Crystal structure of diammonium hydrogen-2-hydroxy-1,2,3-propane-tricarboxylate, $(NH_4)_2(C_6H_6O_7)$

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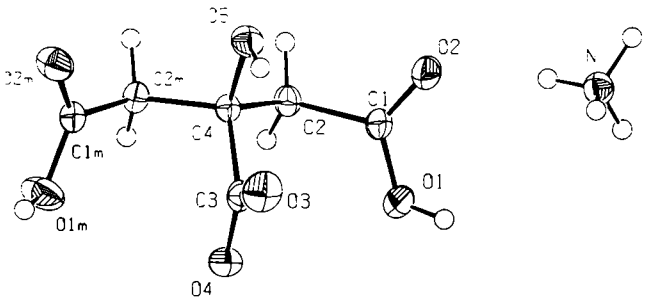

Abstract

$C_6H_{14}N_2O_7$, orthorhombic, *Pnma* (No. 62), $a = 10.775(6)$ Å, $b = 14.715(7)$ Å, $c = 6.165(2)$ Å, $V = 977.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.095$, $T = 293$ K.

Source of material

The compound was synthesized by controlled evaporation, at 313 K, of a water solution of glycine and hydroxylammonium chlorine in the molar ratio 1:1. The small single crystal used for the X-ray data collection was cut from a larger, good quality, single crystal.

Experimental details

The structure was solved by direct methods. An initial attempt to solve the structure in the previously reported non-centrosymmetric space group *Pn2b* [1] showed that the structure was centrosymmetric, with a mirror plane passing through the middle of the citrate ion, with a possible exception of the terminal carboxyl groups. These showed a small asymmetry in their bond lengths that could be interpreted as only one of the groups being ionised. However, refinement in the non-centrosymmetric space group was unstable and showed a large correlation between the refined structural parameters, as expected from the missing inversion symmetry. Thus, the structure was eventually refined in the centrosymmetric space group *Pnma*, with an hydrogen atom attached to each of the terminal carboxyl groups with 50% occupancy. This refinement converged smoothly. It can not be reliably inferred from our X-ray data whether the structure is truly centrosymmetric with disordered anions across the mirror plane or in fact pseudo-centrosymmetric, with just the carboxylic H atom breaking the inversion symmetry. All hydrogen atoms involved in C-H bonds were initially placed at idealized positions using SHELXL-97 [2] defaults and later refined isotropically. The carboxylic H atoms were located in a difference Fourier synthesis and also refined isotropically. The final structure was examined with PLATON [3] showing that there are no solvent-accessible voids in the crystal structure.

Discussion

The asymmetric unit contains one hydrogen citrate ion and two ammonium ions. Examination of the interatomic distances shows that the doubly ionized citrate molecule does not appear to be in the fully extended configuration as is frequently observed in other alkali citrates [4]. The central carboxyl and one terminal carboxyl groups are ionised. This agrees with previous evidence on the order of ionisation of the citric acid [5] in which the central carboxyl group is first ionised followed by the terminal carboxyl groups. The central hydroxyl and carboxyl groups lye on the mirror symmetry plane of the citric acid molecule. This plane is almost perpendicular to the plane of the C atom backbone (85.2(6)°), similarly to what was found for the 1:1 adduct of trimethylglycine and citric acid [6]. The plane of the end carboxyl groups lies at an angle of 82.8(1)° with the C atom backbone. The hydrogen citrate ions are hydrogen bonded head to tail via the disordered hydroxyl group which is involved in a very strong hydrogen bond [d(O1–H1···O1) = 2.442(3) Å]. Further examination of the crystal structure shows alternate (0 0 1) layers of ammonium ions and hydrogen citrate ions at a distance of 1/4 a. These layers are interconnected by a three dimensional network of hydrogen bonds via the ammonium ions (N···O distance within the range 2.815(2) Å – 2.947(2) Å). Each H atom of the ammonium cation participates in at least one hydrogen bond. One of these hydrogen bonds is bifurcated and points towards two oxygen atoms, one of the central carboxylate and one of the end carboxyl groups of the hydrogen citrate ion. The three other hydrogen bonds are established with the end oxygen atom (O2) of two neighbouring hydrogen citrate ions and with one oxygen atom (O3) of the central carboxyl group.

Table 1. Data collection and handling.

Crystal:	colourless truncated square pyramide, size 0.25 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.41 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, $\omega/2\theta$
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1681, 1130
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 862
$N(param)_{refined}$:	108
Programs:	SHELXS-97 [7],SHELXL-97 [2], PLATON [3]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8*d*	0.50	0.503(9)	0.015(6)	0.03(1)	0.08(2)
H(5)	4*c*		0.305(3)	1/4	0.263(7)	0.07(1)
H(2A)	8*d*		0.626(2)	0.171(1)	0.362(3)	0.024(4)
H(2B)	8*d*		0.520(2)	0.163(1)	0.542(3)	0.024(4)
H(1A)	8*d*		0.203(2)	0.068(2)	0.746(4)	0.048(6)
H(1B)	8*d*		0.182(2)	0.151(2)	0.624(3)	0.049(6)
H(1C)	8*d*		0.292(2)	0.147(1)	0.786(4)	0.046(6)
H(1D)	8*d*		0.298(2)	0.094(2)	0.567(4)	0.056(6)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8*d*	0.5531(1)	0.05170(9)	0.1240(2)	0.0530(8)	0.0332(7)	0.0462(8)	–0.0144(6)	0.0240(7)	–0.0173(6)
O(2)	8*d*	0.3907(1)	0.04291(8)	0.3432(2)	0.0338(6)	0.0283(6)	0.0384(7)	–0.0096(5)	0.0098(5)	–0.0102(5)
O(3)	4*c*	0.3636(2)	1/4	–0.0361(3)	0.0364(9)	0.044(1)	0.0296(9)	0	–0.0144(8)	0
O(4)	4*c*	0.5714(2)	1/4	–0.0456(3)	0.0393(9)	0.0294(8)	0.0287(8)	0	0.0105(7)	0
O(5)	4*c*	0.3463(1)	1/4	0.3781(3)	0.0190(7)	0.0283(8)	0.0320(9)	0	0.0040(7)	0
C(1)	8*d*	0.4875(1)	0.0795(1)	0.2834(2)	0.0269(7)	0.0171(7)	0.0246(7)	0.0017(6)	0.0009(6)	0.0005(6)
C(2)	8*d*	0.5360(1)	0.1645(1)	0.3903(2)	0.0231(7)	0.0185(7)	0.0228(7)	0.0004(6)	–0.0026(6)	0.0013(6)
C(3)	4*c*	0.4699(2)	1/4	0.0496(3)	0.028(1)	0.0159(9)	0.022(1)	0	–0.0023(9)	0
C(4)	4*c*	0.4704(2)	1/4	0.3019(3)	0.0162(9)	0.0173(9)	0.021(1)	0	–0.0009(8)	0
N	8*d*	0.2445(1)	0.1140(1)	0.6815(2)	0.0278(7)	0.0250(7)	0.0266(7)	–0.0032(6)	0.0009(6)	0.0002(6)

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