

Hydrogen Bonding in Salts of Poly-carboxylic Acids. Crystal Structures of Ethylenediammonium Hydrogen Tetrahydrofuran-tetracarboxylate hydrate (1:2:1:1) and Ammonium Hydrogen Tetrahydrofuran-tetracarboxylate Hydrate (3:1:1:2).

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Summary: Hydrogen bonding in ethylenediammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (1:2:1:1) and ammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (3:1:1:2) leads to extended ring structures. The conformations of the anions in the two salts are different because of the formation of a strong internal hydrogen bond in the ethylenediammonium salt whereas the ammonium compound has an anion pair with very short hydrogen bonds.

Introduction

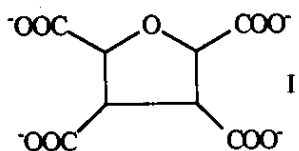
Hydrogen bonding to give supramolecular arrays forms a major factor in the design of the crystal structures of polycarboxylic acids and their ammonium salts [1]. The extensive literature on mono- and di-carboxylic acids has been codified by Etter, MacDonald and Bernstein [2] and reviewed by Etter [3] and most recently by Bernstein, Davis, Shimani and Chang [4] using network analysis to describe the structural elements.

There are relatively few published structures of tri- or tetra-carboxylic acids or their salts. We have recently reported the structures of β -methyl tricarballylic acids, tricarballylic acid mono-ammonium salt hemihydrate and 1,2,3,4-butane-tetracarboxylic acid tetraammonium salt monohydrate [5] and some camphoric acid derivatives [6]. The interest in these structures lies in the contribution of hydrogen bonding to crystal packing. In contrast to the skeletal flexibility of linear polycarboxylates, the tetrahydrofuran-tetracarboxylate ion [1] has limited steric freedom although the conformations of the anions in the two amine salts reported below are significantly different.

Good crystals gave a very satisfactory structure for ethylene diammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (1:2:1:1),

$[\text{NH}_3\text{CH}_2\text{NH}_3]^{2+}[\text{C}_4\text{H}_4\text{O}(\text{COOH})_2(\text{COO})_2]^{2-}\cdot\text{H}_2\text{O}$, [II] but for ammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (3:1:1:2), (3NH_4^+) , $[\text{C}_4\text{H}_4\text{O}(\text{COOH})(\text{COO})_3]^{3-}\cdot 2\text{H}_2\text{O}$ [III] the crystal quality was poor, however the architecture of the structure is clear in spite of the high final R-value. We have previously investigated the calcium, caesium and tris(1,2-diaminoethane) cobalt(III) salts of racemic trans, cis, trans tetrahydrofuran-tetracarboxylic acid [7,8]. As yet, no crystals of diffraction quality have been prepared for the free acid.

Polycarboxylic acids and their ammonium salts can form many local hydrogen bond networks, which must often be of similar energy. In consequence many compounds form syrups which do not readily yield crystals. Only one of the possible ammonium salts was successfully crystallised for each of the linear polycarboxylic acids [5] and only compound III in the present study. With 1,2-diaminoethane, samples of 1:1 and 2:1 compounds were prepared. The crystal structure of the 1:1 compound has been determined but the crystals of the 2:1 compound were so poor that no intensity data could be collected. The 2:1 compound appears to be triclinic with cell dimensions approximately 23.1, 9.2 and 8.1 Å, consistent with four formula weights in the unit cell.



Results and Discussion

a) The individual anions

The anions in II and III show the expected trans, cis, trans configuration. The stereochemistry in II is similar to that in the calcium, caesium and tris (1,2-diaminoethane) cobalt(III) salts, with O1, C2, C3 and C5 within 0.003 Å of their mean plane and 0.513(3) Å out of the plane (Fig. 1). The torsion angles between the carboxylate carbon atoms are C6-C2-C3-C9-93.0(2), C9-C3-C4-C12

39.9(2) and C12-C4-C5-C15 -148.6(2)°. A short (but normal) intramolecular hydrogen bond O7-H71...017 (2.54 (5) Å) constrains the angles between the mean planes of the ring and the carboxylate groups to 68.6(4)° (C6), 30.5(5)° (C9), 90.0(4)° (C12) and 79.2(4)° (C15), in close agreement with the values in the caesium salt and the one anion of the tris(1,2-diaminoethane)cobalt(III) salt in which this hydrogen bond is also present.

