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.

References

BACKER, C. C., HALSTEAD, G. W. & RAYMOND, K. N. (1976). *Struct. Bonding (Berlin)*, **25**, 34–51.

BURNS, J. H. & LAUBEREAU, P. G. (1971). *Inorg. Chem.* **10**, 2789–2792.

Enraf–Nonius (1981). *Structure Determination Package*. Version 18. Enraf–Nonius, Delft.

HOHMANN, M. & ZIEGLER, M. (1978). Diplomarbeit of M. HOHMANN, Anorganisch-Chemisches Institut, Univ. of Heidelberg, Federal Republic of Germany.

International Tables for X-ray Crystallograpy (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MEUNIER-PIERET, J., GERMAIN, G., DECLERCQ, J.-P. & VAN MEERSSCHE, M. (1980). *Bull. Soc. Chim. Belg.* **89**, 241–245.

REBIZANT, J., SPIRLET, M. R. & GOFFART, J. (1983). *Acta Cryst.* C**39**, 1041–1043.

REBIZANT, J., SPIRLET, M. R. & GOFFART, J. (1985). *Acta Cryst.* C**41**, 334–336.

SPIRLET, M. R., REBIZANT, J. & GOFFART, J. (1982). *Acta Cryst.* B**38**, 2400–2404.

Acta Cryst. (1986). C**42**, 1500–1502

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

BY CHRISTER SVENSSON AND JÖRGEN ALBERTSSON

Inorganic Chemistry 2, *Chemical Center, University of Lund, PO Box* 124, *S*-22100 *Lund, Sweden*

AND LENNART EBERSON

Organic Chemistry 3, *Chemical Center, University of Lund, PO Box* 124, *S*-221 00 *Lund, Sweden*

(*Received* 16 *April* 1986; *accepted* 20 *June* 1986)

Abstract. $Cs[Br(C_4H_4BrNO_2)_3]$, $M_r = 746.8$, trigonal, $R\bar{3}$, $a = 14.013$ (2), $c = 17.921$ (9) Å, $V = 3047$ (1) Å^3, $Z = 6$, $D_m = 2.45$ (1), $D_x = 2.441$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 96.6$ cm^{-1}, $F(000) = 2088$, $T = 296$ K, $R = 0.047$ for 1876 observed reflections. The structure comprises trigonal pyramidal $[Br(C_4H_4BrNO_2)_3]^-$ complexes with Br···Br bond lengths of 3.038 (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^- complexes 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, polymaleimide 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 monochromator, Mo $K\alpha$ radiation, crystal 0.25 × 0.25 × 0.25 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 $0.07 \leq \sin\theta/\lambda \leq 0.60$ Å^{-1},

0108-2701/86/111500-03$01.50

$0 \le h \le 16$, $-h \le k \le 16$ and $-21 \le l \le 21$; $\omega/2\theta$ scan, $\Delta\omega = 0{\cdot}60° + 0{\cdot}50° \tan\theta$, max. counting time 180 s; three control reflections (327, $\bar{3}7\bar{4}$, $43\bar{5}$) every 2 h, no significant variation. 2677 unique reflections measured, 1876 observed with $I \ge 3\sigma_c(I)$ (σ_c from counting statistics). Lorentz, polarization and absorption corrections, transmission factor between 0·13 and 0·21. Cs and Br atoms located by direct methods (*MULTAN*80: Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); C, N and O atoms from $\Delta\rho$ maps. H-atom positions calculated with fixed thermal parameter $U_{iso} = 0{\cdot}060$ Å^2 (CH_2 groups). Full-matrix least-squares refinement of structural model minimizing $\sum w(\Delta F)^2$, $w = [\sigma_c^2(|F_o| + (0{\cdot}05|F_o|)^2 + 5{\cdot}00]^{-1}$. Isotropic secondary-extinction corrections, $g = 8{\cdot}4(5) \times 10^3$, r.m.s. mosaic spread 6·9″ (Becker & Coppens, 1974). Refinement converged to $R = 0{\cdot}047$, $wR = 0{\cdot}062$, $S = 1{\cdot}047$, $(\Delta/\sigma) < 0{\cdot}06$. The δR plot (Abrahams & Keve, 1971) is close to linear with slope 1·01 and intercept 0·06. Final $\Delta\rho$ map without significant features; max. and min. values 0·65 and −0·45 e Å^{-3}. Atomic scattering factors for ions Cs^+, Br^- and neutral atoms in SBr, and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All computer programs used are described by Lundgren (1982).

