

Structure of Tetraethylammonium Mono(*N*-bromosuccinimide)bromate(1-)

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$N(C_2H_5)_4 [BrC_4H_4BrNO_2]$, $M_r = 388.14$, monoclinic, $P2_1/n$, $a = 18.091(3)$, $b = 8.925(2)$, $c = 10.587(4)$ Å, $\beta = 103.10(2)^\circ$, $V = 1664.9(5)$ Å³, $Z = 4$, $D_x = 1.549$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu = 48.20$ cm⁻¹, $F(000) = 784$, $T = 296$ K, $R = 0.062$ for 1731 observed reflections. *N*-Bromosuccinimide and bromide form a linear 1:1 complex with $Br \cdots Br = 2.836(1)$ Å and $N-Br = 1.896(6)$ Å.

Apart from possessing its well-known radical-mediated brominating reactivity, *N*-bromosuccinimide (1-bromo-2,5-pyrrolidinedione; abbreviated SBr) is a good electron acceptor, forming stable complexes with typical donor species, such as 1,4-diazabicyclo[2.2.2]octane,¹ succinimide anion² and halogenide ion.³ If the standard potential of the donor atom is low enough, SBr will act as a one-electron transfer oxidant.⁴

There is evidence that SBr/Br⁻ complexes play an important role in the reactions of SBr. Thus it has been shown⁵ that the SBr/Br⁻ complex slowly decomposes in solution to give such succinimide, polymaleimide and tribromide ion, this last species being responsible for the addition of bromine observed when SBr is allowed to react with olefins in the presence of a source of bromide ion.⁶ In the electron-transfer mediated oxidation of ferrocene to ferrocinium ion by SBr, the addition of bromide ion strongly enhances the rate of electron transfer, presumably via the SBr/Br⁻ complex.⁴

In order to study the possible formation of SBr \cdots Br⁻ bonds and their influence upon the N-Br bond in SBr, we determined the crystal structure of SBr \cdot $\frac{1}{3}$ CsBr⁷ and found distinct Br-Br bonds of length 3.038(1) Å between Br⁻ and SBr: about 0.8 Å shorter than normal Br \cdots Br contact distances. Since the bromide ion

of this complex is bound to three SBr molecules, the Br-Br bond presumably is not optimally strong, and we have therefore prepared a 1:1 complex, SBr \cdot Br⁻Et₄N⁺, to elucidate the effect of the increased availability of electrons for bond formation from the bromide ion. This paper describes the crystal structure of this complex.

Experimental

The title compound was prepared as described in Ref. 5. The yellowish stout prismatic crystals formed were filtered off and air-dried. A crystal of dimensions 0.25 \times 0.25 \times 0.25 mm³ was selected for X-ray experiments. The measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite monochromator and MoK α radiation ($\lambda = 0.71073$ Å). Cell dimensions were determined by least-squares calculations from the θ angles of 25 strong reflections in the range $26.0 \leq 2\theta \leq 37.0^\circ$. Reflections $h0l$, $h+l$ odd, and $0k0$, k odd, are systematically absent indicating monoclinic space group $P2_1/n$. Crystal data are given in the abstract. 2919 independent reflections with $-20 \leq h \leq 20$, $0 \leq k \leq 10$, $0 \leq l \leq 12$ and $\sin \theta/\lambda \leq 0.60$ Å⁻¹ were measured with $\omega/2\theta$ scans and $\Delta\omega = 60^\circ + 0.50^\circ \tan \theta$. A maximum counting time of 240 s resulted in $\sigma_c(I)/I \leq 0.030$ for a majority of the reflections [$\sigma_c(I)$ is based on counting statistics]. The intensities of three standard reflections (8-5-3, 1 7-1 and 10 0 2) were measured every

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second hour. The crystal decomposes slowly causing a linear decline of the intensities with exposure time; in 104 h the decrease was, on average, 17.1%. The intensity data set was rescaled with the fitted linear equation. The quantities I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects. Before we had time to determine the morphology of the crystal its disintegration had gone so far that many faces were disrupted. For the absorption correction its shape was then approximated with a sphere of radius $R = 0.15$ mm ($\mu R = 0.723$). The range of transmission factors was 0.353–0.364.