The stereochemistry of III is quite different, Fig. 2. It approaches an idealised model with a vertical mirror plane through O1 and the mid point of C3 and C4 and a torsion angle C9-C3-C4-C12 of zero. The best plane among the ring atoms of III is C2, C3, C4 and C5 (maximum deviation 0.015 Å),

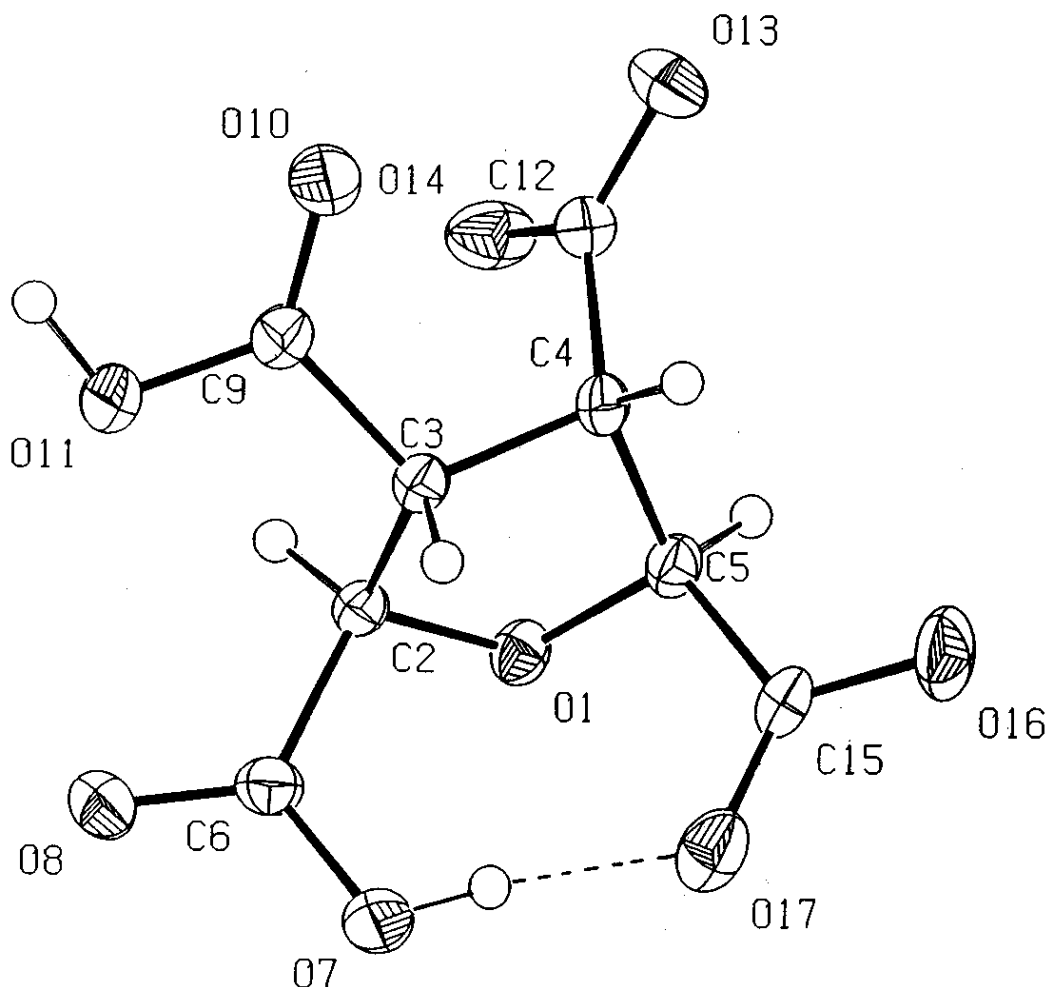


Fig. 1: The tetrahydrofuran tetracarboxylate anion in II. Ellipsoids drawn at 50% probability.

