Complexes between Nucleotide Base and Amino Acid. II. Crystal Structure of 5-Bromocytosine : *N*-Tosyl-L-glutamic Acid

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The complex crystals of 5-bromocytosine and *N*-tosyl-L-glutamic acid were obtained from their aqueous solution. The space group is P1 with dimensions of $a=10.843(1)$, $b=11.690(2)$, $c=10.879(2)$ Å, $\alpha=122.15(1)$, $\beta=121.38(1)$, $\gamma=69.93(1)°$, and $Z=2$. The structure was solved by the heavy atom method and refined by a block-diagonal least-squares method. The undissociated γ-carboxyl group of glutamic acid is bound with O(2) and N(4) of 5-bromocytosine through hydrogen bonds. This interaction mode is different from those found in some cytosine : glycine complexes and cytidine : *N*-benzyloxycarbonyl-L-glutamic acid complex dihydrate in which the dissociated α-carboxyl group plays a role. This is the first example of interaction between cytosine and the acidic side group of amino acid.

Interactions between nucleic acids and proteins take an important part in several biological processes, though the precise molecular mechanism is still unknown. We have been engaged in preparing complexes of nucleotide base and amino acid followed by X-ray crystallographic studies, which will provide stereochemical basis for the mutual recognition between nucleic acid and protein.

One interaction mode is hydrogen bonds between the dissociated α-carboxyl group of amino acid and protonated N(3) and amino group of cytosine, as found in cytosine : glycine dreivatives[1,2] and in cytidine: *N*-benzyloxycarbonyl-L-glutamic acid complex.[3] We have revealed another type of interaction between γ-carboxyl group of glutamic acid and cytosine in the complex of 5-bromocytosine : *N*-tosyl-L-glutamic acid,[4] and the present paper is a full account of its crystal structure.

Experimental

Prismatic crystals were obtained from an aqueous solution containing equimolar 5-bromocytosine and *N*-tosyl-L-glutamic acid. The complex formation was confirmed by IR spectroscopy and an elementary analysis of these crystals. Found: C, 39.06; H, 3.96; N, 11.15%. Calcd for $C_4H_4N_3OBr \cdot C_{12}H_{15}NO_6S$: C, 39.11; H, 3.91; N, 11.41%. Diffraction pattern of the crystal indicated the crystal system to be triclinic. As the amino acid is L-form, the space group should be P1. The unit-cell dimensions were determined by least-squares calculations with 113 spacings from equator Weissenberg photographs about three different axes, calibration being made with superposed silicon lines ($a=5.43075$ Å). The density measured by flotation in a $CHBr_3$–CCl_4 mixture indicated that there are two 1 : 1 molecular complexes in the unit cell. Crystal data are given in Table 1.

TABLE 1. CRYSTAL DATA

5-Bromocytosine : *N*-tosyl-L-glutamic acid		
$C_4H_4N_3OBr$: $C_{12}H_{15}NO_6S$ F. W. = 491.35		
Crystal system: triclinic		
Space group: P1		
$a=10.843(1)$ Å	$b=11.690(2)$ Å	$c=10.879(2)$ Å
$\alpha=122.15(1)°$	$\beta=121.38(1)°$	$\gamma=69.93(1)°$
$U=992.6(2)$ Å^3	$Z=2$	
$D_x=1.644$ g cm^{-3}	$D_m=1.66$ g cm^{-3}	
μ(Cu $K\alpha$) = 45.56 cm^{-1}		

Diffraction data were collected on equi-inclination Weissenberg photographs (0*kl*-8*kl* and *h*0*l*-*h*8*l*) using Ni-filtered Cu $K\alpha$ radiation and the intensities were measured by a TV densitometer.[5] The crystal used for the a- and b-axis rotations were $0.22\times0.20\times0.43$ mm and $0.20\times0.30\times0.40$ mm, respectively. Corrections were made for Lorentz and polarization effects and spot size, but not for absorption. A total of 4259 independent reflexions were obtained, of which zero-reflexions numbered 803. The $N(z)$ test[6] was consistent with non-centrosymmetric space group.