Discussion. Atomic coordinates are given in Table 1, selected bond lengths and bond angles in Table 2.* The main feature of the structure is the trigonal pyramidal complex $[Br(SBr)_3]^-$ formed by three SBr molecules bonded to a Br^- ion. This complex and the environments of the two Cs^+ ions are depicted in Fig. 1. The Br(2) ion is located above the centre of a Br(1) triangle with Br(1)—Br(2) 0·833 (1) Å shorter than the Br(1)—Br(1) contact distances. The Br(1)—Br(2)—Br(1) angle of 79·2 (1)° is about 20° larger than expected for non-bonded Br(1)···Br(2) contacts. Taking the coordination number 3 of the Br^- ion into account the SBr···Br^- distances are comparable to the long Br···Br^- bond distances in unsymmetrical Br_3^- ions. In $CsBr_3$ the distances are Br—Br: 2·440 (6), Br···Br^-: 2·698 (6) Å (Breneman & Willet, 1969) and in $(PBr_4)Br_3$ they are Br—Br: 2·39 (1), Br···Br^-: 2·91 (1) Å (Breneman & Willet, 1967). The $[Br(SBr)_3]^-$ complex bears some resemblance to the CBr_4/Br^- complex in solid $[(C_6H_5)_4P]^+[CBr_5]^-$ (Lindner & Kitschke-von Gross, 1976) where the Br···Br^- interaction is much weaker, the average distance being 3·260 (4) Å.

* Lists of structure amplitudes, anisotropic thermal parameters and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43166 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$, $\times 10^5$ *for* Cs *and* Br) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$, Å$^2 \times 10^4$ *for* Cs *and* Br)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cs(1)	0	0	0	344 (3)
Cs(2)	0	0	50000	389 (3)
Br(2)	0	0	20372 (5)	334 (3)
Br(1)	279 (5)	16085 (5)	31855 (3)	360 (3)
N(1)	85 (4)	2626 (4)	3883 (3)	32 (2)
C(2)	769 (5)	2954 (5)	4499 (3)	33 (2)
O(2)	1375 (4)	2589 (4)	4647 (3)	49 (2)
C(3)	589 (6)	3769 (6)	4916 (4)	42 (3)
C(4)	−360 (6)	3789 (5)	4526 (4)	40 (3)
C(5)	−647 (5)	3011 (5)	3875 (4)	36 (3)
O(5)	−1361 (4)	2761 (4)	3421 (3)	54 (2)
H(31)	425	3568	5426	60
H(32)	1233	4477	4916	60
H(41)	9028	3568	4851	60
H(42)	9837	4512	4367	60

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

The superscripts indicate the following sites: (i) $x-y, x, 1-z$; (ii) $-\frac{2}{3}+y, -\frac{1}{3}+y-x, \frac{2}{3}-z$; (iii) $-y, x-y, z$; (iv) $\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$; (v) $-\frac{1}{3}+y-x, \frac{1}{3}-x, \frac{1}{3}+z$; (vi) $\frac{1}{3}+x-y, \frac{2}{3}+x, \frac{2}{3}-z$.

