

Bis(tetraethylammonium) 2,2'-bipyridine-4,4'-dicarboxylate tetrahydrate

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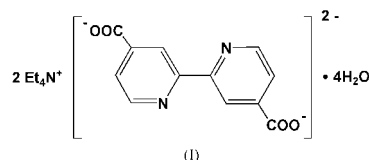
Key indicators

Single-crystal X-ray study
 $T = 297\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.059
 wR factor = 0.187
Data-to-parameter ratio = 19.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $2\text{C}_8\text{H}_{20}\text{N}^+ \cdot \text{C}_{12}\text{H}_6\text{N}_2\text{O}_4^{2-} \cdot 4\text{H}_2\text{O}$, which is one of the precursors of the dye for DSC (dye-sensitized solar cells), consists of tetraethylammonium cations, 2,2'-bipyridine-4,4'-dicarboxylate anions and water molecules. The anion has a centre of symmetry and the pyridine ring is inclined to the carboxylate group by $7.9(3)^\circ$. A two-dimensional network is formed through intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds between water molecules and the carboxylate groups of the anions.

Comment

Ruthenium complexes containing 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2dcbpy) have received much attention as photosensitizers (Grätzel, 2003). The molecular structures of these complexes have been reported (Shklover *et al.*, 1997, 1998). It is important for chemical and materials science applications to elucidate the properties of the H_2dcbpy ligand in the solid state. We report here the crystal structure of the title compound, $2\text{Et}_4\text{N}^+ \cdot \text{dcbpy}^{2-} \cdot 4\text{H}_2\text{O}$, (I).



In (I), the dcbpy^{2-} anion has a centre of symmetry, as shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The $\text{C1}-\text{N1}-\text{C5}$ bond angle of $116.97(13)^\circ$ in the pyridine ring is similar to those for free pyridine (for example, about 117° in a pyridine derivative; Fujihara *et al.*, 2004). The pyridine ring ($\text{N1}/\text{C1}-\text{C5}$) is planar, the largest deviation from the plane being that of atom C1 [$0.004(1)\text{ \AA}$]. The dihedral angle between the pyridine ring and the carboxyl group ($\text{C6}/\text{O1}/\text{O2}$) is $7.9(3)^\circ$.

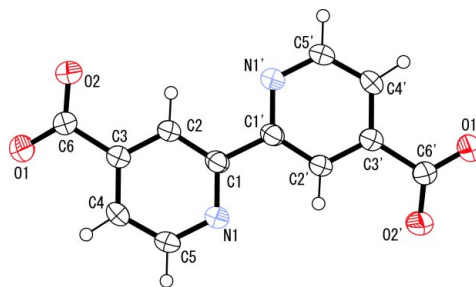


Figure 1

View of the dcbpy^{2-} anion in (I), with 50% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with a prime are at symmetry position $(2-x, 1-y, -z)$.

The carboxylate O1 and O2 atoms act as hydrogen-bond acceptors, forming intermolecular hydrogen bonds with water molecules O3 and O4 (Fig. 2 and Table 2). Hydrogen bonds between water molecules link the dcbpy^{2-} anions, forming a two-dimensional network. The dihedral angle between the two dcbpy^{2-} anions in the same layer is $12.3(1)^\circ$, and the almost planar sheet structure suggests anisotropic electronic properties of the single crystals, which have not been explored. The tetraethylammonium cations are located between layers of dcbpy^{2-} anions in the crystal structure (Fig. 3).

Experimental

2,2'-Bipyridine-4,4'-dicarboxylic acid (0.415 g, 1.7 mmol), synthesized according to a published procedure (Garelli & Vierling, 1992), was added to an aqueous solution (10 ml) containing tetraethylammonium hydroxide (0.50 g, 3.4 mmol) and the solvent evaporated to afford the crude product of (I) as a colourless powder. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution. Elemental analysis (C/H/N) found: 58.47, 9.45, 9.78%; calculated for $\text{C}_{28}\text{H}_{54}\text{N}_4\text{O}_8$: 58.51, 9.47, 9.75%.

Crystal data

$2\text{C}_8\text{H}_{20}\text{N}^+ \cdot \text{C}_{12}\text{H}_6\text{N}_2\text{O}_4^{2-} \cdot 4\text{H}_2\text{O}$	$D_x = 1.161 \text{ Mg m}^{-3}$
$M_r = 574.76$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3258 reflections
$a = 10.740(2) \text{ \AA}$	$\theta = 2.7\text{--}26.1^\circ$
$b = 7.5172(15) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 20.398(4) \text{ \AA}$	$T = 297(2) \text{ K}$
$\beta = 93.40(3)^\circ$	Needle, colourless
$V = 1643.9(6) \text{ \AA}^3$	$0.51 \times 0.22 \times 0.21 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3924 independent reflections
φ and ω scans	2868 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.976$, $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 28.0^\circ$
11634 measured reflections	$h = -14 \rightarrow 12$
	$k = -9 \rightarrow 9$
	$l = -26 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1096P)^2 + 0.1896P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.187$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
3924 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
201 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—N1	1.3452 (19)	C3—C6	1.524 (2)
C1—C2	1.389 (2)	C4—C5	1.378 (2)
C1—C1 ⁱ	1.482 (3)	C5—N1	1.3353 (19)
C2—C3	1.3788 (19)	C6—O2	1.2286 (19)
C3—C4	1.391 (2)	C6—O1	1.2331 (19)
N1—C1—C2	122.62 (12)	C3—C2—C1	119.92 (13)
N1—C5—C4	123.79 (14)	C5—C4—C3	119.29 (13)
C2—C3—C4	117.41 (13)	C5—N1—C1	116.97 (13)

