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The crystal structure of 4,4'-bipyridinium bis(3-carboxy-2-nitrobenzoate) tetrahydrate, $C_{13}H_{13}N_2O_8$

Table 1: Data collection and handling.

Crystal:	Colorless needle
Size:	0.25 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.2°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14035, 2535, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2059
$N(\text{param})_{\text{refined}}$:	209
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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Abstract

$C_{13}H_{13}N_2O_8$, triclinic, $P\bar{1}$ (no. 2), $a = 7.8590(6)$ Å, $b = 9.3108(8)$ Å, $c = 11.0816(8)$ Å, $\alpha = 66.950(3)^\circ$, $\beta = 71.558(3)^\circ$, $\gamma = 77.203(4)^\circ$, $V = 703.38(10)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0389$, $wR_{\text{ref}}(F^2) = 0.1075$, $T = 149(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All the starting materials are used as received. An amount of 1.56 g 4,4'-bipyridine (1 mmol) and 4.20 g 2-nitroisophthalic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2590(2)	0.7332(2)	0.13143(17)	0.0239(4)
C2	0.1192(2)	0.6259(2)	0.22712(16)	0.0205(4)
C3	−0.0630(2)	0.6799(2)	0.24016(17)	0.0233(4)
H3	−0.0978(2)	0.7835(2)	0.18540(17)	0.0280(5)*
C4	−0.1942(2)	0.5853(2)	0.33159(18)	0.0253(4)
H4	−0.3182(2)	0.6236(2)	0.33907(18)	0.0304(5)*
C5	−0.1443(2)	0.4343(2)	0.41248(17)	0.0219(4)
H5	−0.2351(2)	0.3703(2)	0.47605(17)	0.0263(5)*
C6	0.0367(2)	0.37510(19)	0.40201(16)	0.0186(4)
C7	0.1659(2)	0.47334(19)	0.30822(16)	0.0185(4)
C8	0.0840(2)	0.2093(2)	0.49207(17)	0.0215(4)
C9	−0.0006(2)	0.58106(19)	0.94973(16)	0.0187(4)
C10	−0.1603(2)	0.6787(2)	0.93760(18)	0.0251(4)
H10	−0.2723(2)	0.6437(2)	0.99619(18)	0.0301(5)*
C11	−0.1554(3)	0.8259(2)	0.84055(19)	0.0285(4)
H11	−0.2654(3)	0.8917(2)	0.83241(19)	0.0342(5)*
C12	0.1539(3)	0.7897(2)	0.7685(2)	0.0352(5)
H12	0.2638(3)	0.8295(2)	0.7102(2)	0.0423(6)*
C13	0.1584(3)	0.6403(2)	0.8630(2)	0.0346(5)
H13	0.2708(3)	0.5776(2)	0.8688(2)	0.0416(6)*
N1	0.35924(19)	0.41137(17)	0.29123(15)	0.0232(3)
N2	−0.0012(2)	0.87890(17)	0.75764(15)	0.0266(4)
H2	−0.0020(2)	0.97335(17)	0.69541(15)	0.0319(4)*
O1	0.18947(19)	0.86345(16)	0.05184(14)	0.0363(4)
H1	0.2726(3)	0.9172(13)	−0.0038(16)	0.0545(5)*
O2	0.41792(18)	0.70310(16)	0.12970(13)	0.0336(3)
O3	−0.04938(18)	0.14733(15)	0.58489(13)	0.0344(3)

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Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O4	0.24093(17)	0.14612(15)	0.47314(14)	0.0325(3)
O5	0.43726(17)	0.41781(16)	0.36757(13)	0.0311(3)
O6	0.42763(17)	0.35738(17)	0.20058(14)	0.0353(3)
O2W	0.41799(18)	0.05078(16)	0.87492(10)	0.0342(3)
H2Wa	0.4567(19)	0.1279(11)	0.8807(2)	0.0513(5)*
H2Wb	0.44643(16)	0.06749(13)	0.78837(10)	0.0513(5)*
O1W	0.5133(2)	0.09097(19)	0.61236(11)	0.0507(5)
H1Wa	0.4306(3)	0.1042(18)	0.5710(4)	0.0761(7)*
H1Wb	0.5976(14)	0.0250(11)	0.5836(3)	0.0761(7)*

acid (2 mmol) are dissolved in 30 mL ethanol under stirring. Then the solution was heated to 50 degree for 10 min. After cooling to room temperature, the solution was filtered, evaporated in air. Colorless crystals were harvested after two weeks, yield 65.2% (based on 4,4'-bipyridine).

Experimental details

The structure was solved by direct methods with the SHELX program. All H-atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $1.2U_{\text{eq}}(\text{N})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, respectively) using a riding model with C—H = 0.95 Å, N—H = 0.88 Å, O(carboxyl)—H = 0.84 Å and O(water)—H = 0.87 Å.

Comment

As 4,4'-bipyridine can be protonated partially or totally acting as mono- or dication, aromatic polycarboxylic acids can be deprotonated partially or totally, acting as mono- or polyanions. 4,4'-Bipyridine can form organic salts with aromatic di- [5–7], tri- [8, 9], tetra- [10–14] and pentacarboxylic acids [15] in 1:1, 1:2 and other mole ratios (base vs. acid). Salt formation, co-crystal formation with water and/or organic molecules gives new compounds with predictable structures using the *crystal engineering* approach [16, 17]. However, to the best of our knowledge, only one organic salt consisting of 4,4'-bipyridine and isophthalic acid derivative, 5-amino-2,4,6-tri-iodoisophthalic acid, has been reported [18].

As shown in the figure, the asymmetric unit of the title structure contains one hydrogen 2-nitroisophthalate anion, half a centrosymmetric 4,4'-bipyridinium cation and two water molecules. Bond lengths and angles are in the expected ranges [19]. There are extensive hydrogen-bonding interactions between the protonated N atoms, deprotonated (or not) carboxyl groups, and water molecules of the title organic salt. Two of the hydrogen 2-nitroisophthalate anions are linked by two water molecules with O—H...O hydrogen bonds to generate one dimer. The dimers are linked by N—H...O

hydrogen bonds to a chain, which further generate a three-dimensional structure by O(water)—H...O(water) hydrogen bonds.

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