Cs(1)—O(5)	(6×)	3·244 (5)	Cs(2)—O(2)	(6×)	3·207 (5)
Cs(1)—Br(2)	(2×)	3·651 (2)	Cs(2)—Br(1)	(6×)	3·946 (1)
O(2)—O(2^{i})	(2×)	3·389 (6)	O(5)—O(5^{ii})	(2×)	3·255 (5)
Br(1)—Br(2)	(3×)	3·038 (1)	Br(1)—Br(1^{iii})	(2×)	3·871 (1)
Br(1)—N(1)		1·869 (5)	Br(1)—O(2^{iv})		3·780 (5)
N(1)—C(2)		1·381 (7)	N(1)—O(2^{i})		3·183 (7)
C(2)—O(2)		1·219 (8)	C(2)—O(2^{i})		2·968 (8)
C(2)—C(3)		1·488 (9)	C(3)—O(2^{i})		3·126 (8)
C(3)—C(4)		1·515 (10)	C(3)—O(5^{v})		3·501 (8)
C(4)—C(5)		1·507 (9)	C(4)—O(2^{i})		3·319 (8)
C(5)—O(5)		1·198 (8)	C(4)—O(5^{vi})		3·380 (8)
C(5)—N(1)		1·377 (8)	C(5)—O(2^{i})		3·328 (8)
Br(1)—C(2^{iv})		3·765 (6)	C(5)—O(5^{vi})		3·506 (8)
Br(1)—N(1)—C(2)		123·1 (4)	C(2)—C(3)—C(4)		105·7 (5)
Br(1)—N(1)—C(5)		122·4 (4)	C(3)—C(4)—C(5)		105·3 (5)
C(2)—N(1)—C(5)		114·1 (5)	C(4)—C(5)—O(5)		128·3 (6)
N(1)—C(2)—C(3)		107·4 (5)	N(1)—C(5)—C(4)		107·0 (5)
N(1)—C(2)—O(2)		123·3 (5)	N(1)—C(5)—O(5)		124·7 (6)
O(2)—C(2)—C(3)		129·3 (6)			

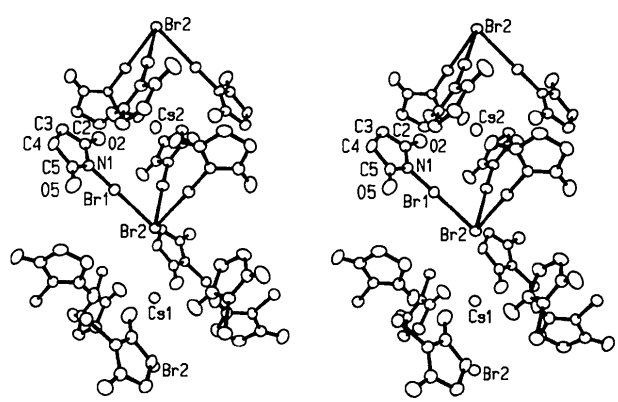

Fig. 1. Stereoview of the $[Br(SBr)_3]^-$ complex and the Cs coordination.

Apart from the N(1)—Br(1) bond length the geometry of the SBr molecule does not differ from that of pure solid SBr (Jabay, Pritzkow & Jander, 1977), *N*-chlorosuccinimide (Brown, 1961) and succinimide (Mason, 1961). The N(1)—Br(1) bond is 0·052 (8) Å longer in the $[Br(SBr)_3]^-$ complex than in pure SBr. The endocyclic torsion angles* indicate a small twist of the succinimide ring. The Br(1) atom is in the least-squares plane through the N and C atoms of SBr, but both O atoms are on the same side of the plane. The angle between the planes through O(2)C(2)N(1)C(3) and O(5)C(5)N(1)C(4) is 8·0 (2)°.

The Cs(1) ion is surrounded by six O(5) atoms and two Br(2) ions in a slightly puckered hexagonal bipyramid. The Cs(2) ion is enclosed in a cage formed by two $[Br(SBr)_3]^-$ complexes. It has six O(2) atoms as nearest neighbours forming a puckered hexagon. Twelve-coordination is completed by six Br(1) atoms at 3·946 (1) Å. There are six C(2) atoms at 3·826 (6) Å.