Structure Determination and Refinement

The approximate structure was obtained by the usual heavy atom method. The structure was refined by a block-diagonal least-squares methos; the minimized function was $\sum w\Delta F^2$, where $\Delta F=|F_o|-|F_c|$. In this refinement, the zero-reflexions were assumed to have the value of $|F_o|_{min}(=1.55)$. The zero-reflexions, for which $|F_c|$ values at each cycle were smaller than $|F_o|_{min}$, were omitted from the refinement. The weight function used was as follows: $w=\exp(-as^2-bt^2-cst-ds-et-f)$ for $|F_o|>|F_o|_{min}$, where $s=|F_o|$ and $t=\sin\theta/\lambda$; $w=1/\langle\Delta F^2\rangle$ for $|F_o|=|F_o|_{min}$. The coefficients, *a*, *b*, *c*, *d*, *e*, and *f*, were evaluated by least-squares at each cycle of the structure refinement so that $\langle w\Delta F^2\rangle=1$. The convergence was slow owing to quasi-centrosymmetric structure of the crystal. The refinement was terminated when the maximum shifts of positional and thermal parameters were less than 0.15σ and 0.25σ, respectively. At the final cycle, the coefficients of weight function were −0.0001747, 36.59, 0.03631, 0.05322, −36.13, and 7.320, respectively, and weight for $|F_o|_{min}$ was 0.609. The final value of *R* factor is 0.082 ($R_w=0.080$), and the *R* for reflexions of $|F_o|>3\sigma$ ($\sigma=1/\sqrt{w}$) is 0.065. The comparison between observed and calculated structure factors is given in Table 2.[7] Atomic scattering factors used were taken from "International Tables for X-Ray Crystallography."[8] The positional and thermal parameters are given in Table 3.

Results and Discussion

Bond lengths and angles of the two independent molecules are listed in Table 4. For a few pairs, discrepancy between the lengths of corresponding bonds looks significant; however, this may be attributable to

