organic compounds

Tetra-n-butylammonium bromide–water (1/38)

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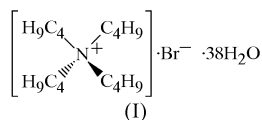
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Tetra-n-butylammonium bromide forms the title semi-clathrate hydrate crystal, $C_{16}H_{36}N^+ \cdot Br^- \cdot 38H_2O$, under atmospheric pressure. The cation and anion lie at sites with mm symmetry and seven water molecules lie at sites with m symmetry in space group Pmma. Br^- anions construct a cage structure with the water molecules. Tetra-n-butylammonium cations are disordered and are located at the centre of four cages, viz. two tetrakaidecahedra and two pentakaidecahedra in ideal cage structures, while all the dodecahedral cages are empty.

Comment

Clathrate hydrate crystals consist of cage structures composed of water molecules, and each cage can encage a molecule that would otherwise be a gas or volatile liquid. The structures consist of a combination of several types of cages, depending on the encaged gas molecules (Sloan, 1989). Clathrate hydrates encaging gas molecules (gas hydrates) are stable only under high pressure and low temperature. On the other hand, tetra-n-butylammonium bromide (TBAB) forms a semi-clathrate hydrate crystal with water molecules even at atmospheric pressure. In TBAB semi-clathrate hydrate, Br forms cage structures with water molecules and the tetra-n-butylammonium cation occupies four cages (Davidson, 1973). Such a hydrate is called a semi-clathrate hydrate crystal because a part of the cage structure is broken in order to encage the large tetra-n-butylammonium molecule, and it has been

$$\left[\begin{array}{c} H_9C_4 \\ H_9C_4 \end{array} \underset{N^+}{\overset{C_4H_9}{\diagdown}} \begin{array}{c} C_4H_9 \\ C_4H_9 \end{array} \right] \cdot Br^- \cdot 38H_2O$$

(I)

suggested that the semi-clathrate hydrate crystal does not encage gas molecules (Davidson, 1973).

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Recently, we found that TBAB hydrate can encage small gas molecules which fit in a dodecahedral cage (Shimada et al., 2003). Additionally, it has been reported that there are two types of TBAB hydrate, denoted A and B (Shimada et al., 2003; Fukushima et al., 1999). Unfortunately, Davidson (1973) reported an outline of only the type A TBAB hydrate structure, while the existence of the type B TBAB hydrate was not known. The congruent melting point of type B TBAB hydrate is 283 K with 32 wt% water solution (Oyama et al., 2005). This shows that the hydration number of type B TBAB hydrate is 38: one TBAB and 38 H_2O molecules form the hydrate crystal. In this paper, we report the crystal structure of the title compound, (I), which is a type B TBAB hydrate, and discuss the mechanism by which gas molecules are included.

Fig. 1 shows the structure of (I). Solid lines show the unit cell, which consists of two TBAB cations and 76 H_2O mole-
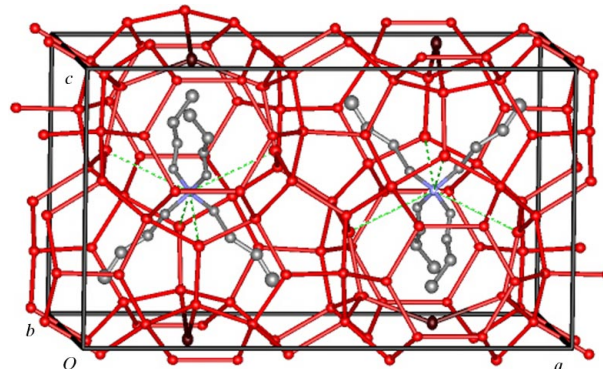
Figure 1
The structure of (I). The unit cell is indicated by solid lines. Br atoms and water molecules form the cage structure. Tetra-n-butylammonium is located at the centre of four cages (part of the cage structure is broken, as indicated by dashed lines). H atoms have been omitted for clarity.
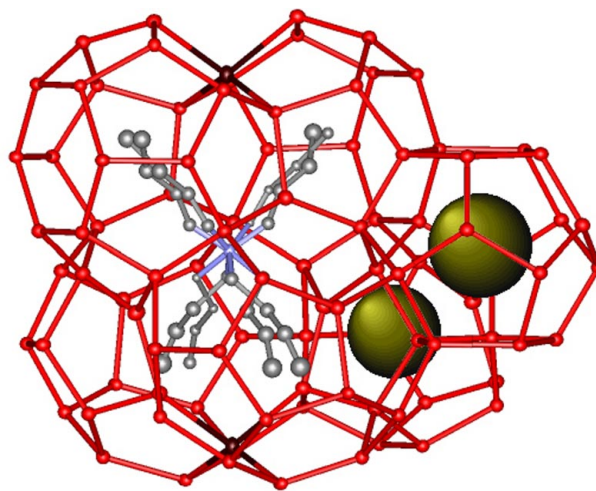
Figure 2
The structure around the tetra-n-butylammonium cation, located at the centre of four cages, viz. two tetrakaidecahedra and two pentakaidecahedra. The butyl groups have two possible sites, with occupancy factors of 50% each. On the other hand, the dodecahedral cages are empty. Therefore, small molecules could be encaged, as shown by the shaded areas.

