

A novel coordination geometry for the uranyl ion. Rhombohedral uranium environment in $[\text{UO}_2(\text{OTf})_2(\text{bpy})_2]$ and $[\text{UO}_2(\text{phen})_3][\text{OTf}]_2$

Jean-Claude Berthet,* Martine Nierlich and Michel Ephritikhine

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA Saclay, 91191 Gif-sur-Yvette, France. E-mail: berthet@drecam.cea.fr; Fax: +33(0)169086640; Tel: +33(0)169086436

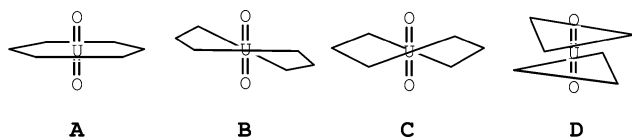
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In the title compounds, the six coordinating ligands atoms of the UO_2^{2+} ion are separated into two parallel and staggered equilateral triangles; the UO_2 axis is perpendicular to these triangles, passing through their centre, and the U atom is equidistant from the two planes at a distance of ca. 0.6 Å.

The most ubiquitous species in actinide(vi) chemistry are the trans dioxo ions AnO_2^{2+} ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) which attract considerable attention for their physico-chemical properties and their behaviour in the nuclear industry and natural environments.¹ In view of the crystal structures of the enormous quantity of uranyl complexes with a great variety of neutral and anionic ligands, it is a well established fact that these compounds adopt inherently a bipyramidal configuration with the linear UO_2 moiety perpendicular to the equatorial plane defined by the uranium and coordinating ligands atoms (A in Scheme 1).²

In some uranyl compounds, one of these atoms is very displaced from the equatorial plane, likely because of steric requirements due to the ligand geometry.^{3,4} Complexes in which several of the coordinating atoms deviate significantly from planarity (by more than ± 0.2 Å) are very rare, being limited quite exclusively to hexacoordinated uranyl derivatives with bi- or polydentate ligands.^{5–10} The heteroatoms form in that case a puckered hexagon around the UO_2^{2+} ion and most generally, four of those are displaced from the equatorial plane while the other two belong or are very close to this plane, occupying 1,2 and 1,4 positions of the hexagonal frame, respectively (B and C in Scheme 1). Thus, the uranium centre in uranyl compounds has always been found in a more or less distorted polygonal bipyramidal configuration, and there is no exception to this rule. Here we present the X-ray crystal structures of $[\text{UO}_2(\text{OTf})_2(\text{bpy})_2]$ (**1**) and a solvate of $[\text{UO}_2(\text{phen})_3][\text{OTf}]_2$ (**2**) (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) which exhibit an unprecedented rhombohedral coordination geometry around the uranium centre (D in Scheme 1).



Scheme 1 Coordination geometries of hexacoordinated uranyl complexes; distortion from hexagonal bipyramid A to rhombohedron D.

Complex **1** was readily obtained from a 1 : 2 mixture of $\text{UO}_2(\text{OTf})_2$ ¹¹ and bpy in acetonitrile and was isolated as a yellow powder in 90% yield. While **1** is stable in the presence of an excess of bpy, addition of 3 equivalents of phen to $\text{UO}_2(\text{OTf})_2$ in the same solvent led to the immediate and almost quantitative formation of **2**. Compounds **1** and **2** were characterized by their elemental analyses, ¹H NMR spectra,[†] and X-ray crystal structure.[‡]

The structure of the centrosymmetric molecule of **1** is shown in Fig. 1. The crystals of the solvate $2 \cdot (\text{phen}) \cdot (\text{py})_{1.5} \cdot (\text{THF})_{0.5}$ are composed of discrete $[\text{UO}_2(\text{phen})_3]^{2+}$ cations and OTf^- anions in the ratio 1 : 2, and free phen and solvent molecules; a

view of the cation is represented in Fig. 2. The interatomic bond lengths in both compounds are unexceptional. The $\text{U}=\text{O}$ distances of the linear UO_2 fragments [1.754(3) Å in **1**, 1.752(5) and 1.755(5) Å in **2**] are typical of uranyl complexes. The triflate ligand in **1** is monodentate and the $\text{U}-\text{O}$ distance of 2.448(3) Å is slightly longer than those of 2.370(2) and 2.394(2) Å in $[\text{UO}_2(\text{OTf})_2(\text{py})_3]$.¹¹ The $\text{U}-\text{N}$ bond lengths, which are

