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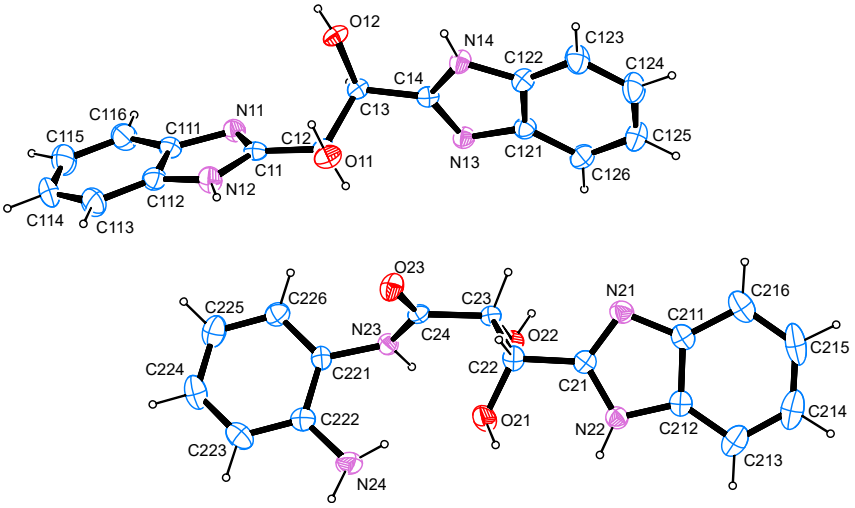
The crystal structure of 1,2-bis(1*H*-benzo[*d*]imidazol-2-yl)ethane-1,2-diol — *N*-(2-aminophenyl)-3-(1*H*-benzo[*d*]imidazol-2-yl)-2,3-dihydroxypropanamide (1/1), $C_{32}H_{30}N_8O_5$



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Abstract

$C_{32}H_{30}N_8O_5$, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.1258(4) Å, b = 10.6225(5) Å, c = 30.1870(14) Å, V = 2926.3(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0367, $wR_{ref}(F^2)$ = 0.0837, T = 200 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.

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Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	0.55 × 0.15 × 0.06 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	39064, 7280, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 6175
$N(param)_{refined}$:	446
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Source of material