organic compounds
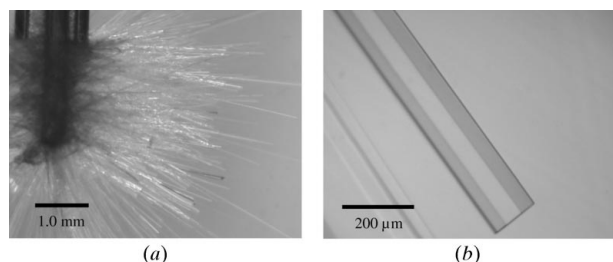
Figure 3
Photographs of (*a*) nucleation around a chilled wire and (*b*) a single-crystal of (I), the morphology being a hexagonal pillar.

cules. Br atoms, which are shown as dark spheres, construct the cage structure with the water molecules. The range of O···O distances is 2.725 (2)–2.820 (4) Å and the range of Br···O distances is 3.248 (3)–3.283 (3) Å. These indicate that the cage structure is constructed by a hydrogen-bonding network. The ideal unit cell is composed of six dodecahedra, four tetrakaidecahedra and four pentakaidecahedra. In reality, because of the presence of tetra-*n*-butylammonium cations, part of the cage structure is broken, as shown by dotted lines.

Fig. 2 shows the structure around the tetra-*n*-butylammonium cation, which is located at the centre of four cages, *viz*. two tetrakaidecahedra and two pentakaidecahedra. Four butyl groups are accommodated in two tetrakaidecahedra (upper cages) and two pentakaidecahedra (lower cages). Each butyl group is disordered over two possible sites, with occupancy factors of 50% each. The tetrakaidecahedra and pentakaidecahedra are occupied by tetra-*n*-butylammonium cations, whereas the dodecahedral cages are empty (Fig. 1). These empty cages could encage small molecules, as is shown in Fig. 2 by the shaded areas, and may function as a sieve for gas molecules.

Experimental

A growth cell was made from stainless steel with glass windows. The temperature of the cell was controlled to within 0.1 K using a cooling bath. The growth cell was filled with an aqueous solution of 10 wt% TBAB, which was then supercooled. For the growth of crystals of (I), a thin glass capillary was immersed in the growth cell and a wire chilled by liquid nitrogen was inserted into the glass capillary tube. Many crystals nucleated at the tip of the chilled wire in the capillary, and some crystals emerged at the tip of the capillary and grew freely in the solution (Fig. 3*a*). After completion of crystal growth, a single crystal of (I) (Fig. 3*b*) was picked up using a nylon loop.

Crystal data

$C_{16}H_{36}N^+ \cdot Br^- \cdot 38H_2O$	Mo $K\alpha$ radiation
$M_r = 1006.95$	Cell parameters from 27 337 reflections
Orthorhombic, $Pmma$	$\theta = 3.0–30.1°$
$a = 21.060$ (5) Å	$\mu = 0.72$ mm^{-1}
$b = 12.643$ (4) Å	$T = 93.1$ K
$c = 12.018$ (8) Å	Needle, colourless
$V = 3199$ (2) Å^3	$0.60 \times 0.10 \times 0.05$ mm
$Z = 2$	
$D_x = 1.045$ Mg m^{-3}	

Water H atoms were not located because they have disordered configurations. The H atoms of the cation were positioned geometrically and treated as riding, with C—H distances of 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The maximum and minimum peaks in the final difference Fourier map are located 1.94 Å from Br1 and 0.36 Å from O2, respectively. The crystal structure contains voids of 64 Å^3, which correspond to the shaded area (dodecahedral cage) in Fig. 2. Bubble formation during dissociation of (I) was observed, suggesting that gas molecules were held in this area.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

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