Structure of Tetrakis(1–3-η-2-indenyl)thorium(IV)

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Abstract. [Th(C$_9$H$_9$)$_4$], $M_r = 692 \cdot 66$, orthorhombic, $Pna2_1$, $a = 22 \cdot 403$ (5), $b = 36 \cdot 034$ (7), $c = 9 \cdot 566$ (2) Å, $V = 7722$ (5) Å^3, $Z = 12$, $D_x = 1 \cdot 787$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 6 \cdot 017$ mm^{-1}, $F(000) = 4008$, $T = 295$ (1) K, $R = 0 \cdot 04$ for 3468 observed reflections. The unit cell contains four parallel rows, each containing three independent molecules stacked along **b**. In each molecule, the Th atom is surrounded by four indenide rings in an approximately tetrahedral configuration. The Th—C distances to the five-membered rings of the indenide ligands suggest trihapto metal–carbon bonding, Th—C, 2·66 (3)–2·97 (4) Å.

Introduction. The largest proportion of structural investigations of organoactinoid species reported in the literature concerns complexes of uranium with the cyclopentadienide ligand or its derivatives. To date, structural data for organoactinide(IV) complexes with the indenide ligand only exist for [Th(C$_{12}$H$_{13}$)$_3$]Cl (Spirlet, Rebizant & Goffart, 1982), [U(C$_9$H$_7$)$_3$]Cl (Burns & Laubereau, 1971), [U(C$_9$H$_7$)]Cl$_3$.2C$_4$H$_8$O (Rebizant, Spirlet & Goffart, 1983), [U(C$_9$H$_7$)]Br$_3$.-2C$_4$H$_8$O (Rebizant, Spirlet & Goffart, 1985) and [U(C$_9$H$_7$)]Br$_3$.C$_4$H$_8$O.OP(C$_6$H$_5$)$_3$ (Meunier-Pieret, Germain, Declercq & Van Meerssche, 1980).

The present work provides further insight into actinide–C π bonding with a novel example of inter-action between thorium and the indenide ligand.

The crystal structure of tetrakis(indenyl)thorium was previously investigated by Hohmann & Ziegler (1978). These reported cell parameters and identified the space group as *Pnma*. Their unsuccessful attempts to solve the structure were attributed to high atomic thermal motion. Our reinvestigation indicates that the space group was incorrect, being actually $Pna2_1$, $Pn2_1a$ in the alternative setting chosen by Hohmann & Ziegler (1978).

Experimental. Tetrakis(indenyl))thorium(IV) was pre-pared by the reaction of pure thorium tetrachloride with the stoichiometric amount of potassium indenide in boiling benzene. After 46 d reaction time, benzene was removed by distillation under vacuum and the residue extracted with benzene. The extraction product was then dried under an Ar atmosphere and crystallized from pentane. The complex crystallized as fine yellow needles of some millimeters length. A single crystal (0·32 × 0·12 × 0·13 mm) suitable for X-ray analysis was selected and sealed in a quartz capillary under an inert atmosphere. Intensity data recorded on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Systematic absences consistent with space group $Pna2_1$ and $Pnam$. 21862 reflections measured (θ–2θ scan mode) in range $4 \leq 2\theta \leq 46°$, 15002 considered observed [$I \geq 1\sigma(I)$, $\pm h, \pm k, -l$], averaged to 5776 unique reflections ($R_{int} = 0 \cdot 02$). Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors 78·76 to 99·94%). The solution of the structure was investigated in the two possible space groups. E maps calculated with the set of phases presenting the highest combined figure of merit given by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions for Th atoms. A large number of difference Fourier maps, alternating with full-matrix least-squares calculations [minimizing $\sum w(\Delta F)^2$] were necessary to locate the C atoms and the procedure only succeeded in space group $Pna2_1$. Last cycles of refinement with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, on 3468 independent reflections with $F^2 \geq 1 \cdot 5\sigma(F^2)$, index range h 0/24, k 0/39, l 0/10. Anisotropic thermal parameters for Th atoms; isotropic for C; H atoms in

calculated positions, included in final structure-factor calculation with $B_{iso} = 5 \cdot 0 \, \text{Å}^2$. $R = 0 \cdot 04$, $wR = 0 \cdot 04$, $S = 0 \cdot 896$, $(\Delta/\sigma)_{max}$ $0 \cdot 01$, $\Delta\rho$ in final difference Fourier map within $+0 \cdot 937$ and $-0 \cdot 925$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1981) *SDP* programs.

