Note

Air-stable liquid clathrates. 1. Crystal structure of $[NBu_4][Br_3]$ and reactivity of the $[NBu_4][Br_3] \cdot 5 C_6H_6$ liquid clathrate

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[NBu₄][Br₃] interacts with C₆H₆ to form an air-stable liquid clathrate. The tribromide anion reacts with phenol to give para-bromophenol in >95% yield. The HBr which is generated in the reaction combines with the Br⁻ anion to form [Br-H-Br]⁻. The latter forms the basis for a new liquid clathrate, [NBu₄][Br-H-Br] \cdot n C₆H₆. The parent salt, [NBu₄][Br₃], crystallizes in the monoclinic space group C2/c with a = 12.983(5), b = 10.380(7), c = 16.222(6) Å, $\beta = 93.93(3)^{\circ}$, and $D_c = 1.47$ g cm⁻³ for Z = 4. The final R value is 0.068 based on 787 observed reflections.

Introduction

A liquid clathrate (Atwood, 1984) is a semiordered, highly ionic system in combination with an aromatic solvent. Their use in coal liquefaction (Atwood, 1982) and separation science (Atwood, 1986) has received attention. However, the reported liquid clathrates possess the drawback of being extremely airsensitive and highly reactive. These problems have thus far limited the use of liquid clathrates as potential carriers for catalytic systems or in more general use in organic chemistry. We have recently begun to develop air- and moisture-stable liquid clathrates of much lower or specific reactivity, one such being the [NBu₄][Br₃] · 5 C_6H_6 liquid clathrate.

Experimental

Synthesis and reactivity

 $[NBu_4][Br_3]$ was prepared by the addition of 1 equivalent of Br_2 to a CCl_4 solution of $[NBu_4]Br$ (Buckles *et al.*, 1951). The reaction of $[NBu_4][Br_3]$ with

phenol (obtained from Aldrich Chemical Company and used without further purification) was carried out in a 1:1 ratio (10 mmol) and monitored by NMR (Nicolet NT 200). The reaction was complete in <2 min and was selective for para bromination. The yield was >95%.

The presence of the $[NBu_4][Br-H-Br]$ liquid clathrate was noted by a comparison of the NMR spectrum with that of an authentic sample (Means, 1988).

X-ray structure analysis

Suitable crystals for X-ray diffraction were grown from a benzene liquid clathrate by slow evaporation of the benzene. Single crystals were sealed in thin-walled glass capillaries. Final lattice parameters as determined from 25 high-angle reflections $(2\theta > 30^\circ)$ carefully centered on an Enraf-Nonius CAD-4 are given in Table 1. Intensity data were recorded on the diffractometer in the usual manner (Holton *et al.*, 1979). A summary of data collection parameters is also presented in Table 1. The intensities were corrected for Lorentz, polarization, and absorption effects (by the psi scan method).

Structure solution was accomplished by means of the direct methods program MULTAN (Germain *et al.*,

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Table 1. Crystal data and summary of data collection

| Mol wt | 482.3 | | |
|-----------------------------------|---------------------------|--|--|
| Space group | C2/c | | |
| Cell constants | | | |
| <i>a</i> , Å | 12.983(5) | | |
| b, Å | 10.380(7) | | |
| <i>c</i> , Å | 16.222(6) | | |
| β , deg | 93.93(3) | | |
| Cell vol, Å ³ | 2181 | | |
| Molecules/unit cell | 4 | | |
| ρ (calc), g cm ⁻³ | 1.47 | | |
| μ (calc), cm ⁻¹ | 54.96 | | |
| Radiation | ΜοΚα | | |
| Scan width | $0.80 + 0.20 \tan \theta$ | | |
| Standard reflections | 0012, 440, 440 | | |
| Variation of standards | <2% | | |
| 2θ range | 2-40 | | |
| Reflections collected | 1165 | | |
| Reflections observed | 787 | | |
| No. of parameters varied | 93 | | |
| GOF 0.89 | | | |
| R | 0.068 | | |
| R _w | 0.064 | | |
| | | | |

