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THE CRYSTAL STRUCTURE OF 2:1 TETRAPROPYLAMMONIUM GUANIDINIUM BROMIDE COMPLEX, $[N(C_3H_7)_4]^+{}_2[C(NH_2)_3]^+Br^-{}_3$

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

The crystal structure of the title compound is a distorted CaF_2 type of ionic crystal. The guanidinium ion is bound to the three bromide ions by the NH···Br hydrogen bonds and forms a rigid divalent anionic group. The two tetrapropylammonium groups have the different conformations represented by the symmetry, $\bar{4}2m$ and $\bar{4}$.

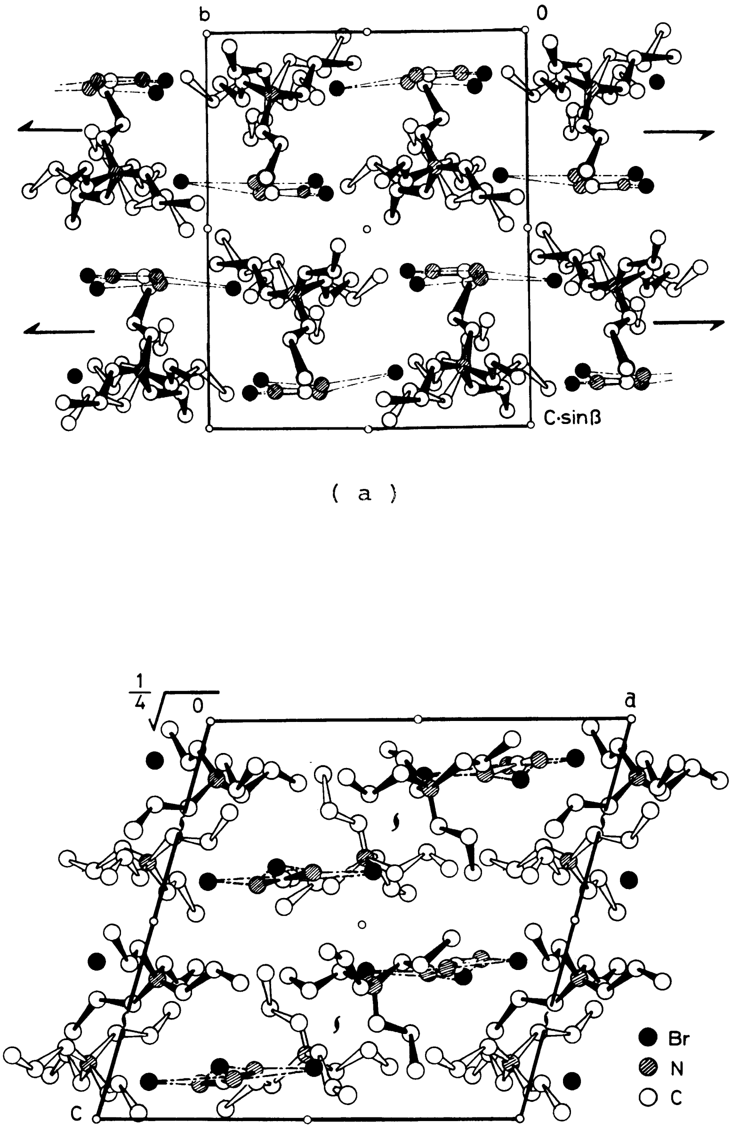
The structural feature of tetraalkylammonium guanidinium halide complex salts in the solution and in the solid states was interested in relation to the denaturation property of protein by the guanidinium ion.[1] This report describes the crystal structure of the title compound as one of the X-ray studies on these complex salts.

The monoclinic single crystals, which were very unstable in the air, were obtained by the evaporation method. Preliminary X-ray photographs showed that the cell dimensions were a=17.45(6), b=13.00(8), c=16.81(6) Å and β=105.7(2)°, and the space group $P2_1/c$ as indicated by the systematic absences of h0ℓ for ℓ odd and 0k0 for k odd. Z=4, Dx=1.217 g/cm^3 and Dm=1.215 g/cm^3. The Weissenberg photographs were taken by rotating the crystals about the b- and c-axes, using Cu Kα radiation. Intensity data of 1194 independent reflections were collected from these films by the use of a SYNTEX AD-1 densitometer. Absorption correction for a spherical crystal was applied for these data (μR=3.8). Although the number of the observed reflections corresponded to only 13.3 % of the theoretically observable reflections within the Cu Kα sphere, the structure was solved by the heavy atom method and refined by the block-diagonal least-squares method. Several cycles of the refinement with the anisotropic thermal parameters gave an R-value of 0.133. The positional parameters at this stage are listed in Table 1. The crystal structures projected along the a- and b-axes are shown in Fig. 1 (a) and (b), respectively.

The dihedral angle between the plane of the guanidinium group and the ab plane of the crystal is 11(1)°. The three bromide ions approximately lie on the guanidinium plane, and the maximum deviation of the bromide ions from the least-squaresplane of the four atoms of guanidinium ion is 0.6 Å. These bromide ions are tightly bound to the nitrogens of guanidinium ion by the NH···Br hydrogen

Table 1. The Positional Parameters of Tetrapropylammonium Guanidinium Bromide Complex.

