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Dimeric dioxocations, $(NpO_2^+)_2$, in the structure of bis(μ-2-fluorobenzoato-κ^2O:O')di-μ-oxo-bis[(2,2′-bipyridine-κ^2N,N')oxoneptunium(V)]

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Key indicators

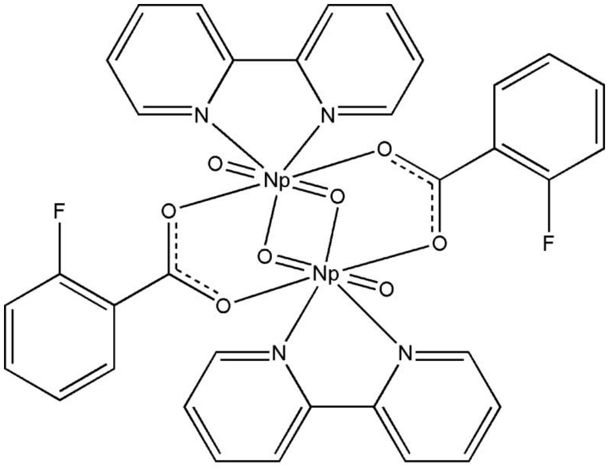
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.023
wR factor = 0.043
Data-to-parameter ratio = 21.2

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

The centrosymmetric title compound, $[(NpO_2)_2(C_7H_4FO_2)_2(C_{10}H_8N_2)_2]$, contains the dimeric dioxocation $(NpO_2^+)_2$ in which two of the four O atoms bridge the Np atoms. Two bidentate chelating-bridging fluorobenzoate anions link the Np atoms of the dimeric cation. The N atoms of the 2,2′-bipyridine ligand occupy two positions in the equatorial plane of the distorted pentagonal bipyramid, forming a five-membered metallacycle.

Comment

Mutual coordination of linear dioxocations or cation–cation (CC) interaction is an important structure-forming feature of Np^V and U^{VI} compounds (Krot & Grigoriev, 2004); recently, an example of CC interaction in a Pu^V compound was reported (Bessonov *et al.*, 2005). Among a wide variety of CC interaction patterns known for Np^V compounds, there is only one published structure with dimeric dioxocations $(NpO_2^+)_2$, for which one of two O atoms of each NpO_2^+ cation bridge two Np atoms, *viz.* the sodium salt of the neptunium(V) derivative of mellitic acid, $Na_4(NpO_2)_2C_{12}O_{12}\cdot 8H_2O$ (Cousson *et al.*, 1984). Here we present one more structure of an Np^V complex with dimeric dioxocations and present evidence for the existence of similar dimeric dioxocations for Pu^V.



(I)

As shown in Fig. 1, the centrosymmetrictitle compound, (I), also contains dimeric dioxocations $(NpO_2^+)_2$. The Np···Np distance in the dimeric dioxocation is 3.4381 (3) Å, compared with 3.482 Å in the mellitate complex (Cousson *et al.*, 1984). Two bidentate chelating-bridging fluorobenzoate anions link Np atoms of the same cationic pair. The N atoms of the 2,2′-bipyridine ligands occupy two positions in the equatorial plane of the distorted pentagonal bipyramid around the metal atom,

