(Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978) .

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1203). 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**, 597–600

Bis(cyclooctatetraenyl)neptunium(IV)

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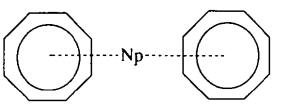
(*Received 30 June 1995; accepted 20 September 1995*)

Abstract

The crystal structure of neptunocene, $[Np(C_8H_8)_2]$, has been determined by single-crystal X-ray diffraction and is isostructural with thorocene and uranocene. A number of crystallographic and geometric parameters of these three compounds are compared.

Comment

The crystal and molecular structures of the two isostructural cyclooctatetraene dianion π-complexes thorocene and uranocene, $[Th(C_8H_8)_2]$ and $[U(C_8H_8)_2]$, have been described by Avdeef, Raymond, Hodgson & Zalkin (1972). Karraker, Stone, Jones & Edelstein (1970) obtained X-ray powder diffractograms of uranocene and of the neptunium (neptunocene) and plutonium (plutonocene) analogues showing evidence that all three actinide(IV)–cyclooctatetraenes are isomorphous. Two groups, Goffart, Fuger, Brown & Duyckaerts (1974), and Starks, Parsons, Streitwieser & Edelstein (1974), have, independently from each other and almost simultaneously, shown that the protactinium analogue is isostructural with the lower actinides mentioned above. In the present paper the molecular and crystal structure of neptunocene, (I), is described and its geometry with respect to thorocene and uranocene discussed.



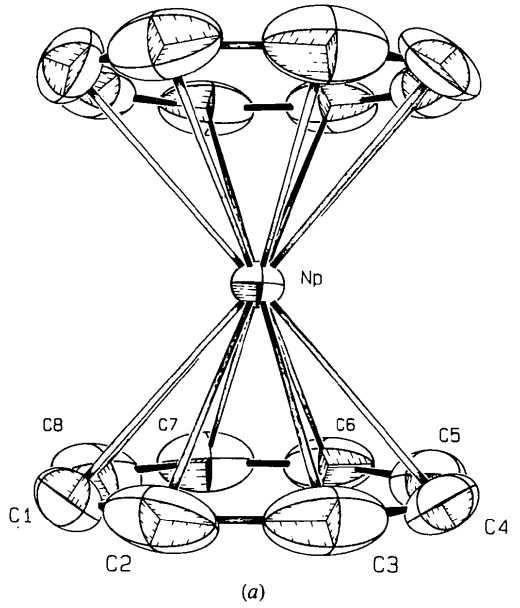
(I)

The molecular structure of the title compound, (I), consists of a central Np atom symmetrically π-bonded to two aromatic cyclooctatetraene dianion rings related by a crystallographic inversion centre. Neptunocene has D_{8h} symmetry: the molecular eightfold axis passes through the centre of the two rings and the Np atom (Fig. 1).

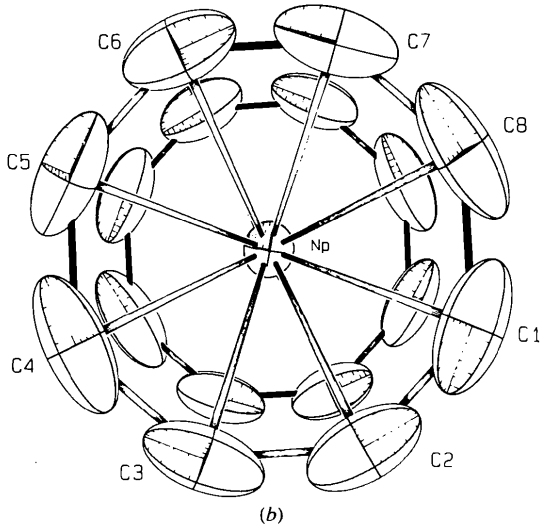
The cyclooctatetraene dianion rings are planar within the limits of accuracy, the maximum deviation of a ring atom through the least-squares plane being 0.014 (8) Å (C3). The planarity of the ring and the mean bond lengths [1.385 (5) Å] and angles [135.0 (3)°] demonstrate the aromatic nature of the 10-π-electron dianion rings in (I). The aromaticity is also confirmed by a comparison of the two averages for alternate sets of four C—C bonds. Such a comparison is a much more severe test for the aromaticity of the anion than bond-by-bond comparisons of the overall average since the averages must be equal in an aromatic hydrocarbon ring. In the title compound the averages, 1.388 (7) and 1.383 (7) Å, are equal to within one e.s.d.

