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The crystal structure of 1,4-bis((1*H*-benzimidazol-2-yl)methyl)-piperazine-2,5-dione dihydrate, $C_{20}H_{22}N_6O_4$

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Abstract

$C_{20}H_{22}N_6O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 11.2208(8)$ Å, $b = 6.0358(4)$ Å, $c = 14.6702(10)$ Å, $\beta = 92.565(1)^\circ$, $V = 992.57(12)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0639$, $wR_{ref}(F^2) = 0.1726$, $T = 296(2)$ 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 reagents and solvents were used as obtained. The title compound was prepared according to a modified method described by Adams *et al.* [5] in which the molar amount ratio of raw material iminodiacetic acid (13.3 g, 0.10 mol) and 1,2-diaminobenzene (10.8 g, 0.10 mol) being 1/1. A small amount of $MnCl_2 \cdot (H_2O)_4$ (1.0 g, 5.0 mmol) was also added as the catalyst (Yield: 9.40 g, 41.5%). Crystals were obtained two weeks later by slow evaporation of the title compound in ethanol (95%).

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.16 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ⁻¹
Diffractometer, scan mode:	φ and ω
θ_{max} , completeness:	27.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	10,383, 2143, 0.033
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1623
$N(param)_{refined}$:	145
Programs:	Bruker [1], SHELX [2–4], Diamond [3], Olex2 [4]

Experimental details

H atoms bonded to C atoms were located in difference maps and subsequently treated as riding, with C–H distances of 0.93 Å (aromatic) and 0.97 Å (methylene); $U_{iso}(H) = 1.2U_{eq}$ (aromatic and methylene C). H atoms bonded to N and methanol O atoms were also found in difference maps, and refined with restraints of N–H = 0.86(1) Å and O–H = 0.82(1) Å; $U_{iso}(H)$ values were set equal to 1.2 or 1.5 times of the U_{eq} of their carrier atoms for N and O atoms, respectively.

Comment

The title compound (BMP) belongs to a new class of bridging ligand containing nitrogen and oxygen donor atoms, which is used in the design and synthesis of very few metal complexes [6]. The mechanism of the synthesis of BMP is still debatable whether it is a byproduct of the synthesis of the bis[N-(benzimidazol-2-ylmethyl)]amine

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.8975 (3)	0.0783 (4)	0.67284 (17)	0.0484 (7)
H1A	0.961332	0.098363	0.718864	0.058*
H1B	0.853067	−0.052909	0.688787	0.058*
C2	0.8158 (2)	0.2759 (4)	0.67395 (15)	0.0395 (6)
C3	0.6863 (2)	0.5290 (4)	0.62803 (17)	0.0421 (6)
C4	0.6078 (3)	0.6729 (5)	0.5818 (2)	0.0601 (8)
H4	0.587237	0.654994	0.520084	0.072*
C5	0.5622 (3)	0.8431 (5)	0.6320 (3)	0.0680 (9)
H5	0.509678	0.942751	0.603315	0.082*
C6	0.5921 (3)	0.8708 (5)	0.7241 (3)	0.0665 (9)
H6	0.559195	0.987950	0.755626	0.080*
C7	0.6694 (2)	0.7284 (5)	0.7696 (2)	0.0537 (7)
H7	0.689858	0.747404	0.831281	0.064*
C8	0.7162 (2)	0.5545 (4)	0.72018 (16)	0.0414 (6)
C9	0.9128 (2)	−0.1527 (4)	0.53247 (18)	0.0488 (7)
H9A	0.827063	−0.145699	0.520891	0.059*
H9B	0.929307	−0.281685	0.570366	0.059*
C10	1.0302 (2)	0.1872 (4)	0.55691 (17)	0.0416 (6)
N1	0.94946 (18)	0.0432 (3)	0.58413 (13)	0.0409 (5)
N2	0.75113 (19)	0.3470 (4)	0.60041 (13)	0.0436 (5)
H2	0.758 (2)	0.307 (5)	0.5443 (9)	0.052*
N3	0.79867 (19)	0.3917 (4)	0.74791 (13)	0.0439 (5)
O1	1.05869 (19)	0.3503 (3)	0.60343 (13)	0.0595 (6)
O2	0.7938 (3)	0.2943 (4)	0.42089 (14)	0.0821 (8)
H2A	0.838 (4)	0.401 (5)	0.415 (3)	0.123*
H2B	0.791 (4)	0.230 (7)	0.3716 (17)	0.123*

(IDB) or from the IDB ligand decomposition under the catalysis by a metal complex, further producing the semi-condensation product BMP [6]. In this work, we have investigated its formation process by a modified method by using the MnCl₂·(H₂O)₄ as the catalyst and the molar ratio of the raw materials iminodiacetic acid and 1,2-diaminobenzene being 1/1. In comparison to the reaction without a catalyst, the product yield of BMP was significantly improved. The colorless crystals can be obtained by a recrystallization of BMP from ethanol solution.

The title compound crystallized in the monoclinic space group *P*2₁/*c*. In its asymmetric unit, there is one half of a BMP and one water molecules with an inversion center residing at

the piperazine-2,5-dione centroid. Due to the conjugate effects of the two carbonyl groups, the six-membered piperazine-2,5-dione ring is found to be planar. In comparison with the conformation of a BMP incorporated into a crystal of a metal complex [6], these two benzimidazole groups are also in a *trans* position to the central piperazine ring, leading to the chair-like conformation. The intermolecular connection between all moieties is furnished by N–H···O and O–H···O hydrogen bonds. The benzo groups are oriented in a perpendicular arrangement to interact by C–H···π interactions.

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