Table 3. Final positional and thermal parameters

Standard deviations are given in parentheses. The temperature factor has the form, $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. All parameters have been multiplied by 10^4.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1A)	−1360(7)	−533(8)	176(7)	116(7)	152(8)	105(7)	−71(13)	77(12)	128(13)
C(2A)	−264(8)	−196(7)	1685(7)	108(8)	102(7)	96(8)	−53(12)	76(13)	85(12)
N(3A)	−432(8)	−194(7)	2828(7)	130(8)	141(8)	112(8)	−100(13)	100(13)	103(12)
C(4A)	−1644(7)	−583(8)	2453(8)	88(7)	110(7)	110(8)	−51(12)	46(13)	114(13)
C(5A)	−2752(8)	−1068(9)	833(9)	104(8)	134(9)	112(9)	−86(14)	13(14)	120(14)
C(6A)	−2572(8)	−991(9)	−247(8)	105(8)	143(9)	95(8)	−89(14)	27(13)	106(14)
O(2A)	885(6)	106(7)	1948(6)	106(6)	182(8)	117(7)	−129(12)	45(10)	141(12)
N(4A)	−1822(8)	−529(9)	3607(8)	126(8)	168(9)	147(10)	−76(15)	98(15)	161(16)
Br(5A)	−4420(1)	−1712(1)	273(1)	118(1)	217(1)	186(1)	−139(2)	64(2)	200(2)
N(1B)	1282(7)	678(7)	9866(7)	92(6)	125(7)	106(7)	−85(11)	29(11)	113(12)
C(2B)	214(8)	256(8)	8317(8)	100(7)	111(7)	115(9)	−69(12)	50(13)	109(13)
N(3B)	414(6)	204(6)	7178(6)	97(6)	110(6)	92(7)	−63(10)	35(11)	91(11)
C(4B)	1638(8)	571(8)	7524(9)	116(8)	100(7)	138(9)	−31(13)	98(15)	123(13)
C(5B)	2743(9)	1056(8)	9135(10)	143(10)	109(8)	154(11)	−23(14)	166(18)	121(15)
C(6B)	2535(8)	1090(8)	10284(9)	98(8)	120(8)	141(10)	−57(13)	64(14)	129(15)
O(2B)	−919(6)	−73(6)	8065(6)	102(6)	140(7)	128(7)	−86(10)	56(10)	123(11)
N(4B)	1830(8)	479(9)	6366(8)	140(9)	180(10)	118(8)	−127(16)	77(14)	137(15)
Br(5B)	4449(1)	1665(1)	9714(1)	111(1)	183(1)	172(1)	−109(2)	77(2)	166(2)
O(3A)	−9550(7)	−3524(7)	531(8)	112(7)	128(7)	213(10)	−42(11)	126(14)	147(14)
O(4A)	−7997(8)	−5323(8)	728(12)	130(8)	144(8)	359(18)	−7(13)	199(20)	285(20)
C(7A)	−8319(9)	−4129(9)	794(9)	120(9)	138(10)	127(10)	−80(16)	64(16)	122(16)
C(8A)	−7072(8)	−3517(9)	1182(9)	100(8)	126(9)	150(11)	−79(14)	84(15)	114(15)
C(9A)	−6300(9)	−2650(9)	2970(8)	124(9)	153(10)	96(8)	−113(16)	53(14)	95(15)
C(10A)	−5116(8)	−1992(8)	3304(8)	109(8)	127(9)	99(8)	−90(14)	54(14)	74(13)
C(11A)	−3999(9)	−1414(8)	5036(8)	117(9)	111(8)	118(9)	−54(14)	80(15)	90(14)
O(5A)	−2965(7)	−936(8)	5201(7)	131(7)	202(9)	126(7)	−191(14)	20(12)	147(13)
O(6A)	−4047(8)	−1406(9)	6123(7)	174(9)	215(10)	122(8)	−146(16)	80(14)	171(14)
N(5A)	−7533(7)	−2712(7)	310(7)	112(7)	113(7)	121(8)	−82(12)	64(13)	92(12)
S(1A)	−7740(2)	−3465(2)	−1535(2)	112(2)	118(2)	117(2)	−55(3)	90(3)	93(3)
O(7A)	−8034(8)	−2377(6)	−1917(7)	192(10)	117(6)	155(8)	−97(13)	141(15)	112(11)
O(8A)	−6492(6)	−4397(7)	−1602(7)	105(6)	157(8)	153(8)	−35(11)	107(12)	121(13)
C(12A)	−9264(9)	−4372(8)	−2711(9)	137(10)	89(7)	127(10)	−30(13)	107(16)	74(13)
C(13A)	−9082(12)	−5785(10)	−3193(12)	161(13)	123(10)	190(14)	−50(18)	127(22)	108(19)
C(14A)	−10311(14)	−6458(11)	−4070(14)	194(15)	117(10)	210(16)	−55(19)	150(26)	126(20)
C(15A)	−11670(11)	−5809(10)	−4460(9)	169(12)	158(11)	117(10)	−140(19)	84(18)	103(17)
C(16A)	−11827(10)	−4433(11)	−3962(11)	120(10)	172(12)	147(12)	−124(18)	36(17)	130(19)
C(17A)	−10619(9)	−3728(10)	−3121(10)	118(9)	136(10)	130(10)	−68(15)	55(16)	104(16)
C(18A)	−13018(16)	−6587(16)	−5465(16)	214(18)	225(18)	219(18)	−236(32)	81(29)	202(29)
O(3B)	9703(7)	3379(7)	9303(11)	121(7)	138(7)	322(16)	−30(12)	206(18)	217(18)
O(4B)	8165(8)	5204(8)	9396(13)	142(9)	137(8)	349(18)	−51(14)	168(20)	236(19)
C(7B)	8505(9)	3989(9)	9201(10)	108(9)	106(8)	151(11)	−54(13)	74(16)	100(14)
C(8B)	7312(8)	3291(8)	8826(9)	109(8)	127(9)	122(9)	−55(14)	71(14)	119(15)
C(9B)	6179(9)	2868(9)	7096(10)	115(9)	142(10)	164(12)	−71(16)	116(17)	138(17)
C(10B)	5017(10)	2165(11)	6766(10)	142(10)	170(11)	130(10)	−163(19)	72(17)	110(17)
C(11B)	3950(9)	1594(8)	5068(9)	121(9)	112(8)	126(9)	−66(14)	86(15)	103(14)
O(5B)	2897(7)	1110(8)	4878(6)	132(7)	199(9)	112(7)	−158(14)	52(11)	131(12)
O(6B)	4009(8)	1528(8)	3943(7)	161(8)	182(9)	130(8)	−143(14)	89(13)	129(13)
N(5B)	6632(7)	4131(8)	9910(8)	109(7)	142(8)	121(8)	−77(13)	68(13)	106(13)
S(1B)	7310(2)	4083(2)	11625(2)	111(2)	124(2)	127(2)	−64(3)	84(4)	107(3)
O(7B)	6370(7)	5036(8)	12371(8)	141(8)	171(8)	155(9)	−32(13)	155(14)	111(14)
O(8B)	7513(9)	2729(8)	11332(9)	186(10)	170(9)	189(10)	−157(16)	54(17)	198(16)
C(12B)	9047(9)	4724(8)	12783(9)	126(9)	103(7)	122(9)	−34(14)	83(15)	98(13)
C(13B)	9139(10)	6040(12)	13329(13)	114(10)	164(12)	200(15)	−62(18)	71(20)	156(22)
C(14B)	10505(12)	6514(11)	14152(12)	145(12)	148(11)	184(14)	−126(19)	33(21)	127(20)
C(15B)	11751(9)	5657(11)	14380(11)	101(9)	193(13)	160(12)	−56(17)	59(17)	210(21)
C(16B)	11586(11)	4296(13)	13765(14)	120(11)	191(14)	206(16)	12(20)	97(21)	227(25)
C(17B)	10259(12)	3807(11)	12958(13)	161(12)	134(10)	198(15)	1(18)	128(22)	178(21)
C(18B)	13186(13)	6175(19)	15287(14)	150(13)	331(26)	171(15)	−216(31)	39(23)	249(32)

