

## The supramolecular architecture in 4,4'-bipyridinium bis(hydrogen oxalate)

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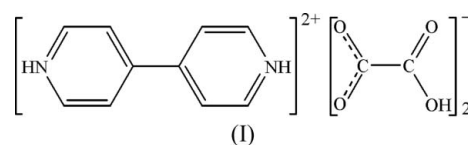
The asymmetric unit of the title compound,  $C_{10}H_{10}N_2^{2+} \cdot 2C_2HO_4^-$ , consists of one half of a 4,4'-bipyridinium cation, which has inversion symmetry, and a hydrogen oxalate anion, in which an intramolecular hydrogen bond exists. The cations and anions are connected by  $O-H \cdots O$ ,  $N-H \cdots O$  and  $C-H \cdots O$  hydrogen bonds, forming a two-dimensional network, whereas  $\pi-\pi$  stacking interactions involving the 4,4'-bipyridinium cations lead to the formation of a three-dimensional supramolecular structure. An unusual deca-atomic ring is formed between two hydrogen oxalate anions, which are linked side-to-side *via*  $O-H \cdots O$  hydrogen-bonding interactions.

### Comment

In crystal engineering, the construction of functional materials with desired properties from molecules or ions is achieved by the use of appropriate building blocks. These constituents can adopt a large number of conformations in the crystal; therefore, it is very difficult to predict the final structure. However, the most widely used structural organizing forces in crystal engineering have been hydrogen bonds, owing to such properties as directionality, selectivity and strength, allowing the preparation of predictable structural aggregates which may have different characteristics. It is well known that the utilization of ions which can make hydrogen bonds allows the simultaneous exploitation of the directionality and reproducibility of these interactions and the strength of the Coulomb field generated by the ionic charges (Braga *et al.*, 2002). In general, noncovalent intermolecular interactions such as hydrogen bonds and  $\pi-\pi$  stacking are widely used in molecular aggregation because they can adjust the dimensionality (one-, two- and three-dimensional supramolecular networks) and lead to new topologies and desired functions of supramolecular assemblies.

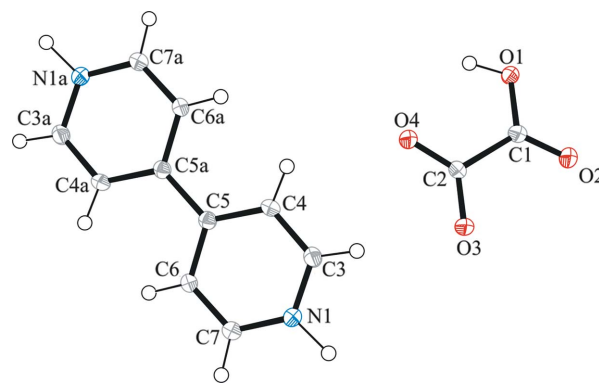
4,4'-Bipyridine is an excellent synthon owing to its rigidity and ability to act as a metal-binding ligand or hydrogen-bonding acceptor and, when protonated, the resulting cation

can serve as a hydrogen-bond donor. In addition, it can also participate in  $\pi-\pi$  stacking interactions. So far, many supramolecular architectures involving 4,4'-bipyridine as a versatile molecular building block have been reported (*e.g.* Jayaraman *et al.*, 2006; Ruiz-Pérez *et al.*, 2004; Iyere *et al.*, 2003). In metal-organic frameworks, especially in the class of porous polymeric materials, metal ions are often linked by this organic bridging ligand (James, 2003). Oxalic acid and its anions can act as both donors and acceptors for hydrogen bonds. It is interesting to note that, because of the extraordinary coordination and electronic properties of the oxalate anion, a huge number of homo- and heteropolynuclear oxalate-based complexes of different nuclearity and dimensionality have been prepared (*e.g.* Jurić *et al.*, 2006).

