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Tris(η^5-cyclopentadienyl)phenolatoneptunium(IV)

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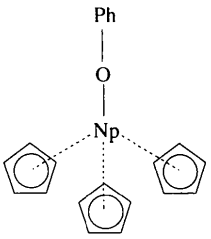
Abstract

The geometry of $[(\eta^5\text{-}C_5H_5)_3Np^{IV}(OC_6H_5)]$ is compared with that of the isostructural uranium analogue.

Comment

The metal coordination polyhedron in the large class of complexes of the type Cp_3MY, where Cp is a cyclopentadienyl ring, M is an actinide or a lanthanide, Y a monodentate Lewis base, anion or η^1-bonded Cp ring, is best described as a flattened tetrahedron (Lippard, 1979) in which the Cp rings are shifted towards the sterically less bulky Y ligand, increasing the Cp—M—Cp angles and decreasing the Y—M—Cp (centroid) angles. Within this class, organometallic uranium(IV) complexes have been widely investigated in recent years but little has been reported on the mixed-ligand complexes $Cp_3U(XR)$, where R = alkyl or aryl substituent, X = Group 16 donor atom (*e.g.* O or S). A complex of the latter class, in which $XR = OC_6H_5$, has been described previously (Spirlet, Rebizant, Apostolidis, Van den Bossche & Kanellakopulos, 1990) and is now compared with the isostructural neptunium complex (1).



(1)

The molecular structure consists of one Np atom coordinated by the O atom of the phenoxide and by three η^5-coordinated cyclopentadienyl rings. If the coordination polyhedron is considered to be formed by the O atom and the centres of the cyclopentadienyl rings, the coordination about the Np atom displays approximate C_{3v} symmetry, with the O atom at the apex and the cyclopentadienyl rings at the base of a flattened tetrahedron (Fig. 1). Thus the Cp_3MY geometry is maintained in this complex; the Cp—Np—Cp angles are nearly identical and significantly greater than 109° while the O—Np—Cp angles are significantly smaller than 109°. The deviation of the structure from a regular tetrahedron is also shown by the distance of the Np atom from the plane defined by the centres of the three cyclopentadienyl rings. If one assumes tetrahedral geometry about the Np atom and an average neptunium to ring-centre distance of 2.47 (1) Å, then the Np atom should be located 0.823 Å above the plane. The distance in (1) is 0.452 (4) Å and is a measure for the trigonal distortion from tetrahedral geometry.

The phenyl and the three cyclopentadienyl rings are planar within the limits of accuracy; the maximum deviation of a ring atom from the corresponding least-squares plane is 0.017 (8) Å (C15). The O atom lies 0.038 (14) Å from the phenyl plane. The phenyl and cyclopentadienyl C—C distances are in the ranges 1.36 (2)–1.40 (2) and 1.29 (2)–1.44 (3) Å, respectively, and the internal ring angles are 118.8 (12)–122.2 (11) and 105.1 (16)–111.9 (18)°, respectively.

The position of the phenyl ring divides the cyclopentadienyl rings into two classes. Cp I is nearly parallel to the phenyl ring [the angle is 11.5 (4)°] while the corresponding angles for Cp II and Cp III are 61.0 (6) and 72.9 (4)°. In addition, the O—Np···Cp I(centroid)

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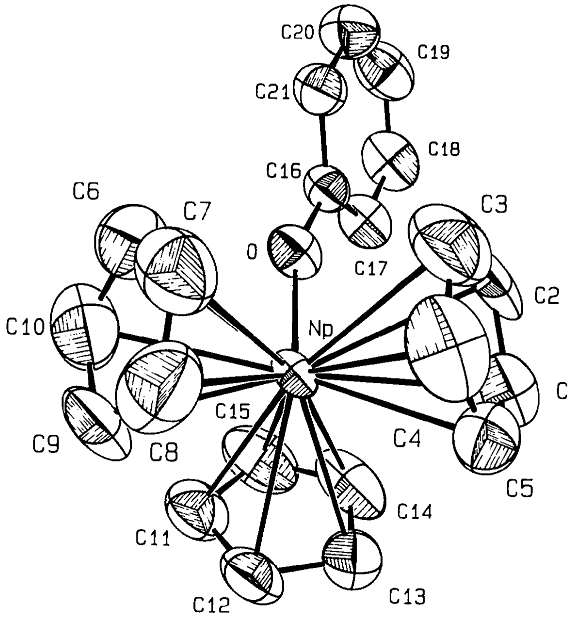

Fig. 1. *ORTEP* (Johnson, 1976) drawing showing the numbering system of (1), with displacement ellipsoids at the 50% probability level. The H atoms are not shown.

angle is significantly smaller than those for the other two Cp rings.