Approximately 0.1 mol o-phenylene diamine and 0.1 mol tartaric acid were refluxed in 100 mL 4 M HCl in a round bottomed flask for 1 h. The flask was allowed to cool to room temperature and then the purple solution was neutralized with conc. NH_3 solution. The brown precipitate was filtered off and recrystallised from a mixture of water and ethanol. Brown crystals were formed.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O11	0.14620 (17)	0.52437 (13)	0.55431 (5)	0.0254 (3)
O12	−0.04913 (15)	0.33833 (14)	0.52593 (5)	0.0221 (3)
O21	0.7834 (2)	0.71613 (16)	0.48936 (5)	0.0356 (4)
O22	0.73500 (15)	0.47932 (13)	0.45153 (5)	0.0201 (3)
O23	0.47180 (16)	0.58894 (14)	0.53054 (5)	0.0278 (3)
N11	0.18880 (19)	0.21491 (16)	0.60449 (6)	0.0222 (4)
N12	0.1950 (2)	0.40536 (18)	0.63450 (6)	0.0273 (4)
N13	0.26775 (18)	0.35960 (16)	0.45259 (6)	0.0216 (4)
N14	0.03971 (19)	0.43346 (17)	0.44705 (6)	0.0221 (4)
N21	0.6082 (2)	0.70821 (17)	0.38000 (6)	0.0254 (4)
N22	0.8329 (2)	0.76985 (17)	0.40019 (6)	0.0228 (4)
N23	0.67444 (18)	0.46668 (16)	0.53706 (5)	0.0198 (3)
N24	0.8680 (2)	0.61172 (19)	0.58518 (7)	0.0300 (4)
C11	0.1880 (2)	0.33647 (18)	0.59689 (7)	0.0202 (4)
C12	0.1913 (2)	0.39755 (17)	0.55193 (7)	0.0198 (4)
H12	0.295697	0.397524	0.541840	0.024*
C13	0.1030 (2)	0.32362 (18)	0.51742 (6)	0.0182 (4)
H13	0.129238	0.232391	0.519356	0.022*
C14	0.1389 (2)	0.37158 (18)	0.47207 (7)	0.0189 (4)
C21	0.7007 (2)	0.72366 (18)	0.41284 (7)	0.0200 (4)
C22	0.6637 (2)	0.69591 (19)	0.46038 (7)	0.0227 (4)
H22	0.580261	0.750863	0.469710	0.027*
C23	0.6184 (2)	0.55756 (17)	0.46556 (6)	0.0175 (4)
H23	0.529794	0.540544	0.446994	0.021*
C24	0.5809 (2)	0.53774 (17)	0.51421 (6)	0.0178 (4)
C111	0.1984 (2)	0.2035 (2)	0.65061 (7)	0.0231 (4)
C112	0.2029 (2)	0.3229 (2)	0.66990 (7)	0.0263 (5)
C113	0.2149 (3)	0.3402 (2)	0.71540 (8)	0.0379 (6)
H113	0.218860	0.421892	0.728172	0.045*
C114	0.2207 (3)	0.2331 (3)	0.74101 (8)	0.0409 (6)
H114	0.230735	0.240989	0.772212	0.049*
C115	0.2123 (3)	0.1138 (2)	0.72231 (8)	0.0404 (6)
H115	0.214259	0.042204	0.741147	0.049*
C116	0.2012 (3)	0.0964 (2)	0.67706 (8)	0.0324 (5)
H116	0.195752	0.014530	0.664536	0.039*
C121	0.2502 (2)	0.41740 (19)	0.41123 (7)	0.0221 (4)
C122	0.1071 (2)	0.4637 (2)	0.40741 (7)	0.0233 (4)
C123	0.0568 (2)	0.5225 (2)	0.36916 (7)	0.0317 (5)
H123	−0.040979	0.552381	0.366800	0.038*
C124	0.1552 (3)	0.5354 (2)	0.33483 (8)	0.0372 (6)
H124	0.124946	0.575539	0.308245	0.045*
C125	0.2991 (3)	0.4905 (2)	0.33839 (8)	0.0360 (6)
H125	0.364626	0.501291	0.314226	0.043*
C126	0.3478 (2)	0.4308 (2)	0.37630 (7)	0.0303 (5)
H126	0.445218	0.399878	0.378392	0.036*
C211	0.6842 (2)	0.75012 (19)	0.34284 (7)	0.0243 (4)
C212	0.8252 (2)	0.7899 (2)	0.35496 (7)	0.0239 (4)
C213	0.9257 (3)	0.8358 (2)	0.32441 (9)	0.0387 (6)
H213	1.020769	0.862466	0.333108	0.046*
C214	0.8807 (4)	0.8407 (3)	0.28080 (9)	0.0468 (7)
H214	0.946478	0.871479	0.258947	0.056*
C215	0.7421 (4)	0.8020 (2)	0.26809 (8)	0.0460 (7)
H215	0.715366	0.806900	0.237728	0.055*
C216	0.6415 (3)	0.7563 (2)	0.29834 (8)	0.0372 (6)
H216	0.546641	0.729935	0.289245	0.045*
C221	0.6754 (2)	0.45380 (19)	0.58432 (7)	0.0207 (4)
C222	0.7771 (2)	0.5266 (2)	0.60795 (7)	0.0247 (4)
C223	0.7911 (3)	0.5056 (2)	0.65315 (8)	0.0339 (5)
H223	0.860700	0.552393	0.669779	0.041*
C224	0.7040 (3)	0.4169 (2)	0.67414 (8)	0.0380 (6)
H224	0.715266	0.402953	0.705039	0.046*
C225	0.6012 (3)	0.3484 (2)	0.65080 (8)	0.0350 (5)
H225	0.540528	0.289258	0.665631	0.042*
C226	0.5873 (2)	0.3668 (2)	0.60562 (7)	0.0263 (5)
H226	0.517305	0.319681	0.589239	0.032*
H1A	0.826 (3)	0.642 (2)	0.5593 (9)	0.035 (7)*
H1B	0.912 (3)	0.675 (3)	0.6043 (9)	0.049 (8)*
H11A	0.056 (3)	0.526 (3)	0.5610 (9)	0.040 (8)*
H12A	0.200 (3)	0.485 (3)	0.6350 (9)	0.043 (8)*
H12B	−0.091 (3)	0.270 (3)	0.5320 (9)	0.036 (7)*
H14A	−0.048 (3)	0.449 (2)	0.4546 (8)	0.028 (6)*
H21A	0.818 (4)	0.788 (3)	0.4879 (10)	0.059 (10)*
H22A	0.708 (3)	0.422 (3)	0.4327 (9)	0.042 (8)*
H22B	0.898 (3)	0.801 (3)	0.4180 (9)	0.041 (8)*
H23A	0.758 (3)	0.440 (2)	0.5230 (9)	0.035 (7)*

