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Single crystal neutron diffraction study of triglycine sulphate revisited

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Abstract. In order to get the exact hydrogen-bonding scheme in triglycine sulphate (TGS), which is an important hydrogen bonded ferroelectric, a single crystal neutron diffraction study was undertaken. The structure was refined to an R-factor of $R[F^2] = 0.034$. Earlier neutron structure of TGS was reported with a very limited data set and large standard deviations. The differences between the present and the earlier reported neutron structure of TGS are discussed.

Keywords. Triglycine sulphate; single crystal; neutron diffraction; ferroelectric.

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1. Introduction

Triglycine sulphate ($(NH_2CH_2COOH)_3H_2SO_4$) is one of the important and well-studied ferroelectric crystals of great technological relevance [1]. In triglycine sulphate (TGS), crystal structure and physical properties are primarily affected by the hydrogen bond interactions between three glycine ions, namely GI, GII and GIII and the tetrahedral negative acidic residue ions SO_4^{2-} [2]. Hence it is important to know the exact hydrogen-bonding scheme in these crystals in order to understand and modify their properties. Cambridge crystallographic database [3] has 17 structures of TGS determined under different conditions but surprisingly only one neutron structure [4] has been reported till date and that too with a very limited data set (only 648 unique reflections were used for structure refinement, and as a result standard deviations were high). With an intention to get the exact hydrogen atom positions in TGS crystals, neutron diffraction study on TGS was once again undertaken, since neutron diffraction is known to be the only method, which gives exact hydrogen atom position.

2. Experiment

A clear rectangular single crystal of TGS of dimension $3 \times 3.5 \times 3$ mm was loaded on a goniometer, which was then mounted on a four-circle single crystal diffractometer

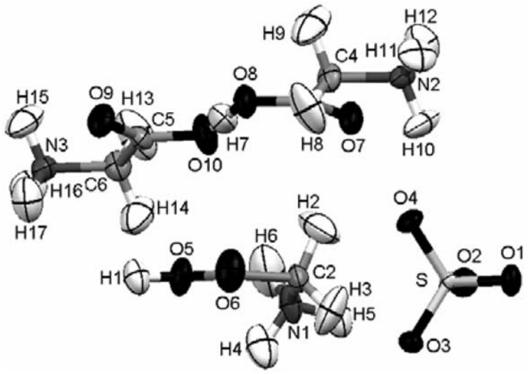

Figure 1. Picture of TGS asymmetric unit.

with BF_3 point detector located at Dhruva Reactor at Trombay. The neutron wavelength used was 1.216 Å obtained from pyrolitic graphite monochromator. The cell constants and orientation matrix were refined by least square technique from optimized 2θ angles of 50 reflections using REFINE program. The reflections were chosen to represent the randomly distributed reciprocal space within $\sin\theta/\lambda \sim 0.58$ Å^{-1}. The refined values are $a = 9.416(7)$ Å, $b = 12.643(1)$ Å, $c = 5.734(3)$ Å and $\beta = 110.33(3)^\circ$. The unit cell is monoclinic, with space group $P2_1$, and systematic absences $0k0$ for k odd.

The integrated neutron counts for 1420 unique Bragg reflections having $\sin\theta/\lambda \sim 0.58$ Å^{-1} were recorded in the symmetrical setting of the diffractometer using θ–2θ coupled step scan mode (0.1° step in 2θ). The background was scanned for a minimum of 1° on either side. The standard reflection was measured after every 50 reflections. The variation of the standard reflection intensity was within 3%. Squared observed structure factors were obtained from integrated intensities using the program DATRED. These were corrected for absorption. The calculated linear absorption coefficient $\mu = 1.59$ cm^{-1}. The structural parameters obtained from earlier neutron diffraction study were used as the starting parameters and were subjected to a series of isotropic and anisotropic full matrix least square refinements using SHELXL [5]. The nuclear scattering lengths used are: $b_{\mathrm{N}} = 0.936$, $b_{\mathrm{C}} = 0.6646$, $b_{\mathrm{H}} = -0.3739$, $b_{\mathrm{S}} = 0.2847$, $b_{\mathrm{O}} = 0.5803 \times 10^{-12}$ cm. All the reflections including negative Fo^2 were used for refinement. In the initial stages of refinement, weight (w) was taken to be $1/\sigma(\mathrm{Fo}^2)$, which was derived using counting statistics. The refined coordinates and anisotropic thermal parameters are given in table 1. Figure 1 shows the picture of TGS asymmetric unit. The final R-factor obtained are as follows: $R[F^2 > 2\sigma(F^2)] = 0.034$, $wR(F^2) = 0.090$ and $S = 1.082$.