TABLE 4. BOND LENGTHS AND ANGLES OF THE TWO INDEPENDENT MOLECULES
Standard deviations are given in parentheses.

	Molecule A	Molecule B
Bond lengths (l/Å)		
N(1)-C(2)	1.37(1)	1.38(1)
N(3)-C(4)	1.33(1)	1.34(1)
C(5)-C(6)	1.34(1)	1.36(1)
C(2)-O(2)	1.26(1)	1.26(1)
C(5)-Br(5)	1.87(1)	1.88(1)
C(2)-N(3)	1.35(1)	1.33(1)
C(4)-C(5)	1.44(1)	1.43(1)
C(6)-N(1)	1.35(1)	1.36(1)
C(4)-N(4)	1.33(1)	1.33(1)
C(7)-O(3)	1.24(1)	1.23(1)
C(7)-C(8)	1.51(1)	1.53(1)
C(8)-C(9)	1.52(1)	1.52(1)
C(10)-C(11)	1.52(1)	1.48(2)
C(11)-O(6)	1.21(1)	1.22(1)
C(7)-O(4)	1.29(1)	1.26(1)
C(8)-N(5)	1.47(1)	1.44(1)
C(9)-C(10)	1.51(1)	1.52(1)
C(11)-O(5)	1.31(1)	1.32(1)
N(5)-S(1)	1.63(1)	1.64(1)
S(1)-O(8)	1.43(1)	1.40(1)
C(12)-C(13)	1.42(2)	1.34(2)
C(14)-C(15)	1.36(2)	1.37(2)
C(16)-C(17)	1.39(2)	1.37(2)
C(15)-C(18)	1.53(2)	1.47(2)
S(1)-O(7)	1.43(1)	1.44(1)
S(1)-C(12)	1.75(1)	1.79(1)
C(13)-C(14)	1.38(2)	1.40(2)
C(15)-C(16)	1.38(2)	1.40(2)
C(17)-C(12)	1.36(1)	1.38(2)
Bond angles (ϕ/°)		
C(2)-N(1)-C(6)	121.1(8)	121.5(8)
N(1)-C(2)-O(2)	117.4(8)	116.4(8)
N(1)-C(2)-N(3)	120.3(8)	120.0(8)
O(2)-C(2)-N(3)	122.3(8)	123.6(8)
C(2)-N(3)-C(4)	119.3(8)	120.6(8)
N(3)-C(4)-C(5)	121.2(8)	120.4(8)
N(3)-C(4)-N(4)	118.7(8)	119.7(9)
C(5)-C(4)-N(4)	120.0(8)	119.9(9)
C(4)-C(5)-C(6)	117.4(9)	118.4(9)
C(4)-C(5)-Br(5)	121.4(7)	122.4(7)
C(6)-C(5)-Br(5)	121.2(7)	119.2(8)
C(5)-C(6)-N(1)	120.3(9)	119.0(9)
O(3)-C(7)-O(4)	124.0(10)	124.1(11)
O(3)-C(7)-C(8)	121.5(9)	120.4(9)
O(4)-C(7)-C(8)	114.5(9)	115.5(9)
C(7)-C(8)-N(5)	112.2(8)	111.5(8)
C(7)-C(8)-C(9)	111.4(8)	112.1(8)
N(5)-C(8)-C(9)	109.8(8)	110.3(8)
C(8)-C(9)-C(10)	109.9(8)	110.5(9)
C(9)-C(10)-C(11)	115.5(8)	114.2(9)
C(10)-C(11)-O(5)	111.5(8)	111.5(9)
C(10)-C(11)-O(6)	124.5(9)	126.3(9)
O(5)-C(11)-O(6)	124.1(9)	122.2(9)
C(8)-N(5)-S(1)	119.9(6)	120.3(7)
N(5)-S(1)-O(7)	104.1(5)	104.8(5)
N(5)-S(1)-O(8)	107.2(4)	108.4(5)
N(5)-S(1)-C(12)	107.3(4)	106.4(5)
O(7)-S(1)-O(8)	119.0(5)	119.9(6)
O(7)-S(1)-C(12)	109.6(5)	108.3(5)
O(8)-S(1)-C(12)	108.9(5)	108.3(5)
S(1)-C(12)-C(13)	119.6(8)	119.9(8)
S(1)-C(12)-C(17)	120.6(8)	117.8(8)
C(13)-C(12)-C(17)	119.8(10)	122.1(11)
C(12)-C(13)-C(14)	117.9(11)	119.4(12)
C(13)-C(14)-C(15)	122.4(13)	121.4(12)
C(14)-C(15)-C(16)	118.9(11)	116.6(11)
C(14)-C(15)-C(18)	121.3(12)	120.9(12)
C(16)-C(15)-C(18)	119.8(11)	122.5(12)
C(15)-C(16)-C(17)	120.4(11)	123.1(13)
C(16)-C(17)-C(12)	120.5(10)	117.4(12)