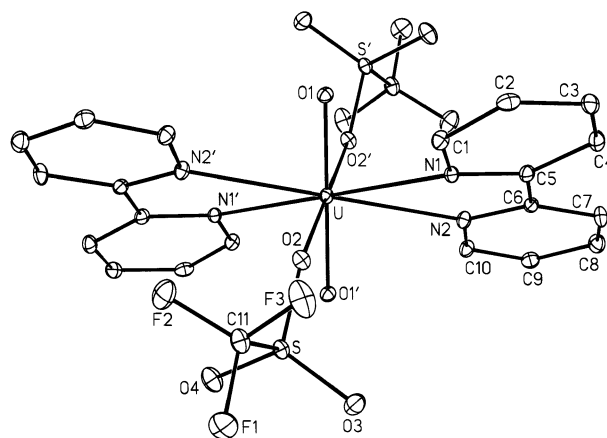


Fig. 1 View of $\text{UO}_2(\text{bpy})_2(\text{OTf})_2$ with displacement ellipsoids at the 30% probability level. Atoms labeled prime are related to the non-labeled ones by the centre of symmetry (symmetry code: $-x, -y, -z$). Selected bond lengths [Å] and angles [°]: $\text{U}-\text{O}1$ 1.754(3), $\text{U}-\text{O}2$ 2.448(3), $\text{U}-\text{N}1$ 2.633(4), $\text{U}-\text{N}2$ 2.605(4); $\text{O}1-\text{U}-\text{O}2$ 100.75(12), $\text{O}1-\text{U}-\text{N}1$ 74.13(13), $\text{O}1-\text{U}-\text{N}2$ 104.17(13), $\text{N}1-\text{U}-\text{N}2$ 60.77(12), $\text{O}2-\text{U}-\text{N}1'$ 111.88(11), $\text{O}2-\text{U}-\text{N}2$ 112.59(11).

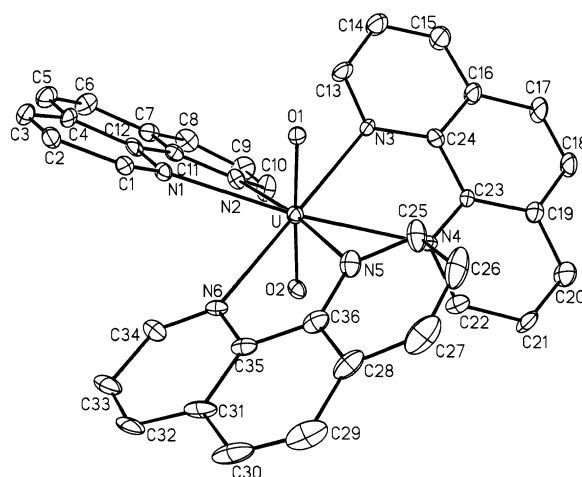


Fig. 2 View of the cation $[\text{UO}_2(\text{phen})_3]^{2+}$ in the solvate of **2** with displacement ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: $\text{U}-\text{O}1$ 1.752(5), $\text{U}-\text{O}2$ 1.755(5), $\text{U}-\text{N}1$ 2.616(7), $\text{U}-\text{N}2$ 2.599(7), $\text{U}-\text{N}3$ 2.613(8), $\text{U}-\text{N}4$ 2.624(7), $\text{U}-\text{N}5$ 2.577(8), $\text{U}-\text{N}6$ 2.596(7); $\text{O}1-\text{U}-\text{O}2$ 177.4(3), $\text{O}1-\text{U}-\text{N}1$ 74.7(2), $\text{O}1-\text{U}-\text{N}2$ 105.0(3), $\text{O}1-\text{U}-\text{N}3$ 74.3(3), $\text{O}1-\text{U}-\text{N}4$ 102.5(2), $\text{O}1-\text{U}-\text{N}5$ 77.4(3), $\text{O}1-\text{U}-\text{N}6$ 105.1(3), $\text{N}1-\text{U}-\text{N}2$ 62.1(2), $\text{N}3-\text{U}-\text{N}4$ 62.5(2), $\text{N}5-\text{U}-\text{N}6$ 62.7(2).

equal to 2.633(4) and 2.605(4) Å in **1**, and range from 2.577(8) to 2.624(7) Å with an average value of 2.60(3) Å in **2**, can be compared with that of 2.578(13) Å in [UO₂(NO₃)₂(bpy)]⁵ and 2.557(22) Å in [UO₂(NO₃)₂(phen)]⁶.

The striking feature of these two structures is the arrangement of the coordinating ligands atoms around the UO₂²⁺ ion. These are far from coplanar, the least-squares plane UN₄O₂ in **1** and UN₆ in **2** being within ± 0.519 and ± 0.554 Å, respectively. The six atoms are separated into two parallel equilateral triangles, forming a trigonal antiprism which is bicapped by the two uranyl oxygen atoms. The two triangles N1–N2'–O2' and N1'–N2–O2 in **1** are parallel due to the imposed symmetry, while the triangles N1–N3–N5 and N2–N4–N6 in **2** form a dihedral angle of 3°. The UO₂ axis is perpendicular to these triangles, passing through their centre, and the U atom is equidistant from the two planes, at a distance of 0.605(1) Å in **1**, and 0.637(7) and 0.651(7) Å in **2**. The bpy ligand is planar within ± 0.06 Å and forms an angle of 75.7° with the UO₂ axis. Complex **2** exhibits a propeller type structure, with the planar phen molecules tilted with respect to the UO₂ axis by an average angle of 73(10)°; this conformation minimizes the interactions between the pyridyl groups.¹² Compounds **1** and **2** adopt a remarkable rhombohedral structure (Fig. 3) in which all the six coordinating ligands atoms are alternately up and down the UN₄O₂ or UN₆ mean plane, at an equal distance of ca. 0.6 Å. The unique structures of **1** and **2** can also be assessed from the angles between the UO₂ axis and the U–O or U–N single bonds which all deviate from orthogonality by an angle of 14(3)°. Compounds **1** and **2** are the first hexacoordinated uranyl complexes which are not found in a hexagonal bipyramidal configuration.