Structure determination and refinement. The structure was solved by using the SHELXS-86 program.⁸ All non-hydrogen atoms were located in the E -maps. Subsequent electron-density difference maps gave the positions of the hydrogen atoms. The structure was refined by the least-squares method minimizing $\sum w(F_o - F_c)^2$ with $w = [\sigma_c^2(F_o) + (0.06F_o)^2]^{-1}$. 1188 reflections with $I < 3\sigma_c(I)$ were given zero weight. The program used was UPALS⁹ with atomic scattering factors for neutral atoms and anomalous dispersion corrections taken from Ref. 10. The non-hydrogen atoms were assigned anisotropic thermal parameters and the hydrogen atoms were assigned the fixed isotropic thermal parameter $U_{iso} = 0.080$ Å². An isotropic extinction correction was made in the least-squares refinement with coefficient $q = 0.69(14) \times 10^4$ corresponding to a mosaic spread of 8.5". The maximum correction [on $F_o(301)$] was 1.32. Refinement converged to $R = 0.062$, $R_w = 0.072$, $S = 1.156$ and $\Delta/\sigma < 0.15$ for

non-hydrogen atoms and <0.50 for hydrogen atoms. The δR plot¹¹ has slope 1.06 and intercept 0.07, i.e. the random errors on F_o are, on average, correctly estimated and there are only small systematic errors affecting the model. The final $\Delta\rho$ map was almost featureless with the max. and min. values $+0.57$ and -0.45 e Å⁻³ located near the bromine atoms.

Results

Atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2.* The structure contains linear 1:1 complexes between the bromide ions and the *N*-bromosuccinimide molecules as shown in Fig. 1. The Br(1)⋯Br(2) distance is about the same as the long Br⋯Br⁻ distance in unsymmetrical Br₃⁻ ions: 2.836(1) Å compared with 2.298(6) Å in CsBr₃¹² and 2.91(1) Å in PBr₇.¹³ The distance is 0.202(1) Å shorter than in the [Br(SBr)₃]⁻ complex formed in the previously investigated caesium compound SBr · $\frac{1}{3}$ CsBr.⁷ The Br⋯Br bond might thus be slightly stronger in the 1:1 than in the 1:3 complex as may be further inferred from a comparison of the NBr bond distances, 1.896(6) Å in the 1:1 and 1.869(5) Å in the 1:3 complex.

The bond distances and angles in the SBr molecule which do not involve Br are the same in the 1:1 and 1:3 complexes within the limits of error,

*Lists of anisotropic thermal parameters for the non-hydrogen atoms, selected torsion angles, least-squares plane data and structure factors are available on request from one of the authors (J.A.)

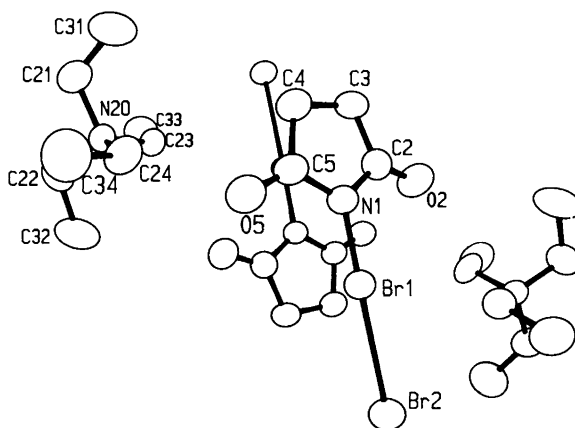


Fig. 1. A perspective drawing, viewed in the $[-101]$ direction, of a pair of 1:1 SBr/Br⁻ complexes and two tetraethylammonium ions with the molecular numbering. The thermal ellipsoids are scaled to include 50% probability.

