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An organouranium coordination polymer containing infinite metal oxide chains

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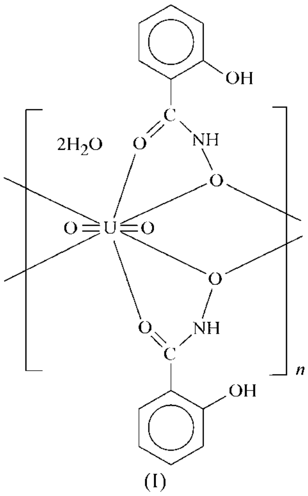
The title compound, *catena*-poly[[[dioxouranium(VI)]-bis(μ-2-hydroxybenzohydroxamato)] dihydrate], $\{[U(C_7H_6NO_3)_2O_2]\cdot 2H_2O\}_n$, is a uranyl coordination polymer based on the salicylhydroxamate ligand. The ligand acts both as a chelate, forming five-membered rings, and as a bridge between two U atoms. The coordination around each U atom is a distorted hexagonal bipyramid. Infinite chains running along [001] are formed *via* bridging salicylhydroxamate O atoms. The chains have C_2 symmetry, with U atoms in special positions on twofold axes. The water molecules are not coordinated to the metal but crosslink, through hydrogen bonding, adjacent coordination polymer chains in the [110] and [$1\bar{1}0$] directions.

Comment

Actinide compounds show great structural variety and complexity, owing to the implication of 5*f* orbitals in the formation of chemical bonds, and in recent years they have been studied in the search for new materials with peculiar optical, magnetic and catalytic properties (Hutchings *et al.*, 1996; Francis *et al.*, 1998; Bean *et al.*, 2001). In this context, a promising area is that of metal–organic coordination polymers built up from U—O units. For these materials, interesting electronic (*e.g.* semiconducting) and optical properties are foreseen (Chen *et al.*, 2003). Up to now, only a few examples of uranyl coordination polymers have been reported. In some cases, the polymers contain an additional metal besides uranium (Chen *et al.*, 2003; Yu *et al.*, 2004) and, moreover, they are generally based on more than one type of ligand (Thuéry, 2007).

During a study of complex formation equilibria between metal ions and salicylhydroxamic acid, we succeeded in the synthesis of the title compound, (I), which is a rare example of a uranyl coordination polymer containing uranium as the only metal and based on only one type of ligand, here 2-hydroxybenzohydroxamate (or salicylhydroxamate), the water molecules not being coordinated to the metal.



(I)

The hydroxamate group occurs in natural products having biological activity (Kehl, 1982); some are inhibitors of enzymes such as peroxidases, metalloproteinases and ureases. The biological effects have been attributed to the affinity of the hydroxamate anion for metal ions. Actually, X-ray crystallographic studies have shown that the salicylhydroxamate group behaves as an *O*,*O*′-bidentate ligand, forming a five-membered chelate ring with several transition metal ions. All

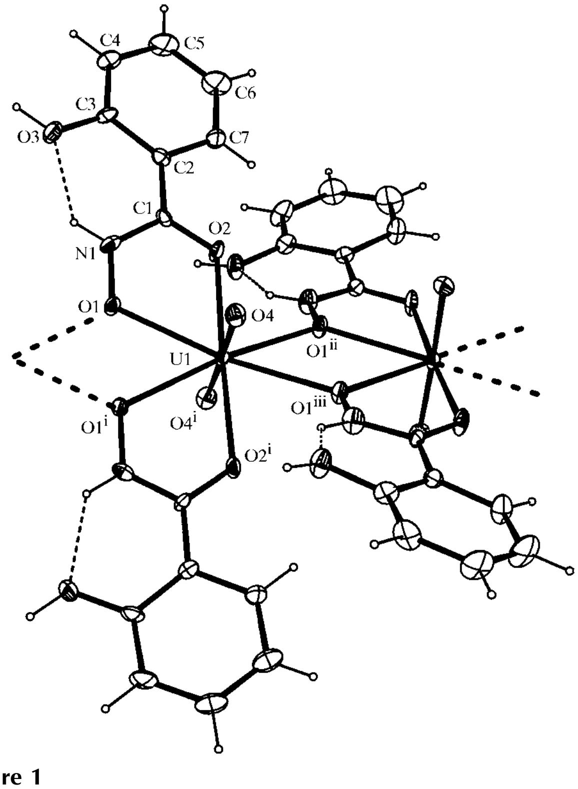


Figure 1
A view of part of the coordination polymer of (I), showing the atom numbering. Displacement ellipsoids are drawn at the 30% probability level. The water molecule has been omitted for clarity. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

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metal complexes of this ligand reported to date, however, have a mononuclear structure (Comman *et al.*, 1992; Sharipov *et al.*, 1983; Gao *et al.*, 1998) and only one has a dinuclear structure (Stemmler *et al.*, 1995). This report is the first in which the salicylhydroxamate ligand is involved in the formation of a coordination polymer.

