Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A three-dimensional hydrogen-bonded network in bis(4-hydroxyanilinium) selenate(VI) dihydrate

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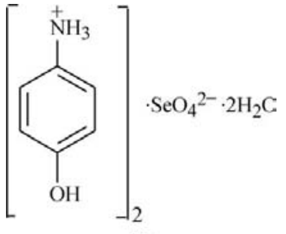
Received 6 February 2009
Accepted 18 February 2009
Online 27 February 2009

The title compound, $2C_6H_8NO^+ \cdot SeO_4^{2-} \cdot 2H_2O$, contains 4-hydroxyanilinium cations, selenate(VI) anions and water molecules. One of the two independent cations is nearly planar (excluding the ammonium H atoms), while the other is markedly nonplanar, with the hydroxy and ammonium groups displaced from the plane of the benzene ring. This results from the antiparallel orientation of the cations, which interact through oppositely polarized ammonium and hydroxy groups. Ionic and hydrogen-bonding interactions join the oppositely charged units into a three-dimensional network. This work demonstrates the usefulness of 4-aminophenol in the crystal engineering of organic–inorganic hybrid compounds.

Comment

In recent years, studies on the self-assembly of acid–base hydrogen-bond interactions and molecular recognition in the solid state have shown a great variety of physical and chemical properties in this class of materials. These hybrid crystals are potentially good materials for exhibiting nonlinear optical properties (Chemla & Zyss, 1987; Marchewka *et al.*, 2003): the anionic acid part is responsible for favourable chemical and mechanical properties due to the formation of strongly directional hydrogen bonds, while the organic base is mainly responsible for nonlinear optical properties due to its relatively high hyperpolarizability (Bhattacharya *et al.*, 1994; Blagden & Seddon, 1999; Głowiak *et al.*, 2001). Continuing our studies on the characterization of acid–base hybrid crystals (Janczak & Perpétuo, 2007), we report here the structure of bis(4-hydroxyanilinium) selenate(VI) dihydrate, (I).

The asymmetric unit of (I) consists of two 4-hydroxyanilinium cations (denoted $4AP^+$), one selenate(VI) anion and two water molecules (Fig. 1). One of the water molecules (O6) acts as a hydrogen-bond donor to two anions, while the other water molecule (O7) acts as a donor to an anion and a cation (Table 1). Additionally, water atom O7 acts as an acceptor from both ammonium cations (denoted *M*1 and *M*2), while water atom O6 acts as an acceptor from one cation only.



(I)

The geometry of the selenate(VI) anion is slightly distorted tetrahedral, with typical values for the Se—O bonds. The two independent cations exhibit different geometries: *M*2 is almost planar (excluding the ammonium H atoms), while *M*1 is nonplanar. In *M*1, the O and N atoms are displaced from the ring plane by 0.167 (2) and 0.187 (2) Å, respectively, while in *M*2 the respective displacements are less than 0.006 (2) Å. Thus, in *M*1 the C—N and C—O bonds are inclined to the benzene ring by 7.3 (1)°. This nonplanar conformation of *M*1 results from an antiparallel orientation of the dipolar $4AP^+$ units that interact *via* oppositely charged ammonium and hydroxy groups, forming a centrosymmetric dimer.

Considering the geometry of the N—H···O hydrogen bond in the $(4AP^+)_2$ dimer, it was observed that the H···O distance of 2.542 (2) Å is longer than the 1.2–2.2 Å range typically observed for N—H···O hydrogen bonds (Jeffrey, 1997). However, the H···O distance in (I) is slightly shorter than the sum of the van der Waals radii of H and O atoms (2.65 Å; r_H = 1.10 Å and r_O = 1.55 Å; Bondi, 1964; Rowland & Taylor, 1996); thus, the N—H···O interaction between the ammonium and hydroxy groups in the $(4AP^+)_2$ dimer is significant and is responsible for the inclination of both groups to the plane of the benzene ring. In addition, ammonium atom H11 is involved in a three-centre hydrogen bond, where the N—H···$(O)_2$ contacts are generally longer than in a two-centre system.

Extensive N—H···O and O—H···O hydrogen bonding (Table 1) links the oppositely charged $4AP^+$ and SeO_4^{2-} units, forming stacks along [001], while the water molecules inter-

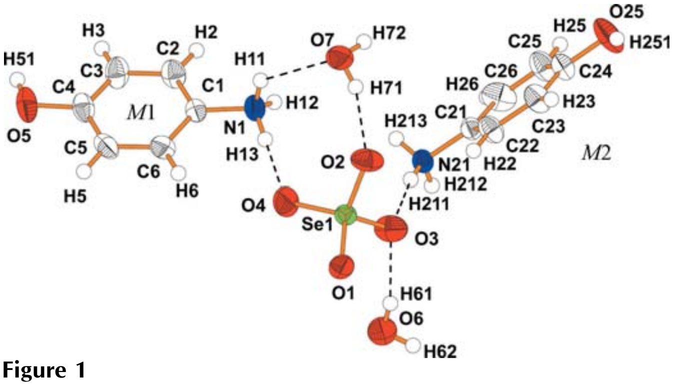


Figure 1
A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Dashed lines indicate hydrogen-bond contacts. *M*1 and *M*2 denote the nonplanar and planar $4AP^+$ cations, respectively.