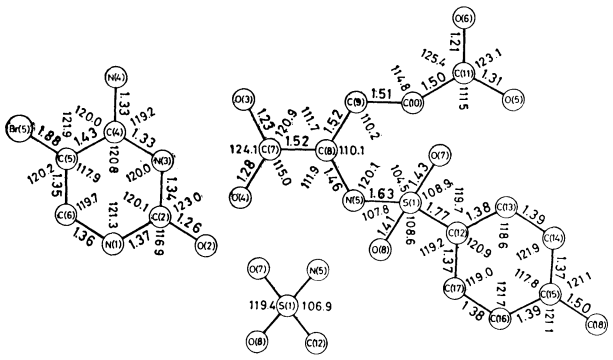

Fig. 1. Average bond lengths and angles of the two independent 5-bromocytosine and *N*-tosyl-L-glutamic acid molecules.

the difficulty in convergence due to pseudo symmetry of the crystal. Their averaged values shown in Fig. 1 are close to authentic ones.

The crystal structure is shown in Fig. 2. The molecules are arranged in layers parallel to the $(1\bar{2}0)$ plane. The complexes are formed by hydrogen bonds in the layer and come in van der Waals contancts with those in adjacent layers. The hydrogen bond scheme in the layer is illustrated in Fig. 3, relevant distances and angles being listed in Table 5. The 5-bromocytosine molecules form a ribbon elongated along [001], by the hydrogen bonds, N(1A)H···O(2B), N(1B)H···O(2A), N(4A)H···N(3B), and N(4B)H···N(3A), the former two and the latter two being related around each of pseudo-center of symmetry. The dihedral angle between the mean planes of cytosines A and B

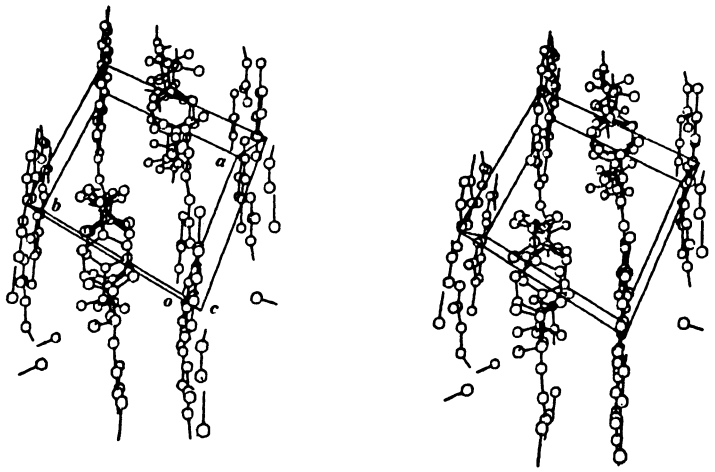

Fig. 2. A stereoscopic view of the crystal structure.

