# metal-organic compounds

# {2,6-Bis[(dimethylamino)methyl]-pyridine-$\kappa^3N$}(2,2-methylene-diphenolato-$\kappa^2O,O'$)dioxo-uranium(VI) acetone solvate

## Bernardo Masci[a]* and Pierre Thuéry[b]*

[a]Dipartimento di Chimica and IMC-CNR Sezione Meccanismi di Reazione, Università 'La Sapienza', Box 34, Roma 62, P.le Aldo Moro 5, 00185 Roma, Italy, and [b]CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France
Correspondence e-mail: bernardo.masci@uniroma1.it, thuery@drecam.cea.fr

In the title compound, $[UO_2(C_{13}H_{10}O_2)(C_{11}H_{19}N_3)]\cdot C_3H_6O$, the U atom is in a pentagonal–bipyramidal environment, with the three N atoms of the 2,6-bis[(dimethylamino)methyl]-pyridine ligand and the two O atoms of the dianionic 2,2'-methylenediphenolate ligand in the equatorial plane. The geometry is compared with that of previously reported 1:2 uranyl–diphenoxide complexes.

## Comment

Reports of uranyl complexes with acyclic polyphenoxides are rather scarce (Thuéry & Nierlich, 1997; Thuéry et al., 2000, 2002; Salmon et al., 2004), at least when compared with the numerous studies of uranyl complexes with cyclic poly-(phenol/phenoxides) in the calixarene and homooxacali-xarene families (Thuéry et al., 2001). Also, few uranium(IV) complexes with acyclic polyphenoxides have been described to date (Salmon et al., 2003). In the case of uranyl, in parti-cular, the complex with the simple ligand 2,2'-methylenedi-phenolate could not be obtained (Thuéry et al., 2000), although 1:2 complexes with related molecules possessing terminal hydroxymethyl or pyridiniomethyl groups have been characterized, in which the uranyl ion is surrounded by two diphenoxide species (Thuéry et al., 2002; Salmon et al., 2004). We have also shown that some triphenols complex the uranyl ion as diphenoxide ligands only, the third phenolic group being uncoordinated (Thuéry et al., 2000, 2002). In an attempt to synthesize uranyl complexes with mixed ligands, the title complex, (I), was obtained, in which the uranyl ion is bound both to the bidentate chelating 2,2'-methylenediphenolate ligand and to the tridentate bis-ortho-chelating 2,6-bis[(di-methylamino)methyl]pyridine ligand. Several structures of complexes of the latter molecule with d-block transition metal atoms have been reported and are present in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002), but, to

the best of our knowledge, (I) is the first complex of uranium with this ligand to be crystallographically characterized.



(I)
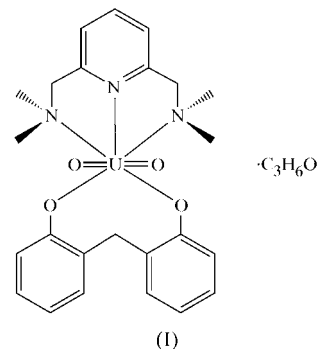
Compound (I) crystallizes as an acetone solvate, with one complete molecule in the asymmetric unit. The uranyl ion is surrounded by the two chelating ligands, i.e. the tridentate neutral 2,6-bis[(dimethylamino)methyl]pyridine molecule and the bidentate bis(2-oxidophenyl)methane dianion, resulting in a neutral complex. The five donor atoms are located near the equatorial plane of the uranyl ion and define a mean plane with an r.m.s. deviation of 0.17 Å and individual deviations of −0.224 (3), 0.144 (2), −0.153 (3), 0.003 (3) and 0.230 (3) Å for atoms O1, O2, N1, N2 and N3, respectively. The U atom is located 0.0003 (19) Å from this plane and is thus in a slightly distorted pentagonal–bipyramidal environment, with O(oxo)−U−(O,N) angles in the range 81.11 (15)–97.17 (15)°. The U−N bond lengths are slightly larger for the side-arm tertiary amine groups [mean value = 2.647 (13) Å] than for the central pyridine N atom [2.613 (4) Å]; an even more
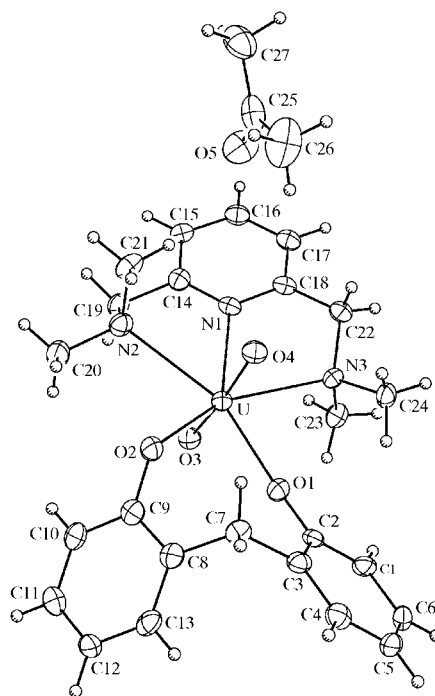