In order to keep a reasonable value for the ratio of intensity data to parameters, the C atoms were not refined anisotropically, even though they usually exhibit larger anisotropic thermal vibrations within the indenyl rings (Spirlet *et al.*, 1982).

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are listed in Table 2. The crystal structure (Fig. 1) consists of twelve discrete molecules of $Th(C_9H_7)_4$ per unit cell, the asymmetric unit consisting of three independent molecules. The molecules are packed, along the *b* axis, in four parallel rows that lie alternately at intervals of half the unit-cell length along the *c* axis. In each row, three distinct (symmetrically independent) molecules succeed one another at regular intervals of about one third of the *b* axial length. They differ in their orientation and slight discrepancies also occur in their geometries (Table 2). In each molecule the Th atom is bonded to C atoms of the five-membered-ring portion of the indenide ligands (Table 2).
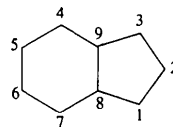
The coordination polyhedron about Th has the indenide five-membered rings at the apices of a distorted tetrahedron. The extent of deviation from a regular tetrahedron is shown by the angles of the type (centroid of one ring)–Th–(centroid of another ring) reported in Table 2.

Most of the indenyl rings exhibit small ($<4\sigma$) deviations from planarity. Dihedral angles ranging from 6 (2) to 9 (2)° occur between the five- and the six-membered-ring portions. These deviations probably result from steric hindrance between the bulky indenyl ligands around the Th atom. Indeed there are some short intramolecular contacts in the coordination sphere.*

Within each indenide ligand, the closest Th–C distances involve the three non-bridging C atoms (ring positions 1, 2 and 3) of the five-membered ring. The lengthening of the Th–C distances to the bridging C atoms (positions 8 and 9) in comparison with the Th–C bond lengths to the non-bridging C atoms cannot be

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, C–C bond lengths and bond angles and intramolecular contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43161 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

For Th equivalent isotropic thermal parameters are listed with $B_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{B}}$.

Numbering scheme

Th(1)	Indenide I	[C(1)⋯C(9)]
	Indenide II	[C(10)⋯C(18)]
	Indenide III	[C(19)⋯C(27)]
	Indenide IV	[C(28)⋯C(36)]
Th(2)	Indenide V	[C(37)⋯C(45)]
	Indenide VI	[C(46)⋯C(54)]
	Indenide VII	[C(55)⋯C(63)]
	Indenide VIII	[C(64)⋯C(72)]
Th(3)	Indenide IX	[C(73)⋯C(81)]
	Indenide X	[C(82)⋯C(90)]
	Indenide XI	[C(91)⋯C(99)]
	Indenide XII	[C(100)⋯C(108)]