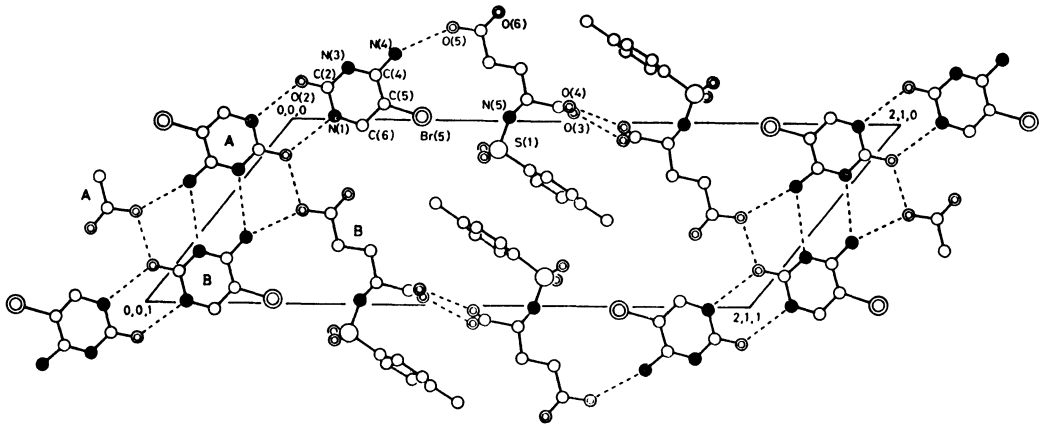

Fig. 3. The hydrogen bond scheme in the 5-bromocytosine : *N*-tosyl-L-glutamic acid. Crystallographically independent molecules are indicated as A and B. These are related to each other by pseudo-inversions.

Table 5. Distances and angles of hydrogen bonds
CH···O contacts are also listed in this table.

Distance (l/Å)					
N(1A)···O(2B)[a]	2.90	N(1B)···O(2A)[b]	2.93	N(4A)···N(3B)[c]	3.13
N(4B)···N(3A)[c]	3.12	N(4A)···O(5A)[c]	2.88	N(4B)···O(5B)[c]	2.88
O(5A)···O(2B)[c]	2.58	O(5B)···O(2A)[c]	2.61	O(4A)···O(3B)[d]	2.65
O(4B)···O(3A)[e]	2.70	C(6A)···O(6A)[a]	3.21	C(6B)···O(6B)[b]	3.23
Angle (ϕ/°)					
N(1A)···O(2B)[a]-C(2B)[a]	127.8	C(2A)-N(1A)···O(2B)[a]	115.1	C(6A)-N(1A)···O(2B)[a]	123.7
N(1B)···O(2A)[b]-C(2A)[b]	126.5	C(2B)-N(1B)···O(2A)[b]	114.4	C(6B)-N(1B)···O(2A)[b]	123.1
N(4A)···N(3B)[c]-C(2B)[c]	127.0	N(4A)···N(3B)[c]-C(4B)[c]	112.2	C(4A)-N(4A)···N(3B)[c]	128.0
N(4B)···N(3A)[c]-C(2A)[c]	127.3	N(4B)···N(3A)[c]-C(4A)[c]	113.3	C(4B)-N(4B)···N(3A)[c]	127.5
N(4A)···O(5A)[c]-C(11A)[c]	146.1	N(4A)···O(5A)[c]···O(2B)[c]	99.7	C(4A)-N(4A)···O(5A)[c]	161.2
N(4B)···O(5B)[c]-C(11B)[c]	146.2	N(4B)···O(5B)[c]···O(2A)[c]	98.2	C(4B)-N(4B)···O(5B)[c]	158.2
O(5A)···O(2B)[c]-C(2B)[c]	119.3	O(5A)···N(4A)[c]···N(3B)[c]	70.0	O(5A)···O(2B)[c]···N(1A)[b]	127.5
C(11A)-O(5A)···O(2B)[c]	114.1	O(5B)···O(2B)[c]-C(2B)[c]	119.9	O(5B)···N(4B)[c]···N(3A)[c]	70.8
O(5B)···O(2A)[c]···N(1B)[a]	110.5	C(11B)-O(5B)···O(2A)[c]	115.4	O(4A)···O(3B)[d]-C(7B)[d]	121.6
C(7A)-O(4A)···O(3B)[d]	113.3	O(4B)···O(3A)[e]-C(7A)[e]	120.6	C(7B)-O(4B)···O(3A)[e]	113.2
C(6A)···O(6A)[a]-C(11A)[a]	151.0	N(1A)-C(6A)···O(6A)[a]	94.8	C(5A)-C(6A)···O(6A)[a]	144.9
C(6B)···O(6B)[b]-C(11B)[b]	151.5	N(1B)-C(6B)···O(6B)[b]	95.1	C(5B)-C(6B)···O(6B)[b]	145.5