Symmetry code: (i) $2 - x, 1 - y, -z$.

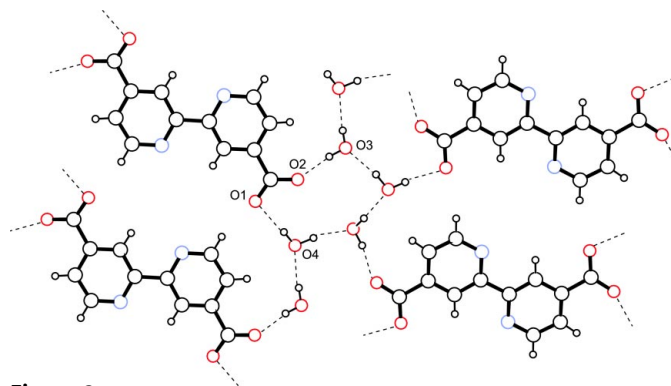


Figure 2

A schematic view of the two-dimensional network. The dashed lines indicate the intralayer hydrogen bonds.

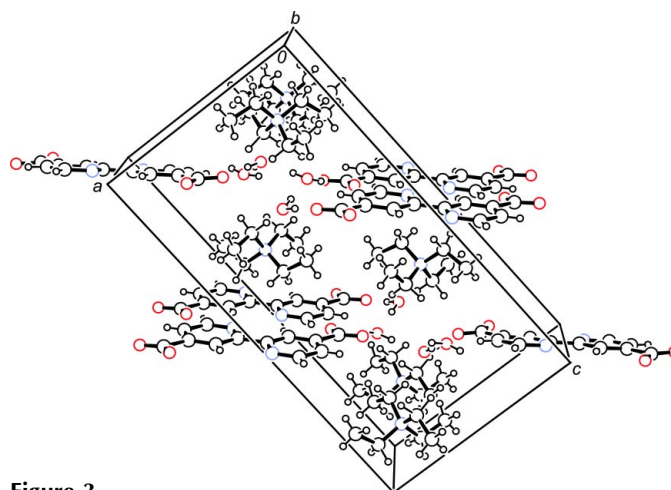


Figure 3

A molecular packing diagram of (I).

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O4—H4A···O1	0.84 (3)	1.97 (3)	2.813 (2)	174 (3)
O3—H3A···O2	0.88 (2)	1.82 (2)	2.688 (2)	168 (2)
O3—H3B···O4 ⁱⁱ	0.87 (3)	1.95 (3)	2.811 (2)	169 (2)
O4—H4B···O3 ⁱⁱⁱ	0.91 (2)	1.88 (2)	2.776 (2)	167 (2)

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

Water H atoms were located in difference Fourier maps and refined isotropically. Other H atoms were placed in calculated positions, with C—H = 0.93 \AA (dcbpy^{2-}) or 0.97 \AA (Et_4N^+) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: SMART-W2K/NT (Bruker, 2003); cell refinement: SMART-W2K/NT; data reduction: SAINT-W2K/NT (Bruker, 2003); program(s) used to solve structure: SHELXTL-NT (Bruker, 2003); program(s) used to refine structure: SHELXTL-NT; molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL-NT.

This research was carried out as a part of the 'Sai-no-Kuni' Consortium of Saitama Prefecture, Japan.

References

- Bruker (2003). *SAINT-W2K/NT* (Version 5.0), *SMART-W2K/NT* (Version 5.6) and *SHELXTL-NT* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fujihara, T., Saito, M. & Nagasawa, A. (2004). *Acta Cryst.* **E60**, o262–o263.
- Garelli, N. & Vierling, P. (1992). *J. Org. Chem.* **57**, 3046–3051.
- Grätzel, M. (2003). *J. Photochem. Photobiol. C*, **4**, 145–153.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Shklover, V., Haibach, T., Bolliger, B., Hochstrasser, M., Erbudak, M., Nissen, H.-U., Zakeeruddin, S. M., Nazeeruddin, M. K. & Grätzel, M. (1997). *J. Solid State Chem.* **132**, 60–72.
- Shklover, V., Ovchinnikov, Yu. E., Braginsky, L. S., Zakeeruddin, S. M. & Grätzel, M. (1998). *Chem. Mater.* **10**, 2533–2541.