The crystallographically independent unit of (I) contains one-half of a uranyl group, where atom U1 sits on a C_2 axis, one salicylhydroxamate unit and one water molecule (Fig. 1). The conformation of the ligand shows, as expected, the 2-hydroxy group (C3—O3) and the C1—N1 bond in a *syn* conformation in order to establish an intramolecular hydrogen bond (Table 2). The carbonyl O atom is coordinated to one U atom only, while the hydroxamate O atom acts as a slightly asymmetric bridge between two U atoms. The bond geometry around the hydroxamate O atoms is substantially trigonal planar (Table 1).

The coordination environment of uranyl contains two chelate five-atom rings and four bridging O atoms (Fig. 1). Each chelate ring is planar within 0.056 (4) Å, and the two rings and the U atom are coplanar within 0.101 (6) Å. This coordination can be described as a distorted hexagonal bipyramid, with axial O uranyl atoms (Cotton *et al.*, 2005). The distortion is mainly due to the μ-O atoms being 0.588 (7) Å above and 0.588 (7) Å below the average plane of atom U1 and the two chelate rings.

In the crystal structure, the bridging of the U atoms by the salicylhydroxamate ligands leads to infinite chains running parallel to [001] (Figs. 1 and 2), whose direction coincides with the macroscopic elongation axis of the prismatic single crystals. The chains are formed, *via* bridging hydroxamate O atoms, through the two *c*-glide planes and, because those glide planes are mutually perpendicular, the chains have overall C_2 symmetry about the U1 atoms. Owing to the distorted coordination geometry around the U atom, adjacent chelate rings along the direction of the chain axis are not coplanar [the dihedral angle is 37.2 (1)°], thus relieving the overcrowding of the benzene groups.

The water molecules are not coordinated to the metal atoms; they are located between adjacent coordination polymer chains and crosslink them in the [110] and $[1\bar{1}0]$ directions, thereby contributing to the stability of the crystal packing by completing a three-dimensional framework. The water molecule is involved as an acceptor of a hydrogen bond from the 2-hydroxy group of a neighbouring salicylhydroxamate ligand and as a donor in weaker hydrogen bonds with atoms O2 and O4 of symmetry-related units (Table 2).

Finally, we stress the relevant feature of the structure of (I) as compared with the few polymeric structures of uranyl reported to date, *i.e.* that all O atoms coordinated to the uranyl group belong to the organic ligand. Thus, in principle, it could be possible to influence the metal-to-ligand electronic system (and hence the spectroscopic properties) by introducing suitable substituents onto the aromatic ring (*e.g.* electron-withdrawing groups, such as nitro or cyano, or electron-releasing groups, such as dialkylamino).

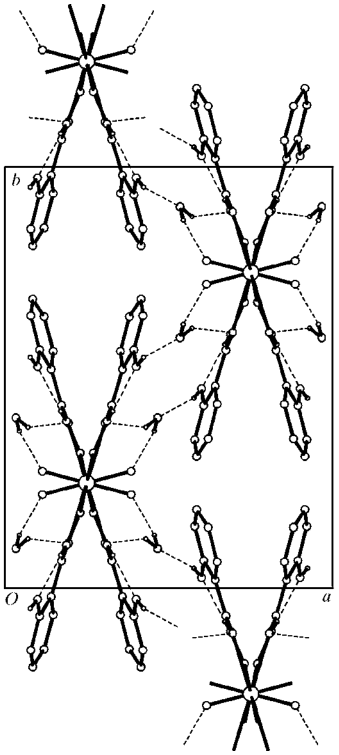

Figure 2
The crystal packing of (I), viewed along *c*. The benzene H atoms have been omitted for clarity and hydrogen bonds are shown as dashed lines.