3. Results and discussion

The standard deviation for both fractional coordinates as well as the anisotropic thermal parameters were found to be almost an order of magnitude smaller in this study as compared to the earlier neutron structure reported way back in 1973 indicating that our structure is more precise than earlier structures.

Table 1. Fractional coordinates and anisotropic thermal parameters of TGS.

Atom	x	y	z	b11 $\times 10^4$	b22 $\times 10^4$	b33 $\times 10^4$	b23 $\times 10^4$	b13 $\times 10^4$	b12 $\times 10^4$
S	0.0004(5)	0.2449(5)	0.2247(8)	33(5)	19(2)	115(14)	−23(16)	77(14)	−13(9)
O1	0.8576(2)	0.2474(3)	0.0065(4)	39(3)	45(1)	135(7)	−6(10)	45(8)	−1(6)
O2	0.9657(3)	0.2439(3)	0.4562(4)	82(3)	38(1)	127(7)	0(9)	125(9)	−3(6)
O3	0.0848(4)	0.1503(2)	0.2090(8)	61(4)	20(1)	231(14)	−4(7)	106(12)	8(4)
O4	0.0875(4)	0.3401(3)	0.2140(8)	68(4)	25(2)	250(15)	−11(8)	118(13)	−31(4)
GI									
N1	0.3578(4)	0.2096(3)	1.1634(6)	55(4)	69(3)	207(11)	20(7)	117(9)	27(4)
NIP	0.3564(28)	0.2860(20)	1.1622(52)	260(100)					
C1	0.4895(2)	0.2563(2)	0.8725(4)	51(2)	32(1)	176(7)	−2(7)	78(7)	−1(4)
C2	0.3407(2)	0.2509(3)	0.9146(5)	44(2)	37(1)	226(8)	26(9)	55(9)	14(5)
O5	0.6065(3)	0.2532(4)	1.0755(5)	49(3)	67(2)	175(9)	0(12)	65(10)	−17(6)
O6	0.4945(4)	0.2624(4)	0.6664(6)	83(4)	86(3)	170(9)	49(10)	91(10)	−8(7)
H1	0.7074(6)	0.2522(7)	1.0433(10)	67(6)	59(3)	266(17)	32(19)	118(17)	18(11)
H2	0.2926(11)	0.3297(6)	0.8994(23)	174(13)	52(4)	776(56)	162(27)	413(48)	93(14)
H3	0.2658(8)	0.2000(8)	0.7827(13)	104(9)	110(6)	285(22)	−91(22)	107(26)	−120(14)
H4	0.4223(9)	0.1433(7)	1.1993(14)	105(10)	88(6)	305(25)	138(20)	130(25)	39(14)
H5	0.2543(9)	0.1917(7)	1.1774(14)	97(10)	89(5)	345(27)	76(20)	166(27)	52(12)