The $R\bar{3}$ symmetry locates the SBr molecules in six columns per unit cell with the centres of the five-rings very near the 3_1 axes. Each $[Br(SBr)_3]^-$ complex is bonded to five Cs^+ ions, two of which are located on the same $\bar{3}$ axis as the central Br(2) ion (*cf.* Fig. 1) with the other three on three adjacent $\bar{3}$ axes. The Cs—O, Cs—Br and Br···Br bonds connect the structure in three dimensions. There are only a few short intermolecular contact distances (*cf.* Table 2).

The structure of $Cs[Br(SBr)_3]$ illustrates well the properties to be expected for an SBr/Br^- complex capable of undergoing the reactions described in the introduction. There is a distinct SBr···Br bond and the N—Br bond is slightly elongated. The bonding situation around the N atom facilitates the *X*-philic mechanism in which the Br—Br bond is formed with the succinimide anion leaving synchronously. Also, the formation of the Br—Br bond is expected to enhance the oxidizing power of the complex.

* See deposition footnote.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.
BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A**30**, 129–153.
BRAUDE, E. A. & WAIGHT, E. S. (1952). *J. Chem. Soc.* pp. 1116–1122.
BRENEMAN, G. L. & WILLET, R. D. (1967). *Acta Cryst.* **23**, 467–471.
BRENEMAN, G. L. & WILLET, R. D. (1969). *Acta Cryst.* B**25**, 1073–1076.
BROWN, R. N. (1961). *Acta Cryst.* **14**, 711–715.
EBERSON, L., BARRY, J. E., FINKELSTEIN, M., MOORE, W. M. & ROSS, S. D. (1986). *Acta Chem. Scand. Ser. B*, **40**, 402–403.
FILLER, R. (1963). *Chem. Rev.* **63**, 21–43.
FINKELSTEIN, M., HART, S. A., MOORE, W. M., ROSS, S. D. & EBERSON, L. (1986). *J. Org. Chem.* In the press.
HORNER, L. & WINKELMANN, E. H. (1959). *Angew. Chem.* **71**, 349–392.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht).
JABAY, O., PRITZKOW, H. & JANDER, J. (1977). *Z. Naturforsch. Teil B*, **32**, 1416–1470.
LINDNER, H. J. & KITSCHKE-VON GROSS, B. (1976). *Chem. Ber.* **109**, 314–319.
LUNDGREN, J.-O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MASON, R. (1961). *Acta Cryst.* **14**, 720–724.
ZEFIROV, N. S. & MAKHENKOV, D. I. (1982). *Chem. Rev.* **82**, 615–624.

Acta Cryst. (1986). C**42**, 1502–1505

Structure du Complexe Uranyle Pentahydraté de l'Acide Hydroxyméthylphosphonique

PAR A. BRITEL,* M. WOZNIAK,† J. C. BOIVIN,* G. NOWOGROCKI* ET D. THOMAS*

Equipe de Cristallochimie et Physicochimie du Solide UA CNRA n° 452 et Laboratoire d'Hydrométallurgie, Ecole Nationale Supérieure de Chimie de Lille, BP 108, 59652 Villeneuve d'Ascq CEDEX, France

(*Reçu le 18 décembre 1985, accepté le 2 mai 1986*)

Abstract. Uranyl hydroxymethylphosphonate pentahydrate, $UO_2(HOCH_2PO_3).5H_2O$, $M_r = 470·1$, monoclinic, $P2_1/c$, $a = 7·004$ (9), $b = 8·579$ (4), $c = 16·754$ (9) Å, $\beta = 90·65$ (5)°, $V = 1007$ (2) Å^3, $Z = 4$, $D_m = 3·04$ (5), $D_x = 3·10$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 154$ cm^{-1}, $F(000) = 856$, $T = 298$ K, $R = 0·04$ for 1495 independent reflexions. Linear UO_2^{2+} ions are coordinated to five additional oxygens located in a plane perpendicular to the uranyl axis. The O of the

* Equipe de Cristallochimie et Physicochimie du Solide.
† Laboratoire d'Hydrométallurgie.

0108-2701/86/111502-04$01.50