In the crystal, the molecules alternate in a herringbone motif up the twofold screw axis, parallel to *b* (Fig. 2). The same motif has been found in the thorium and uranium analogues (Avdeef, Raymond, Hodgson & Zalkin, 1972).

The molecular structure corroborates the Mössbauer studies of Karraker, Stone, Jones & Edelstein (1970), which indicated 'the presence of at least some π-interaction between the ligand molecular orbitals and metal 5*f* orbitals', and by Adrian, Appel, Bohlander, Haffner, Kanellakopulos & Krüger (1986).



(a)



(b)

Fig. 1. *ORTEP*II (Johnson, 1976) drawings showing the numbering system of the title compound, with displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. (*a*) Perspective view perpendicular to the eightfold axis. (*b*) Perspective view along the eightfold axis.

The relatively large anisotropic thermal motion of the $C_8H_8^{2-}$ ring C atoms (Fig. 1*b*) is similar to that observed in thorocene and uranocene (Avdeef, Raymond, Hodgson & Zalkin, 1972) and in mixed-sandwich compounds like $(C_5H_5)Ti(C_8H_8)$ (Kroon & Helmoldt, 1970), $[Ce(C_8H_8)Cl.2OC_4H_8]_2$ (Hodgson & Raymond, 1972), $(C_8H_8)Lu(C_5Me_5)$ (Schumann, Köhn, Reier, Dietrich & Pickardt, 1989), $(C_8H_8)Y(C_5H_4CH_3)$(thf) (Schumann, Sun & Dietrich, 1990) and $(C_8H_8)Tb(C_5H_3{}^tBu_2)$ (Schumann, Winterfeld, Köhn, Esser, Sun & Dietrich, 1993). The preferential oscillation is around the eightfold axis with an average root-mean-square amplitude of vibration

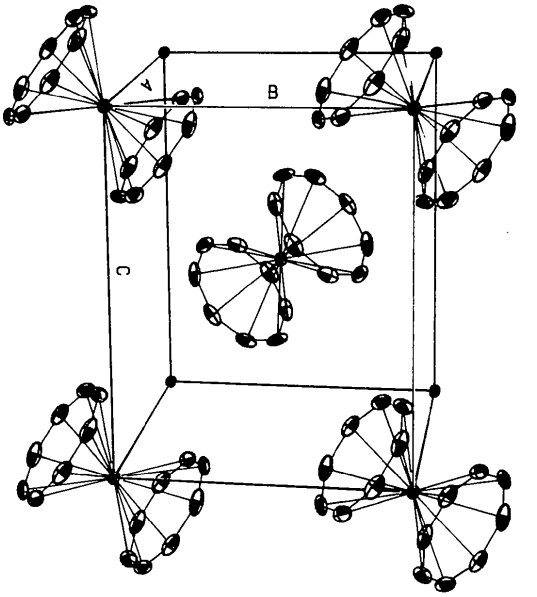


Fig. 2. Packing drawing of the unit cell; *b* axis horizontal, *c* axis vertical. H atoms have been omitted for clarity.

along the major ellipsoid axis of 0.37 Å. The values for thorocene and uranocene are 0.39 and 0.37 Å, respectively (Avdeef, Raymond, Hodgson & Zalkin, 1972).

The title compound is the first π-sandwich structure of neptunium to be published. A similar neptunium π-sandwich structure has been found for bis(phtalocyanine)neptunium(IV) (Lux, Apostolidis & Rebizant, unpublished results).

A number of crystallographic and geometric parameters for thorocene, protactinocene (only crystallographic data), uranocene and the title compound have been collected in Table 3. The crystallographic data for protactinocene have been taken from Goffart, Fuger, Brown & Duyckaerts (1974) since these data are more accurate than those determined by Starks, Parsons, Streitwieser & Edelstein (1974), the reason being that the former used Cr whereas the latter used Cu radiation. However, the cell parameters of the latter [a = 7.09 (4), b = 8.75 (4), c = 10.62 (4) Å, β = 98,5(4)°] do not differ much from those of the former (Table 3). No cell parameters have been given for plutonocene by Karraker, Stone, Jones & Edelstein (1970), so this compound is not included in Table 3. Going from Th to Np, the dimension of the a axis and the value of β increases whereas the dimensions of the b and c axes decrease. The metal–carbon, and consequently the metal–centroid distances decrease when going from Th to Np. This correlates with the ionic radii which are 1.06, 1.00 and 0.98 Å for Th, U and Np, respectively [values for M^{4+} ions with coordination number VIII (Shannon & Prewitt, 1969)]. The average C_i—M—C_{i+1} and C_i—M—C_{i+4} angles of the title compound compare well with the values for uranocene; both values are somewhat greater than those for thorocene.

