Crystal structure of bis(2-aminopyridinium) 2,2′-dithiobis(benzoate) dihydrate, $[C_5H_7N_2]_2[C_{14}H_8O_4S_2] \cdot 2H_2O$

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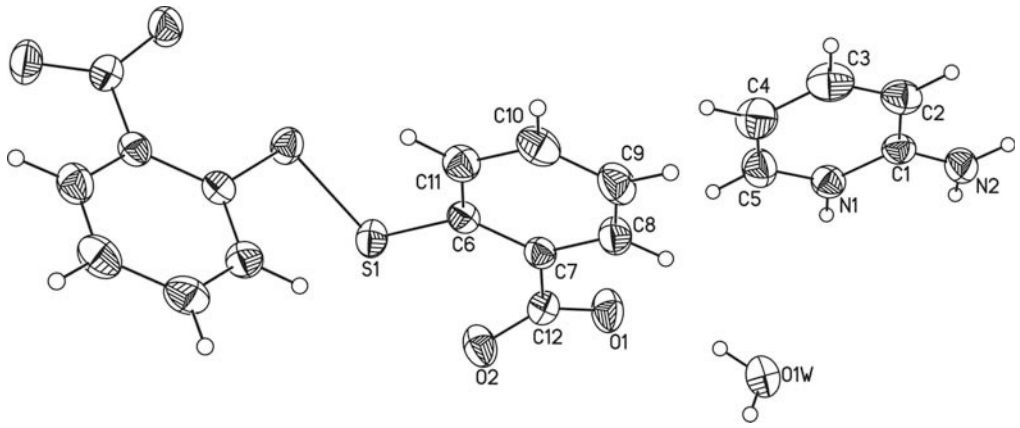

Abstract

$C_{24}H_{26}N_4O_6S_2$, monoclinic, *C*12/*c*1 (no. 15), a = 13.429(1) Å, b = 9.7934(9) Å, c = 20.331(2) Å, β = 105.808(2)°, V = 2572.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.098, T = 296 K.

Source of material

All reagents were commercially available and of analytical grade. The 5 ml ethanol soloution of 2-aminopyridine (1.0 mmol, 0.094 g) was slowly added to an aqueous solution (25 ml) of 2,2′-dithiodibenzoic acid (1.0 mmol, 0.301 g). The mixture was stirred for 10 minutes at 100 °C. The solution was filtered, and the filtrate was kept at the room temperature. After 6 d, crystals suitable for single crystal X-ray diffraction were obtained.

Experimental details

Hydrogen atoms bonded to N and O were located in difference Fourier maps and refined isotropically with distance restraints d(N—H) = 0.89(2), d(O—H) = 0.82(2) and d(H—H) = 1.34(2) Å, respectively. All the remaining H atoms were positioned geometrically and treated as riding with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

Rational design and assembly of novel supramolecular aducts through hydrogen bonding interaction are still an important research area due to their striking structures [1,2]. This work continues our previously investigations of supra-molecular interactions between aromatic molecular salts and adducts [3].

The asymmetric unit of the title crystal structure consists of two 2-aminopyridinium cations, one 2,2′-dithiobis(benzoate) anion and two discrete water molecules. 2,2′-Dithiobis(benzoate) anion has an inversion centre at the midpoint of the S1—S1 (–*x*,*y*,–*z*+½) bond. Two benzene rings of 2,2′-dithiobis(benzoate) anion are nearly perpendicular to each other with the dihedral angles of 103.4° and C6–S1–S1A angle of 105°. 3-Aminopyridinium cation and 2,2′-dithiobis(benzoate) anion are linked together through a pair of N–H···O hydrogen bonds forming a $R_2^2(6)$ motif, in which 3-aminopyridinium cation uses another N–H donor contacting to one water molecule *via* N–H···O hydrogen bonds. In addition, each $R_2^2(6)$ motif interacts with neighbor two water molecule through O···H–O hydrogen bonds. In contrast, each water molecule links adjacent three $R_2^2(6)$ motifs leading to an infinite three-dimensional hydrogen-bonded framework.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.13 × 0.18 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.53 cm^{-1}
Diffractometer, scan mode:	Bruker SMART Apex CCD, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6999, 2520
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1851
$N(param)_{refined}$:	183
Programs:	SHELXS-97, SHELXL-97, SHELXTL [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1WA)	8*f*	0.451(2)	0.203(3)	0.510(1)	0.10(1)
H(1WB)	8*f*	0.458(2)	0.290(3)	0.558(1)	0.11(1)
H(1A)	8*f*	0.668(2)	0.011(2)	0.4773(9)	0.059(6)
H(2A)	8*f*	0.890(1)	0.156(2)	0.474(1)	0.065(7)
H(2B)	8*f*	0.842(2)	0.051(2)	0.5093(9)	0.061(7)
H(2)	8*f*	0.7818	0.2865	0.3761	0.078
H(3)	8*f*	0.6190	0.3172	0.3061	0.091
H(4)	8*f*	0.4810	0.1893	0.3208	0.094
H(5)	8*f*	0.5097	0.0357	0.4081	0.083
H(8)	8*f*	0.3688	0.3350	0.3997	0.069
H(9)	8*f*	0.3538	0.4996	0.3172	0.079
H(10)	8*f*	0.2080	0.5062	0.2255	0.078
H(11)	8*f*	0.0775	0.3482	0.2167	0.067

