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The Crystal Structure of the 1:2 Tetrapropylammonium Guanidinium Bromide Complex

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Synopsis. The crystal of the title complex is monoclinic, $P2_1/a$ with these unit cell dimensions: $a=16.16$, $b=19.18$, $c=15.46$ Å, and $\beta=98°$. The crystal structure has layers of hydrogen-bond networks formed by the guanidinium and bromide ions. Two different conformers of the tetrapropylammonium ions are packed between the networks.

This work is one of a series of X-ray studies on the crystal structures of tetraalkylammonium guanidinium halide complexes.[1-3] Two kinds of the crystals of tetrapropylammonium guanidinium bromide complexes, 1:2 and 2:1 $(Pr)_4NBr$–GuBr, were obtained from the aqueous solutions of the mixed tetrapropylammonium bromide and guanidinium bromide salts.[1] The crystal structure of the 1:2 complex described in this note received attention in relation to that of the 2:1 complex reported previously.[2]

Experimental

The crystals obtained by the evaporation method were very unstable in the air. Thus, the X-ray experiments were performed by sealing the crystals in a capillary tube. The crystals are monoclinic, space group $P2_1/a$, as indicated by the systematic absences of $h0l$ for h odd and $0k0$ for k odd. The cell dimensions are $a=16.65(9)$, $b=19.18(5)$, $c=15.46(14)$ Å, and $\beta=98(2)°$. The observed crystal density is 1.415 g/cm^3, while the calculated density is 1.485 g/cm^3 if eight chemical unit, $[N(C_3H_5)_4][C(NH_2)_3]_2\,Br_3$, are assumed in the unit cell. The higher order reflections were not observed in the Weissenberg films taken by rotating the crystals about the b- and c-axes, using Ni-filtered Cu $K\alpha$ radiation. Intensity data of 1498 reflections were collected by the use of a SYNTEX AD-1 densitometer.

The structure was solved by the heavy-atom method. The six bromide ions were determined by the direct method using the program MULTAN. The structure was refined by successive cycles of the block-diagonal and full-matrix least-squares methods with the anisotropic thermal parameters of the bromide ions. The refinement was terminated at the stage where an R-value was reduced to 0.15, since the temperature factor of this crystal is large ($\bar{B}=4.9$). All computations were performed on a FACOM M-190 in the Data Processing Center of Kyoto University, using the program system KPAX which included the UNICS program.

Results and Discussion

Table 1 lists the positional parameters and their estimated standard deviations, and Figs. 1 and 2 show the crystal structures projected along the a- and b-axes, respectively.

The structure is composed of the two-dimensional hydrogen-bond network formed by the guanidinium ions and the bromide ions. The tetrapropylammonium groups are packed between these hydrogen-bond networks. This layer-like structure resembles that observed previously in the crystal of tetrabutylammonium guanidinium bromide monohydrate complex.[3] However, an interesting aspect of this crystal structure is found in its unique hydrogen-bond networks. Each guanidinium ion is bonded to three bromide ions by the six NH···Br hydrogen-bonds, and forms a rigid triangular $GuBr_3$ group; the average N···Br distance is 3.45 Å. The $GuBr_3$ groups are linked together in a

TABLE 1. POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

The values have been multiplied by 10^4.

