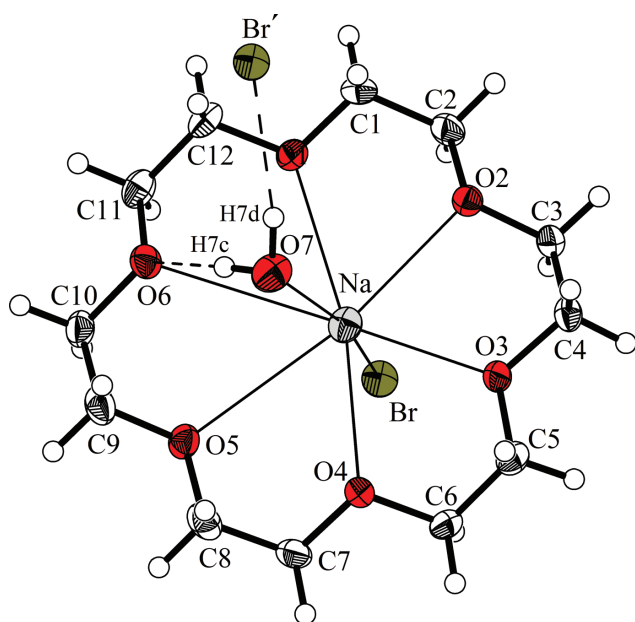


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# Crystal structure of (1,4,7,10,13,16-hexaoxacyclooctadecane- $\kappa^6 O_6$ ) sodium bromide hydrate, $[Na(18-crown-6)]Br \cdot H_2O$ , $C_{12}H_{26}BrNaO_7$



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## Abstract

$C_{12}H_{26}BrNaO_7$ , monoclinic,  $Pc$  (no. 7),  $a = 7.9362(6)$  Å,  $b = 14.1331(7)$  Å,  $c = 7.7734(6)$  Å,  $\beta = 96.701(6)^\circ$ ,  $V = 865.93(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{gt}(F) = 0.0257$ ,  $wR_{ref}(F^2) = 0.0598$ ,  $T = 173(2)$  K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless fragment
Size:	0.30 × 0.25 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
$\mu$ :	2.43 mm <sup>-1</sup>
Diffractometer, scan mode:	STOE StadiVari, $\omega$
$\theta_{max}$ , completeness:	26.0°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	22969, 3392, 0.030
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2 \sigma(I_{obs})$ , 2988
$N(param)_{refined}$ :	196
Programs:	X-AREA [1], SHELX [2, 3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{iso}^*/U_{eq}$
Br	0.3677(2)	0.24930(3)	0.5761(2)	0.02736(12)
Na	0.5000	0.22716(11)	0.2500	0.0267(4)
O1	0.1938(4)	0.2932(2)	0.0714(4)	0.0246(6)
O2	0.2748(4)	0.09921(18)	0.1386(4)	0.0218(6)
O3	0.5714(4)	0.06417(17)	0.3444(4)	0.0254(6)
O4	0.8154(4)	0.20027(18)	0.4065(4)	0.0231(6)
O5	0.7341(4)	0.39236(19)	0.3238(4)	0.0263(6)
O6	0.4532(4)	0.4303(2)	0.0857(5)	0.0253(7)
C1	0.0995(6)	0.2167(3)	-0.0120(6)	0.0292(9)
H1A	0.1488	0.1981	-0.1183	0.035*
H1B	-0.0197	0.2361	-0.0451	0.035*
C2	0.1064(5)	0.1351(3)	0.1116(6)	0.0281(9)
H2A	0.0705	0.1561	0.2233	0.034*
H2B	0.0278	0.0847	0.0637	0.034*
C3	0.2875(5)	0.0228(3)	0.2593(6)	0.0239(8)
H3A	0.2090	-0.0287	0.2165	0.029*
H3B	0.2563	0.0446	0.3724	0.029*
C4	0.4664(6)	-0.0127(3)	0.2799(6)	0.0234(8)
H4A	0.4788	-0.0665	0.3622	0.028*
H4B	0.4985	-0.0344	0.1671	0.028*
C5	0.7393(5)	0.0382(3)	0.4053(6)	0.0269(9)
H5A	0.8046	0.0259	0.3066	0.032*
H5B	0.7399	-0.0200	0.4763	0.032*
C6	0.8175(6)	0.1192(3)	0.5131(6)	0.0262(8)
H6A	0.7521	0.1313	0.6118	0.031*
H6B	0.9357	0.1034	0.5596	0.031*
C7	0.8902(6)	0.2793(3)	0.5033(6)	0.0292(9)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H7A	1.0051	0.2625	0.5584	0.035*
H7B	0.8200	0.2971	0.5954	0.035*
C8	0.9006(5)	0.3601(3)	0.3813(7)	0.0315(10)
H8A	0.9680	0.4121	0.4404	0.038*
H8B	0.9574	0.3394	0.2808	0.038*
C9	0.7328(6)	0.4685(3)	0.2041(6)	0.0305(9)
H9A	0.7731	0.4464	0.0952	0.037*
H9B	0.8090	0.5196	0.2532	0.037*
C10	0.5558(6)	0.5043(3)	0.1690(6)	0.0287(9)
H10A	0.5127	0.5225	0.2789	0.034*
H10B	0.5523	0.5607	0.0932	0.034*
C11	0.2771(6)	0.4537(3)	0.0635(7)	0.0284(10)
H11A	0.2590	0.5138	−0.0015	0.034*
H11B	0.2356	0.4618	0.1779	0.034*
C12	0.1830(6)	0.3757(3)	−0.0337(6)	0.0278(9)
H12A	0.0627	0.3940	−0.0637	0.033*
H12B	0.2327	0.3632	−0.1425	0.033*
O7	0.5955(5)	0.2589(2)	−0.0307(5)	0.0349(7)
H7C	0.566(7)	0.316(5)	−0.020(8)	0.052*
H7D	0.539(9)	0.248(3)	−0.136(10)	0.052*

