Crystal structure of [1,3-bis(benzimidazol-3-ium-1-yl)propane][bis(2,3-dicarboxy-5-nitrobenzoate)], $(C_{17}H_{18}N_4).(O_2NC_9H_4O_6)_2$, $C_{35}H_{26}N_6O_{16}$

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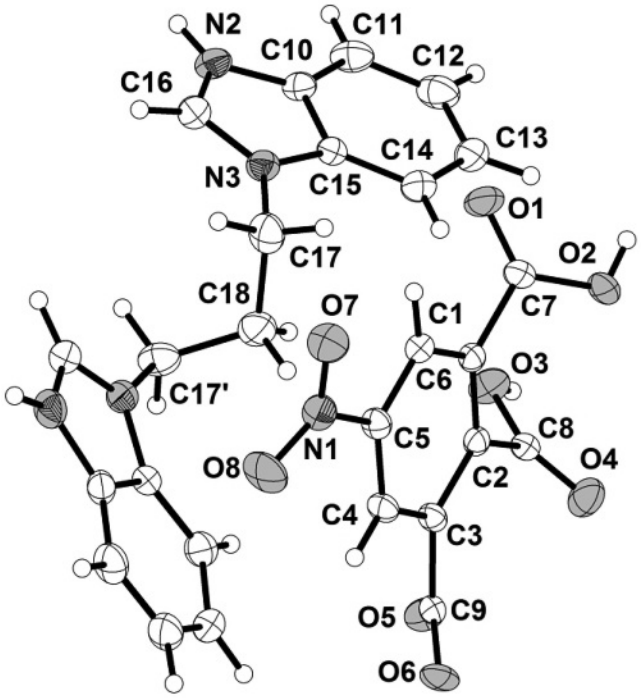

Abstract

$C_{35}H_{26}N_6O_{16}$, monoclinic, *P*2/*n* (no. 13), a = 12.0121(6) Å, b = 9.5473(5) Å, c = 14.1503(6) Å, β = 96.390(4)°, V = 1612.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0474, $wR_{ref}(F^2)$ = 0.0994, T = 293 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.16×0.17×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.31 cm^{-1}
Diffractometer, scan mode:	multiwire proportional, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6124, 3006
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2097
$N(param)_{refined}$:	260
Programs:	SHELX [12]

Source of material

A mixture of H_3nbtc (5-nitro-1,2,3-benzenecarboxylic acid, 0.1 mmol, 23 mg), *bbp* (1,3-bis(benzimidazol-1-yl)propane, 0.1 mmol, 27 mg), and H_2O 10 mL was placed in a Teflon-lined stainless steel vessel, heated to 423 K for 3 days, and then cooled to room temperature over 24 h. Colourless block crystals of the title complex were obtained.

Discussion

The design and synthesis of supramolecular coordination polymeric networks, especialy those constructed by hydrogen bonding and intermolecular weak interactions have been a field of rapid growth due to their special physical properties and potential application in functional materials [1-6]. One of the most successful strategies for preparing these materials has been the assembly reaction of organic bridging ligand which have O and N atoms. 1,3-Bis(benzimidazol-1-yl)propane (*bbp*), one of the extensively studied bidentate ligand, is often used for the construction of various supramolecular architectures by means of coordination and hydrogen bonds due to its two potential binding sites [7, 8]. On the other hand, multicarboxylate ligands, such as 5-nitrobenzene-1,2,3-benzenecarboxylic acid (H_3nbtc) possess several interesting characteristics: (a) it has three carboxyl groups which may be completely or partially deprotonated, including various coordination modes and allowing interesting structures with higher dimensions; (b) it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the numbers of deprotonated carboxyl groups [9-11]. In the title structure, the asymmetric unit comprises one H_2nbtc^- anion and one half H_2bbp^{2+} dication which resides on a crystallographic 2 fold axis (figure). One carboxyl group of H_3nbtc is deprotonated and two N atoms of the *bbp* accepts two protons coming from two H_3nbtc molecules to produce the H_2bbp^{2+} dication. The 1-COOH of H_3nbtc are ionized, which is confirmed by the bond distances of O5–C9 (1.253(2) Å) and O6–C9 (1.254(2) Å) for the carboxylates. These give rise to a conjugated structure. There exist strong electrostatic interactions between charged cation units of NH^+ and the anion of H_2nbtc^-. It is noteworthy that hydrogen bonding and π-π interactions play an important role in the structure of the title compound. There exist two kinds of π-π interaction: (a) between the aromatic rings of the adjacent H_2bbp^{2+} molecules with Cg-Cg distance of 3.504 Å; (b) between the aromatic rings of the adjacent H_2nbtc^- anions with Cg-Cg distance of 3.760 Å. The H_2bbp^{2+} molecules are linked together by π-π interactions to form a 1D chain. Two anions generate a bicomponent adduct π-π interactions. Such kind of bicomponent adducts were linked together by the O–H···O among anions groups with O···O distances of 2.539(2) and 2.651(2) Å to form a 2D layer. The 1D chains are located by hydrogen bonding N^+–H3···O^- between the NH^+ cation and the carboxylic groups with N–O distances of 3.127(3) and 2.984(3) Å in the voids of 2D layer. Then an extended two-dimensional network with hydrogen bonding and π-π interactions is formed, which contributes to the stability of the crystal structure.