	x	y	z	B_{eq}/B_{iso}
Th(1)	0·33705 (4)	0·20827 (2)	0·750	2·80 (2)
Th(2)	0·33347 (4)	0·54047 (2)	0·7344 (1)	2·79 (2)
Th(3)	0·36261 (4)	0·88741 (2)	0·7104 (1)	2·61 (2)
C(1)	0·257 (1)	0·1775 (7)	0·543 (3)	3·7 (6)
C(2)	0·276 (1)	0·1508 (7)	0·645 (3)	5·1 (7)
C(3)	0·239 (1)	0·1533 (6)	0·770 (3)	4·3 (6)
C(4)	0·144 (1)	0·1931 (7)	0·813 (3)	5·2 (7)
C(5)	0·105 (1)	0·2187 (6)	0·755 (3)	5·0 (6)
C(6)	0·114 (1)	0·2332 (8)	0·618 (3)	5·3 (8)
C(7)	0·162 (1)	0·2216 (7)	0·533 (3)	5·3 (7)
C(8)	0·207 (1)	0·1959 (7)	0·598 (3)	4·7 (7)
C(9)	0·195 (1)	0·1816 (6)	0·737 (3)	4·0 (5)
C(10)	0·297 (1)	0·2743 (6)	0·851 (3)	3·1 (6)
C(11)	0·2577 (9)	0·2659 (5)	0·747 (3)	3·1 (5)
C(12)	0·288 (1)	0·2727 (7)	0·613 (3)	3·8 (6)
C(13)	0·390 (1)	0·3035 (7)	0·554 (3)	4·1 (6)
C(14)	0·438 (1)	0·3189 (8)	0·614 (3)	5·5 (8)
C(15)	0·449 (1)	0·3182 (6)	0·762 (3)	4·5 (6)
C(16)	0·405 (1)	0·3031 (7)	0·848 (3)	5·3 (7)
C(17)	0·3523 (9)	0·2895 (5)	0·792 (2)	2·3 (5)
C(18)	0·342 (1)	0·2871 (6)	0·640 (2)	3·1 (5)
C(19)	0·412 (1)	0·2048 (7)	1·001 (3)	4·7 (7)
C(20)	0·403 (1)	0·1661 (7)	0·958 (3)	4·7 (7)
C(21)	0·342 (1)	0·1587 (7)	0·987 (3)	4·0 (6)
C(22)	0·256 (1)	0·1988 (8)	1·101 (3)	4·9 (7)
C(23)	0·251 (1)	0·2328 (7)	1·181 (3)	5·1 (7)
C(24)	0·296 (1)	0·2571 (6)	1·205 (3)	4·5 (6)
C(25)	0·353 (1)	0·2537 (7)	1·157 (3)	5·2 (7)
C(26)	0·365 (1)	0·2193 (7)	1·067 (3)	4·4 (7)
C(27)	0·313 (1)	0·1909 (7)	1·051 (3)	4·3 (7)
C(28)	0·407 (1)	0·2145 (7)	0·513 (3)	4·5 (7)
C(29)	0·442 (1)	0·2234 (7)	0·625 (3)	3·9 (6)
C(30)	0·460 (1)	0·1896 (6)	0·691 (3)	4·2 (6)
C(31)	0·436 (1)	0·1200 (7)	0·653 (3)	4·8 (7)
C(32)	0·409 (1)	0·0964 (8)	0·542 (4)	6·8 (9)
C(33)	0·381 (1)	0·1110 (8)	0·426 (3)	6·4 (8)
C(34)	0·376 (1)	0·1497 (7)	0·399 (3)	4·2 (6)
C(35)	0·400 (1)	0·1741 (7)	0·501 (3)	4·2 (6)
C(36)	0·433 (1)	0·1594 (7)	0·626 (3)	4·4 (7)
C(37)	0·301 (1)	0·4996 (7)	0·496 (3)	4·9 (7)
C(38)	0·295 (1)	0·4755 (6)	0·619 (3)	3·0 (6)
C(39)	0·243 (1)	0·4848 (6)	0·691 (3)	4·2 (6)
C(40)	0·155 (1)	0·5315 (8)	0·638 (3)	6·6 (9)
C(41)	0·137 (1)	0·5539 (8)	0·526 (3)	6·1 (8)
C(42)	0·168 (1)	0·5599 (8)	0·401 (3)	5·9 (7)
C(43)	0·229 (1)	0·5456 (7)	0·380 (3)	5·0 (7)
C(44)	0·253 (1)	0·5203 (7)	0·488 (3)	3·7 (6)
C(45)	0·211 (1)	0·5145 (7)	0·612 (3)	3·5 (6)
C(46)	0·445 (1)	0·5288 (7)	0·591 (3)	3·7 (6)
C(47)	0·4568 (9)	0·5479 (5)	0·727 (4)	3·8 (5)
C(48)	0·446 (1)	0·5238 (6)	0·839 (3)	3·3 (6)
C(49)	0·423 (1)	0·4537 (7)	0·851 (3)	5·0 (7)
C(50)	0·417 (1)	0·4226 (6)	0·760 (3)	4·5 (6)
C(51)	0·420 (1)	0·4253 (8)	0·613 (3)	5·4 (8)
C(52)	0·428 (1)	0·4585 (6)	0·543 (3)	3·5 (6)
C(53)	0·434 (1)	0·4911 (6)	0·631 (2)	2·9 (6)
C(54)	0·431 (1)	0·4878 (5)	0·778 (2)	3·0 (5)
C(55)	0·308 (1)	0·6188 (6)	0·745 (3)	5·0 (6)
C(56)	0·282 (1)	0·6024 (7)	0·624 (3)	3·8 (6)
C(57)	0·328 (1)	0·5961 (7)	0·526 (3)	4·6 (7)

Table 1 (cont.)