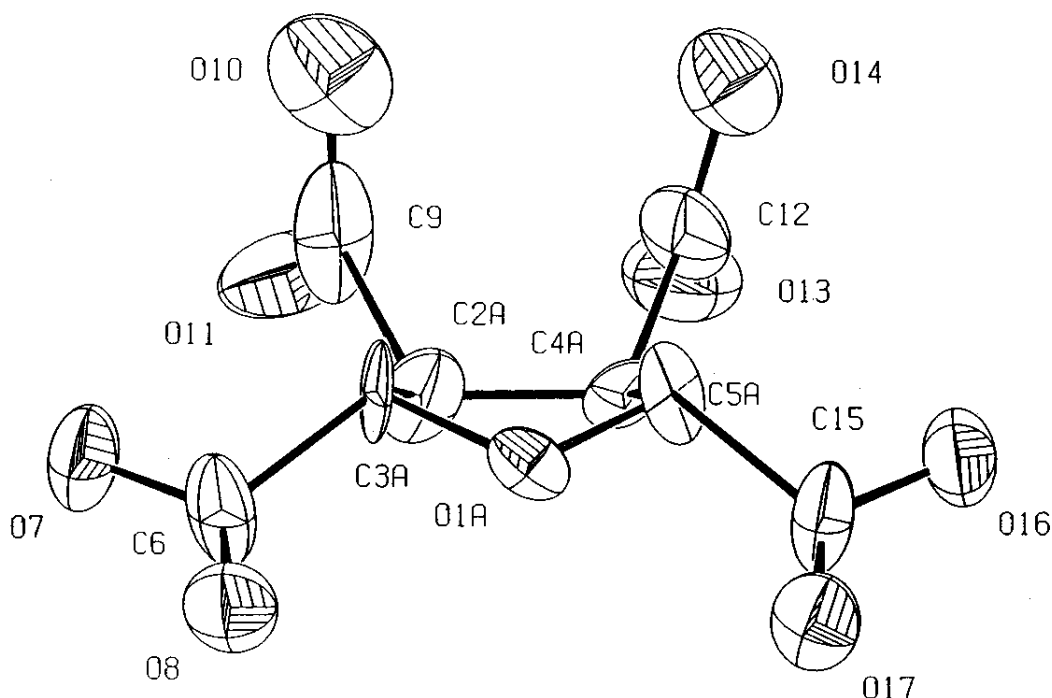


Fig. 2: The tetrahydrofuran tetracarboxylate anion in III. Position A of the disordered structure is shown with an anisotropic refinement of the ring atoms. Ellipsoids drawn at 50% probability.

with O1 0.501 Å out of this plane. The torsion angles between the carboxylate carbon atoms are C6-C2-C3-C9 99.0(3), C9-C3-C4-C12 6.3(3) and C-12-C4-C5-C15 -100.5(2)°. The angles between the mean planes of the ring and the carboxylate groups are 35.9(3)° (C6), 97.1(5)° (C9), 71.0(4)° (C12) and 41.3(3)° (C15). This stereochemistry allows the anions to pair by forming very short hydrogen bonds O10...O10' and O14...O14' (see below).

b. Intermolecular hydrogen-bonding networks

The lengths and symmetry relationships of the hydrogen bonds are given in Tables 3b and 6b. Hydrogen bonds have been accepted only where the angles in the C-O...N-C (etc.) fragment are reasonable. In most cases protons are found close to the proposed line for the bond. There are many other O...O and N...O contacts under 3.0 Å which for geometric reasons cannot be hydrogen bonds. Fig. 3 shows that the intermolecular hydrogen bonding in II is a complex pattern of fused rings, giving layers in the *ac* plane with cross-links in the *b*-direction. The protons of the water molecule,

Table-1: Crystal data and structure refinement for II

Identification code	jcb16
Empirical formula	C ₁₀ H ₁₈ N ₂ O ₁₀
Formula weight	326.26
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 12.531(2) Å b = 8.4658(6) Å beta = 98.024(10) deg. c = 12.8730(14) Å
Volume	1352.3(2) Å ³
Z	4
Density (calculated)	1.603 Mg/m ³
Absorption coefficient	0.145 mm ⁻¹
F(000)	688
Crystal size	0.54 x 0.44 x 0.40 mm
Theta range for data collection	2.12 to 27.47 deg.
Index ranges	0 <= h <= 16, 0 <= k <= 10, -16 <= l <= 16
Reflections collected	3224
Independent reflections	3089 [R (int) = 0.0061]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3089/0/219
Goodness-of-fit on F ²	1.018
Final R indices	R1 = 0.0392, wR2 = 0.1070
[I > 2sigma (I)]	
R indices (all data)	R1 = 0.0445, wR2 = 0.1120
Extinction coefficient	0.012(2)
Large diff. peak and hole	0.399 and -0.269 e. Å ⁻³