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2D)	4*g*		0.1906	–0.1995	–0.0472	0.045
H(2)	4*g*		–0.1583	0.4481	0.1778	0.056
H(3)	4*g*		0.1492	0.5008	0.1785	0.056
H(4)	4*g*		0.1543	0.3443	0.5908	0.034
H(6)	4*g*		–0.0877	0.1759	0.4075	0.033
H(11)	4*g*		0.1533	0.0167	–0.1862	0.049
H(12)	4*g*		0.0992	0.2494	–0.1954	0.053
H(13)	4*g*		0.0624	0.3727	–0.0629	0.049
H(14)	4*g*		0.0873	0.2706	0.0869	0.043
H(16)	4*g*		0.1923	–0.2133	0.1190	0.045
H(17A)	4*g*		0.1450	–0.0539	0.2527	0.050
H(17B)	4*g*		0.0801	0.0837	0.2199	0.050
H(18A)	4*g*	0.5	0.2310	0.1765	0.3011	0.054
H(18B)	4*g*	0.5	0.2690	0.1765	0.1989	0.054

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}
N(1)	4*g*	0.0096(2)	0.1393(2)	0.5788(1)	0.042(1)	0.034(1)	0.025(1)	0.003(1)	0.006(1)	0.001(1)
N(2)	4*g*	0.1768(2)	–0.1299(2)	–0.0117(1)	0.039(1)	0.034(1)	0.039(1)	–0.001(1)	0.001(1)	–0.012(1)
N(3)	4*g*	0.1509(2)	–0.0103(2)	0.1144(1)	0.035(1)	0.030(1)	0.028(1)	–0.001(1)	0.0004(9)	–0.0010(9)
O(1)	4*g*	–0.1096(2)	0.2270(2)	0.2214(1)	0.103(2)	0.030(1)	0.053(1)	–0.000(1)	–0.043(1)	–0.007(1)
O(2)	4*g*	–0.1171(2)	0.4581(2)	0.2276(1)	0.045(1)	0.034(1)	0.029(1)	0.0004(9)	–0.0144(8)	0.0064(8)
O(3)	4*g*	0.1274(2)	0.4515(2)	0.2202(1)	0.054(1)	0.036(1)	0.0242(9)	–0.0060(9)	0.0113(8)	–0.0021(8)
O(4)	4*g*	0.1126(2)	0.6558(2)	0.2962(1)	0.066(1)	0.029(1)	0.037(1)	0.001(1)	0.0017(9)	0.0038(9)
O(5)	4*g*	0.3052(1)	0.5595(2)	0.4273(1)	0.042(1)	0.037(1)	0.0296(9)	–0.0078(9)	0.0099(8)	–0.0040(8)
O(6)	4*g*	0.2478(1)	0.5880(2)	0.5694(1)	0.035(1)	0.046(1)	0.0208(9)	–0.0027(9)	–0.0043(7)	–0.0102(8)
O(7)	4*g*	–0.0781(2)	0.0725(2)	0.5658(1)	0.043(1)	0.044(1)	0.044(1)	–0.009(1)	0.0089(9)	0.0067(9)
O(8)	4*g*	0.0808(2)	0.1214(2)	0.6460(1)	0.064(1)	0.061(2)	0.032(1)	–0.007(1)	–0.013(1)	0.019(1)