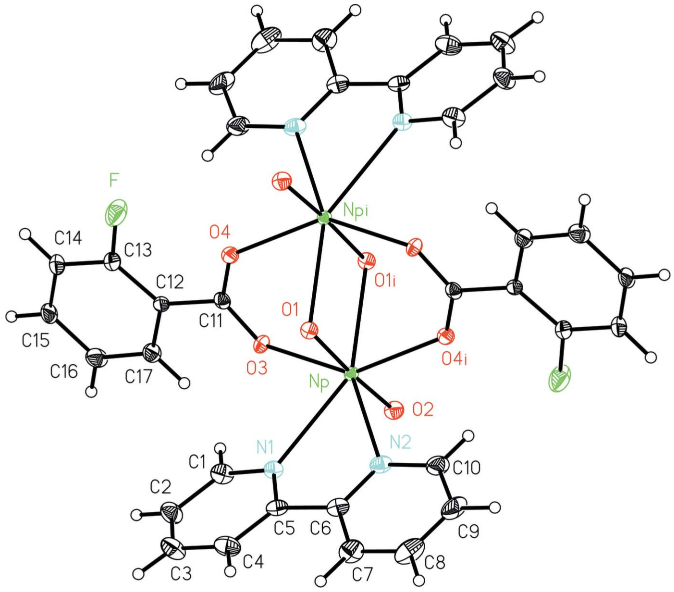


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radius. [Symmetry code: (i) $2 - x, 1 - y, 1 - z$.]

resulting in the formation of a five-membered metallacycle. The carboxylate groups play the same role as in the mellitate complex, and possibly also help to stabilize the dioxocations. The Np atom is displaced by 0.2076 (10) Å from the equatorial plane.

The partcipation of NpO_2^+ cations in CC bonding makes them somewhat bent (Table 1). The elongation of the Np—O1 bond (with a bridging O atom) compared with Np—O2 is about 0.05 Å.

The X-ray powder diffraction patterns of Np^V and Pu^V complexes, but with non-fluorinated benzoate anions (Bessonov *et al.*, 2007), are similar to that of (I), showing that these compounds are isostructural with (I).

Experimental

A water–ethanol (1:1) solution (5 ml) of NpO_2NO_3 (concentration about 5×10^{-3} *M*), orthofluorobenzoic acid and 2,2′-bipyridine (in about 10% molar excess) was heated in a Pyrex tube at 350 K for several hours until the volume of the solution was reduced to half. The crystallization of (I) took place upon slow cooling of the solution. After the formation of crystals, the tube was hermetically sealed. A crystal for analysis was obtained after 24 h.

Crystal data

$[Np_2(C_7H_4FO_2)_2O_4(C_{10}H_8N_2)_2]$
$M_r = 1128.67$
Monoclinic, $P2_1/n$
$a = 9.3373$ (5) Å
$b = 10.1342$ (6) Å
$c = 17.5070$ (10) Å
$\beta = 97.6551$ (11)°
$V = 1641.85$ (16) Å^3

$Z = 2$
$D_x = 2.283$ Mg m$^{-3$}
Mo $K\alpha$ radiation
$\mu = 6.36$ mm^{-1}
$T = 100$ (2) K
Parallelepiped, green
$0.28 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.519$, $T_{max} = 0.802$
(expected range = 0.389–0.601)

20861 measured reflections
4784 independent reflections
3900 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.043$
$S = 0.99$
4784 reflections
226 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.96$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Np—O1	1.863 (2)	Np—O4^i	2.431 (2)
Np—O2	1.810 (2)	Np—N1	2.640 (3)
Np—O3	2.443 (2)	Np—N2	2.624 (3)
Np—O1^i	2.488 (2)	Np—Np^i	3.4381 (3)
O1—Np—O2	175.93 (9)	O2—Np—O4^i	94.31 (9)
O1—Np—O3	84.90 (8)	O2—Np—N1	92.83 (9)
O1—Np—O1^i	76.51 (8)	O2—Np—N2	92.40 (9)
O1—Np—O4^i	84.31 (8)	O3—Np—O1^i	73.47 (7)
O1—Np—N1	90.78 (8)	O4^i—Np—O1^i	72.12 (7)
O1—Np—N2	90.97 (8)	O3—Np—N1	76.04 (7)
O2—Np—O3	94.15 (8)	O4^i—Np—N2	75.50 (8)
O2—Np—O1^i	99.42 (8)	N1—Np—N2	61.62 (8)

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

The H atoms of CH groups were refined as riding in idealized geometrical positions (C—H = 0.95 Å) with displacement parameters set equal to 1.2 times U_{eq} of the attached C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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m562 Grigoriev *et al.* • $[Np_2(C_7H_4FO_2)_2O_4(C_{10}H_8N_2)_2]$ *Acta Cryst.* (2007). E**63**, m561–m562