**Figure 1**
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

pronounced difference is observed in a ruthenium(II) complex with the same ligand (Back *et al.*, 2001). This trend is opposite to that found in the mono- and dinuclear uranyl complexes with pyridine-2,6-dicarboxylic acid, which we have described elsewhere (Masci & Thuéry, 2004). In these complexes, the U—N bond lengths range from 2.535 (5) to 2.626 (2) Å [mean value = 2.56 (3) Å] and the U—O(carboxylate) bond lengths range from 2.366 (4) to 2.4730 (19) Å [mean value = 2.40 (3) Å], *i.e.* the N atom is farther from U than the carboxylate O atoms, both distances being smaller than in (I). This is obviously due to the different geometries of the pyridine substituents, particularly apparent when the distances to the aromatic plane of the side-arm donor atoms are considered, since they amount to 0.751 (9) and −0.504 (9) Å for atoms N2 and N3, respectively, in (I), and to 0.23 Å at most for the O atoms in the dicarboxylate complexes. The mean plane of the pyridine ring (r.m.s. deviation = 0.007 Å) makes a dihedral angle of 19.94 (12)° with the uranyl equatorial plane.

The mean value of the U—O(phenoxide) bond lengths in (I) is 2.208 (2) Å, in agreement with the lower values usually observed in polyphenoxide uranyl complexes (Thuéry *et al.*, 2001) and particularly in the acyclic polyphenoxide complexes cited above. The mean values in the diphenoxide 1:2 complexes previously described are 2.25 (2) (Thuéry *et al.*, 2002) and 2.256 (6) Å (Salmon *et al.*, 2004), the difference probably being due to the replacement of one diphenoxide species by a neutral N-donor ligand in complex (I).

The angles around the U atom defined by adjacent donor atoms in the equatorial plane are not equivalent, with mean values of 63.2 (6) and 76.6 (12)° for the N—U—N and O—U—N angles, respectively, the larger angle being that defined by the diphenoxide ligand, *viz.* O1—U—O2 of 82.12 (13)°. This last value is, however, smaller than those in the 1:2 uranyl complexes with substituted diphenoxide ligands previously reported, which are in the range 86.7 (5)–89.9 (4)°, and the O1···O2 distance in (I) of 2.900 (5) Å is accordingly smaller than in the other cases. This difference is likely to be the result of the uranyl equatorial environment being more crowded in the pentagonal complex, (I), than in the square-planar 1:2 complexes.