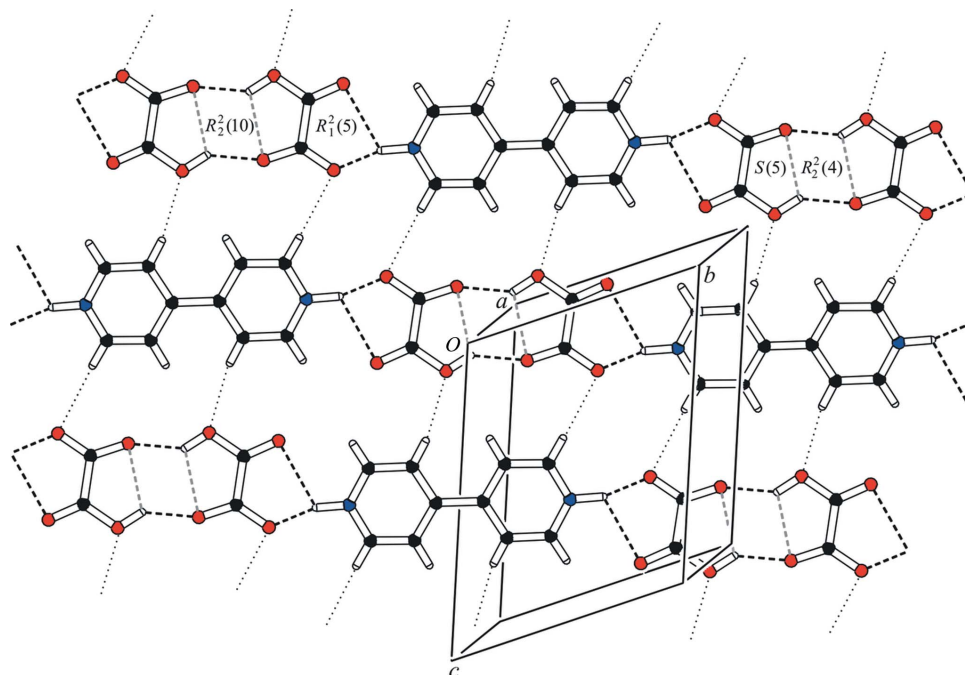


Related to our current magneto-structural studies on oxalate-based mono- and polynuclear transition metal complexes, we have recently extended our investigations to the reactions of oxalate salts with N-donor ligands, with the aim of preparing new organic frameworks. Our interest has been to determine the influence of particular components of such systems on the structural and functional characteristics of new supramolecular assemblies. We report herein on the supramolecular crystal structure of 4,4'-bipyridinium bis(hydrogen oxalate), (I), which contains hydrogen bonds and  $\pi-\pi$  stacking interactions. Further research on other similar oxalate systems is in progress.

The molecular structure of (I) (Fig. 1) consists of a diprotonated 4,4'-bipyridine cation and two hydrogen oxalate anions which are linked together by noncovalent interactions giving a three-dimensional architecture. There is a crystallographic inversion centre in the middle of the cation, so that



**Figure 1**  
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The two halves of the 4,4'-bipyridinium cation are related by the symmetry operator (a)  $-x, -y, -z + 1$ .



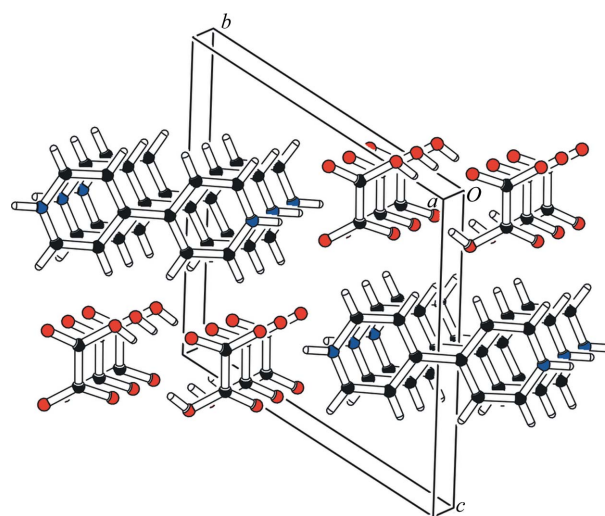
**Figure 2**

Hydrogen-bonding pattern with marked motifs parallel to the  $(\bar{1}\bar{2}1)$  plane in the crystal packing of (I). Black and grey dashed lines represent inter- and intramolecular hydrogen bonds, respectively, whereas dotted lines represent C—H...O hydrogen bonds.