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C). All oxygen- and nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Comment

Chelate ligands have found widespread use in coordination chemistry due to the increased stability of coordination compounds they can form in comparison to monodentate ligands. The stability of these compounds is enhanced further if the denticity of the ligand is increased upon incorporation of more and more potential donor sites [7]. Especially dicarboxylic acids are interesting in this aspect as chemical factors such as pH values could influence on the protonation/deprotonation of acidic functional groups and fine-tune the denticity of the resulting ligand species. Examples in this aspect are imidazole-dicarboxylic acids that can be synthesized according to a published procedure [8]. The structure of piperazine-1,4-diium bis(hydrogen 2-propyl-1*H*-imidazole-4,5-dicarboxylate) monohydrate has been reported earlier and confirms the validity of the general synthetic protocol [9]. In continuation of our studies of the

structures of polyfunctional carboxylic acids [10–13], we attempted the synthesis of a novel imidazole-dicarboxylic acid.

The structure solution shows a surprising result confirming that the synthesis reaction was interrupted too early for the complete conversion of the starting materials. The asymmetric unit contains two complete, neutral molecular species 1,2-bis(1H-benzo[*d*]imidazol-2-yl)ethane-1,2--diol and *N*-(2-aminophenyl)-3-(1*H*-benzo[*d*]imidazol-2-yl)-2,3-dihydroxypropanamide. The latter can be expected as a first step on the conversion pathway of the educts to the intended product. C–N bond lengths in the symmetric molecular entity clearly show the distinction between the imino and the amino-type nitrogen atom with values of 1.312(3) and 1.320(3) Å for the former and 1.352(3) and 1.350(3) Å for the latter with regards to the bond towards the carbon atom connected to both nitrogen atoms within each heterocyclic moiety. These values also tally with the corresponding bond lengths in the benzimidazole motif of the asymmetric second molecular entity present in the asymmetric unit of the crystal structures where values of 1.312(3) and 1.358(3) Å are apparent. In each case, these values are in good agreement with other benzimidazole derivatives whose molecular and crystal structures were determined by means of diffraction studies performed on single crystals and whose metrical parameters have been deposited with the Cambridge Structural Database. The C=O bond in the asymmetric benzimidazol moiety present in the crystal structure is found at 1.237(2) Å. The least-squares planes as defined by the respective non-hydrogen atoms of the two benzimidazole systems present in the 1,2-bis(2-benzimidazyl)-1,2,-dihydroxyethane molecule intersect at an angle of 75.04(7)° while the least-squares planes as defined by the respective non-hydrogen atoms of the benzimidazole moiety on the one hand and the non-hydrogen atoms of the aminophenyl moiety on the other hand in the asymmetric molecule present in the crystal structure intersect at an angle of 23.86(7)° only.

In the crystal, classical hydrogen bonds of the O–H···O, O–H···N, N–H···O and N–H···N type are present next to C–H···N contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. All hydrogen atoms bonded to heteroatoms act as donors while all imino-type nitrogen atoms as well as all oxygen atoms act as acceptors. These classical hydrogen bonds are established between the two molecular entities of the title compound as well as symmetry-generated equivalents thereof. One intramolecular N–H···O hydrogen bond is formed by the amino group of the aminophenyl moiety. The C–H···N contact is supported by one of the hydrogen atoms in *ortho* position to the heterocyclic five-membered ring in the 1,1,2-bis(1*H*-benzo[d]imidazol-2-yl)ethane-1,2-diol molecule. In terms of graph-set analysis [14], the descriptor for these contacts is $S(9)DDDDC_1^1(5)C_1^1(6)\ C_1^1(7)\ C_1^1(9)C_1^1(10)$. In total, the entities present in the asymmetric unit are connected to sheets perpendicular to the crystallographic *c* axis. Furthermore, a number of N–H···π as well as C–H···π interactions could be discussed whose metrical details have been tabulated.

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