Atom	x	y	z	Atom	x	y	z
Br(1)	3797(5)	1728(4)	4054(5)	N(P1)	3625(28)	3065(22)	6308(31)
Br(2)	13(6)	−20(5)	2409(6)	C(11)	3311(60)	3371(47)	7142(62)
Br(3)	3842(5)	1755(4)	8725(5)	C(12)	2764(57)	3804(48)	7048(64)
Br(4)	2400(4)	5047(4)	4808(6)	C(13)	2418(45)	4055(37)	7930(51)
Br(5)	2704(5)	303(6)	222(6)	C(21)	3918(31)	3601(25)	5791(37)
Br(6)	31(5)	4719(5)	2504(6)	C(22)	4325(49)	3554(39)	5080(54)
				C(23)	4760(44)	4089(36)	4746(49)
C(G1)	505(46)	4261(38)	5526(53)	C(31)	4228(44)	2518(36)	6557(52)
N(11)	958(31)	4740(25)	5989(34)	C(32)	5075(54)	2689(44)	7212(61)
N(12)	642(25)	4049(20)	4814(29)	C(33)	5721(53)	2272(44)	7484(60)
N(13)	−238(27)	4210(21)	5770(30)	C(41)	3062(50)	2742(42)	5740(57)
				C(42)	2414(70)	2145(56)	6087(76)
C(G2)	513(36)	4345(29)	333(43)	C(43)	1671(38)	2043(32)	5254(44)
N(21)	1079(31)	4642(27)	880(35)				
N(22)	541(35)	4274(30)	−452(40)	N(P2)	3509(23)	3079(20)	1265(27)
N(23)	−99(26)	3988(22)	575(31)	C(51)	2932(42)	3508(35)	1904(48)
				C(52)	2511(59)	3077(50)	2469(64)
C(G3)	2137(58)	759(47)	2230(62)	C(53)	2333(44)	3549(37)	3139(49)
N(31)	2860(30)	885(24)	2225(33)	C(61)	3804(44)	3678(36)	784(50)
N(32)	1506(32)	667(26)	1570(37)	C(62)	4349(64)	3349(50)	105(68)
N(33)	1849(32)	882(25)	3092(37)	C(63)	4624(49)	4028(40)	−196(53)
				C(71)	4184(31)	2630(26)	1836(38)
C(G4)	2201(49)	655(40)	7314(55)	C(72)	4737(40)	2966(33)	2355(45)
N(41)	2936(34)	601(29)	7359(38)	C(73)	5453(35)	2460(29)	2751(43)
N(42)	1629(36)	297(30)	6718(40)	C(81)	2825(44)	2643(37)	659(51)
N(43)	1878(35)	772(28)	8041(40)	C(82)	2105(33)	2979(28)	105(38)
				C(83)	1477(65)	2323(55)	−219(75)

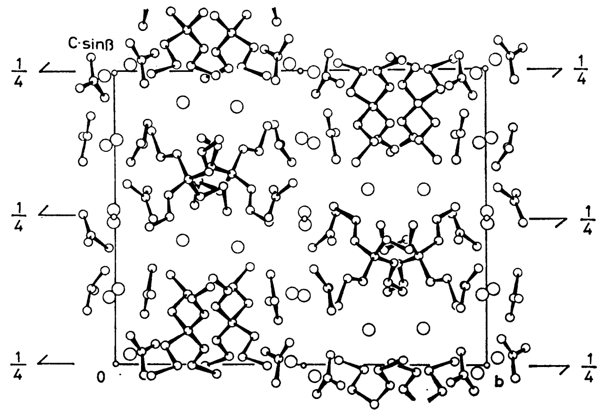

Fig. 1. The [100] projection of the structure of 1:2 tetrapropylammonium guanidinium bromide complex. The large circle indicates a bromide ion.