the asymmetric unit contains half a cation and one anion. In the cation, as in other 4,4'-bipyridinium salts (e.g. Ma *et al.*, 2005; Muthiah *et al.*, 2003; Wang & Wei, 2006), there is an increase of the internal angle [C3—N1—C7 = 121.63 (14)°] compared with the corresponding angle in the neutral 4,4'-bipyridine molecule [115.45 (19)°; Boag *et al.*, 1999]. This increase in angle confirms the protonation of the N atoms in 4,4'-bipyridine. The pyridyl ring of the cation is planar [maximum deviation from the mean plane = 0.004 (2) Å]. The hydrogen oxalate anion is almost planar, with O1—C1—C2—O4 and O2—C1—C2—O3 torsion angles of 0.7 (2) and 1.1 (2)°, respectively.

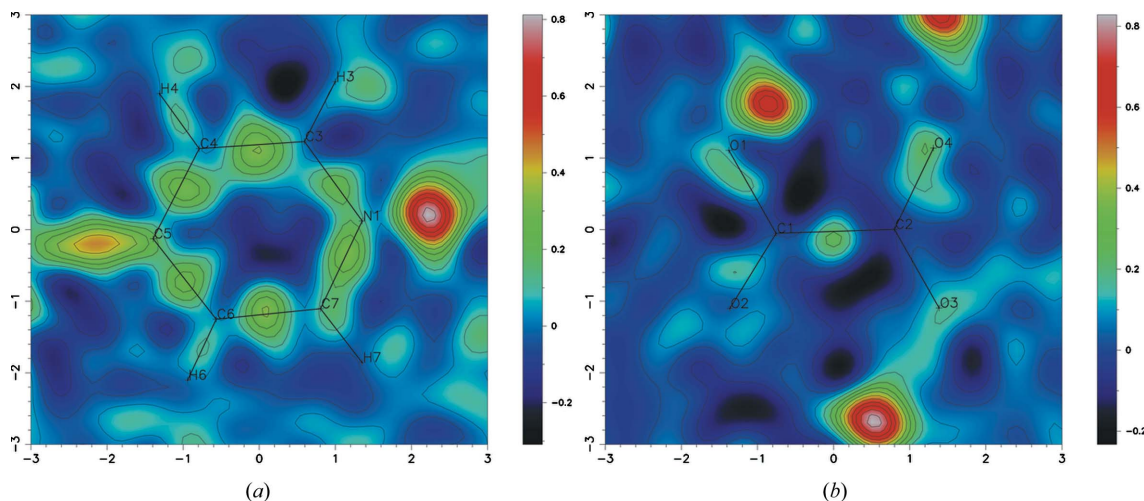
According to Steiner (2002),  $D-H\cdots A$  interactions with distances of up to 3.0 or even 3.2 Å should be considered as potential hydrogen bonding. Also, an angular cutoff can be set at  $>90^\circ$  or, somewhat more conservatively, at  $>110^\circ$ . Based on these values, an intramolecular O—H...O hydrogen bond exists in the hydrogen oxalate anion [Table 1 and Fig. 2 (grey dashed lines)], with graph-set descriptor  $S(5)$  (Etter *et al.*, 1990). Further, the cations and anions are interconnected by means of three  $D-H\cdots A$  hydrogen bonds forming an extended one-dimensional motif parallel to the  $[1\bar{2}1]$  direction (Table 1 and Fig. 2). Taking into consideration the classification of hydrogen bonds by Jeffrey (Steiner, 2002), the H1N atom from the protonated pyridyl ring of the cation is involved in one moderate and one weak hydrogen bond with O atoms of the hydrogen oxalate anion from the neighbouring symmetry unit (entries 3 and 4 in Table 1), making the ring motif  $R_1^2(5)$  (Fig. 2). With regard to the intramolecular hydrogen bond, an  $R_2^2(4)$  ring motif linking two inversion-related hydrogen oxalate anions can be recognized in Fig. 2. However, a second-order hydrogen-bonded ring motif,  $R_2^2(10)$ ,