	x	y	z	B_{eq}/B_{iso}
C(58)	0.443 (1)	0.6174 (7)	0.530 (3)	4.4 (7)
C(59)	0.484 (1)	0.6412 (9)	0.602 (3)	7.1 (9)
C(60)	0.467 (1)	0.6507 (7)	0.738 (4)	6.2 (7)
C(61)	0.414 (1)	0.6477 (6)	0.791 (3)	4.8 (7)
C(62)	0.371 (1)	0.6260 (6)	0.717 (3)	5.0 (6)
C(63)	0.384 (1)	0.6120 (6)	0.580 (2)	3.0 (5)
C(64)	0.266 (1)	0.5646 (7)	0.964 (3)	4.4 (6)
C(65)	0.243 (1)	0.5273 (7)	0.951 (3)	4.9 (7)
C(66)	0.299 (1)	0.5061 (7)	0.999 (3)	4.4 (7)
C(67)	0.397 (1)	0.5212 (8)	1.150 (3)	6.2 (8)
C(68)	0.426 (1)	0.5531 (7)	1.189 (3)	5.3 (7)
C(69)	0.411 (1)	0.5881 (8)	1.154 (4)	8 (1)
C(70)	0.356 (1)	0.5973 (7)	1.073 (3)	5.2 (7)
C(71)	0.322 (1)	0.5673 (7)	1.035 (3)	3.6 (6)
C(72)	0.341 (1)	0.5269 (8)	1.057 (3)	5.5 (7)
C(73)	0.324 (1)	0.9643 (7)	0.660 (3)	4.2 (7)
C(74)	0.287 (1)	0.9372 (7)	0.604 (3)	4.5 (7)
C(75)	0.311 (1)	0.9221 (7)	0.481 (3)	4.2 (7)
C(76)	0.411 (1)	0.9396 (8)	0.346 (3)	6.2 (8)
C(77)	0.458 (1)	0.9645 (8)	0.351 (4)	6.7 (9)
C(78)	0.471 (1)	0.9870 (8)	0.476 (3)	6.1 (8)
C(79)	0.427 (1)	0.9889 (8)	0.581 (3)	5.7 (8)
C(80)	0.375 (1)	0.9660 (6)	0.581 (3)	3.6 (6)
C(81)	0.369 (1)	0.9390 (7)	0.455 (3)	4.1 (6)
C(82)	0.289 (1)	0.8331 (6)	0.841 (2)	2.7 (5)
C(83)	0.3179 (9)	0.8179 (5)	0.731 (3)	3.0 (5)
C(84)	0.294 (1)	0.8291 (7)	0.588 (3)	3.7 (6)
C(85)	0.199 (1)	0.8683 (7)	0.544 (3)	4.1 (6)
C(86)	0.150 (1)	0.8870 (8)	0.601 (3)	6.3 (8)
C(87)	0.149 (1)	0.8914 (6)	0.753 (3)	5.2 (6)
C(88)	0.192 (1)	0.8786 (7)	0.841 (3)	4.9 (7)
C(89)	0.239 (1)	0.8573 (6)	0.781 (3)	3.3 (6)
C(90)	0.247 (1)	0.8511 (7)	0.627 (3)	4.3 (7)
C(91)	0.338 (1)	0.9340 (8)	0.961 (3)	5.6 (7)
C(92)	0.396 (1)	0.9413 (9)	0.918 (4)	7.2 (9)
C(93)	0.434 (1)	0.9094 (8)	0.954 (3)	6.6 (9)
C(94)	0.401 (1)	0.8469 (9)	1.091 (3)	6.8 (9)
C(95)	0.352 (1)	0.8325 (8)	1.166 (3)	6.9 (9)
C(96)	0.299 (1)	0.8507 (7)	1.187 (3)	5.7 (7)
C(97)	0.288 (1)	0.8835 (7)	1.122 (3)	4.9 (7)
C(98)	0.332 (1)	0.9008 (7)	1.032 (3)	4.2 (6)
C(99)	0.395 (1)	0.8797 (7)	1.026 (3)	4.5 (7)
C(100)	0.435 (1)	0.8616 (6)	0.489 (3)	3.8 (6)
C(101)	0.469 (1)	0.8865 (8)	0.570 (3)	5.5 (8)
C(102)	0.485 (1)	0.8704 (6)	0.694 (3)	4.6 (6)
C(103)	0.476 (1)	0.8000 (8)	0.788 (4)	7.1 (9)
C(104)	0.455 (1)	0.7676 (6)	0.741 (4)	5.7 (6)
C(105)	0.429 (1)	0.7599 (7)	0.609 (3)	4.4 (7)
C(106)	0.418 (1)	0.7897 (7)	0.523 (3)	4.1 (6)
C(107)	0.437 (1)	0.8257 (7)	0.562 (3)	4.4 (7)
C(108)	0.467 (1)	0.2898 (7)	0.697 (3)	5.1 (7)