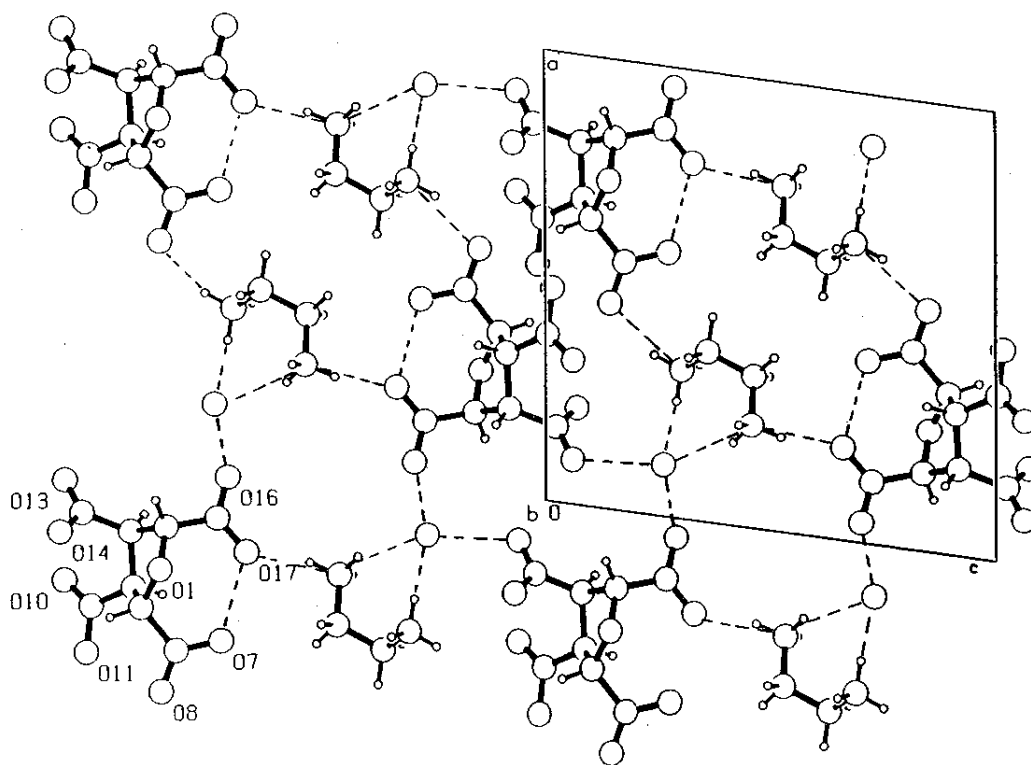


Fig. 3: Hydrogen bonds in the section $-0.25 < y < 0.25$ of the b -axis projection of ethylenediammonium hydrogen tetrahydrofuran tetracarboxylate hydrate (1:2:1:1).

Table-2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for II. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	7283(1)	540(1)	1464(1)	22(1)
C(2)	6389(1)	-420(2)	1035(1)	20(1)
C(3)	6852(1)	-2074(2)	880(1)	20(1)
C(4)	8063(1)	-1780(2)	847(1)	21(1)
C(5)	8264(1)	-343(2)	1579(1)	21(1)
C(6)	5549(1)	-434(2)	1786(1)	24(1)
O(7)	5904(1)	-478(2)	2794(1)	37(1)
O(8)	4594(1)	-415(2)	1470(1)	36(1)
C(9)	6288(1)	-2956(2)	-64(1)	24(1)
O(10)	6767(1)	-3723(2)	-636(1)	43(1)
O(11)	5237(1)	-2829(2)	-177(1)	37(1)
C(12)	8320(1)	-1380(2)	-259(1)	25(1)
O(13)	9003(1)	-2224(1)	-630(1)	36(1)
O(14)	7839(1)	-233(1)	-720(1)	37(1)
C(15)	8599(1)	-849(2)	2722(1)	23(1)
O(16)	9563(1)	-1259(2)	2952(1)	42(1)
O(17)	7917(1)	-837(1)	3344(1)	30(1)
O(18)	11157(1)	1050(2)	2674(1)	40(1)
N(21)	2297(1)	2191(2)	4638(1)	29(1)
C(22)	3408(1)	1540(2)	4714(1)	32(1)
C(23)	3799(1)	1368(2)	3663(1)	35(1)
N(24)	3331(1)	-47(2)	3083(1)	32(1)