Table 1. Final atomic coordinates with e.s.d.s of tetraethylammonium mono(*N*-bromosuccinimide)-bromate (1⁻).^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso} /Å ²
Br(1)	0.92661(4)	-0.10141(8)	0.66173(7)	0.0478(3)
Br(2)	0.90736(4)	-0.39915(9)	0.74224(8)	0.0583(3)
N(1)	0.9466(3)	0.0934(7)	0.6063(6)	0.049(2)
O(2)	1.0681(3)	0.1126(7)	0.7268(6)	0.073(2)
C(2)	1.0148(4)	0.1654(9)	0.6509(7)	0.050(3)
C(3)	1.0097(5)	0.3159(10)	0.5867(9)	0.056(3)
C(4)	0.9325(5)	0.3197(11)	0.4939(10)	0.064(3)
C(5)	0.8951(4)	0.1756(9)	0.5164(8)	0.054(3)
O(5)	0.8312(4)	0.1349(7)	0.4647(7)	0.079(3)
N(20)	0.8352(3)	0.2259(7)	0.0260(5)	0.047(2)
C(21)	0.8193(6)	0.3875(11)	-0.0202(11)	0.063(3)
C(31)	0.8539(9)	0.5076(14)	0.0681(14)	0.092(5)
C(22)	0.7963(6)	0.1239(11)	-0.0818(10)	0.069(3)
C(32)	0.8057(9)	-0.0435(16)	-0.0514(17)	0.108(7)
C(23)	0.9203(4)	0.1975(11)	0.0599(8)	0.053(3)
C(33)	0.9593(6)	0.2165(13)	-0.0511(11)	0.072(4)
C(24)	0.8092(5)	0.1979(13)	0.1494(9)	0.064(4)
C(34)	0.7257(6)	0.2180(18)	0.1366(14)	0.094(5)
H(31)	1.007(6)	0.362(10)	0.649(10)	0.08
H(32)	1.049(5)	0.323(11)	0.531(9)	0.08
H(41)	0.912(6)	0.380(11)	0.535(11)	0.08
H(42)	0.944(5)	0.297(12)	0.424(9)	0.08
H(211)	0.837(6)	0.386(11)	-0.085(10)	0.08
H(212)	0.778(6)	0.392(11)	-0.029(10)	0.08
H(311)	0.833(5)	0.630(11)	0.031(9)	0.08
H(312)	0.844(6)	0.507(13)	0.136(10)	0.08
H(313)	0.908(5)	0.495(11)	0.130(9)	0.08
H(221)	0.737(6)	0.152(11)	-0.082(9)	0.08
H(222)	0.819(5)	0.165(11)	-0.165(9)	0.08
H(321)	0.791(7)	-0.077(13)	-0.109(11)	0.08
H(322)	0.871(6)	-0.091(10)	-0.043(9)	0.08
H(323)	0.791(5)	-0.069(11)	0.054(10)	0.08
H(231)	0.941(5)	0.279(11)	0.134(9)	0.08
H(232)	0.924(5)	0.091(10)	0.105(10)	0.08
H(331)	0.947(5)	0.307(13)	-0.103(9)	0.08
H(332)	1.018(5)	0.196(12)	-0.001(8)	0.08
H(333)	0.932(5)	0.145(11)	-0.134(10)	0.08
H(241)	0.830(6)	0.102(10)	0.168(10)	0.08
H(242)	0.833(5)	0.248(12)	0.210(10)	0.08
H(341)	0.722(6)	0.315(13)	0.147(11)	0.08
H(342)	0.691(6)	0.175(13)	0.079(10)	0.08
H(343)	0.722(4)	0.196(12)	0.239(9)	0.08

^aFor the non-hydrogen atoms the equivalent isotropic temperature factor is calculated from the average of the anisotropic temperature factor over all directions.

and do not differ from those in pure SBr, *N*-chlorosuccinimide and succinimide.¹⁴⁻¹⁶ As in the 1:3 complex the endocyclic torsion angles indicate a small twist of the succinimide ring in the present compound. The r.m.s. deviation from the

least-squares plane through the N and C atoms of SBr is 0.015 Å, with Br(1) 0.025(1) and Br(2) 0.214(1) Å from the plane. The N-Br...Br angle is 175.6(2)° as compared with 178.4(2)° in the 1:3 complex.