H6	0.4101(9)	0.2619(12)	1.3020(17)	126(10)	129(9)	326(28)	−160(40)	93(30)	46(20)
GII									
O7	0.2212(4)	0.5012(3)	0.7768(8)	58(4)	52(2)	185(12)	70(9)	53(13)	−0(5)
O8	0.4605(4)	0.5276(3)	0.7988(9)	52(4)	52(2)	226(14)	36(9)	28(13)	7(7)
C3	0.3174(3)	0.5272(2)	0.6874(6)	44(3)	29(1)	167(10)	21(6)	42(10)	2(4)
C4	0.2694(4)	0.5648(2)	0.4203(7)	58(3)	40(2)	183(12)	46(7)	105(11)	−0(4)
N2	0.1042(2)	0.5665(1)	0.3018(4)	67(2)	26(1)	126(9)	7(6)	36(8)	−16(3)
H8	0.3190(12)	0.5171(9)	0.3184(1)	139(13)	122(8)	419(37)	13(29)	280(39)	128(17)
H9	0.3113(12)	0.6463(8)	0.4161(21)	153(12)	72(6)	415(41)	166(22)	1(36)	−87(15)
H10	0.0614(10)	0.4923(8)	0.2903(15)	135(11)	38(4)	287(30)	22(15)	5(29)	−71(11)
H11	0.0713(10)	0.5999(6)	0.1287(15)	143(11)	52(4)	200(30)	85(19)	62(27)	22(11)
H12	0.0597(10)	0.6179(7)	0.4021(17)	120(10)	71(5)	247(29)	−22(20)	159(30)	35(12)
GIII									
O9	0.7870(4)	0.4978(3)	0.2400(7)	71(5)	53(2)	165(13)	64(10)	88(13)	−14(5)
O10	0.5512(5)	0.4755(4)	0.2415(10)	58(4)	76(3)	259(15)	46(11)	089(15)	40(6)
C5	0.6975(3)	0.4706(2)	0.3386(6)	57(3)	28(1)	146(9)	23(6)	40(10)	16(4)
C6	0.7502(4)	0.4264(2)	0.5994(6)	72(4)	42(2)	155(10)	39(7)	108(11)	6(5)
N3	0.9163(2)	0.4230(1)	0.7060(4)	68(3)	27(1)	123(9)	9(6)	34(9)	−7(3)
H7	0.5116(9)	0.5010(6)	1.0432(19)	82(8)	39(3)	537(48)	−11(19)	128(33)	12(8)
H13	0.7079(11)	0.4754(9)	0.7167(18)	166(13)	118(7)	270(28)	2(22)	278(35)	122(17)
H14	0.7051(11)	0.3491(7)	0.5955(22)	118(10)	69(5)	436(40)	123(22)	67(32)	−53(13)
H15	0.9611(11)	0.4960(7)	0.7092(17)	143(12)	50(5)	337(34)	69(19)	34(32)	−72(12)
H16	0.9521(10)	0.3929(5)	0.8820(14)	133(10)	51(4)	159(27)	25(17)	59(23)	−10(11)
H17	0.9548(10)	0.3740(7)	0.6002(17)	91(9)	95(6)	224(28)	−49(23)	103(26)	18(12)