 Table 2. Final fractional coordinates and thermal parameters

| Atom | x/a | y/b | z/c | $U(eqv)^a$ |
|-------|------------|------------|-----------|------------|
| Br(1) | 0.2500 | 0.2500 | 0.5000 | 0.064(15) |
| Br(2) | 0.2870(1) | 0.0453(1) | 0.5822(1) | 0.089(12) |
| N(1) | 0.0000 | -0.144(1) | 0.7500 | 0.042(13) |
| C(1) | -0.0156(7) | -0.2306(9) | 0.8225(7) | 0.045(17) |
| C(2) | -0.0308(8) | -0.167(1) | 0.9037(7) | 0.053(15) |
| C(3) | -0.0641(9) | -0.259(1) | 0.9681(8) | 0.067(18) |
| C(4) | -0.079(1) | -0.197(1) | 1.0508(8) | 0.082(8) |
| C(5) | 0.0924(7) | -0.0545(9) | 0.7668(7) | 0.048(23) |
| C(6) | 0.1968(7) | -0.123(1) | 0.7781(7) | 0.055(28) |
| C(7) | 0.2784(8) | -0.031(1) | 0.8135(8) | 0.063(15) |
| C(8) | 0.3865(9) | -0.094(1) | 0.817(1) | 0.086(52) |

 $^{a}U(\text{eqv}) = 1/3(U_{11} + U_{22} + U_{33}).$

1971) and the subsequent calculation of a difference Fourier map using the SHELX system of computer programs afforded the location of all nonhydrogen atoms. Refinement of the structure with anisotropic thermal parameters for all nonhydrogen atoms and placement of methylene hydrogen atoms in calculated positions led to a final conventional R value of 0.068. The final values of the positional parameters are given in Table 2. The cell packing plot was done using ORTEP.

Results and Discussion

The $[NBu_4][Br_3] \cdot 5 C_6H_6$ liquid clathrate is stable at 25°C and shows no sensitivity to air or atmospheric moisture. The toluene liquid clathrate forms upon heating to 60°C, but the parent salt recrystallizes rapidly at room temperature.

Addition of phenol to the system leads to a rapid decoloration. The reaction



occurs and yields selectivity similar to that observed with $[NBu_4][Br_3]$ in CHCl₃ (Berthelot *et al.*, 1986). The 4-bromophenol product remains in the liquid clathrate layer, and the liquid clathrate layer is maintained. This



Fig. 1. Stereoscopic view of the packing of the ions in the unit cell. The C-C distances range from 1.50 to 1.55 Å; the N-C is 1.53(1) Å; the C-C-C angles range from 110 to 114°; the angle at the N atom is $111.7(6)^{\circ}$.

is due to the formation of the $[Br-H-Br]^-$ anion (Emsley, 1980).

A stereoscopic view of the packing of the ions in the crystal structure of $[NBu_4][Br_3]$ is shown in Fig. 1. The Br_3^- anions exist in channels formed by the packing of the cations. It is interesting to note that the butyl groups are fully extended, as was found in the structure of $[NBu_4][AII_4]$ (Rogers *et al.*, 1984).

The cation resides on a crystallographic two-fold axis, while the anion exists on a center of inversion. The independent Br—Br distance is 2.536(2) Å. This is well within the range observed in other studies (Bruce *et al.*, 1985; Cotton *et al.*, 1986), and is quite close to the values found in tribromide ions constrained by crystallographic symmetry: 2.548(1) Å in [VBr₂(MeCN)₄][Br₃] (Cotton *et al.*, 1986) and 2.550(1) Å in [PPh₄][Br₃] (Bogaard and Rae, 1982).

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Complete bond distances and angles, hydrogen atom coordinates, anisotropic thermal parameters, and structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 67041 (8 pages).