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4,4′-Bipyridylium bis(hydrogen 2,2′-dithiodibenzoate) dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.058
wR factor = 0.186
Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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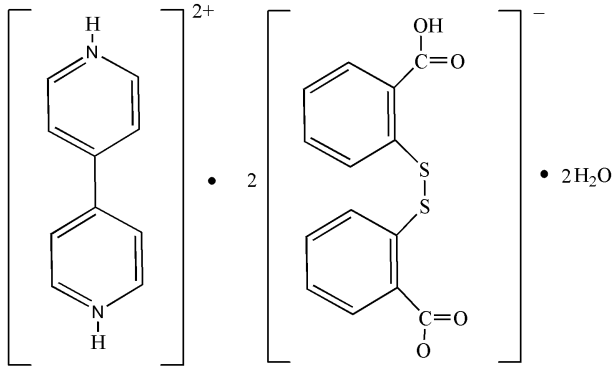
The title compound, $C_{10}H_{10}N_2^{2+}\cdot 2C_{14}H_9O_4S_2^{-}\cdot 2H_2O$, was obtained by the reaction of $Zn(NO_3)_2$ with 2,2′-dithiodibenzoic acid and 4,4′-bipyridine in ethanol. The compound consists of hydrogen 2,2′-dithiodibenzoate anions, centrosymmetric 4,4′-bipyridylium cations and water molecules. Hydrogen-bonding interactions between the components lead to the formation a three-dimensional network.

Comment

The design and synthesis of novel coordination architectures has resulted in a great number of research efforts, due not only to their intriguing structural topologies, but also to their unexpected properties as functional materials (Sato *et al.*, 1996; Yaghi *et al.*, 1998; Harrison *et al.*, 2002). The main strategy popularly used in this area is the building-block approach. 2,2′-Dithiodibenzoic acid is a good choice in the design of novel coordination architectures, since its four coordination sites are likely to engage in coordination to metal ions. The title compound, (I), was unexpectedly obtained during our attempt to react 2,2′-dithiodibenzoic acid and 4,4′-bipyridine with metal ions.



(I)

X-ray diffraction analysis of (I) reveals that its crystal structure is similar to that of the co-crystal 2,2′-dithiodibenzoic acid 4,4′-bipyridine (1/1) (Bi *et al.*, 2002). As depicted in Fig. 1, the asymmetric unit of (I) contains one hydrogen 2,2′-dithiodibenzoate anion, half a centrosymmetric 4,4′-bipyridylium cation and one water molecule.

There are extensive hydrogen-bonding interactions between the carboxyl groups, protonated N atoms and water molecules of (I). As shown in Fig. 2, hydrogen-bonding interactions link water molecules to $C_{14}H_9O_4S_2^{-}$ anions and $C_{10}H_{10}N_2^{2+}$ cations, to form an extended three-dimensional network.

Experimental

A mixture of 2,2′-dithiodibenzoic acid (0.153 g, 0.50 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.149 g, 0.5 mmol) was dissolved in ethanol (15 ml) and the resulting solution was stirred at 333 K for 30 min. A solution of 4,4′-bipyridine (0.047 g, 0.3 mmol) in methanol (5 ml) was added and the resulting mixture was stirred for 1.5 h and then filtered. After allowing the solution to stand for two weeks, colourless crystals of (I) were obtained in 40% yield.

Crystal data

$C_{10}H_{10}N_2^{2+}{\cdot}2C_{14}H_9O_4S_2^-{\cdot}2H_2O$
M_r = 804.90
Triclinic, $P\overline{1}$
a = 7.913 (2) Å
b = 11.192 (2) Å
c = 11.438 (3) Å
α = 64.80 (2)°
β = 82.26 (3)°
γ = 77.32 (3)°
V = 893.3 (4) Å^3
Z = 1
D_x = 1.496 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2035 reflections
θ = 2.0–25.0°
μ = 0.33 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.961, T_{max} = 0.984
5746 measured reflections
3140 independent reflections
2300 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.186
S = 1.16
3140 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2 + 0.5264P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.798 (4)	N1—C15	1.329 (6)
S1—S2	2.0602 (15)	N1—C19	1.337 (6)
S2—C8	1.802 (4)	C15—C16	1.372 (6)
O1—C7	1.312 (5)	C16—C17	1.374 (6)
O2—C7	1.216 (5)	C17—C18	1.392 (6)
O3—C14	1.260 (5)	C17—C17^{i}	1.490 (8)
O4—C14	1.259 (5)	C18—C19	1.369 (6)
C1—S1—S2	105.11 (14)	C8—S2—S1	106.17 (13)
C1—S1—S2—C8	83.48 (19)	S2—S1—C1—C6	162.9 (3)
S2—S1—C1—C2	−18.4 (4)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{ii}	0.82	1.75	2.566 (5)	177
O1W—H1WA···O4^{iii}	0.84	1.74	2.569 (4)	167
N1—H1A···O1W	0.86	1.76	2.605 (5)	165
O1W—H1WB···O2	0.84	1.95	2.738 (5)	157

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

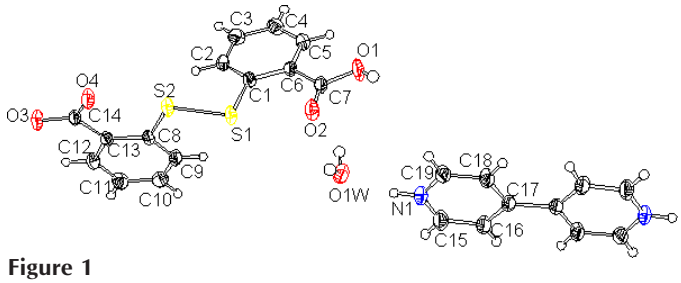


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by $-x, 2-y, 1-z$.

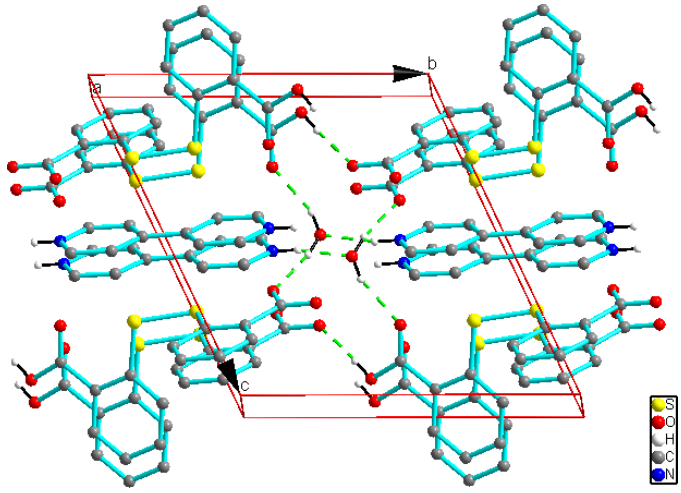


Figure 2
The three-dimensional packing structure of (I). H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonds are shown as dashed lines.

The H atoms of the water molecule were located in a difference map and were allowed to ride on the parent O atom, with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O). The remaining H atoms were positioned geometrically (O—H = 0.82, N—H = 0.86 and C—H = 0.93 Å) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,N). Owing to the large fraction of weak data at higher angles, the 2θ maximum was limited to 50°.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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