An unusual two-dimensional hydrogen-bonding network in bis(2,9-dimethyl-1,10-phenanthrolin-1-ium) peroxodisulfate dihydrate

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The title compound, $2C_{14}H_{13}N_2^+ \cdot S_2O_8^{2-} \cdot 2H_2O$, is a protonated amine salt which is formed from two rather uncommon ionic species, namely a peroxodisulfate (pds^{2-}) anion, which lies across a crystallographic inversion centre, and a 2,9-dimethyl-1,10-phenanthrolin-1-ium ($Hdmph^+$) cation lying in a general position. Each pds^{2-} anion binds to two water molecules through strong water–peroxo $O-H\cdots O$ interactions, giving rise to an unprecedented planar network of hydrogen-bonded macrocycles which run parallel to (100). The atoms of the large $R_8^8(30)$ rings are provided by four water molecules bridging in fully extended form ($\cdots H-O-H\cdots$) and four pds^{2-} anions alternately acting as long ($\cdots O-S-O-O-S-O\cdots$) and short ($\cdots O-S-O\cdots$) bridges. The $Hdmph^+$ cations, in turn, bind to these units through hydrogen bonds involving their protonated N atoms. In addition, the crystal structure also contains $\pi-\pi$ and aromatic–peroxo $C-H\cdots O$ interactions.

Comment

In spite of not being an extensively explored species, the peroxodisulfate anion (pds, $S_2O_8^{2-}$) has been shown to be a versatile ligand towards transition metals; the few relevant entries in the Cambridge Structural Database (CSD; Version 5.29, January 2008 update; Allen, 2002) show that its binding mode can be either monodentate, chelating or bridging, but it can also behave as a counter-ion. Somewhat curiously, in all the reported cases, the cation is coordinated by an aromatic amine; these are 2,2′-bipyridine (Harvey, Baggio, Garland & Baggio, 2001; Harrison & Hathaway, 1980; Blackman *et al.*, 1991; Díaz de Vivar *et al.*, 2005), 1,10-phenanthroline (Harvey,

Baggio, Garland, Burton & Baggio, 2001; Skogareva *et al.*, 2004), 2,2′:6′,2′′-terpyridine (Harvey, Baggio, Garland & Baggio, 2001; Harvey *et al.*, 2004; Díaz de Vivar *et al.*, 2005), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (Harvey *et al.*, 2004), 2,6-bis(2-benzimidazolyl)pyridine (Harvey *et al.*, 2004, 2005) and 2,9-dimethyl-1,10-phenanthroline (dmph) (Harvey, Baggio, Garland, Burton & Baggio, 2001; revisited by Marsh, 2004).

While exploring some new synthetic routes to the (scarcely reported) dmph/pds complexes, the title salt, $2Hdmph^+ \cdot pds^{2-} \cdot 2H_2O$, (I), was obtained, where the cationic role is fulfilled by a protonated $Hdmph^+$ group.
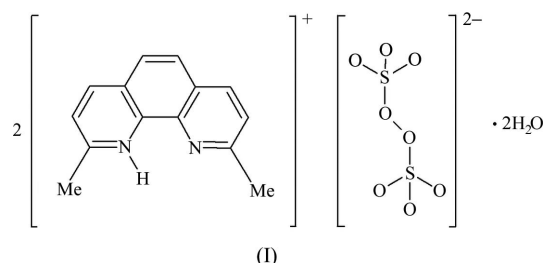

(I)

Fig. 1 shows a view of the asymmetric unit of (I); the pds^{2-} anion lies across a crystallographic inversion centre and compensates the single positive charge introduced by the extra H atom of $Hdmph^+$, thus achieving charge balance. As expected, the $Hdmph^+$ cation is planar [the mean deviation from the least-squares plane is 0.007 (1) Å and the maximum deviation is 0.022 (1) Å for the protonated N1 atom] and forms a weak intramolecular $N1-H1\cdots N2$ contact (Table 1) defining an $S_1^1(5)$ pattern [for graph-set notation, see Bernstein *et al.* (1995)]. This is an inherent characteristic of the rigid atomic arrangement in the $Hdmph^+$ cation and has already been described elsewhere (Yu *et al.*, 2006).
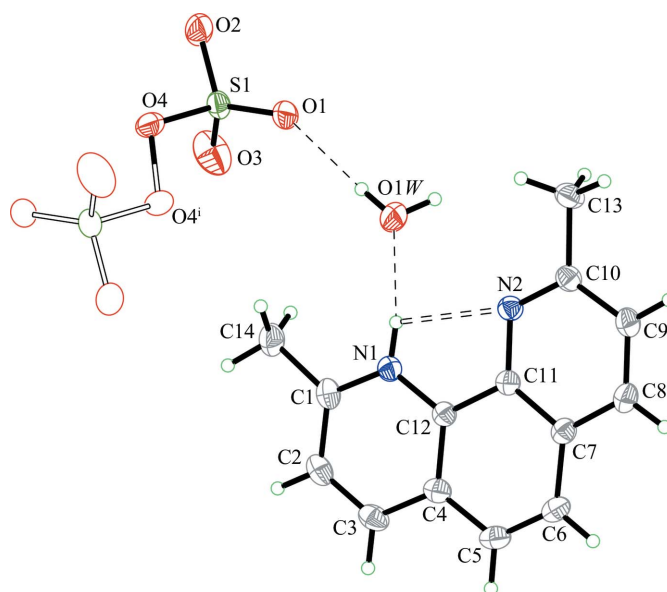