O18, connect to O13 and O16 of different anions to give an 18-membered ring with two hydrogen bonds. $R_2^2(18)$ in the Etter notation, centered at the origin. N21 and N24 of a single ethylenediammonium cation donate protons to hydrogen bonds with the lone pairs of electrons on O18, forming a hydrogen bonded chelate ring $R_2^2(7)$. In addition N21 interacts with O17 to complete a ring $R_6^6(16)$ centred at $(0,0,0.5)$ in the ac -plane and to O14 to give another $R_6^6(16)$ ring in the b -direction. N24 connects to 8 for a ring $R_6^6(22)$ centered at $(0.5,0,5.0)$ and 13 to give an $R_4^4(18)$ ring in the b -direction.

Examination of the C-O distances in the anion of III would suggest that all four acid groups were deprotonated. This is not the case. The disorder in the anion makes the C-O distances unreliable. Fig. 4 shows that O10 and O14 are connected to O10' and O14' respectively of the molecule at $(1-x, y, 0.5-z)$ by "very short hydrogen bonds" [9] of 2.368 (12) and 2.470(14) Å. In these

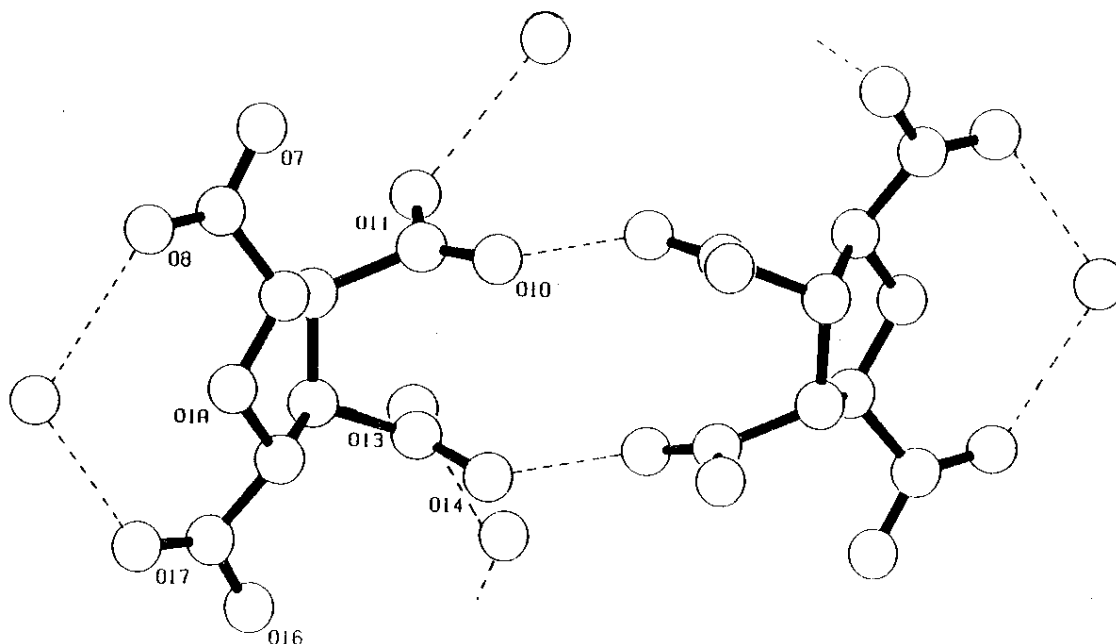


Fig. 4: The short hydrogen bonds 010...010' and 014...014' forming an anion pair in ammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (3:1:1:2).

bonds the proton is required by symmetry to lie on the special position (0.5,y,0.25) (Wyckoff position 4e) at the midpoint of the bond. Thus on average the anion has one proton. This O10/O14 system forms a ring $R_2^2(14)$ in the *a*-direction.

Two other hydrogen bond arrays involve the anion. The ammonium ion N21 bridges 08 and 017 of the same molecule to form a local ring $R_2^2(10)$. Secondly, the anions are linked into chains in the *b*-direction by O7...N23...O13' and O11...N22...016' to form a ring $R_{22}(18)$. These hydrogen bonds have O...N about 2.8 Å and C-O...N angles in the range 100-120°. The water molecules O24W and O25W are involved in hydrogen bonds to the ammonium ions but not to the anions.