is more obvious; this unusual deca-atomic ring is formed between two hydrogen oxalate anions linked side-to-side via  $^-O-H\cdots O^-$  hydrogen-bonding interactions (Table 1 and Fig. 2; Braga *et al.*, 2002). An intramolecular O—H...O hydrogen bond may be the cause of the relatively acute hydrogen-bond angle between two hydrogen oxalate anions [O1—H1...O4<sup>i</sup> = 142.5 (16)°; symmetry code: (i)  $-x + 1, -y, -z$ ; Table 1]. In addition, it is well known that in cyclic hydrogen-bonded dimers fairly short H...H contacts occur and destabilize such arrays, forcing angles to be very bent (Steiner, 2002).



**Figure 3**

The crystal packing of the 4,4'-bipyridinium cations linked by the  $\pi$ - $\pi$  interactions of aromatic rings parallel to the  $a$  axis, and hydrogen oxalate anions.



**Figure 4**

Difference Fourier maps for the structure of (I), showing (a) the environment of the 4,4'-bipyridinium cation and (b) the environment of the hydrogen oxalate anion, indicate that the H atoms attached to the N1 and O1 atoms could be located and they were refined freely.

All of these ring hydrogen-bonding motifs are further linked into a chain by hydrogen-bonding motifs with the graph-set descriptors  $C_3^3(17)$ ,  $C_3^3(18)$  or  $C_3^3(19)$ , depending on the choice of the different paths chosen through the hydrogen bonds. The extended one-dimensional chains are connected via C—H...O hydrogen bonds generating a two-dimensional network (Fig. 2 and Table 1).

Stacking interactions of the aromatic systems play an equally important role in the structure of (I), linking the two-dimensional hydrogen-bonding pattern to form a three-dimensional supramolecular architecture. The 4,4'-bipyridinium cations related by the inversion centres are grouped through  $\pi$ - $\pi$  interactions parallel to the *a* axis (Fig. 3), each cation belonging to a different hydrogen-bonding layer. The centroid-centroid distance of two pyridyl rings related by an inversion centre is 4.3865 (10) Å, but the distance between the centres of the two stacking pyridyl rings is equal to the *a*-axis length, *i.e.* 3.6954 (2) Å, whereas the perpendicular distance between their mean planes is 3.3373 (6) Å. The above structural analysis, taking into account the  $\pi$ - $\pi$  interactions in compound (I), is consistent with the view that the aromatic groups stack when the parallel molecular planes are separated approximately by the interplanar distances of *ca* 3.3–3.8 Å (Janiak, 2000). A pyridine-fragment search made by Janiak (2000) has revealed that centroid-centroid contacts between two pyridine fragments start slightly below 3.4 Å (strong interactions are around 3.3 Å and weaker interactions lie above 3.6 Å) and a relative maximum in a number of examples was found around 3.8 Å.