Experimental

3.65 g (20 mmol) of potassium cyclooctatetraenide and 3.79 g (10 mmol) of neptunium tetrachloride were intensively stirred in diethyl ether. After ten days the solvent was removed; the yellow–brown residue was extracted with benzene yielding 2.71 g of dark brown crystals. The crystals were washed with diethyl ether and dried under vacuum. All reactions were carried out under an argon atmosphere (Bohlander, 1986). After recrystallization with *n*-pentane a crystal suitable for X-ray diffraction was obtained.

Crystal data

$[Np(C_8H_8)_2]$
$M_r = 445.29$
Monoclinic
$P2_1/n$
$a = 7.124\ (4)$ Å
$b = 8.687\ (3)$ Å
$c = 10.6064\ (13)$ Å
$\beta = 98.85\ (4)°$
$V = 648.6\ (4)$ Å^3
$Z = 2$
$D_x = 2.280$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 11.7–24.5°$
$\mu = 7.985$ mm^{-1}
$T = 293\ (2)$ K
Needle
$0.72 \times 0.12 \times 0.09$ mm
Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.825$, $T_{max} = 1.000$
3913 measured reflections
1884 independent reflections
1408 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0334$
$\theta_{max} = 29.98°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.031$
$wR = 0.038$
$S = 1.065$
1125 reflections
80 parameters
Riding H atoms at 0.95 Å from their carrier atom, with $U_{iso} = 1.3U_{eq}$
$w = 4F^2/[\sigma^2(I) + (0.06F^2)^2]$
$(\Delta/\sigma)_{max} = 0.09$
$\Delta\rho_{max} = 0.782$ e Å^{-3}
$\Delta\rho_{min} = -0.990$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $1.21\ (4) \times 10^{-6}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	0	0	0.02660 (5)
C1	0.259 (2)	0.0201 (7)	0.205 (1)	0.068 (3)
C2	0.335 (1)	0.092 (1)	0.1128 (9)	0.062 (3)
C3	0.278 (1)	0.1992 (9)	0.0229 (8)	0.062 (3)
C4	0.110 (1)	0.2879 (9)	−0.0114 (7)	0.072 (3)
C5	−0.066 (1)	0.293 (1)	0.0344 (8)	0.065 (3)
C6	−0.1452 (9)	0.2193 (9)	0.1283 (7)	0.058 (3)
C7	−0.088 (1)	0.112 (1)	0.2140 (7)	0.063 (3)
C8	0.077 (2)	0.0261 (9)	0.2501 (8)	0.080 (4)

Table 2. *Selected geometric parameters (Å)*

Np—C1	2.63 (1)	C1—C2	1.35 (1)
Np—C2	2.624 (7)	C1—C8	1.45 (2)
Np—C3	2.616 (7)	C2—C3	1.35 (1)
Np—C4	2.629 (8)	C3—C4	1.43 (1)
Np—C5	2.628 (9)	C4—C5	1.41 (1)
Np—C6	2.643 (8)	C5—C6	1.38 (1)
Np—C7	2.633 (8)	C6—C7	1.32 (1)
Np—C8	2.634 (8)	C7—C8	1.39 (2)

Table 3. *Comparison of crystallographic and geometric data of the title compound with that of the isostructural Th, Pa and U compounds (Å, °)*

Crystallographic data	Th[a]	Pa[b]	U[a]	Np[c]
a	7.058 (1)	7.06 (1)	7.084 (3)	7.124 (4)
b	8.819 (2)	8.83 (1)	8.710 (3)	8.687 (3)
c	10.704 (2)	10.72 (1)	10.631 (5)	10.606 (1)
β	98.44 (3)	98.4 (1)	98.75 (3)	98.85 (4)
Geometric data[d]				
⟨M—C⟩	2.701 (4)	–	2.647 (4)	2.630 (3)
M—centroid	2.0036 (5)	–	1.9264 (5)	1.9088 (3)
⟨C—C⟩	1.386 (7)	–	1.392 (7)	1.385 (5)
⟨C_i—M—C_{i+1}⟩[e]	29.7 (2)	–	30.5 (3)	30.5 (1)
⟨C_i—M—C_{i+4}⟩[f]	84.2 (2)	–	86.8 (1)	86.9 (1)

Notes: (*a*) Avdeef, Raymond, Hodgson & Zalkin (1972); (*b*) Goffart, Fuger, Brown & Duyckaerts (1974); (*c*) this work; (*d*) the values and the e.s.d.'s for thorocene and uranocene have been recalculated; (*e*) atoms i and i+1 are adjacent in the cyclooctatetraene ring; (*f*) atoms i and i+4 are separated by three C atoms in the cyclooctatetraene ring.