There are several short intramolecular contacts between the ligands that may reflect steric congestion in the coordination sphere of neptunium (see Table 3).

The title complex, (1), is isostructural with that of uranium, (2) (Spirlet, Rebizant, Apostolidis, Van den Bossche & Kanellakopulos, 1990). The cell dimensions of the two structures compare very well, the cell volume of (1) being somewhat larger [1745.2 (7) *versus* 1730 (2) Å^3]. The largest difference of a lattice dimension is that for the c axis [23.441 (4) *versus* 23.337 (5) Å]. It should be remarked that the configuration of (1) is inverted with respect to that reported for (2). Matching of the non-H atoms of (1) with those of the uranium homologue (2) resulted in a r.m.s. value of 0.06 Å.

Only one other (η^5-C_5H_5)Np^{IV} complex has been recorded in the Cambridge Structural Database (Allen *et al.*, 1991). The average Np—C distance observed in [trichloro(η^5-cyclopentadienyl)bis(methyldiphenylphosphine oxide)neptunium(IV)] (Bagnall, Payne, Alcock, Flanders & Brown, 1986) is smaller than in (1) [2.70 (1) *versus* 2.733 (3) Å]. Consequently the Np—Cp distance is also smaller than the average distance in (1) [2.444 (11) *versus* 2.47 (1) Å]. These differences can presumably be ascribed to higher steric hindrance in (1). The average Np—O distance of 2.277 (6) Å is significantly greater than in (1). This difference can be explained by the fact that in (1), Np—O is a σ-bond whereas in the other compound Np—O is a coordinative bond.

Experimental

Reaction of tris(cyclopentadienyl)neptunium chloride with potassium phenoxide in tetrahydrofuran (von Ammon, Fischer & Kanellakopulos, 1972) yielded the title complex, (1). Extraction with n-pentane followed by crystallization produced single crystals suitable for X-ray analysis. A selected specimen was sealed in a thin-walled glass capillary under an inert atmosphere.

Crystal data

$[Np(C_6H_5O)(C_5H_5)_3]$
$M_r = 525.37$
Orthorhombic
$P2_12_12_1$
$a = 8.370(3)$ Å
$b = 8.8948(14)$ Å
$c = 23.441(4)$ Å
$V = 1745.2(7)$ Å^3
$Z = 4$
$D_x = 2.00$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.9$–$17.4°$
$\mu = 5.956$ mm^{-1}
$T = 295(2)$ K
Needle
0.80 × 0.25 × 0.12 mm
Brown–red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.888$, $T_{max} = 1.000$
4869 measured reflections
2265 independent reflections

2239 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0179$
$\theta_{max} = 22.48°$
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -25 \rightarrow 25$
3 standard reflections frequency: 120 min intensity decay: 4.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.077$
$S = 0.978$
2265 reflections
208 parameters
H atoms: riding at 0.93 Å from their carrier atom, with $U_{iso}(H) = 1.2U_{eq}(C)$
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 3.9101P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 1.12$ e Å^{-3}
$\Delta\rho_{min} = -2.73$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.03 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Np	0.22421 (4)	0.90526 (4)	0.85631 (1)	0.0401 (2)
O	0.3710 (9)	1.0585 (8)	0.9030 (3)	0.057 (2)
C1	0.439 (2)	0.863 (1)	0.7702 (6)	0.075 (4)
C2	0.533 (1)	0.866 (2)	0.8185 (8)	0.091 (5)
C3	0.497 (2)	0.740 (2)	0.8511 (8)	0.107 (6)
C4	0.381 (2)	0.656 (2)	0.8193 (8)	0.100 (6)
C5	0.347 (2)	0.737 (1)	0.7694 (5)	0.075 (3)
C6	0.178 (2)	0.805 (2)	0.9647 (6)	0.093 (5)
C7	0.188 (2)	0.681 (2)	0.9365 (8)	0.097 (5)