A search of the Cambridge Structural Database (CSD, Version 3.2, update of May 2011; Allen, 2002) revealed that there are a large number of structures containing the 4,4'-bipyridinium cation or the hydrogen oxalate anion, with different simple or complex organic (metal-organic) anions or cations, respectively. Only one structure containing both the 4,4'-bipyridinium cation and an hydrogen oxalate anion was found in the CSD, but the structure also incorporates a

complex anion with bivalent Fe (Yang *et al.*, 2007). These three kinds of ions generate a supramolecular architecture which is different from that of (I). There are only three structures so far (Vaidyanathan *et al.*, 2001; Braga *et al.*, 2002) in which hydrogen oxalate anions form a deca-atomic dimer joined together via the  $\text{O}-\text{H}\cdots\text{O}^-$  interaction, as observed in (I). The intradimer O1...O4 distance [2.5941 (16) Å] in (I) is shorter than the corresponding distances in the structures mentioned above, where the O(H)...O distances are in the range 2.619 (3)–2.741 (3) Å.

## Experimental

An oxalatoantantate(V) solution (1 ml) [ $m(\text{Ta}) = 17.8$  mg, 0.1 mmol; Androš *et al.*, 2010] was added dropwise with stirring at room temperature to a mixture of an aqueous solution (5 ml) of 4,4'-bipyridine (40.8 mg, 0.2 mmol) and 1 M HCl (2 ml). A small amount of white precipitate soon formed and was removed by filtration. Over a period of 2 d, colourless plate-shaped crystals of (I) were obtained. These were separated and dried in air (yield 15%). Elemental analysis for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_8$  found: C 49.89, H 3.52, N 8.01%; calculated: C 50.01, H 3.59, N 8.23%.

### Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_2^{2+}\cdot 2\text{C}_2\text{HO}_4^-$	$\gamma = 97.487$ (5)°
$M_r = 336.26$	$V = 331.00$ (4) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 1$
$a = 3.6954$ (2) Å	Mo $K\alpha$ radiation
$b = 9.8579$ (7) Å	$\mu = 0.14$ mm <sup>-1</sup>
$c = 10.4254$ (8) Å	$T = 150$ K
$\alpha = 116.081$ (7)°	$0.3 \times 0.2 \times 0.1$ mm
$\beta = 97.214$ (5)°	

### Data collection

Oxford Diffraction KM-4/Xcalibur diffractometer with a Sapphire3 detector	2408 measured reflections
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2006)	1475 independent reflections
$T_{\min} = 0.682$ , $T_{\max} = 1.000$	1134 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	117 parameters
$wR(F^2) = 0.096$	All H-atom parameters refined
$S = 0.99$	$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
1475 reflections	$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O4	0.92 (2)	2.222 (18)	2.6885 (14)	110.8 (14)
O1—H1 $\cdots$ O4 <sup>i</sup>	0.92 (2)	1.81 (2)	2.5941 (16)	142.5 (16)
N1—H1N $\cdots$ O2 <sup>ii</sup>	1.05 (2)	2.423 (18)	3.0190 (16)	114.8 (14)
N1—H1N $\cdots$ O3 <sup>ii</sup>	1.05 (2)	1.62 (2)	2.6359 (18)	162.1 (16)
C3—H3 $\cdots$ O3	0.93	2.47	3.3498 (18)	157
C6—H6 $\cdots$ O1 <sup>iii</sup>	0.93	2.37	3.2291 (18)	153

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

C-bound H atoms were included in calculated positions and treated as riding [ $C-H = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. Difference Fourier maps for the structure of (I) (Fig. 4) indicate that the H atoms attached to N1 and O1 of the 4,4'-bipyridine and carboxylate groups, respectively, could be located and were refined freely. These H atoms are involved in relatively strong or moderate hydrogen bonds, which could be the reason why the N1—H1N and O1—H1 distances are refined as relatively long. In support of this view, one can find in the review article of Steiner (2002) that the internuclear  $D-H$  bond length is fairly constant only in weak and moderate hydrogen bonds, whereas it is significantly elongated in strong ones. Additionally, the N-bound H atom of the pyridinium ring participates in two hydrogen bonds (entries 3 and 4 in Table 1) and hence these are more likely to be elongated.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3065). Services for accessing these data are described at the back of the journal.

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