### Source of material

[Na(18-crown-6)]Br·H<sub>2</sub>O was crystallized from an aqueous solution of equimolar amounts of NaBr and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). 103 mg NaBr (1 mmol, Merck, p.a.) and 264 mg 18-crown-6 (1 mmol; Merck, p.a.) were dissolved in 5 mL H<sub>2</sub>O, and the solution was stored at room temperature until the water was almost completely evaporated. After several weeks colourless, column-shaped crystals of the title compound were grown.

### Experimental details

The crystal structure has been refined as an inversion twin with a Flack parameter of 0.212(12). All H atoms have been located from the difference Fourier map and can be refined freely resulting in virtually the same residual values as presented in the final refinement, e.g.  $wR_{\text{ref}}(F^2) = 0.0567$  instead of 0.0570. However, to reduce the number of parameters the methylene H atoms have been refined using a riding model with *U*<sub>iso</sub> set to 1.2 *U*<sub>eq</sub>(C). The H atoms of the water molecule are refined with free positional parameters and an *U*<sub>iso</sub> of 1.5 *U*<sub>eq</sub>(O) [3].

### Comment

[Na(18-crown-6)]Br·H<sub>2</sub>O has been obtained for the first time by accident in the course of the investigation of ionic ozonides [5, 6] and was prepared purely by crystallisation from aqueous solution of NaBr and 18-crown-6. The crystal structure

consists of sodium cations which are coordinated by one bromide anion, one crown ether molecule, and one water molecule, respectively, with one formula as asymmetric unit. All complexes are oriented in the same direction e.g. the Br anions are situated at higher *z* coordinates than the coordinated Na cations so the non-centrosymmetry is obvious. The Na<sup>+</sup> ion is in plane with the crown ether molecule, however, it is considerably off-centred with one short (Na–O3 2.464(3) Å), two medium (Na–O2 2.618(3) Å, Na–O4 2.679(3) Å), and three Na–O distances longer than 2.8 Å indicating that 18-crown-6 is slightly too large for Na<sup>+</sup> [7]. While the mean Na–O value of 2.786 Å excellently fits with the six almost equal Na–O bonds of 2.781–2.833 Å found in [Na(18-crown-6)]Br<sub>3</sub> [8], only the shortest bond represents a more usual Na–O bond length of about 2.40–2.45 Å as observed for similar coordination numbers in [Na(15-crown-5)]Br [9] or in binary compounds [5, 10, 11]. In compounds containing 18-crown-6 such short bonds can be achieved by distortion of the sequestering molecules agent like the strongly folded crown ether in [Na(18-crown-6)]I [12]. In the present case a closer packing is realized by the additional coordination by one water molecule and the Br anion at opposite sides of the crown ether. The Na–O bond of 2.434(4) Å is in an expected range, while the Na–Br distance of 2.871(2) Å is relatively short with respect to NaBr (2.985 Å) and NaBr·2H<sub>2</sub>O (2.966 Å, 2.974 Å) [13], but, however, longer than in [Na(15-crown-5)]Br (2.773 Å) [9]. The water molecule forms hydrogen bonds to the Br anion of the neighbouring complex (O7–H7d 0.90(7), H7d–Br' 2.48(8), O7–Br' 3.368(3) Å; O7–H7d–Br' 169(4)°) as well as to one oxygen atom of the crown ether (O7–H7c 0.85(6), H7c–O6 2.06(6), O7–O6 2.865(4) Å; O7–H7c–O6 157(6)°). This special arrangement seems to be the reason for the asymmetric coordination of the Na/18-crown-6 complex. Taking into account the hydrogen bonds, the complex molecules form strands along the crystallographic *c* axis. The compound is not stable at normal conditions in air. After removing the mother liquor completely, the dry compound decomposes with NaBr as the only solid residue.

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