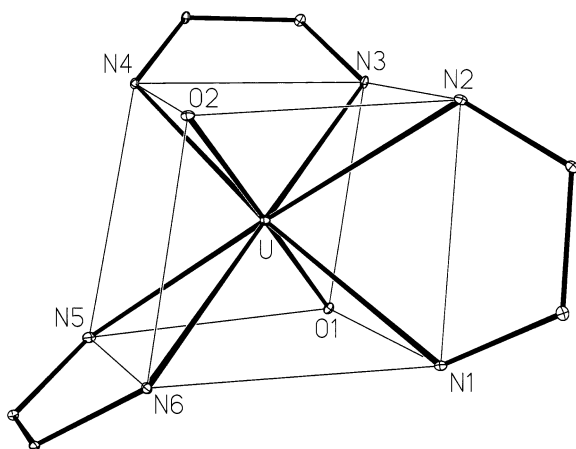


Fig. 3 Line-drawing showing the rhombohedral coordination geometry of the cation [UO₂(phen)₃]²⁺.

In conclusion, the first bis-bpy and tris-phen adducts of the uranyl ion have been isolated; their syntheses were possible by combining the use of triflate as the weakly coordinating counterion and anhydrous organic solvent. Under these conditions, UO₂²⁺ accommodates the set of ligands by forming compounds with a rhombohedral coordination geometry. These results strongly indicate that the development of nonaqueous uranyl chemistry, which is an emerging area of research after

the easy preparation of the anhydrous derivatives UO₂(OTf)₂¹¹ and UO₂Cl₂(THF)₃,¹³ will reveal the existence of unforeseen structural features. That the uranyl ion can adopt a coordination geometry other than the ubiquitous polygonal bipyramidal is of interest for both fundamental and applied aspects, in particular the design of new ligands for the selective complexation and extraction of actinyl ions.

Notes and references

† Characterizing data: ¹H NMR (200 MHz, 20 °C in [D₂H₅]acetonitrile): **1**, δ 9.0 (4 H, br d, *J* = 7.5 Hz), 8.45 (2 H, t, *J* = 7.5 Hz), 7.68 (2 H, t, *J* = 6.4 Hz); **2**, δ 9.17 (1 H, d, *J* = 5.0 Hz), 9.01 (1 H, d, *J* = 8.1 Hz), 8.53 (1 H, s), 7.91 (1 H, dd, *J* = 8.1 and 5.0 Hz). Elemental analyses (%) (calculated values in parentheses): **1**: C, 30.0 (29.8); H, 1.8 (1.95); N, 6.35 (6.5). **2**: C, 41.15 (41.3); H, 2.2 (2.3); N, 7.6 (7.4).

‡ Crystal data: for compound **1**: C₂₂H₁₆F₆N₄O₈S₂U, *M* = 880.54, triclinic, space group *P*-1, *a* = 6.0290(12), *b* = 10.031(2), *c* = 11.462(2) Å, α = 102.13(3)°, β = 92.66(3)°, γ = 102.87(3)°, *V* = 657.5(2) Å³, *Z* = 1, *D*_c = 2.224 g cm⁻³, *T* = 123(2) K, μ = 6.429 mm⁻¹, 4085 measured reflections, 2016 independent, 2015 > 2σ(*I*), 196 parameters, *R*₁ = 0.0248, *wR*₂ = 0.0621, GOF = 0.949.

For compound **2**:(phen)_{1.5}:(THF)_{0.5}: C_{59.5}H_{43.5}F₆N_{9.5}O_{8.5}S₂U, *M* = 1443.69, monoclinic, space group *C2/c*, *a* = 35.859(7), *b* = 12.269(3), *c* = 29.128(6) Å, β = 118.34(3)°, *V* = 11279(4) Å³, *Z* = 8, *D*_c = 1.700 g cm⁻³, *T* = 123 K, μ = 3.039 mm⁻¹, 33199 measured reflections, 9433 independent, 6026 > 2σ(*I*), 780 parameters, *R*₁ = 0.0558, *wR*₂ = 0.1074, GOF = 0.932.

The data were collected on a Nonius Kappa CCD diffractometer with MoKα radiation (λ = 0.71073 Å). Absorption effects were empirically corrected. CCDC 202642 and 202643. See <http://www.rsc.org/suppdata/cc/b3/b303255h/> for crystallographic data in .cif format.

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