Experimental

Aqueous 1,2-diaminoethane (B.D.H.) and tetrahydrofuran-tetracarboxylic acid (Aldrich) (5 mmol) were mixed in 1:1 and 2:1 ratios and allowed to crystallise at room temperature (295K). The resulting brown masses were dissolved in ethanol and decolourised with charcoal before crystallisation. Only a few crystals of possible

diffraction quality could be separated from the bulk of overgrown and dendritic material.

A plate of the 1:1 compound was mounted on an Enraf-Nonius CAD4 diffractometer and data collected at 24.5°C using ω -2 θ scans in bisecting geometry. The structure solved by direct methods (SHELXS-86) [10] and refined by standard Fourier and least-squares methods (SHELXL-93) [11] to R 0.039. Details of the data collection and refinement are given in Table-1. Anisotropic atomic displacement parameters were used for all non hydrogen atoms. Carboxylate and water hydrogen atoms were located on difference maps, other hydrogen atoms were placed at calculated positions and refined by a riding model.

Needles of ammonium hydrogen tetrahydrofuran-tetracarboxylate hydrate (3:1:1:2) were grown by evaporating an aqueous solution containing the acid (5 mmol) and excess saturated ammonia. The crystals decompose slowly in air at 295K so that samples for diffraction photographs were mounted in Lindemann capillaries. The specimen for data collection at 150K was mounted in an oil drop.

Table-3: Bond lengths [Å] and angles [deg] for II

O(1)-C(5)	1.429(2)
O(1)-C(2)	1.431(2)
C(2)-C(6)	1.526(2)
C(2)-C(3)	1.540(2)
C(3)-C(9)	1.515(2)
C(3)-C(4)	1.544(2)
C(4)-C(5)	1.538(2)
C(4)-C(12)	1.541(2)
C(5)-C(15)	1.534(2)
C(6)-O(8)	1.209(2)
C(6)-O(7)	1.312(2)
C(9)-O(10)	1.203(2)
C(9)-O(11)	1.309(2)
C(12)-O(14)	1.248(2)
C(12)-O(13)	1.259(2)
C(15)-O(17)	1.250(2)
C(15)-O(16)	1.251(2)
N(21)-C(22)	1.488(2)
C(22)-C(23)	1.510(2)
C(23)-N(24)	1.488(2)
C(5)-O(1)-C(2)	111.05(9)
O(1)-C(2)-C(6)	109.39(10)
O(1)-C(2)-C(3)	106.08(9)
C(6)-C(2)-C(3)	112.41(10)
C(9)-C(3)-C(2)	114.20(10)
C(9)-C(3)-C(4)	114.10(10)
C(2)-C(3)-C(4)	104.31(10)
C(5)-C(4)-C(12)	110.82(10)
C(5)-C(4)-C(3)	100.82(10)
C(12)-C(4)-C(3)	113.18(10)
O(1)-C(5)-C(4)	111.28(10)
O(1)-C(5)-C(4)	106.58(9)
C(15)-C(5)-C(4)	111.51(10)
O(8)-C(6)-O(7)	121.08(12)
C(8)-C(6)-C(2)	121.64(12)
O(7)-C(6)-C(2)	117.28(11)
O(10)-C(9)-O(11)	123.83(12)
O(10)-C(9)-C(3)	122.65(12)
O(11)-C(9)-C(3)	113.50(11)
O(14)-C(12)-O(13)	124.77(13)
O(14)-C(12)-C(4)	117.43(11)
O(13)-C(12)-C(4)	117.80(12)
O(17)-C(15)-O(16)	125.06(12)
O(17)-C(15)-C(5)	119.41(11)
O(16)-C(15)-C(5)	115.53(12)
N(21)-C(22)-C(23)	113.21(12)
N(24)-C(23)-C(22)	111.92(12)

Symmetry transformations used to generate equivalent atoms

Table-3b: Hydrogen bond lengths [Å] for II.