Figure 1
The symmetry-independent part of the structure of (I), shown with fully shaded ellipsoids (drawn at the 50% probability level) and filled bonds.

We shall now discuss in detail some structural peculiarities of the pds^{2-} and Hdmph$^+$ ions in both the present structure and the few other structures where they occur. For the pds^{2-} anion, it has been shown that, when it appears in an unperturbed noncoordinated form [for instance, in the K$^+$ (Sivertsen & Sorum, 1969) and NH$_4^+$ (Naumov *et al.*, 1997) salts], the anion presents a perfectly planar S—O′—O′—S nucleus (O′ = O$_{core}$); one of the three terminal O atoms (O″) at each side occupies a perfectly *trans* position relative to the core, thus configuring a six-membered O″—S—O′—O′—S—O″ planar entity. These latter O atoms are special in that they subtend an O″—S—O′ angle that is much smaller than the two remaining O″—S—O′ angles. This fact had already been pointed out by Harvey, Baggio, Garland, Burton & Baggio (2001), where it was qualitatively explained in terms of a previous idea put forward by Cruickshank (1961) regarding the availability of 3d orbitals in SO$_4$ groups to form strong π-bonding molecular orbitals; this explanation was confirmed by *ab initio* calculations on the expected geometry of the anion.

The geometry of the pds^{2-} anion in (I) adjusts almost perfectly to these characteristics. In fact, letting O′= O4 and O″= O2:

(i) the core is perfectly planar; in this particular case, for symmetry reasons, the S1—O4—O4^v—S1^v angle is 180° [symmetry code: (v) $-x + 2, -y, -z$];

(ii) O2 is in an almost exactly *trans* position with respect to the planar core: O2—S—O4—O4^v = $-179.56\,(12)°$;

(iii) O2—S1—O4 [96.98 (7)°] is significantly smaller than O3—S1—O4 [106.65 (8)°] and O1—S1—O4 [106.56 (7)°].

Regarding the Hdmph$^+$ group, its peculiarity resides in the fact that protonation introduces differences in the environment of the N atoms, breaking the equivalence that is seen in the unprotonated species. This can be explained by the fact that the charge around the N atoms in the unprotonated case is distributed, in the form of lone pairs. When protonation occurs, in the corresponding N atom this charge concentrates in the form of an N—H single bond, with the consequent reduction in repulsion between the charge cloud and the C—N bond. The result is an opening of the C—N—C angle as compared with the remaining unperturbed N atom. Thus, the C1—N1—C12 angle [123.01 (15)°] in (I) is significantly larger than C10—N2—C11 [118.34 (15)°]. Similar differences can be found in other closely related phenanthrolinium structures [Hphen$^+$ (phen is 1,10-phenanthroline; Hensen *et al.*, 1998) and Hdmph$^+$ (Yu *et al.*, 2006)].

However, the most appealing feature of the structure is the assembly of four different intermolecular interactions which, in addition to the obvious Coulombic forces, can be envisaged as building up the structure in a stepwise fashion, as follows:

(i) the pds^{2-} anion binds to two symmetry-related water molecules through two strong (O—H)$_{water}$···O$_{peroxo}$ hydrogen bonds (Table 1), giving rise to an unusual two-dimensional network of $R_8^8(30)$ macrocycles parallel to (100) (Fig. 2). The 30 atoms involved in each centrosymmetric ring are provided by four water molecules bridging in fully extended form (···H—O—H···) and four pds^{2-} anions, alternately acting as long (···O—S—O—O—S—O···) or short (···O—S—O···)

bridges, leading to an elongated loop with approximate maximum and minimum dimensions of 12.5 and 5.4 Å, respectively.

(ii) These two-dimensional structures serve as the planar base to which the Hdmph$^+$ groups attach *via* N1—H1···O1W hydrogen bonds (above and below the plane in Fig. 2), leaving the bulky hydrophobic side facing outwards.

(iii) The complex two-dimensional structures thus configured stack along [100], as shown in Fig. 3, with interdigitation of aromatic amines to set them at distances from each other typical of graphitic packing; the structure thereby exhibits π–π interactions (Table 2).