a) At x, y, $-1+z$. b) At x, y, $1+z$. c) At x, y, z. d) At $-2+x$, $-1+y$, $-1+z$. e) At $2+x$, $1+y$, $1+z$.

is 3.5°. On the other hand, the two independent *N*-tosyl-L-glutamic acid molecules are associated by the two hydrogen bonds between the α-carboxyl groups, O(4A)H···O(3B) and O(4B)H···O(3A), related by a pseudo-inversion. These dimers are stacked, by overlapping the tosyl groups, in the same direction as the ribbon. The two independent phenyl planes are almost parallel to each other; the dihedral angle between them is 1.7°, and its spacing is 3.59 Å.

The cytosine ribbons and glutamic acid stacks are linked by the other hydrogen bonds in which the side group of the glutamic acid participates. The O(5) atom is the donor to O(2) of 5-bromocytosine and at the same time the acceptor from N(4) of the neighboring base. In addition, the O(6) atom seems to make a CH···O type interaction with C(6) of the third base. Similar C(6)H···O contact is also observed in crystals of the two forms of cytidylic acid,[9,10] 1-methylcytosine hydrochloride,[11] and 1-(β-D-arabinofuranosyl)cytosine hydrochloride.[12]

The hydrogen bond scheme suggests that the protonation to N(3) of cytosine by the carboxyl group does not occur in the present complex. This is supported by the bond lengths and angles of cytosine molecule (Fig. 3); the C(2)–N(3)–C(4) bond angle 120.0° is close to unprotonated form, and the dimensions of α- and γ- carboxyl groups indicate that their hydrogen atoms are bonded to O(4) atom in α-carboxyl group and O(5) atom in γ-carboxyl group.

In the tosyl groups S(1)–O(8) bonds are *cis* to N(5)–C(8) bonds, and the N(5)–S(1)–O(8) bond angles are larger than N(5)–S(1)–O(7).

The conformations of the two independent glutamic acids are extended ones; the relevant torsion angles are given in Table 6. Atoms in the side group of the amino acid are coplanar; the largest deviation of atoms from the mean plane is 0.14 Å at C(8A) and 0.10 Å at C(9B), and the largest deviation in torsion angle from the *trans* conformation arises around C_β–C_γ bond in both A and B molecules; 15.9° and 6.0°, respectively. The α-carboxyl group makes an angle of 80.9° in A and 84.5° in B with the side group mean plane.

In summary, the present complex formation is due to the undissociated γ-carboxyl group of glutamic acid bound with O(2) and N(4) of 5-bromocytosine through hydrogen bonds. It is quite different from those found in cytosine : *N*-benzoylglycine complex monohydrate,[1] cytosine : *N*-formylglycine complex,[2] and cytidine : *N*-benzyloxycarbonyl-L-glutamic acid complex dihydrate,[3] where the dissociated α-carboxyl group plays a role. The present crystal provides the first example of interaction mode between cytosine and acidic side group of amino acid.

Table 6. Torsion angles of the glutamic acids

	Molecule A	Molecule B
O(4)-C(7)-C(8)-N(5)	143.5°	−47.9°
O(3)-C(7)-C(8)-N(5)	−35.0	131.8
C(7)-C(8)-N(5)-S(1)	−81.7	−87.1
C(9)-C(8)-N(5)-S(1)	153.8	147.6
O(4)-C(7)-C(8)-C(9)	−93.0	76.4
O(3)-C(7)-C(8)-C(9)	88.5	−103.9
N(5)-C(8)-C(9)-C(10)	−51.9	−55.6
C(7)-C(8)-C(9)-C(10)	−176.8	179.5
C(8)-C(9)-C(10)-C(11)	−164.1	174.0
C(9)-C(10)-C(11)-O(5)	176.2	−174.2
C(9)-C(10)-C(11)-O(6)	−3.2	7.5

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