O(18)-H(181)...O(13)	(a)	2.793(2)
O(18)-H(182)...O(16)		2.851(2)
O(18)...H(212)-N(21)	(b)	2.891(2)
O(18)...H(242)-N(24)	(b)	2.857(3)
N(21)-H(212)...O(17)	(c)	2.887(2)
N(21)-H(213)...O(14)	(d)	2.718(2)
N(24)-H(241)...O(8)		2.798(2)
N(24)-H(243)...O(13)	(e)	2.900(2)
O(7)-H(71)...O(17)		2.541(2)
O(11)...O(16)	(f)	2.556(3)

Symmetry transformations used to generate equivalent atoms:

(a)	(2-x),	-y,	-z
(b)	(1+x),	y,	z
(c)	(x-0.5),	(0.5-y),	(0.5+z)
(d)	(1-x),	-y,	(1-z)
(e)	(x-0.5),	(-0.5-y),	(0.5+z)
(f)	(x-0.5),	(-0.5-y),	(z-0.5)

Table-4: Crystal data and structure refinement for III

Identification code	nthf
Empirical formula	C ₈ H _{4.25} NO ₁₃
Formula weight	322.37
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 11.752(5) Å alpha = 90 deg. b = 18.668(3) Å beta = 104.08(2) deg. c = 13.279(12) Å gamma = 90 deg.
Volume	2826(3) Å ³
Z	8
Density (calculated)	1.516 Mg/m ³
Absorption coefficient	0.152 mm ⁻¹
F(000)	1306
Crystal size	0.24 x 0.12 x 0.10 mm
Theta range	2.09 to 25.02 deg.
for data collection	
Index ranges	-9<h<13, -20<k<20, -15<l<15
Reflections collected	6329
Independent reflections	2200 [R(int) = 0.1607]
Absorption correction	None
Refinement method	Full-matrix least-square on F ²
Data/restraints/parameters	2177/10/195
Goodness-of-fit on F ²	0.726
Final R indices	R1 = 0.1000, wR2 = 0.2129
[I>2sigma(1)]	
R indices (all data)	R1 = 0.2752, wR2 = 0.3371
Largest diff. peak and hole	0.496 and -0.456 e.Å ⁻³

Table-5: Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for III U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1A)	1527(9)	2557(6)	4128(8)	36(4)
C(2A)	1978(16)	3176(8)	3668(12)	23(5)
C(3A)	2016(18)	2937(9)	2603(13)	37(6)
C(4A)	2041(18)	2079(9)	2664(13)	37(6)
C(5A)	1991(16)	1910(8)	3764(12)	24(5)
O(18)	776(9)	2547(7)	3386(9)	34(4)
C(28)	1319(14)	3155(8)	2993(16)	24(5)
C(38)	2592(14)	2968(10)	3253(19)	36(6)
C(48)	2598(14)	2108(9)	3283(18)	29(6)
C(58)	1332(15)	1899(8)	3097(17)	25(5)
C(6)	1205(10)	3818(5)	3676(9)	44(3)
O(7)	1554(5)	4372(4)	3291(5)	45(2)
O(8)	523(6)	3813(4)	4265(6)	48(2)
C(9)	3217(19)	3271(7)	2445(16)	93(7)
O(10)	4237(8)	3316(6)	2941(8)	84(4)
O(11)	2857(7)	3434(5)	1485(9)	94(3)
C(12)	3187(14)	1796(6)	2405(14)	64(5)
O(13)	2885(7)	1768(5)	1448(9)	84(3)
O(14)	4198(7)	1615(4)	2953(6)	61(3)
C(15)	1211(10)	1285(6)	3811(8)	42(3)
O(16)	1627(5)	706(4)	3541(5)	49(2)
O(17)	482(6)	1347(4)	4324(6)	51(2)
N(21)	4412(6)	2380(5)	-66(6)	54(2)
N(22)	920(7)	568(4)	-539(6)	51(3)
N(23)	1234(6)	5581(4)	4341(5)	31(2)
O(24W)	1159(6)	4945(4)	6267(6)	73(3)
O(25W)	1334(6)	37(4)	1584(6)	75(3)

