CHEMISTRY LETTERS, pp. 921-924, 1977. Published by the Chemical Society of Japan

THE CRYSTAL STRUCTURE OF TETRABUTYLAMMONIUM GUANIDINIUM BROMIDE MONOHYDRATE COMPLEX, $[N(C_4H_9)_4]^+[C(NH_2)_3]^+Br^-{}_2 \cdot H_2O$

Tooru TAGA, Makoto OHASHI, Koichiro MIYAJIMA,
Hiromitsu YOSHIDA, and Kenji OSAKI
Faculty of Pharmaceutical Sciences, Kyoto University,
Yoshidashimoadachi-cho, Sakyo-ku, Kyoto 606

In the crystal structure of the title compound, the two dimensional hydrogen-bond networks are formed between the guanidinium ions, bromide ions and water molecules. The tetrabutylammonium groups are located at the interstitial space between these hydrogen-bond networks, and the neighboring groups have a large number of hydrophobic contacts.

This work is one of a series of our X-ray studies on the crystal structures of tetraalkylammonium guanidinium halide complexes.[1) From thermodynamic studies on the guanidinium salt solutions, the guanidinium ion was found to be 'a structure breaker' for the water structure.[2) In the present work, we were, therefore, interested in the structural feature around the guanidinium ions in the title crystal.

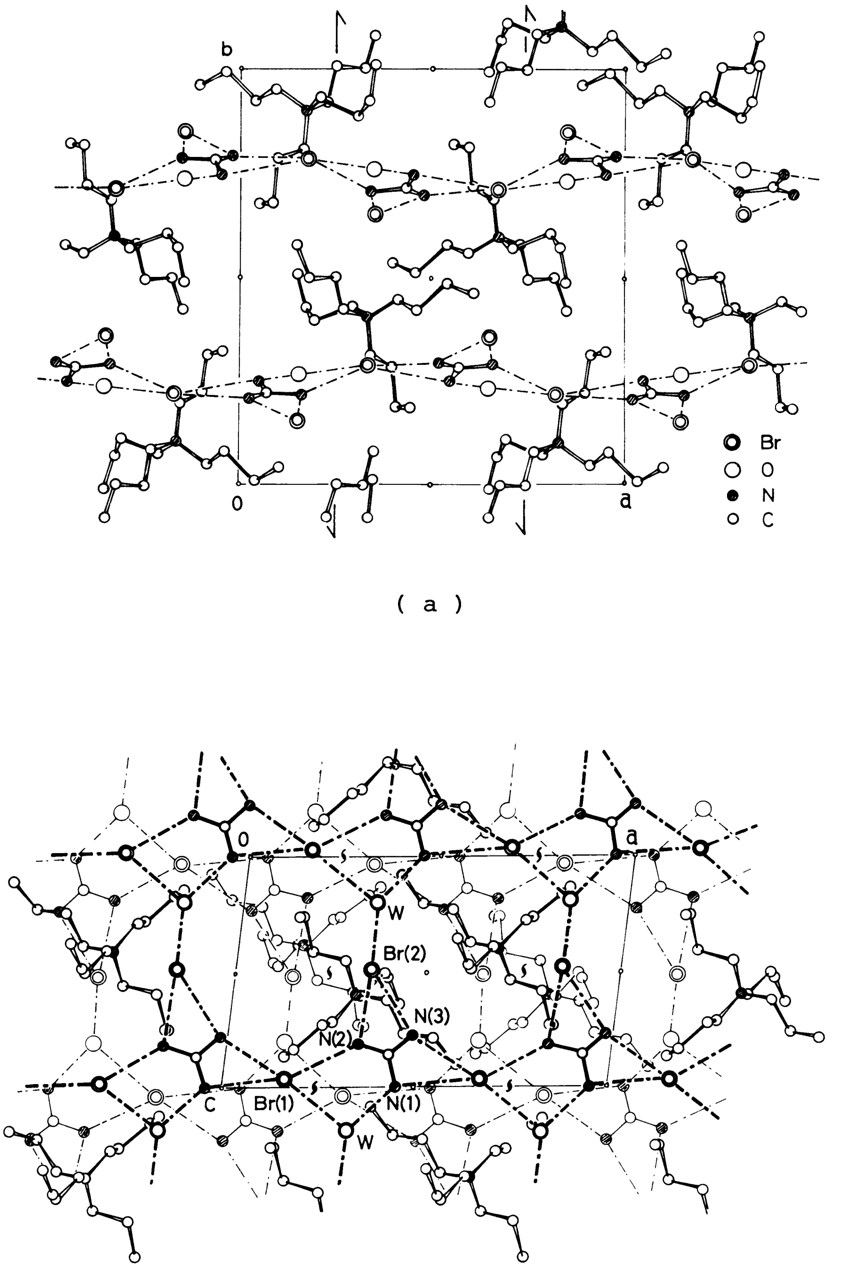
The isomorphous crystals of the title bromide salt (TBG.Br_2) and the bromide-chloride salt (TBG.BrCl) were obtained from aqueous solutions. The crystallographic data for these salts were determined as follows : monoclinic, $P2_1/a$, Z=4, a=15.71(7), b=17.15(2), c=9.56(3) Å, β=97.6(2)° and Dx=1.249 g/cm^3 for TBG.Br_2, and a=15.41(4), b=17.09(5), c=9.67(4) Å, β=97.5(2)° and Dx=1.151 g/cm^3 for TBG.BrCl. Intensity data for TBG.Br_2 were collected by the visual estimation of the Weissenberg films taken by rotating the crystals about the b- and c-axes, using Cu Kα radiation. Absorption correction for a spherical crystal was applied for 1049 observed reflections, which corresponded to 17.9 % of the theoretically observable reflections within the Cu Kα sphere. The structure was solved by the heavy atom method. The C(13), C(14), and C(24) atoms at the side chains of the tetrabutylammonium group were in disordered states, and their positions and occupancies were estimated from the difference Fourier maps. Several cycles of the block-diagonal least-squares refinement with the anisotropic thermal parameters except for those of the disordered atoms gave an R-value of 0.148. The positional parameters at this stage are listed in Table 1.

