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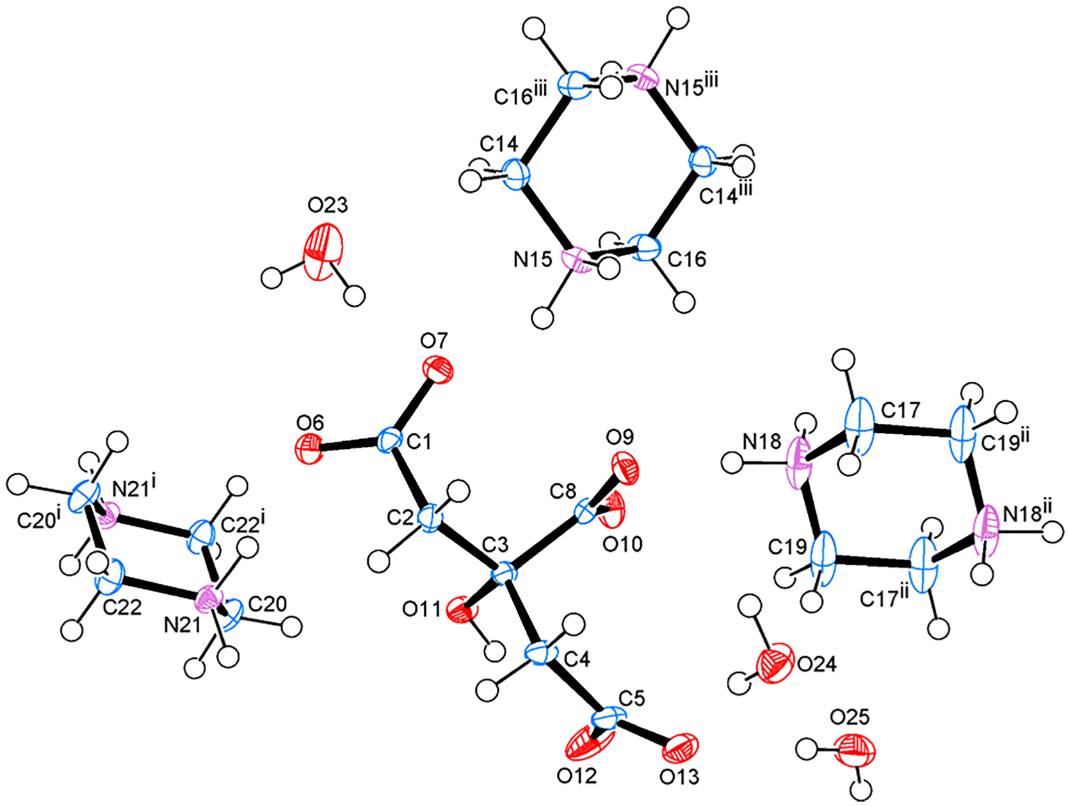
Crystal structure of tris(piperazine-1,4-diium) bis(2-hydroxy-1,2,3-propane-tricarboxylate) pentahydrate, $C_{24}H_{56}N_6O_{19}$



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Abstract

$C_{24}H_{56}N_6O_{19}$, triclinic, $P\bar{1}$ (no. 2), a = 6.0132(12) Å, b = 11.667(2) Å, c = 13.152(3) Å, α = 67.10(3)°, β = 88.54(3)°, γ = 83.18(3)°, V = 843.8(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0606, $wR_{ref}(F^2)$ = 0.1336, T = 173(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

The 2-hydroxy-1,2,3-propane-tricarboxylic acid (citric acid) monohydrate was obtained from UniLAB Saarchem (Merck) and piperazine hexahydrate from BDH laboratories. Diethyl ether was obtained from Merck. The citric acid monohydrate was dried in an oven at 60 °C for 2 h. Citric acid (0.26 mmol, 0.050 g) and piperazine hexahydrate (0.26 mmol, 0.052 g) was dissolved in 2.0 mL of a 1:1 mixture of diethyl

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.27 × 0.17 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II diffractometer, φ and ω scans
θ_{max}, completeness:	28.3°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13092, 4187, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3,830
$N(param)_{refined}$:	278
Programs:	Bruker,[1,2] WinGX,[3] SHELX,[4,5] X-Seed[6]

ether:water with slight heating. The solution was allowed to evaporate at room temperature. Block crystals were obtained after 5 months of slow evaporation.

2 Experimental details

The hydroxyl hydrogen atom, water hydrogen atoms and amine hydrogens were located in the difference electron density map and freely refined with isotropic temperature factors. The C–H atoms were geometrically constrained at 0.99 Å with U_{iso} (H) = 1.2 $Å^2$.

3 Comment

Citric acid is naturally found in citrus fruits, however commercially it is sourced from fermentation processes primarily using the fungus *Aspergillus niger*.[7,8] Citric acid has uses in a wide variety of industries including food, pharmaceutical and chemical industries.[9,10] Recently, cocrystallisation studies of citric acid with selected heterocyclic compounds have been reported.[11] Piperazine is an anthelmintic drug for veterinary use.[12] Piperazine has been used in cocrystallisation studies involving natural products and active pharmaceutical ingredients.[13–15]

The crystal structure of piperazine citrate monohydrate, $(C_4H_{12}N_2)^{2+}(C_6H_6O_7)^{2-}\cdot H_2O$ in the monoclinic space group Pn (a = 9.2055(12) Å, b = 6.8314(9) Å, c = 11.2443 (14) Å, β = 112.047 (2)°, V = 655.41 (15) $Å^3$) has been reported by Liu.[16] The asymmetric unit of $(C_4H_{12}N_2)^{2+}(C_6H_6O_7)^{2-}\cdot H_2O$ contains a double deprotonated citrate anion, a doubly protonated piperazine and one water molecule.

The asymmetric unit of the current structure, $3(C_4H_{12}N_2^{2+})\cdot 2(C_6H_5O_7^{3-})\cdot 5(H_2O)$, contains a triple deprotonated citrate anion, 1.5 piperazinium cations and 2.5 water molecules. The piperazinium cations lie on centres of inversion and all three of the carboxylic acids of citric acid are deprotonated. There are several NH···O, OH···O and CH···O hydrogen bonds in the structure. The piperazinium cations and water molecules are hydrogen bonded to the carboxylate groups of the citrate anion. The hydroxyl group of the citrate forms an intramolecular OH···O contact with one of the carboxylate oxygens. There are numerous hydrogen bonded rings and chains. In particular, two citrate and two piperazinium ions form R_4^4 (24) rings involving four NH···O heterosynthons. Citrate and piperazinium ions are linked *via* NH···O hydrogen bonds creating C_4^4 (26) chains. The two and a half water molecules and one citrate ion produce R_4^4 (10) rings *via* OH···O hydrogen bonds. The water molecules occupy channels parallel to [100] with different water environments present including donor···donor (DD), donor···donor···acceptor (DDA) and donor···donor···acceptor···acceptor (DDAA).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Conflict of interest: The authors declare no conflicts of interest regarding this article.

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