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*f*	0.04241(4)	0.12501(5)	0.30001(3)	0.0473(3)	0.0535(3)	0.0551(3)	–0.0061(2)	0.0060(2)	0.0075(2)
O(1)	8*f*	0.3315(1)	0.1048(2)	0.44974(8)	0.0469(8)	0.083(1)	0.074(1)	–0.0006(7)	0.0017(7)	0.0194(8)
O(2)	8*f*	0.1607(1)	0.0969(2)	0.42730(8)	0.0495(9)	0.086(1)	0.073(1)	–0.0009(8)	0.0145(7)	0.0288(8)
O(1W)	8*f*	0.4947(1)	0.2359(2)	0.5436(1)	0.055(1)	0.100(2)	0.084(1)	–0.009(1)	0.019(1)	–0.007(1)
N(1)	8*f*	0.6610(1)	0.0682(2)	0.44288(9)	0.059(1)	0.056(1)	0.054(1)	0.0000(8)	0.0176(9)	0.0058(9)
N(2)	8*f*	0.8349(2)	0.1142(2)	0.4783(1)	0.061(1)	0.070(1)	0.060(1)	–0.010(1)	0.017(1)	0.007(1)
C(1)	8*f*	0.7437(2)	0.1380(2)	0.4356(1)	0.060(1)	0.051(1)	0.050(1)	–0.001(1)	0.020(1)	–0.0058(9)
C(2)	8*f*	0.7269(2)	0.2352(2)	0.3826(1)	0.081(2)	0.058(1)	0.061(1)	0.000(1)	0.029(1)	0.004(1)
C(3)	8*f*	0.6301(2)	0.2531(3)	0.3411(1)	0.095(2)	0.069(2)	0.066(2)	0.017(1)	0.024(1)	0.015(1)
C(4)	8*f*	0.5471(2)	0.1773(3)	0.3499(1)	0.069(2)	0.090(2)	0.070(2)	0.021(1)	0.010(1)	0.011(1)
C(5)	8*f*	0.5644(2)	0.0865(3)	0.4011(1)	0.054(1)	0.080(2)	0.074(2)	0.002(1)	0.015(1)	0.003(1)
C(6)	8*f*	0.1428(1)	0.2485(2)	0.30453(9)	0.044(1)	0.044(1)	0.048(1)	0.0003(8)	0.0167(8)	–0.0013(8)
C(7)	8*f*	0.2312(1)	0.2437(2)	0.3602(1)	0.043(1)	0.046(1)	0.050(1)	0.0006(8)	0.0165(8)	–0.0050(8)
C(8)	8*f*	0.3094(2)	0.3382(2)	0.3632(1)	0.049(1)	0.061(1)	0.064(1)	–0.008(1)	0.016(1)	–0.008(1)
C(9)	8*f*	0.3010(2)	0.4362(2)	0.3138(1)	0.063(1)	0.059(1)	0.084(2)	–0.017(1)	0.033(1)	–0.005(1)
C(10)	8*f*	0.2140(2)	0.4400(2)	0.2592(1)	0.073(2)	0.057(1)	0.073(2)	–0.004(1)	0.035(1)	0.010(1)
C(11)	8*f*	0.1355(2)	0.3460(2)	0.2542(1)	0.055(1)	0.057(1)	0.056(1)	0.002(1)	0.017(1)	0.0061(9)
C(12)	8*f*	0.2424(2)	0.1409(2)	0.4168(1)	0.049(1)	0.054(1)	0.049(1)	–0.0011(9)	0.0081(9)	–0.0013(9)

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