organic papers

2,2′-(Piperazine-1,4-diium-1,4-diyl)diacetate dihydrate

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The asymmetric unit of the title compound, $C_8H_{14}N_2O_4 \cdot 2H_2O$, contains one water molecule and one half-molecule of piperazine-1,4-diacetic acid in salt form. Intramolecular N—H···O and O—H···O and intermolecular O—H···O hydrogen bonds are involved in the crystal packing. In the centrosymmetric title compound, the six-membered piperazine ring is in a standard chair form, and the two acetates are mutually *trans*. The 2,2′-(piperazine-1,4-diyl)diacetic acid and water molecules are connected through a complex pattern of hydrogen-bonding interactions, resulting in a three-dimensional network.

Comment

The title compound, (I), is an effective chelating agent and some studies of its chelating character have been reported. The presence of carboxy groups enhances its chelating ability and it chelates to Pb effectively at very low concentrations (Chividzhiyan, 1977). The protonation reactions and stable conformations of complexes of (I) and related compounds have been studied by ^{1}H NMR spectroscopy, and molecular mechanics calculations and microcalorimetry measurements have also been carried out (Ascenso *et al.*, 1990). However, the stability constants of complexes of (I) and other related ligands have been measured and it was found that chelation involving both N atoms of the piperazine derivatives does not occur with small ions (Irving & Pettit, 1963). Because of its effective chelating ability, (I) could be used to treat soils polluted by heavy metals (Okey *et al.*, 1997) and could also prevent carnation wilt as a cut-flower preservative (Tanaka & Asada, 1991). This study was undertaken in order to ascertain the crystal structure of (I), which might provide some information about its chelating reactions.

(I)
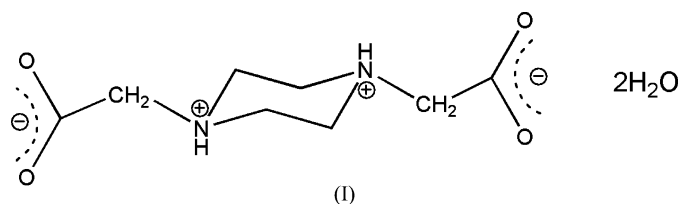
The asymmetric unit of (I) contains one water molecule and one half-molecule of 2,2′-(piperazine-1,4-diyl)diacetic acid (Fig. 1). The C1—O1 [1.248 (2) Å] and C1—O2 [1.248 (2) Å] bonds are equal, and atom N1 of the piperazine is linked to atoms C2, C3 and C4, as well as to atom H1 (Table 1). This means that (I) is in the salt form.
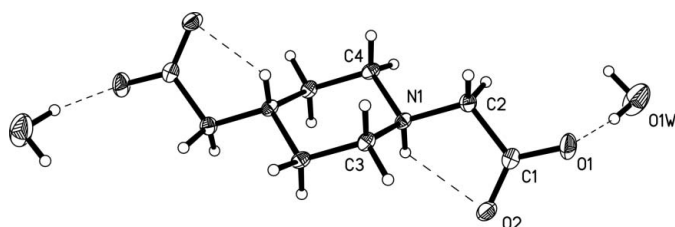
Figure 1
A drawing of the components of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y + 1, -z)$.
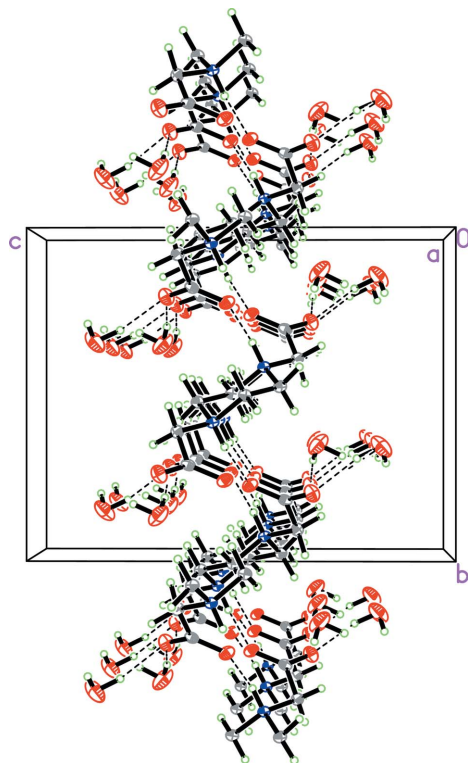
Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

In the centrosymmetric title compound, the six-membered piperazine ring is in a standard chair form, and the two acetates are mutually *trans*. The 2,2′-(piperazine-1,4-diyl)diacetic acid and water molecules are connected through a complex pattern of hydrogen-bonding interactions, resulting in a three-dimensional network. The crystal structure is stabilized by intramolecular N—H···O and O—H···O and intermolecular O—H···O hydrogen bonds (Table 2 and Fig. 2).

Experimental

Compound (I) was synthesized from piperazine (43 mg, 0.5 mmol) and chloroacetic acid (1.0 mmol, 85 ml) as described in the literature (Shen *et al.*, 2006) and suitable colourless crystals of (I) were obtained from a dilute HCl solution (10%) (yield 89 mg, 88%). Analysis found: C 47.52, H 6.98, N 13.85%; calculated for 2,2′-(piperazine-1,4-diyl)-diacetic acid: C 47.49, H 6.99, N 13.87%.

Crystal data

$C_8H_{14}N_2O_4\cdot2H_2O$	$Z = 4$
$M_r = 238.24$	$D_x = 1.470$ Mg m^{-3}
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 6.5060$ (13) Å	$\mu = 0.13$ mm^{-1}
$b = 11.344$ (2) Å	$T = 296$ (2) K
$c = 14.587$ (3) Å	Block, colourless
$V = 1076.6$ (4) Å^3	$0.28 \times 0.24 \times 0.16$ mm

Data collection

Bruker SMART APEX area-detector diffractometer	1049 independent reflections
	762 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.087$
Absorption correction: none	$\theta_{max} = 26.0°$
2031 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
1049 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
110 parameters	Extinction correction: *SHELXL97*
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.047 (5)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.248 (2)	N1—C4	1.499 (2)
O2—C1	1.248 (2)	N1—C3	1.503 (2)
N1—C2	1.493 (3)	N1—H1	0.91 (2)
C2—N1—H1	107.9 (13)	O2—C1—O1	127.19 (18)
C4—N1—H1	108.4 (14)	O2—C1—C2	117.10 (16)
C3—N1—H1	108.2 (13)	O1—C1—C2	115.70 (17)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.91 (2)	2.40 (2)	2.688 (2)	98.3 (15)
O1W—H1WB···O1	0.92 (4)	1.93 (4)	2.834 (3)	168 (3)
O1W—H1WA···O1^i	0.90 (5)	2.02 (5)	2.899 (3)	165 (4)

Symmetry code: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$.

H atoms were located in a difference synthesis and refined isotropically, with refined distances of O—H = 0.90 (5) and 0.92 (4), N—H = 0.91 (2) and C—H = 0.95 (2)–1.02 (2) Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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