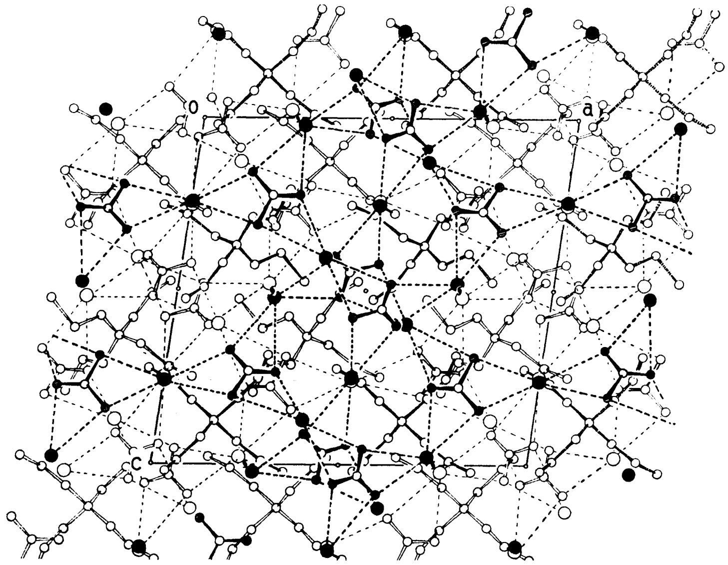

Fig. 2. The [010] projection of the structure of 1 : 2 tetrapropylammonium guanidinium bromide complex. The broken line indicates a NH···Br hydrogen-bond.

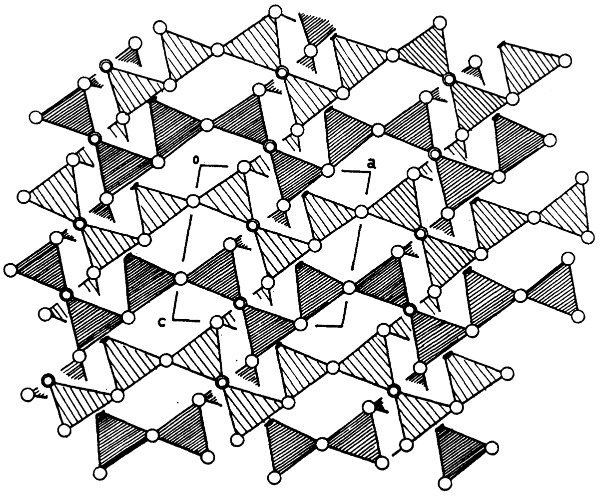

Fig. 3. A schematical drawing of the hydrogen-bond networks composed of the $GuBr_3$ groups.
The two networks weaved into each other are viewed down the b-axis.

manner such that the bromide ion forms four hydrogen-bonds with the nitrogen atoms of the two adjacent guanidinium ions, and they form four-membered rings and eight-membered rings in an infinite two-dimensional network. As is shown schematically in Fig. 3, the two networks related by the $\bar{1}$ symmetry are, furthermore, interwoven with each other; the four-membered rings and the eight-membered rings in the different networks are entangled together. The closest approach of these networks is found between the antiparallel guanidinium planes at the entanglement point of the two rings.

When the crystal structure described above is compared with that of the 2 : 1 complex,[2] one of the common structural features is that two different conformers of tetrapropylammonium groups exist in both structures. The two conformers have approximately $\bar{4}$ mm and $\bar{4}$ symmetries, as reported previously.[2] This common fact will provide the evidence that these two conformations for tetrapropylammonium are energetically very close. The second point of the common features is that the guanidinium ion forms a $GuBr_3$ group with three bromide ions. A similar $GuCl_3$ group has been observed in the crystal structure of guanidinium chloride salt.[4] These facts may indicate that the $GuBr_3$ formation is favorable in a crystalline state. A definite difference between the three structures is how these stable $GuBr_3$ groups link in the structure. In the 2 : 1 complex, each $GuBr_3$ group is apart from the others and act as a divalent anion.[2] On the other hand, in the 1 : 2 complex, the $GuBr_3$ groups are linked together at the bromide ion, and they form a two-dimensional network as mentioned above. In the case of guanidinium chloride salt, three $GuCl_3$ groups are linked together at a chloride ion, and they form a complicate three-dimensional network as a whole.[4] The apparent charge of the $GuBr_3$ group in the 1 : 2 complex is smaller than in the 2 : 1 complex, since each bromide ion contributes half a unit of charge onto the $GuBr_3$ group in the network. Hence, the ionic character of the crystal of the 1 : 2 complex is considered to be smaller than that of the 2 : 1 complex.

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