(iv) Finally, the inter-layer link is complemented by weak C—H···O bonds involving aromatic H atoms and peroxodisulfate O atoms (Table 1, entries 5–7).
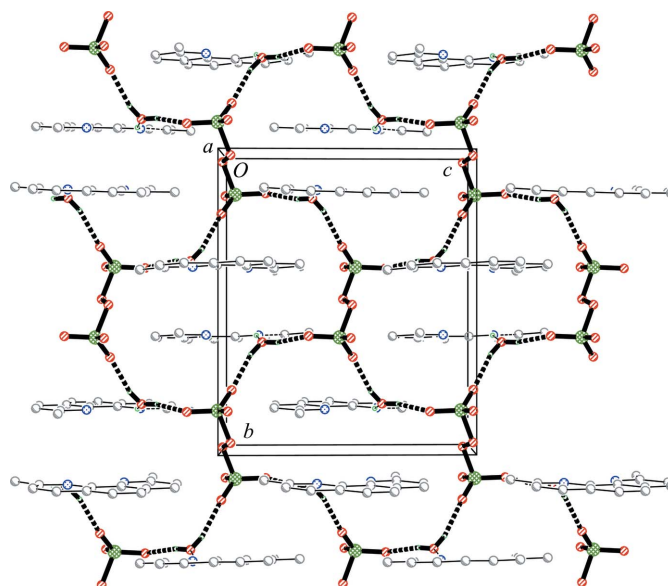

Figure 2
The packing of (I), viewed down the [100] direction, showing in bold the hydrogen-bonded two-dimensional network involving water molecules and pds^{2-} ions. The planar aromatic amines appear vertically in projection.
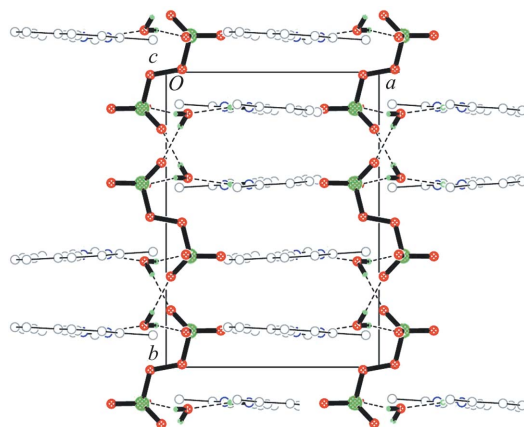

Figure 3
The packing of (I), viewed down the [001] direction, at right angles to the view in Fig. 2, showing the way in which the layers interact through interdigitation of the aromatic amines.

It is worth mentioning that some previously reported pds hydrates, where the pds^{2-} anion is either free or only weakly coordinated, also exhibit interesting hydrogen-bonding motifs, including $C_2^2(6)$ or $C_3^3(8)$ linear chains (Figs. 4a and 4c), and doubly isolated $R_3^3(11)$ or concatenated $R_4^4(12)$ loops (Figs. 4d and 4b), but none are comparable in complexity to the unprecedented array of $R_8^8(30)$ rings displayed in the present structure (Fig. 4e).
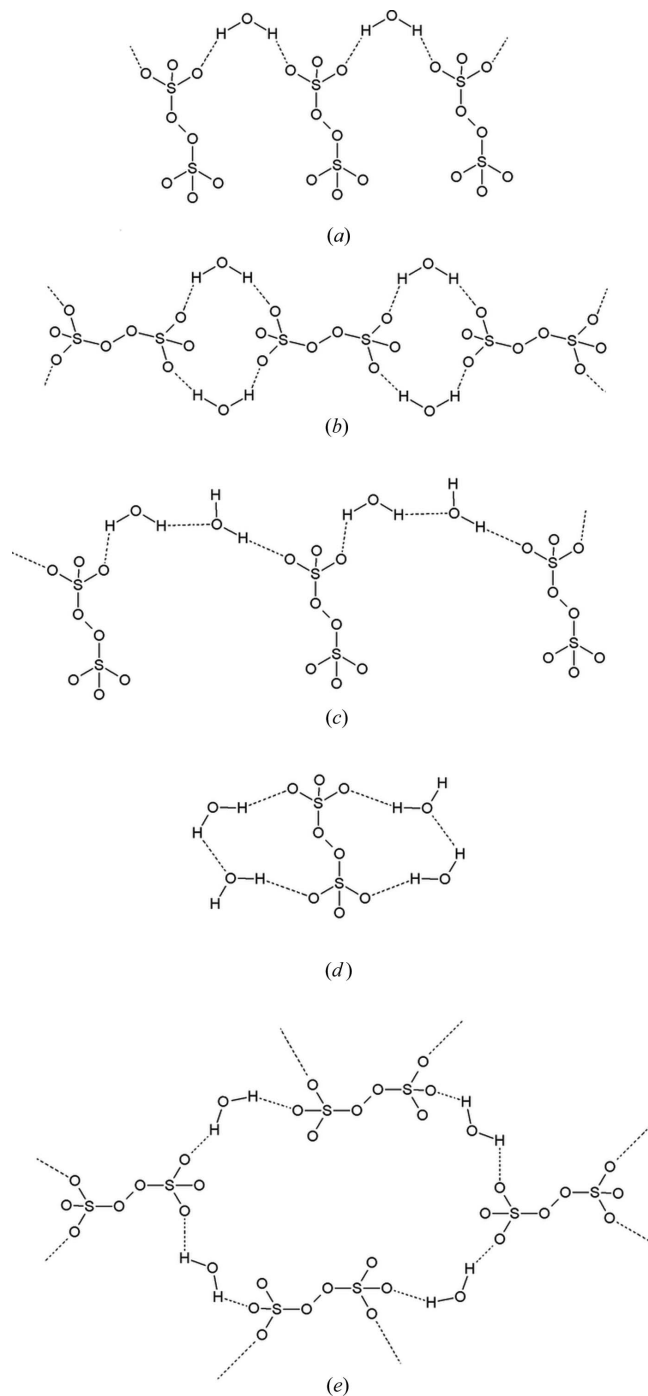