C(1)	4*g*	–0.0101(2)	0.3405(2)	0.3528(2)	0.029(1)	0.024(1)	0.023(1)	0.005(1)	–0.001(1)	–0.003(1)
C(2)	4*g*	0.0780(2)	0.4364(2)	0.3719(1)	0.030(1)	0.022(1)	0.020(1)	0.005(1)	0.000(1)	–0.002(1)
C(3)	4*g*	0.1405(2)	0.4386(2)	0.4620(1)	0.025(1)	0.029(1)	0.020(1)	0.003(1)	0.000(1)	–0.002(1)
C(4)	4*g*	0.1150(2)	0.3430(3)	0.5303(2)	0.032(1)	0.033(2)	0.019(1)	0.002(1)	–0.004(1)	–0.001(1)
C(5)	4*g*	0.0315(2)	0.2463(3)	0.5080(2)	0.029(1)	0.029(2)	0.022(1)	0.002(1)	0.002(1)	0.002(1)
C(6)	4*g*	–0.0317(2)	0.2426(3)	0.4207(2)	0.029(1)	0.023(1)	0.030(1)	0.001(1)	–0.000(1)	–0.002(1)
C(7)	4*g*	–0.0832(2)	0.3347(3)	0.2604(2)	0.034(1)	0.030(2)	0.027(1)	–0.001(1)	–0.007(1)	–0.001(1)
C(8)	4*g*	0.1079(2)	0.5305(3)	0.2929(2)	0.030(1)	0.026(2)	0.026(1)	0.000(1)	–0.006(1)	–0.001(1)
C(9)	4*g*	0.2384(2)	0.5362(2)	0.4875(2)	0.028(1)	0.024(1)	0.024(1)	0.004(1)	–0.003(1)	0.000(1)
C(10)	4*g*	0.1510(2)	0.0050(3)	–0.0431(2)	0.030(1)	0.028(2)	0.034(1)	–0.005(1)	0.001(1)	–0.004(1)
C(11)	4*g*	0.1397(2)	0.0664(3)	–0.1321(2)	0.048(2)	0.046(2)	0.028(1)	–0.010(2)	0.002(1)	–0.006(1)
C(12)	4*g*	0.1073(2)	0.2047(3)	–0.1367(2)	0.053(2)	0.046(2)	0.032(2)	–0.013(2)	–0.007(1)	0.006(1)
C(13)	4*g*	0.0862(2)	0.2801(3)	–0.0563(2)	0.047(2)	0.028(2)	0.045(2)	–0.003(1)	–0.008(1)	0.003(1)
C(14)	4*g*	0.0998(2)	0.2203(3)	0.0328(2)	0.040(2)	0.033(2)	0.033(1)	–0.001(1)	–0.002(1)	–0.005(1)
C(15)	4*g*	0.1329(2)	0.0816(3)	0.0377(2)	0.026(1)	0.026(1)	0.028(1)	–0.001(1)	–0.002(1)	–0.000(1)
C(16)	4*g*	0.1765(2)	–0.1341(3)	0.0816(2)	0.036(2)	0.029(2)	0.045(2)	–0.001(1)	–0.004(1)	0.001(1)
C(17)	4*g*	0.1475(2)	0.0297(3)	0.2141(2)	0.051(2)	0.044(2)	0.029(1)	0.007(1)	0.003(1)	0.005(1)
C(18)	2*e*	$\frac{1}{4}$	0.1165(4)	$\frac{1}{4}$	0.064(3)	0.038(3)	0.029(2)	0	–0.009(2)	0

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