doi:10.1107/S0108270109005782

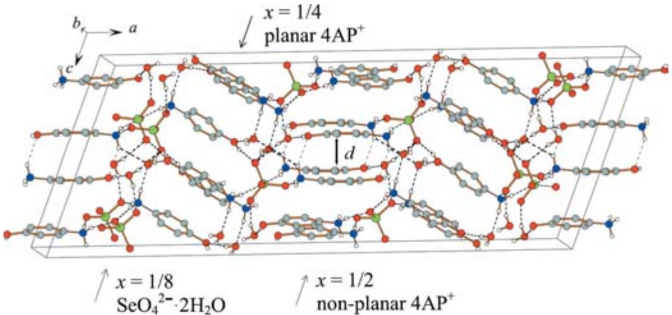


Figure 2
A view of the hydrogen-bonded three-dimensional network of (I), showing layers of planar and nonplanar 4AP$^+$ cations at $x = \frac{1}{4}, \frac{3}{4}$ and at $x = 0, \frac{1}{2}$, respectively, and layers of selenate(VI) anions and water molecules at $x = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. The distance labelled d represents the interplanar spacing of 3.320 (2) Å between two benzene rings.

connect the stacks into a three-dimensional network (Fig. 2). The nonplanar $M1$ 4AP$^+$ cations that form dimers are arranged in stacks, forming layers parallel to (100) (at $x = 0, \frac{1}{2}$, *etc.*). The planar $M2$ 4AP$^+$ cations form layers at $x = \frac{1}{4}$ and $\frac{3}{4}$. The benzene rings of the nonplanar $M1$ 4AP$^+$ cations are almost parallel to (001), while the planar $M2$ 4AP$^+$ units are inclined by ~22° to this plane. Between the phenyl rings of the 4AP$^+$ cations there are weak π–π interactions with an interplanar spacing of 3.320 (2) Å for the $M1\cdots M1^{i}$ dimer [symmetry code: $-x$, $1 - y$, $1 - z$)]. The ring-centroid separation is 3.552 (2) Å and the corresponding ring-centroid offset is 1.262 (2) Å. By contrast, the rings of planar 4AP$^+$ ($M2$) units are inclined to each other so that no effective π–π interactions can occur. It is commonly accepted that interactions between stacks of aromatic rings with approximately parallel molecular planes occur if the planes are separated by 3.3–3.8 Å (Filippini & Gavezzotti, 1993; Janiak, 2000). The layers of $M1$ and $M2$ cations are interconnected by layers of anions and water molecules at $x = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ (Fig. 2), forming a three-dimensional network.

Experimental

An aqueous solution of 4-aminophenol (Aldrich, 99% purity) in selenic acid was prepared and held at a temperature of 360 K. When the solution became homogeneous, it was cooled to 295 K. After several days at room temperature, crystals of (I) suitable for X-ray diffraction analysis were obtained.

Crystal data

$2C_6H_8NO^+\cdot SeO_4^{2-}\cdot 2H_2O$
$M_r = 399.26$
Monoclinic, $C2/c$
$a = 37.632$ (6) Å
$b = 6.520$ (1) Å
$c = 14.431$ (3) Å
$\beta = 109.82$ (1)°
$V = 3331.0$ (10) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 2.30$ mm^{-1}
$T = 295$ (2) K
0.32 × 0.24 × 0.18 mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.532$, $T_{\max} = 0.684$
21626 measured reflections
4283 independent reflections
3056 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.051$
$S = 1.00$
4283 reflections
222 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O7	0.89	2.38	3.045 (2)	131
N1—H11···O5^{i}	0.89	2.54	3.204 (2)	132
N1—H12···O1^{ii}	0.89	1.94	2.781 (2)	157
N1—H13···O4	0.89	1.87	2.752 (2)	171
O5—H51···O6^{iii}	0.82	1.92	2.726 (2)	170
O25—H251···O2^{iv}	0.82	1.84	2.641 (2)	165
N21—H211···O3	0.89	1.87	2.757 (2)	172
N21—H212···O7^{v}	0.89	1.92	2.795 (2)	167
N21—H213···O1^{ii}	0.89	1.90	2.776 (2)	170
O6—H61···O3	0.82	1.95	2.748 (2)	163
O6—H62···O2^{vi}	0.82	2.24	3.035 (2)	166
O7—H71···O2	0.82	1.98	2.746 (2)	156
O7—H72···O25^{vii}	0.82	1.96	2.768 (2)	168

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y+1, z$; (iii) $-x, y+1, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $x, -y+1, z-\frac{1}{2}$; (vi) $x, -y, z-\frac{1}{2}$; (vii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

All H atoms were located in difference maps and then treated as riding, with C—H distances of 0.93 Å, N—H distances of 0.89 Å and O—H distances of 0.82 Å, and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}$(carrier), where $k = 1.2$ for the aryl rings and 1.5 otherwise.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3275). Services for accessing these data are described at the back of the journal.

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