Experimental

Compound (I) was prepared from uranium(VI) perchlorate, 2-hydroxybenzohydroxamic acid and sodium perchlorate. Stock solutions of uranium(VI) perchlorate, perchloric acid and sodium perchlorate were obtained as described previously (Ciavatta *et al.*, 1979). Commercial 2-hydroxybenzohydroxamic acid (Sigma–Aldrich) was recrystallized twice from methanol–water mixtures (Ciavatta *et al.*, 2004). A solution of 0.005 mol dm^{-3} 2-hydroxybenzohydroxamic acid, 0.002 mol dm^{-3} uranium(VI) perchlorate and 1 mol dm^{-3} sodium perchlorate was neutralized quantitatively by the addition of 0.05 mol dm^{-3} NaOH. Subsequently, the acidity of the solution was increased slowly by addition of 0.02 mol dm^{-3} perchloric acid, until incipient precipitation of an orange–red solid. All operations were performed in a thermostatted vessel at 298.00 (5) K. The solutions were purged using a continuous stream of pure nitrogen. The resulting solid, which developed as aggregates of elongated prismatic crystals, was separated from the solution by filtration, washed with 1 mol dm^{-3} sodium perchlorate then with water, and finally dried under vacuum at room temperature. Compound (I) was identified by IR spectroscopy and chemical and thermal analysis. An intense IR band at 914–930 cm^{-1} was observed, which is typical of asymmetric $O{=}U{=}O$ uranyl stretching; typical amide $C{=}O$ stretching at 1600 cm^{-1} was also observed. The composition of the solid was determined by thermogravimetric analysis under a nitrogen gas atmosphere, within the temperature range 323–1073 K, after which the transformation to U_3O_8 was complete. The total weight loss (52.6%) and the water weight loss (5.5%) correspond to the formula $[U(C_7H_6NO_3)_2O_2]\cdot 2H_2O$.

Crystal data

$[U(C_7H_6NO_3)_2O_2]\cdot 2H_2O$
$M_r = 610.32$
Orthorhombic, *Pccn*
$a = 12.649$ (3) Å
$b = 16.258$ (5) Å
$c = 8.756$ (3) Å
$V = 1800.6$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 9.07$ mm^{-1}
$T = 295$ (2) K
$0.08 \times 0.05 \times 0.03$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker–Nonius, 2002) $T_{\min} = 0.520$, $T_{\max} = 0.762$
11824 measured reflections
2062 independent reflections
1122 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.139$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.074$
$S = 1.00$
2062 reflections
123 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.84$ e Å^{-3}
$\Delta\rho_{\min} = -1.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—O4	1.769 (6)	O1—N1	1.343 (9)
U1—O2	2.428 (6)	O2—C1	1.279 (10)
U1—O1	2.464 (5)	N1—C1	1.313 (10)
U1—O1$^{\rm i}$	2.512 (5)		
O4$^{\rm ii}$—U1—O4	177.8 (3)	O2—U1—O1$^{\rm i}$	64.66 (18)
O4—U1—O2	87.9 (2)	O1—U1—O1$^{\rm i}$	124.7 (2)
O2—U1—O2$^{\rm ii}$	177.7 (3)	O4—U1—O1$^{\rm iii}$	78.5 (2)
O4—U1—O1$^{\rm ii}$	87.9 (2)	O2—U1—O1$^{\rm iii}$	113.12 (18)
O2—U1—O1$^{\rm ii}$	119.74 (18)	O1—U1—O1$^{\rm iii}$	168.2 (3)
O4—U1—O1	90.2 (2)	O1$^{\rm i}$—U1—O1$^{\rm iii}$	56.2 (2)
O2—U1—O1	62.56 (18)	N1—O1—U1	117.7 (4)
O1$^{\rm ii}$—U1—O1	57.4 (2)	N1—O1—U1$^{\rm iv}$	118.0 (4)
O4—U1—O1$^{\rm i}$	103.4 (2)	U1—O1—U1$^{\rm iv}$	123.2 (2)
O2—C1—C2—C3	−172.4 (8)		

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y, z-\frac{1}{2}$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y, z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3	0.86	1.97	2.633 (10)	133
O3—H3$\cdots$O5$^{\rm v}$	0.82	1.93	2.691 (9)	153
O5—H5$A\cdots$O4	0.80	2.24	3.020 (9)	164
O5—H5$B\cdots$O2$^{\rm vi}$	0.84	2.36	3.112 (10)	149

Symmetry codes: (v) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

H atoms of the benzene ring were generated stereochemically. All other H atoms were located in a difference map. All H atoms were refined using a riding model, with $U_{\rm iso}$(H) values equal to $U_{\rm eq}$ of the carrier atom. The following feature of the diffraction pattern of (I) has not escaped our attention. Since the U atoms lie in special positions on twofold axes, their contribution to *hkl* reflections with odd *l* is zero. However, uranium alone accounts for a large fraction of the overall electronic density of the compound (32%), so it follows that reflections of *hkl* layers with odd *l* have intensities systematically lower than layers with even *l*. This fraction of low-intensity reflections may account for the relatively high $R_{\rm int}$ value.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3054). Services for accessing these data are described at the back of the journal.

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