered around symmetry centres, hence their N atoms were not located. All H atoms, except those bound to N atoms and those of the disordered pyridine molecules, were introduced at calculated positions as riding atoms with a

**Table 1**

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

U—O5	1.780 (4)	Gd—O4	2.298 (3)
U—Cl3	2.6861 (15)	Gd—N3	2.620 (4)
U—Cl4	2.6501 (15)	Gd—N4	2.609 (4)
Gd—O1	2.601 (4)	Gd—Cl1	2.6695 (14)
Gd—O2	2.302 (3)	Gd—Cl2	2.6869 (14)
Gd—O3	2.635 (3)		
O5—U—Cl4	90.45 (13)	N4—Gd—O3	121.78 (13)
O5—U—Cl3	90.57 (13)	N3—Gd—O3	137.57 (12)
Cl4—U—Cl3	90.29 (5)	O4—Gd—Cl1	89.58 (9)
O4—Gd—O2	128.51 (12)	O2—Gd—Cl1	105.62 (10)
O4—Gd—O1	74.65 (12)	O1—Gd—Cl1	74.25 (9)
O2—Gd—O1	63.54 (12)	N4—Gd—Cl1	76.25 (11)
O4—Gd—N4	76.39 (13)	N3—Gd—Cl1	78.05 (11)
O2—Gd—N4	154.59 (13)	O3—Gd—Cl1	138.38 (8)
O1—Gd—N4	138.34 (13)	O4—Gd—Cl2	103.34 (10)
O4—Gd—N3	156.17 (13)	O2—Gd—Cl2	89.47 (9)
O2—Gd—N3	74.90 (13)	O1—Gd—Cl2	137.57 (9)
O1—Gd—N3	120.13 (13)	N4—Gd—Cl2	78.19 (11)
N4—Gd—N3	80.88 (14)	N3—Gd—Cl2	78.62 (11)
O4—Gd—O3	63.23 (11)	O3—Gd—Cl2	72.88 (8)
O2—Gd—O3	74.10 (12)	Cl1—Gd—Cl2	147.64 (4)
O1—Gd—O3	68.65 (12)		

**Table 2**

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1—H1 $\cdots$ O2	0.97	1.73	2.609 (5)	148
N2—H2 $\cdots$ O4	0.87	1.86	2.592 (6)	140

displacement parameter equal to 1.2 (CH) or 1.5 (CH<sub>3</sub>) times that of the parent atom. Some soft restraints were applied to the bond lengths and displacement parameters of some terminal C atoms of the *tert*-butyl groups. The low completeness of data (91.9%) arises from feeble diffracting power at high  $\theta$ .

Data collection: *KappaCCD 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: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1999) and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1069). Services for accessing these data are described at the back of the journal.

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