The two aromatic rings of the diphenoxide ligand define a dihedral angle of 77.05 (18)°, which is in the usual range for uncomplexed diphenols in the 'butterfly' conformation (Thuéry *et al.*, 2000), whereas in the 1:2 uranyl complex with hydroxymethyl-substituted diphenols, the dihedral angles are in the range 71.4 (6)–79.6 (7)°. A smaller value of 69.66 (17)° has been found for the complex with pyridiniomethyl-substituted diphenoxide ligands (Salmon *et al.*, 2004), this same ligand displaying dihedral angles of 76.3 (2) and 76.2 (4)° in its uranium(IV) complex (Salmon *et al.*, 2003). The bulky and cationic pyridiniomethyl groups, as well as the intermolecular interactions observed in the uranyl complex, are likely to be the origin of this difference in geometry in the former case. The dihedral angles between the mean equatorial N3O2 plane of the uranyl ion and the two phenoxide aromatic rings are 30.91 (12) and 50.83 (14)°, *i.e.* within the range observed in the previous diphenoxide complexes [25.8 (2)–52.4 (5)°].

## Experimental

For the preparation of the title compound, uranyl nitrate hexahydrate (77 mg, 0.15 mmol) in MeOH (1 ml) was added dropwise to a boiling stirred mixture of 2,6-bis[(dimethylamino)methyl]pyridine (21 mg, 0.11 mmol), 2,2′-bis(hydroxyphenyl)methane (30 mg, 0.15 mmol) and triethylamine (250 mg, 2.5 mmol) in MeOH (11 ml). Stirring and heating of the resulting red solution were continued for an additional 5 min. The red crystals which formed on solvent evaporation were recovered and recrystallized from acetone to give dark orange single crystals of (I) suitable for X-ray crystallographic analysis.

*Crystal data*

| | |
|---|---|
| $[U(C_{13}H_{10}O_2)O_2(C_{11}H_{19}N_3)]\cdot$ $C_3H_6O$ | $D_x = 1.773$ Mg m$^{-3}$ |
| $M_r = 719.61$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 18 299 reflections |
| $a = 14.5787$ (6) Å | $\theta = 2.2$–25.7° |
| $b = 11.7099$ (3) Å | $\mu = 6.06$ mm$^{-1}$ |
| $c = 16.7701$ (8) Å | $T = 100$ (2) K |
| $\beta = 109.691$ (2)° | Platelet, dark orange |
| $V = 2695.50$ (19) Å$^3$ | $0.15 \times 0.10 \times 0.04$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | 5120 independent reflections |
| $\varphi$ scans | 4149 reflections with $I > 2\sigma(I)$ |
| Absorption correction: refined on | $R_{int} = 0.068$ |
| $\Delta F$ (*DELABS* in *PLATON*; Spek, 2003) | $\theta_{max} = 25.7°$ |
| $T_{min} = 0.463$, $T_{max} = 0.770$ | $h = -17 \rightarrow 17$ |
| 18 299 measured reflections | $k = -14 \rightarrow 14$ |
| | $l = -20 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | $w = 1/[\sigma^2(F_o^2) + 0.9093P]$ |
| $wR(F^2) = 0.071$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 5120 reflections | $\Delta\rho_{max} = 0.75$ e Å$^{-3}$ |
| 331 parameters | $\Delta\rho_{min} = -1.33$ e Å$^{-3}$ |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| U—N1 | 2.613 (4) | U—O2 | 2.205 (3) |
| U—N2 | 2.661 (4) | U—O3 | 1.798 (4) |
| U—N3 | 2.633 (4) | U—O4 | 1.786 (4) |
| U—O1 | 2.210 (4) | | |
| | | | |
| N1—U—N2 | 62.61 (13) | O2—U—N2 | 77.82 (13) |
| N1—U—N3 | 63.77 (13) | O1—U—O2 | 82.12 (13) |
| O1—U—N3 | 75.36 (13) | O4—U—O3 | 172.52 (16) |

The H atoms were introduced in calculated positions as riding atoms, with C—H distances of 0.93 (aromatic CH), 0.97 (CH$_2$) and 0.96 Å (CH$_3$), and with $U_{iso}$(H) = $1.2U_{eq}$(C) for CH and CH$_2$, and $1.5U_{eq}$(C) for CH$_3$ groups.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 2003) and *PARST*97 (Nardelli, 1995).

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