C8	0.065 (3)	0.666 (2)	0.9024 (7)	0.106 (6)
C9	−0.0347 (17)	0.790 (3)	0.9116 (8)	0.132 (9)
C10	0.045 (2)	0.880 (2)	0.9522 (7)	0.097 (5)
C11	−0.0330 (15)	1.088 (2)	0.8357 (6)	0.076 (4)
C12	−0.0356 (14)	0.984 (2)	0.7916 (6)	0.072 (3)
C13	0.0948 (16)	1.008 (2)	0.7563 (5)	0.076 (4)
C14	0.1798 (17)	1.132 (2)	0.7803 (8)	0.096 (5)
C15	0.098 (2)	1.182 (2)	0.8274 (8)	0.095 (5)
C16	0.4959 (12)	1.1428 (10)	0.9166 (4)	0.046 (2)
C17	0.5283 (14)	1.274 (1)	0.8853 (5)	0.058 (3)
C18	0.6580 (16)	1.363 (1)	0.9014 (6)	0.075 (3)
C19	0.7545 (16)	1.326 (1)	0.9462 (6)	0.080 (4)
C20	0.7213 (17)	1.196 (1)	0.9759 (5)	0.077 (3)
C21	0.5940 (13)	1.105 (1)	0.9611 (4)	0.058 (3)

Table 2. *Selected geometric parameters (Å, °)*

*Cp*I denotes the centre of the cyclopentadienyl ring I (C1–C5), *Cp*II that of ring II (C6–C10) and *Cp*III that of ring III (C11–C15).

Np—O	2.136 (7)	Np—C10	2.71 (1)
Np—C1	2.73 (1)	Np—C11	2.74 (1)
Np—C2	2.75 (1)	Np—C12	2.74 (1)
Np—C3	2.72 (1)	Np—C13	2.74 (1)
Np—C4	2.74 (1)	Np—C14	2.71 (1)
Np—C5	2.73 (1)	Np—C15	2.76 (1)
Np—C6	2.72 (1)	O—C16	1.326 (12)
Np—C7	2.76 (1)	Np···*Cp*I	2.460 (7)
Np—C8	2.73 (2)	Np···*Cp*II	2.477 (8)
Np—C9	2.73 (1)	Np···*Cp*III	2.470 (7)
O—Np···*Cp*I	97.6 (4)	*Cp*I···Np···*Cp*II	116.4 (6)
O—Np···*Cp*II	102.3 (5)	*Cp*I···Np···*Cp*III	116.1 (5)
O—Np···*Cp*III	101.7 (4)	*Cp*II···Np···*Cp*III	117.7 (6)
Np—O—C16	159.8 (6)		

Table 3. *Short interligand distances (Å)*

O···C contacts (< 3.1 Å)			
O···C2	2.95 (2)		
C···C contacts (< 3.4 Å)			
C1···C13	3.17 (2)	C4···C8	3.28 (2)
C1···C14	3.24 (2)	C5···C13	3.22 (2)
C2···C16	3.38 (2)	C9···C11	3.20 (2)
C3···C7	3.31 (2)	C9···C12	3.30 (2)
C4···C7	3.19 (2)	C10···C11	3.36 (2)

In the final difference Fourier map there are four substantial peaks with heights in the range 0.86–1.12 e Å^{-3}, close to the Np atom (0.94–1.18 Å).

Disorder or librational motion of the cyclopentadienyl rings may explain the excessive vibrational anisotropy of C2 and C9: for these atoms the ratio of the maximum to minimum mean-square atomic displacement is greater than 10:1.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1983). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1438–1441

Disodium Aqua[2,5,8-tris(carboxymethyl)-12-phenyl-2,5,8-triaza-11-oxa-1,9-dodecanedicarboxylato(5−)]europate Sesquihydrate

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Abstract

The structure of the disodium salt of the $[Eu(C_{22}H_{26}N_3O_{11})(H_2O)]^{2-}$ complex anion is isomorphous with that of the corresponding gadolinium(III) compound. The Eu^{III} atom is nine-coordinate with the donor atoms disposed at the vertices of a tricapped trigonal prism, the cap positions being occupied by two N atoms of the ligand and the O atom of the ligated water molecule.

Comment

The bis(*N*-methylglucammonium) salt of $[Gd(BOPTA)]^{2-}$ [international non-proprietary name (INN): gadobenate; BOPTA is the pentanion of 2,5,8-tris(carboxymethyl)-12-phenyl-2,5,8-triaza-11-oxa-1,9-dodecanedicarboxylic acid] is a promising contrast agent