Table-6: Selected bond lengths [Å] and angles [deg] for III

O(1A)-C(5A)	1.46(2)
O(1A)-C(2A)	1.46(2)
C(2A)-C(3A)	1.49(2)
C(2A)-C(6)	1.51(2)
C(3A)-C(9)	1.60(2)
C(3A)-C(4A)	1.60(2)
C(4A)-C(5A)	1.51(2)
C(4A)-C(12)	1.56(2)
C(5A)-C(15)	1.49(2)
O(18)-C(28)	1.46(2)
C(18)-C(58)	1.47(2)
C(28)-C(38)	1.49(2)
C(28)-C(6)	1.56(2)
C(38)-C(9)	1.55(2)
C(38)-C(48)	1.61(2)
C(48)-C(58)	1.50(2)
C(48)-C(12)	1.60(2)
C(58)-C(15)	1.52(2)
C(6)-C(8)	1.248(12)
C(6)-O(7)	1.266(11)
C(9)-O(10)	1.22(2)
C(9)-O(11)	1.28(2)
C(12)-O(13)	1.24(2)
C(12)-O(14)	1.28(2)
C(15)-O(17)	1.223(12)
C(15)-O(16)	1.273(12)
C(5A)-O(1A)-C(2A)	108.3(10)
O(1A)-C(2A)-C(3A)	104.9(12)
O(1A)-C(2A)-C(6)	110.2(13)
C(3A)-C(2A)-C(6)	113.7(14)
C(2A)-C(3A)-C(9)	104(2)
C(2A)-C(3A)-C(4A)	104.7(13)
C(9)-C(3A)-C(4A)	113(2)
C(5A)-C(4A)-C(12)	112(2)
C(5A)-C(4A)-C(3A)	104.7(13)
C(12)-C(4A)-C(3A)	110(2)
O(1A)-C(5A)-C(15)	110.6(13)
O(1A)-C(5A)-C(4A)	104.6(11)
C(15)-C(5A)-C(4A)	111.9(14)
O(8)-C(6)-O(7)	125.4(10)
O(8)-C(6)-C(2A)	118.6(11)
O(7)-C(6)-C(2A)	113.1(11)
O(10)-C(9)-O(11)	124.3(14)
O(10)-C(9)-C(3A)	137(2)
O(11)-C(9)-C(3A)	98(2)
O(13)-C(12)-O(14)	124.6(12)
O(13)-C(12)-C(4A)	101(2)
O(14)-C(12)-C(4A)	134(2)
O(17)-C(15)-O(16)	127.3(10)
O(17)-C(15)-C(5A)	118.0(11)
O(16)-C(15)-C(5A)	111.7(11)

Data were collected using an Enraf-Nonius CAD-4 diffractometer fitted with the FAST-MADNESS area detector system. All the non-hydrogen atoms of the anion and some others subsequently assigned as oxygen or nitrogen of water or ammonia were located by direct methods, as above. During refinement it became clear that, although the carboxylate groups are essentially ordered, the

Table-6b: Hydrogen bond lengths [Å] for III

O(7)...N(23)		2.73(2)
O(8)...N(21)	(a)	2.83(1)
O(10)...O(10)	(b)	2.37(1)
O(11)...N(22)	(c)	2.83(2)
O(13)...N(23)	(d)	2.76(1)
O(14)...O(14)	(b)	2.43(1)
O(16)...N(22)	(e)	2.89(2)
O(17)...N(21)	(a)	2.90(2)

Symmetry transformations used to generate equivalent atoms:

(a)	(x-0.5),	(0.5-y)	(0.5+z)
(b)	(1-x)	y,	(0.5-z)
(c)	(0.5-x),	(0.5-y),	-z
(d)	(0.5-x),	(y-0.5),	(0.5-z)
(e)	x,	-y,	(0.5+z)

tetrahydrofuran ring was disordered over two positions (A & B) of equal site occupancy, related by a local horizontal mirror plane. A satisfactory refinement was obtained using isotropic atomic displacement parameters for the ring atoms O1A - C5A and O1B - C5B and anisotropic atomic displacement parameters (which include the small positional disorder) for the carboxylate atoms. Anisotropic refinement of the ring atoms was attempted but rejected as unstable and not meaningful. Details of the data collection and refinement are given in Table-4. With the high final R factor the possibility of twinning was examined but no twin plane could be located. In this case the main factor leading to the poor final R factor was the very limited number of planes with intensities above background. Of the 2177 independent reflections measured only 456 had $I > 2\sigma(I)$.

Atomic coordinates for the structures are given in Tables 2 and 5 respectively, with bond lengths and angles in Tables 3 and 6. Figures were drawn with PLATON-92[12] or PLUTON-92 [13].

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