Since the value calculated for Z was 2, the Np atoms were placed on the symmetry-related special positions 0,0,0 and 1/2,1/2,1/2 with $\bar{1}$ site symmetry. The C atoms were found in a subsequent Fourier analysis.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf–Nonius, 1986). Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

One of the authors (DDR) acknowledges support in the frame of the EC-funded training programme 'Human Capital and Mobility'.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1077). 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**, 600–602

Ferrocenium Tetrachloroantimonate

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(*Received 13 June 1995; accepted 7 August 1995*)

Abstract

The crystal structure of ferrocenium tetrachloroantimonate, $[Fe(C_5H_5)_2][SbCl_4]$, has been determined at 173 K. The cyclopentadiene rings in the ferrocenium cation are in an eclipsed conformation. The Sb atom is coordinated by six Cl ions in an irregular octahedral arrangement. Two Cl^- ions form halogen bridges with neighbouring Sb atoms, resulting in a polymeric chain of anions {the compound may be named *catena*-poly[ferrocinium (dichloroantimonate-di-μ-chloro)]}. The ferrocenium cations are stacked between these polymeric chains and form two-dimensional layers parallel to the *bc* plane.

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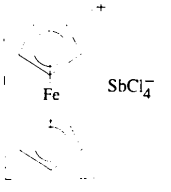
Comment

Although ferrocene is readily oxidized to the ferrocenium cation by Group 15 trihalides such as PCl_3, $AsCl_3$, $SbCl_3$ and $BiCl_3$, the products can be quite complicated due to the presence of highly aggregated halogeno–Group 15 anions (Landers *et al.*, 1976; Mammano, Zalkin, Landers & Rheingold, 1977). Therefore, it can be generalized that the oxidation products of such reactions can have different compositions depending on the molar ratio of metal halide to ferrocene used, and also on the type of solvent. The ability of some metals to expand their coordination number during reaction could further contribute to the complexity of the product. Recrystallization of ferrocenium salts from water or organic solvents is normally very difficult and hence relatively few detailed X-ray structures of ferrocenium salts have been reported. Our literature search on ferrocenium Group 15 halides indicated that so far only the structures of ferrocenium tetrachlorobismuthate, $[\eta^5\text{-}(C_5H_5)_2Fe]_2[As_4Cl_{10}O_2]$ and $\{[\eta^5\text{-}(C_5H_5)_2Fe]_2[Sb_4Cl_{12}O]\}_2.2C_6H_6$ have been reported (Mammano *et al.*, 1977; Churchill, Landers & Rheingold, 1981; Rheingold, Landers, Dahlstrom & Zubieta, 1979). Even though a product from $SbCl_3$ with an empirical formula analogous to that of ferrocenium tetrachlorobismuthate was found, no structural details of the compound were reported (Cowell, Ledwith, White & Wood, 1970) and hence the X-ray structure analysis of the title compound, (I), was undertaken.



(I)

The structure was found to be isomorphous with that of ferrocenium tetrachlorobismuthate. The Sb atom is coordinated by six Cl^- ions, forming an irregular octahedron. The Sb—Cl distances vary from 2.3888 (7) (Sb—Cl1) to 3.3202 (8) Å (Sb—Cl3′). The Sb atoms are connected by Sb—Cl—Sb′ halogen bridges *via* atoms Cl3 and Cl4, leading to a polymeric chain of anions running along the *c* axis. In this chain, the Sb coordination octahedra are found to be 'edge sharing'. Among the six Sb—Cl bonds, the four long bonds involving atoms Cl3, Cl4, Cl3′ and Cl4′ are bridging, whereas the two short bonds, Sb—Cl1 and Sb—Cl2, are non-bridging. The Sb—Cl3—Sb′ and Sb—Cl4—Sb′ angles are 92.9 (1) and 98.2 (1)°, respectively. The octahedron is considerably distorted owing to the vast differences in the relevant bond lengths and angles. The Sb—Cl distances observed in this structure show variations from those observed in pyridinium tetra-