Table 2. Selected distances (Å) and angles (°) with e.s.d.'s in parentheses

(a) Th—C distances

Th(1)–ind. I	2.78 (3)*		Th(2)–ind. V	2.66 (3)*		Th(3)–ind. IX	2.65 (3)*
–C(1)	2.90 (3)		–C(37)	2.81 (4)		–C(73)	2.94 (3)
–C(2)	2.68 (3)		–C(38)	2.73 (3)		–C(74)	2.66 (3)
–C(3)	2.96 (3)		–C(39)	2.89 (3)		–C(75)	2.77 (3)
–C(8)	3.29 (3)		–C(44)	3.06 (3)		–C(80)	3.10 (3)
–C(9)	3.33 (2)		–C(45)	3.12 (3)		–C(81)	3.07 (3)
Th(1)–ind. II	2.61 (3)*		Th(2)–ind. VI	2.61 (3)*		Th(3)–ind. X	2.62 (3)*
–C(10)	2.72 (3)		–C(46)	2.89 (4)		–C(82)	2.85 (3)
–C(11)	2.73 (2)		–C(47)	2.78 (2)		–C(83)	2.70 (2)
–C(12)	2.89 (4)		–C(48)	2.78 (3)		–C(84)	2.86 (3)
–C(17)	2.98 (2)		–C(53)	3.03 (3)		–C(89)	3.04 (3)
–C(18)	3.03 (3)		–C(54)	2.93 (3)		–C(90)	3.02 (3)
Th(1)–ind. III	2.70 (3)*		Th(2)–ind. VII	2.70 (3)*		Th(3)–ind. XI	2.75 (4)*
–C(19)	2.84 (3)		–C(55)	2.88 (2)		–C(91)	2.97 (4)
–C(20)	2.91 (4)		–C(56)	2.73 (3)		–C(92)	2.88 (4)
–C(21)	2.89 (3)		–C(57)	2.83 (3)		–C(93)	2.93 (4)
–C(26)	3.12 (3)		–C(62)	3.20 (2)		–C(98)	3.19 (3)
–C(27)	2.99 (3)		–C(63)	3.18 (3)		–C(99)	3.12 (3)
Th(1)–ind. IV	2.61 (3)*		Th(2)–ind. VIII	2.70 (3)*		Th(3)–ind. XII	2.65 (3)*
–C(28)	2.76 (3)		–C(64)	2.81 (3)		–C(100)	2.82 (3)
–C(29)	2.69 (3)		–C(65)	2.93 (4)		–C(101)	2.73 (3)
C(30)	2.89 (3)		–C(66)	2.92 (3)		–C(102)	2.81 (3)
–C(35)	3.03 (4)		–C(71)	3.05 (3)		–C(107)	3.11 (3)
–C(36)	3.02 (3)		–C(72)	3.13 (4)		–C(108)	3.13 (3)

(b) Ring centroid–Th–ring centroid angles

I–Th(1)–II	102.7 (8)	VI–Th(2)–VII	106.6 (8)
I–Th(1)–III	111.7 (8)	VI–Th(2)–VIII	111.7 (9)
I–Th(1)–IV	110.9 (9)	VII–Th(2)–VIII	110.4 (9)
II–Th(1)–III	113.4 (9)	IX–Th(3)–X	111.6 (8)
II–Th(1)–IV	111.6 (9)	IX–Th(3)–XI	106.6 (8)
III–Th(1)–IV	106.6 (8)	IX–Th(3)–XII	109.5 (8)
V–Th(2)–VI	110.0 (8)	X–Th(3)–XI	108.4 (9)
V–Th(2)–VII	110.3 (9)	X–Th(3)–XII	106.9 (9)
V–Th(2)–VIII	107.8 (8)	XI–Th(3)–XII	113.8 (9)

* Distance to the five-membered-ring centroid.

ascribed solely to steric factors, since short intra-molecular contacts involve both the non-bridging C atoms and the bridging ones. It results, rather, from electronic factors, the negative charge of the indenyl anion residing primarily on the non-bridging C atoms. This inference is corroborated from examination of C—C bond within the indenides: most C—C bonds between the bridging C atoms are significantly longer than the average C—C distance (1.39 Å) in the cyclopentadienyl ring (Backer, Halstead & Raymond, 1976). Further, particularly short Th—C bonds are observed for the C atom at ring position 2.