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

Distances		Angles	
Br(1)–Br(2)	2.836(1)	N(1)–Br(1)–Br(2)	175.8(2)
Br(1)–N(1)	1.896(6)	Br(1)–N(1)–C(2)	122.8(5)
N(1)–C(2)	1.376(10)	Br(1)–N(1)–C(5)	123.6(5)
C(2)–O(2)	1.203(10)	C(2)–N(1)–C(5)	113.6(6)
C(2)–C(3)	1.498(12)	N(1)–C(2)–C(3)	107.8(6)
C(3)–C(4)	1.515(13)	N(1)–C(2)–O(2)	124.5(8)
C(4)–C(5)	1.507(9)	O(2)–C(2)–C(3)	127.7(7)
C(5)–O(5)	1.216(10)	C(2)–C(3)–C(4)	105.5(7)
C(5)–N(1)	1.382(10)	C(3)–C(4)–C(5)	105.1(8)
		C(4)–C(5)–O(5)	127.0(8)
		N(1)–C(5)–C(4)	107.9(7)
		N(1)–C(5)–O(5)	125.1(7)
N(20)–C(21)	1.529(12)	C(21)–N(20)–C(22)	107.9(7)
C(21)–C(31)	1.466(17)	C(21)–N(20)–C(23)	109.9(6)
N(20)–C(22)	1.505(12)	C(21)–N(20)–C(24)	111.1(7)
C(22)–C(32)	1.530(18)	C(22)–N(20)–C(23)	111.0(6)
N(20)–C(23)	1.520(9)	C(22)–N(20)–C(24)	111.9(7)
C(23)–C(33)	1.512(13)	C(23)–N(20)–C(24)	105.4(6)
N(20)–C(24)	1.507(10)	N(20)–C(21)–C(31)	117.6(9)
C(24)–C(34)	1.496(14)	N(20)–C(22)–C(32)	114.9(9)
		N(20)–C(23)–C(33)	115.1(7)
		N(20)–C(24)–C(34)	114.2(8)

The geometry of the tetraethylammonium ion is quite well determined. A comparison with previous investigations of this geometry, e.g. the one described in Ref. 17, shows that there are no unusual values among the various C–C and C–N bond lengths and C–N–C and N–C–C bond angles. The N–C–C angles are all significantly larger than the tetrahedral angle.

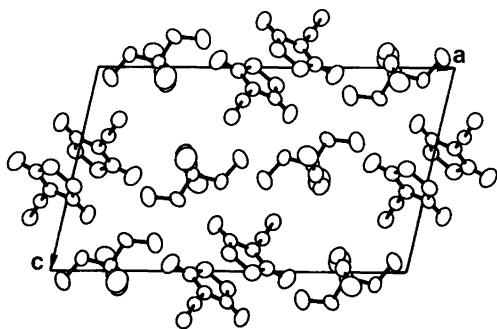


Fig. 2. The molecular packing of the SBr/Br⁻ complexes and the tetraethylammonium ions. The unit-cell content is projected onto the *ac* plane. Thermal ellipsoids as in Fig. 1.

Fig. 2 shows the molecular packing of the 1:1 complex and the tetraethylammonium ion. The complexes form van der Waals bonded pairs of antiparallel molecules about the $\frac{1}{2}y0$ and $0y\frac{1}{2}$ screw axes. The molecules are about 3.7 Å apart in each pair. The tetraethylammonium ions are located in layers parallel to the (101) planes. These layers are intercalated between the layers formed by the complex columns.

The structure of the 1:1 SBr/Br⁻ complex is in agreement with the proposed X-philic mechanism for the addition of bromine to double bonds.⁵ The structure of the activated complex should be quite similar to that investigated with an elongated N–Br bond. The existence of such a complex is compatible with the synchronous formation of the succinimide anion and the covalent Br–Br bond.

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