Since no field was applied during the data collection, the crystal was not single domain but instead both the domains were found to be present with occupancy 88% and 12% as indicated by the refined value of the occupancy of the nitrogen atom of GI in alternate orientation denoted as NIP in table 1. The fractional coordinates, especially those of hydrogen atoms obtained with this study were found to be significantly different from those reported earlier and hence the hydrogen bond

Table 2. Comparison between the hydrogen-bonding scheme as obtained in the previously reported neutron structure [4] and the current structure.

	Current structure				Previous structure [4]			
H-bond	D–H (Å)	D- - -A (Å)	H- - -A (Å)	∠DHA (°)	D–H (Å)	D- - -A (Å)	H- - -A (Å)	∠DHA (°)
GI								
O5–H1- -O1	1.029(07)	2.531(08)	1.502(09)	177.30(9)	0.996	2.516	1.520	178.5
N1–H4- -O8	1.014(11)	2.831(08)	1.830(10)	168.5(10)	0.975	2.803	1.840	168.5
N1–H5- -O3	1.030(10)	2.776(07)	1.748(08)	175.0(08)	1.063	2.785	1.723	176.8
N1–H6- -O6	1.020(13)	2.800(08)	1.960(10)	137.7(08)	1.000	2.802	1.964	139.6
GII								
N2–H10- -O4	1.014(08)	2.900(07)	2.006(09)	145.5(09)	0.986	2.913	2.044	145.8
N2–H10- -O9	1.014(08)	3.011(09)	2.499(10)	110.6(10)	0.986	3.040	2.537	111.4
N2–H11- -O1	1.023(09)	2.989(06)	2.211(11)	131.5(09)	1.056	2.973	2.225	126.0
N2–H11- -O3	1.023(09)	3.042(08)	2.084(09)	155.0(09)	1.056	3.019	2.001	160.8
N2–H12- -O4	1.014(10)	2.833(06)	1.841(08)	145.5(10)	0.969	2.849	1.948	153.5
GIII								
O10–H7- -O8	1.115(12)	2.470(09)	1.356(11)	177.3(09)	1.096	2.501	1.406	176.4
N3–H15- -O3	1.012(09)	2.915(08)	2.086(09)	137.6(08)	1.066	2.906	2.004	140.4
N3–H15- -O7	1.012(09)	2.928(09)	2.344(08)	115.6(10)	1.066	2.899	2.345	110.7
N3–H16- -O4	1.020(08)	2.986(09)	2.002(09)	161.3(08)	0.944	2.986	2.088	158.4
N3–H16- -O1	1.020(08)	2.978(07)	2.264(09)	125.8(07)	0.944	2.978	2.285	129.7
N3–H17- -O2	1.018(11)	2.804(07)	1.859(10)	152.7(08)	1.048	2.769	1.791	153.6

scheme obtained from this structure was compared to that obtained from the earlier structure. Table 2 gives a detailed comparison between the two.

The most important difference is found in the short hydrogen bond (O_{10}–H_7–O_8) connecting GIII and GII, the O_{10}- - -O_8 distance is found to be 0.031 Å smaller than that reported by the earlier neutron study, our value matches more with distance obtained by the different X-ray diffraction studies at room temperature (average O_{10}- - -O_8 in TGS obtained from nine room temperature X-ray structures reported in CCDC is 2.460 Å). It is believed that for O- - -O distance less than $r_c = 2.47$ Å the hydrogen bond energy has a single minimum as opposed to two site state for O- - -O distances greater than r_c [6]. Hence we conclude that the O_{10}–H_7–O_8 bond connecting GII and GIII has an energy contour having a single minimum, the position of which depends entirely on how much identical GII and GIII are. As it is now known, a perfectly symmetrical hydrogen bond exists only between crystallograpically as well as physiochemically identical molecules [7].

We see from table 2 that the above-mentioned O_{10}–H_7–O_8 hydrogen bond is asymmetric. This asymmetry is brought about due to the difference in the crystallographic environment around the donor (O_{10}) and acceptor (O_8) oxygens. Unlike the donor O_{10} atom acceptor oxygen O_8 is also involved in another hydrogen bond of moderate strength, namely, N_1–H_4=O_8 and as a result the donor and acceptor become non-equivalent resulting in the asymmetry of the O_{10}–H_7–O_8 H-bond. The fact that the largest thermal motion of the proton in the above-mentioned hydrogen bond is along the bond (table 1) instead of being normal as in ordinary bonds [8] supports the conclusion that the proton vibrates in a single, broad, flat potential energy well.

The O_{10}- - -O_8 distance was found to be 2.485 Å from the room temperature structure of deuterated TGS reported in CCDC. This is 0.015 Å larger than the O_{10}- - -O_8 distance in hydrated TGS reported here indicating that there is no inverse Ubbelohde effect in TGS as reported earlier by us [9] based on the then available neutron structure of TGS. Inverse Ubbelohde effect is observed for low barrier double well hydrogen bond potential [10] but since this study shows that the hydrogen bond potential for O_{10}–H_7–O_8 in TGS has a single, broad, flat potential energy well no inverse Ubbelohde effect is observed in TGS.

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