Figure 4
A schematic representation of the different pds/water hydrogen-bonding motifs found in the literature. References: (a) Díaz de Vivar *et al.* (2005); (b) Harvey *et al.* (2004); (c) Harvey, Baggio, Garland, Burton & Baggio (2001); (d) Harvey *et al.* (2005); (e) this work.

Experimental

The title salt was obtained while trying to synthesize an Mn^{II} complex, through direct mixing of aqueous solutions of manganese sulfate monohydrate and potassium peroxodisulfate and a methanol solution of 2,9-dimethyl-1,10-phenanthroline (all solutions 0.008 *M*). The crystalline compound obtained was the result of a complicated process of crystallization and digestion which took about 20 d until finally resulting in the yellow platelet-like crystals studied.

Crystal data

2C$_{14}$H$_{13}$N$_2$$^+$·S$_2O_8$$^{2-}$·2H$_2$O	$V = 1414.6$ (5) Å^3
$M_r = 646.68$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.5644$ (19) Å	$\mu = 0.26$ mm^{-1}
$b = 13.228$ (3) Å	$T = 170$ (2) K
$c = 11.201$ (2) Å	$0.38 \times 0.32 \times 0.08$ mm
$\beta = 93.39$ (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	11488 measured reflections
	3039 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	2625 reflections with $I > 2\sigma(I)$
$T_{min} = 0.95$, $T_{max} = 0.98$	$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.126$	
$S = 1.06$	
3039 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
216 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
3 restraints	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1W	0.85 (2)	1.94 (2)	2.768 (2)	163 (2)
N1—H1$\cdots$N2	0.85 (2)	2.39 (2)	2.738 (2)	105 (2)
O1W—H1$WB\cdots$O1	0.84 (2)	1.98 (2)	2.808 (2)	168 (2)
O1W—H1$WA\cdots$O3^i	0.85 (2)	2.05 (2)	2.883 (2)	166 (2)
C2—H2$\cdots$O2^{ii}	0.93	2.52	3.449 (2)	173
C3—H3$\cdots$O1^{ii}	0.93	2.55	3.224 (2)	130
C8—H8$\cdots$O2^{iii}	0.93	2.57	3.395 (2)	148

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

Table 2
π–π contacts (Å, °) for (I).

$Cg1$, $Cg2$ and $Cg3$ are the centroids of the N1/C1–C4/C12, N2/C7–C11 and C4–C7/C11/C12 rings, respectively. ipd (Å) is the interplanar distance (the distance from one plane to the neighbouring centroid); ccd (Å) is the centre-to-centre distance (the distance between ring centroids); sa (°) is the slippage angle (the angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000).

Ring1/ring2	ccd	ipd	sa
$Cg1/Cg2^{iv}$	3.5283 (12)	3.304 (10)	21.05 (4)
$Cg1/Cg3^{iv}$	3.5303 (12)	3.318 (4)	19.92 (15)
$Cg3/Cg3^{iv}$	4.0702 (13)	3.326 (2)	35.21 (1)

Symmetry code: (iv) $-x + 1, -y, -z + 1$.

H atoms attached to N and O atoms were found in a difference Fourier synthesis and refined with O—H and N—H distances

restrained to 0.85 (2) Å, but with free isotropic displacement parameters. H atoms bound to C atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93 or 0.96 Å and U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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