Atom	x	y	z
Br(1)	0.2502(4)	0.0867(5)	0.3615(5)
Br(2)	0.1004(4)	0.6314(5)	0.4002(4)
Br(3)	0.4738(4)	0.6686(5)	0.3704(4)
C(1)	0.273(3)	0.802(5)	0.396(4)
N(1)	0.213(2)	0.839(4)	0.403(3)
N(2)	0.286(3)	0.700(4)	0.400(3)
N(3)	0.335(3)	0.853(4)	0.378(3)
N(4)	0.043(2)	0.792(3)	0.151(3)
C(11)	0.119(2)	0.735(4)	0.181(3)
C(12)	0.169(3)	0.703(5)	0.123(4)
C(13)	0.242(3)	0.647(5)	0.163(4)
C(21)	0.008(3)	0.805(5)	0.227(3)
C(22)	-0.078(3)	0.857(4)	0.206(3)
C(23)	-0.106(3)	0.875(5)	0.277(3)
C(31)	-0.015(3)	0.735(5)	0.071(3)
C(32)	-0.035(3)	0.624(5)	0.086(4)
C(33)	-0.097(4)	0.565(5)	0.012(3)
C(41)	0.059(3)	0.886(4)	0.113(3)
C(42)	0.118(3)	0.978(5)	0.174(4)
C(43)	0.128(3)	1.062(4)	0.120(4)
N(5)	0.447(2)	0.295(3)	0.337(3)
C(51)	0.410(3)	0.322(4)	0.249(3)
C(52)	0.334(3)	0.263(5)	0.227(3)
C(53)	0.293(4)	0.312(5)	0.128(5)
C(61)	0.394(3)	0.310(4)	0.402(3)
C(62)	0.347(3)	0.406(5)	0.401(4)
C(63)	0.302(4)	0.408(6)	0.466(4)
C(71)	0.526(3)	0.369(5)	0.382(3)
C(72)	0.584(3)	0.366(5)	0.325(4)
C(73)	0.651(4)	0.448(5)	0.378(5)
C(81)	0.477(3)	0.192(4)	0.335(4)
C(82)	0.526(3)	0.151(5)	0.420(4)
C(83)	0.561(3)	0.034(4)	0.422(4)



(a)

(b)

Fig. 1. The crystal structure of 2:1 tetrapropylammonium guanidinium bromide complex projected along the a-axis (a) and the b-axis (b).

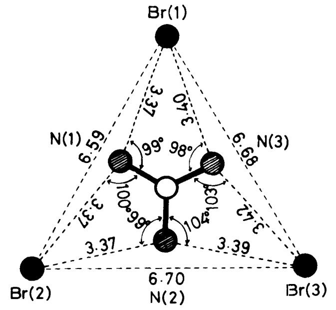


Fig. 2. The dimensions of guanidinium-bromide group. The e.s.ds. for N···Br, Br···Br, and ∠C-N···Br are 0.03 Å, 0.05 Å, and 2.6°, respectively.

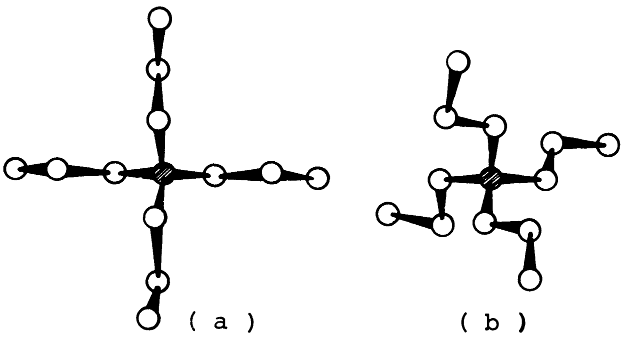


Fig. 3. The two conformations of tetrapropylammonium groups. Both groups are projected along the approximate $\bar{4}$ axis.

bonds, the interatomic distances being shown in Fig. 2. In this rigid guanidinium-bromide group, the positive charge on the central guanidinium cation is compensated by the negative charges of the bromide ions, and this triangular group is probably regarded as a large divalent anion. The two tetrapropylammonium groups have different conformations (see Fig. 3). The structure (a) has an approximate $\bar{4}2m$ symmetry, while the structure (b) has $\bar{4}$. Although the former structure has been observed in many crystal structures determined hitherto,[2] the latter is an unusual form. Brown et al.[3] have, however, found the latter form for the tetraethylammonium group in its indium salt, and they concluded that this form is a more energetically favorable state in the absence of the crystal forces than the former. In the present crystal, both tetrapropylammonium groups are located at similar sites surrounded by the four anionic groups in spite of the different conformations. The anionic group is surrounded by the eight tetrapropylammonium groups. Thus the arrangement of those anionic and cationic groups roughly resembles that of the ions in the CaF_2 structure with inverted signs of the ions. Hence the present crystal can be best described as $[N(C_3H_7)_4]^+_2[C(NH_2)_3Br_3]^{2-}$.

References

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