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Crystal structure of 4,4'-(1,4-phenylene)bis(1H-imidazol-3-ium)bis(2-carboxybenzoate), $C_{30}H_{26}N_4O_8$

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Abstract

$C_{30}H_{26}N_4O_8$, monoclinic, $P2_1/n$ (no. 14), $a = 6.6363(7)$ Å, $b = 9.0231(9)$ Å, $c = 22.082(2)$ Å, $\beta = 92.765(2)^\circ$, $V = 1320.7(2)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0455$, $wR_{\text{ref}}(F^2) = 0.1234$, $T = 296(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.25 \times 0.23 \times 0.22$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.11 mm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
θ_{max} , completeness:	25.0° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6471, 2310, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1664
$N(\text{param})_{\text{refined}}$:	191
Programs:	Bruker [1], SHELX [2, 3]

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.2627(4)	0.4076(3)	0.29001(12)	0.0540(7)
H1A	−0.348507	0.322246	0.285404	0.081*
H1B	−0.336858	0.494691	0.277660	0.081*
H1C	−0.216756	0.417168	0.331717	0.081*
C2	−0.0847(3)	0.3897(3)	0.25135(10)	0.0402(6)
C3	0.0631(3)	0.2869(3)	0.26601(11)	0.0485(6)
H3	0.053044	0.228363	0.300389	0.058*
C4	0.2260(3)	0.2701(3)	0.23010(11)	0.0466(6)
H4	0.321886	0.198302	0.240604	0.056*
C5	0.2527(3)	0.3563(2)	0.17876(10)	0.0366(5)
C6	0.1025(3)	0.4622(2)	0.16302(10)	0.0353(5)
C7	−0.0619(3)	0.4741(2)	0.19960(10)	0.0392(5)
H7	−0.162115	0.542429	0.188724	0.047*
C8	0.0945(4)	0.5663(3)	0.10941(11)	0.0438(6)
C9	0.4410(3)	0.3189(3)	0.14589(11)	0.0424(6)
C10	0.4133(3)	−0.0578(2)	0.04994(10)	0.0392(5)
H10	0.355484	−0.097786	0.083839	0.047*
C11	0.3224(3)	0.0623(2)	0.02077(9)	0.0311(5)
C12	0.4120(3)	0.1194(2)	−0.02970(10)	0.0386(6)
H12	0.353701	0.200054	−0.050076	0.046*
C13	0.1355(3)	0.1243(2)	0.04295(9)	0.0323(5)
C14	0.0330(3)	0.0930(3)	0.09295(10)	0.0400(6)
H14	0.069535	0.023308	0.122493	0.048*
C15	−0.1350(3)	0.2652(3)	0.04348(10)	0.0396(6)
H15	−0.232934	0.335024	0.032212	0.048*
N1	0.0256(2)	0.23360(19)	0.01276(8)	0.0384(5)
H1D	0.047638	0.274144	−0.024163	0.046*
N2	−0.1346(3)	0.1828(2)	0.09228(8)	0.0404(5)
H2A	−0.243234	0.189637	0.122182	0.049*
O1	0.2445(3)	0.5781(2)	0.07602(9)	0.0763(7)
O2	−0.0588(3)	0.6400(2)	0.09838(9)	0.0708(6)
O3	0.4922(3)	0.3959(2)	0.10041(9)	0.0666(6)
H3A	0.377273	0.490218	0.092488	0.080*
O4	0.5442(2)	0.2134(2)	0.16348(8)	0.0583(5)

Source of material

All reagents and solvents were used as obtained without further purification. The ethanol solution (5 mL) of 1,4-di(1H-imidazol-4-yl)benzene (*L*, 0.10 mmol, 0.021 g) was slowly added to an aqueous solution (25 mLs) of 4-methylphthalic acid (H_2A , 0.1 mmol, 0.0181 g). The mixture was stirred for

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half an hour at 353 K. The solution was filtered, and the filtrate was kept at the room temperature. After two weeks later, colorless crystals of the title salt were obtained with a yield of 38%. Analysis calculated (%): C, 63.15; H, 4.59; N, 9.82. Found (%): C, 63.28; H, 4.38; N, 9.72.

Experimental details

Coordinates of hydrogen atoms were added using a riding model. Their U_{iso} values were set to $1.2U_{\text{eq}}$ of the parent atoms except H1A, H1B and H1C of the U_{iso} values were set to $1.5U_{\text{eq}}$ of the parent C1 atom.

Comment

Cocrystal is the type of multi-component crystalline supramolecular polymer that has attracted considerable attention in recent years because of their fascinating structural topologies and potential applications [4, 5]. Polyaza-heteroaromatic compounds in their neutral and anionic forms have been widely exploited in the construction of intriguing metal-organic coordination architectures [6–10]. In addition to their favourable coordination abilities, the rich nitrogen atoms of polyazaheteroaromatic compounds can serve as weak base to accept protons from carboxylic acid or inorganic acid to form acid-base conjugate pair incorporating charge transfer interactions, which might potentially benefit the construction of cocrystals [11, 12].

In this paper, we report the reaction product of the multi-nitrogen compound 1,4-di(1*H*-imidazol-4-yl)benzene (*L*) together with 4-methylphthalic acid (H₂A). The asymmetric unit consists of one half of a dication and one monoanion (*cf.* the figure; $a = 1 - x, -y, -z$). As mentioned above, the nitrogen-rich molecule *L* can serve as weak base to accept protons from carboxylic acid to form HL^+ , and H₂A are deprotonated to be HA^- anion.

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