These observations confirm the conclusions reported for two other tetrahedral indenide complexes, [Th-$(C_{12}H_{13})_3$]Cl (Spirlet et al., 1982) and [U$(C_9H_7)_3$]Cl (Burns & Laubereau, 1971), suggesting trihapto actinide–C π bonding with the ligand. [Th$(C_9H_7)_4$] is the first example of an organoactinide complex with a formal coordination number of 12. On the other hand, in the octahedral derivatives [U(ind)]X_3.2Y (X = halide,

Fig. 1. The crystal structure of [Th$(C_9H_7)_4$]; contents of the unit cell.

Y = neutral donor ligand) (Meunier-Pieret *et al.*, 1980; Rebizant *et al.*, 1983, 1985) the U atom is pentahapto covalently bonded to the indenyl ligand.

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Caesium Tris(*N*-bromosuccinimide)bromate(1−)

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Abstract. $Cs[Br(C_4H_4BrNO_2)_3]$, $M_r = 746\cdot8$, trigonal, $R\bar{3}$, $a = 14\cdot013$ (2), $c = 17\cdot921$ (9) Å, $V = 3047$ (1) Å^3, $Z = 6$, $D_m = 2\cdot45$ (1), $D_x = 2\cdot441$ (1) g cm^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 96\cdot6$ cm^{-1}, $F(000) = 2088$, $T = 296$ K, $R = 0\cdot047$ for 1876 observed reflections. The structure comprises trigonal pyramidal $[Br(C_4H_4BrNO_2)_3]^-$ complexes with Br···Br bond lengths of $3\cdot038$ (1) Å. The central Br$^-$ ions are located on the $\bar{3}$ axes with the Cs$^+$ ions at the centres. One of the Cs$^+$ ions is enclosed in a cage formed by two of the complexes; the other Cs$^+$ ion is surrounded by a puckered hexagonal bipyramid of six O atoms and two Br$^-$ ions.

Introduction. *N*-Bromosuccinimide (SBr: 1-bromo-2,5-pyrrolidinedione) is a well-known brominating agent (Filler, 1963; Horner & Winkelmann, 1959). In the presence of bromide salt, SBr serves to add bromine to double bonds (Braude & Waight, 1952). Bromide ion acts as a catalyst for the electron transfer oxidation of ferrocene to ferricinium ion by SBr, in all probability by forming an SBr/Br$^-$ complex which is a stronger oxidant (Eberson, Barry, Finkelstein, Moore & Ross, 1986). Finkelstein, Hart, Moore, Ross & Eberson (1986) have found evidence that 1:1 SBr/Br$^-$ com-

plexes play a vital role in the mechanism by which tetraalkylammonium bromides promote the reaction of SBr and olefins to give addition products. It was proposed that the complex (which could be isolated) decomposes slowly *via* an *X*-philic mechanism (Zefirov & Makhenkov, 1982) to form succinimide, poly-maleimide and tribromide ion. The latter is the species responsible for the addition reaction. In view of the importance of SBr/Br$^-$ complexes as intermediates in these reactions, we have determined the crystal structure of the title compound in order to study the bonding situation around the N—Br bond.

Experimental. Title compound prepared by stirring caesium bromide (5 mmol) and *N*-bromosuccinimide (5·3 mmol) in acetonitrile (100 ml) with gradual warming to 353 K, filtering the hot solution and keeping the filtrate at 273 K for 24 h. The colourless rhombohedral crystals formed were filtered off and air-dried. Density determined by flotation in $CHBr_3/CHCl_3$. Enraf-Nonius CAD-4 diffractometer with graphite mono-chromator, Mo $K\alpha$ radiation, crystal $0\cdot25 \times 0\cdot25 \times 0\cdot25$ mm. Unit-cell dimensions from 25 reflections with $12 \leq \theta \leq 18°$. Space group $R\bar{3}$. Intensities from 1/3 of reflection sphere with $0\cdot07 \leq \sin\theta/\lambda \leq 0\cdot60$ Å^{-1},