As will be seen in Fig. 1, this crystal structure is composed of two parts in which the hydrophobic and hydrophilic interactions are dominant. The guanidinium ions, the bromide ions, and the water molecules form two dimensional hydrogen-bond networks, being parallel to the ac plane, and the tetrabutylammonium groups occupy the interstitial space between these hydrogen-bond networks. This structural

Table 1. The Positional Parameters of Tetrabutylammonium Guanidinium Bromide Monohydrate Complex.

The occupancy factor Q for each atom is given in the last column.

Atom	x	y	z	Q
Br(1)	0.3294(4)	0.2917(5)	0.0320(8)	1.0
Br(2)	0.1500(4)	0.1543(4)	0.5138(6)	1.0
C(1)	0.074(3)	0.222(3)	0.132(6)	1.0
N(1)	0.042(3)	0.244(3)	0.007(4)	1.0
N(2)	0.159(3)	0.215(3)	0.176(4)	1.0
N(3)	0.028(3)	0.205(3)	0.225(4)	1.0
N(4)	0.321(2)	0.402(3)	0.589(4)	1.0
C(11)	0.338(3)	0.313(3)	0.595(6)	1.0
C(12)	0.393(4)	0.282(4)	0.496(7)	1.0
C(13)	0.403(4)	0.194(4)	0.506(7)	0.8
C(13)'	0.383(19)	0.191(18)	0.333(30)	0.2
C(14)	0.443(8)	0.183(7)	0.616(12)	0.5
C(14)'	0.459(12)	0.170(12)	0.416(20)	0.3
C(14)"	0.310(19)	0.134(18)	0.380(30)	0.2
C(21)	0.269(3)	0.425(3)	0.707(6)	1.0
C(22)	0.248(5)	0.504(3)	0.719(6)	1.0
C(23)	0.182(5)	0.504(4)	0.828(6)	1.0
C(24)	0.157(8)	0.594(8)	0.859(12)	0.5
C(24)'	0.100(8)	0.472(7)	0.779(12)	0.5
C(31)	0.290(3)	0.430(4)	0.450(5)	1.0
C(32)	0.198(3)	0.394(4)	0.402(6)	1.0
C(33)	0.167(5)	0.416(4)	0.258(10)	1.0
C(34)	0.149(4)	0.506(4)	0.261(6)	1.0
C(41)	0.411(3)	0.447(3)	0.626(5)	1.0
C(42)	0.462(3)	0.417(3)	0.759(6)	1.0
C(43)	0.547(5)	0.485(5)	0.792(9)	1.0
C(44)	0.599(4)	0.458(4)	0.922(6)	1.0
O(w)	0.159(2)	0.251(2)	0.800(3)	1.0



(a)

(b)

Fig. 1. The crystal structure of tetrabutylammonium guanidinium bromide monohydrate complex projected along the c-axis (a) and the b-axis (b).
The hydrogen bondings are indicated by the broken lines.
The highest occupancy sites are shown for the disordered atoms.

feature is similar to the clathrate structure observed in tetrabutylammonium fluoride polyhydrate crystal, in which the tetrabutylammonium groups are enclosed into the water-fluoride cage.[3] In the present case, although the waters and the halide ions do not form the cage structure, the ionic nature of the tetrabutylammonium group may be unimportant for the crystal construction, and these groups only fill the vacancy of the hydrogen-bond networks. The hydrocarbon chains of these tetrabutylammonium groups approach each other around the center of symmetry sites between the hydrogen-bond sheets. In particular, the two groups related by the center of symmetry at 0,0,0 or $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ have many van der Waals contacts between their parallel hydrocarbon chains, the shortest C-C distance being 3.96 (8) Å. The guanidinium ion in the hydrogen-bond network is bonded to three bromide ions and one water molecule in approximately the same plane. The N···Br hydrogen-bond distances range from 3.3 to 3.4 Å with their estimated standard deviations less than 0.1 Å. The water molecule accepts one hydrogen atom from the guanidinium nitrogen (2.9 Å) and donates two protons to the bromide ions (3.3 and 3.2 Å). Since the guanidinium ions in an aqueous solution probably form similar hydrogen bonds with the water molecules, the function of guanidinium ion as 'a structure breaker' for the water structure may be explained by the idea that such 'planar hydrogen bonds' around the guanidinium ion disturb the formation of three dimensional hydrogen-bond system in the water.

The isomorphous crystal structure of TBG.BrCl was studied by the synthesis of the difference Fourier maps, using the hk0 and h0ℓ reflection data for both crystals. In these maps, there were no significant difference between the peak heights at the two heavy atom sites. The chloride ions in the TBG.BrCl crystal are, therefore, distributed equally to both sites, and this crystal must be a so-called 'mixed crystal'.

References

1) T. Taga, M. Ohashi, K. Miyajima, H. Yoshida, and K. Osaki, Chem. Lett., 1977, our preceding paper.
2) K. Miyajima, H. Yoshida, and M. Nakagaki, Nippon Kagaku Zasshi, 1976, 366.
3) R. K. McMullan, M. Bonamico, and G. A. Jeffrey, J. Chem. Phys., 39, 3295 (1963).

(Received May 20, 1977)