Crystal structure of bis(2,2'-biimidazole)zinc(II) benzene-1,2-dicarboxylate monohydrate, $\text{Zn}(\text{C}_6\text{H}_6\text{N}_4)_2(\text{C}_8\text{H}_4\text{O}_4) \cdot \text{H}_2\text{O}$

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four nitrogen atoms ($d(\text{Zn1}—\text{N2}) = 2.142(3) \text{ \AA}$, $d(\text{Zn1}—\text{N3}) = 2.168(3) \text{ \AA}$, $d(\text{Zn1}—\text{N5}) = 2.136(4) \text{ \AA}$, $d(\text{Zn1}—\text{N7}) = 2.145(3) \text{ \AA}$) from two different biimidazole ligands, forming a tetragonal pyramid with the $\text{O(N)}—\text{Zn}—\text{O(N)}$ angles ranging from $77.8(1)^\circ$ to $152.9(1)^\circ$. The two carboxyl groups of one DBC are both deprotonated, as proven by the absence of any strong bands around 1700 cm^{-1} in the IR spectrum [2]. Each dianion is coordinated to a Zn(II) ion in a monodentate coordination mode. In this coordination manner, the title complex forms a zero dimensional structure. In the crystal lattice, the $\text{N6} \cdots \text{N8}^i$ distance of $3.334 \text{ \AA}$ between the imidazole rings (containing N6, N8) and its symmetry equivalent (symmetry code i: $1-x, 1-y, -z$), and the $\text{N6} \cdots \text{N1}^{ii}$ distance of $3.515 \text{ \AA}$ between the imidazole ring (contains N6)-imidazole ring (contains N1ⁱⁱ) (symmetry code ii: $1-x, -y, -z$) in an offset fashion, indicates strong $\pi-\pi$ stacking interactions between two neighboring aryl-rings. Otherwise, there are seven types of hydrogen bonds between N atoms from biimidazole and O atoms from both DBC and water molecules. The $\pi-\pi$ interactions and hydrogen bonds result in a three-dimensional supramolecular structure. It is clear that the $\pi-\pi$ interactions and the $\text{N}—\text{H} \cdots \text{O}$, $\text{Ow}—\text{H} \cdots \text{O}$ hydrogen bonds stabilize the title structure [3].

Abstract

$\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_5\text{Zn}$, monoclinic, $P12_1/c1$ (no. 14), $a = 10.0039(8) \text{ \AA}$, $b = 11.6195(9) \text{ \AA}$, $c = 18.197(1) \text{ \AA}$, $\beta = 96.404(1)^\circ$, $V = 2102.0 \text{ \AA}^3$, $Z = 4$, $R_g(F) = 0.045$, $wR_{\text{ref}}(F^2) = 0.156$, $T = 293 \text{ K}$.

Source of material

The title complex was prepared from a mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.184 g), benzene-1,2-dicarboxylic acid (0.166 g), 2,2'-biimidazole (0.270 g) and H_2O (19 ml) in a 30 ml Teflon-lined autoclave under autogenous pressure at 443 K for four days. After cooling to room temperature, colorless block crystals were collected by filtration and washed with distilled water (34 % yield based on Zn). Chemical analysis — found: C, 46.9 %; H, 3.6 %; N, 22.4 %; calculated for $\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_5\text{Zn}$: C, 46.6 %; H, 3.5 %; N, 21.7 %. IR data are available in the CIF.

Discussion

In the title crystal structure there are one Zn(II) ion, one benzene-1,2-dicarboxylate ligand (DBC), two 2,2'-biimidazole ligands and one free water molecule in the asymmetric unit. The coordination number of zinc(II) atom is five, and it is coordinated by one oxygen atoms from a carboxyl of DBC with $d(\text{Zn1}—\text{O1}) = 1.973(3) \text{ \AA}$. This distance is shorter than the normal average $\text{Zn}—\text{O}$ distance [1], the other oxygen atoms are deprotonated to maintain the charge balance. The zinc(II) atom is further coordinated by

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.288 \times 0.321 \times 0.403 \text{ mm}$
Wavelength:	$\text{Mo K}\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	12.22 cm^{-1}
Diffractometer, scan mode:	Bruker Apex II CCD, ω
$2\theta_{\text{max}}$:	52.12°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	17615, 4166
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3040
$N(\text{param})_{\text{refined}}$:	307
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(8A)	4e	0.7141	0.4548	−0.0044	0.066
H(6A)	4e	0.5287	0.4441	−0.1260	0.068
H(1A)	4e	0.3571	−0.1997	0.1675	0.064
H(4A)	4e	0.1688	−0.2018	0.0468	0.071
H(8B)	4e	0.0943	0.2460	0.2047	0.081
H(10A)	4e	−0.1058	0.4870	0.3021	0.086
H(11A)	4e	0.5890	0.0656	0.2136	0.085
H(12A)	4e	0.5373	−0.1279	0.2558	0.085
H(13A)	4e	−0.0626	0.2960	0.2819	0.091
H(14A)	4e	0.6927	0.2533	0.1640	0.084

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(15A)	4e	0.8303	0.4043	0.1151	0.083
H(16A)	4e	0.1315	0.0538	−0.0909	0.119
H(17A)	4e	0.3241	0.3901	−0.2013	0.098
H(18A)	4e	0.0063	0.6243	0.2429	0.104

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(19A)	4e	0.0499	−0.1389	−0.0694	0.107
H(20A)	4e	0.2108	0.2522	−0.1296	0.102
HW(1A)	4e	0.9161	0.5803	−0.0313	0.383
HW(1B)	4e	0.9625	0.5989	0.0399	0.383

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zn(1)	4e	0.37547(4)	0.18045(3)	0.05438(2)	0.0561(3)	0.0254(2)	0.0580(3)	−0.0039(2)	0.0225(2)	0.0019(2)
N(2)	4e	0.4379(3)	0.0424(2)	0.1284(2)	0.061(2)	0.031(2)	0.067(2)	−0.009(1)	0.013(2)	0.001(1)
N(8)	4e	0.6876(3)	0.4035(3)	0.0248(2)	0.058(2)	0.045(2)	0.067(2)	−0.011(2)	0.022(2)	0.006(2)
N(7)	4e	0.5650(3)	0.2687(3)	0.0685(2)	0.055(2)	0.045(2)	0.070(2)	0.001(2)	0.020(2)	0.015(2)
N(5)	4e	0.3706(4)	0.2694(3)	−0.0486(2)	0.069(2)	0.053(2)	0.066(2)	−0.020(2)	0.020(2)	−0.002(2)
N(6)	4e	0.4703(3)	0.3957(3)	−0.1135(2)	0.057(2)	0.050(2)	0.066(2)	−0.006(2)	0.023(2)	0.008(2)
N(1)	4e	0.3939(3)	−0.1330(3)	0.1658(2)	0.064(2)	0.031(2)	0.065(2)	−0.004(2)	0.010(2)	0.007(2)
N(4)	4e	0.1798(4)	−0.1365(3)	0.0260(2)	0.082(2)	0.032(2)	0.062(2)	−0.010(2)	0.005(2)	−0.001(2)
N(3)	4e	0.2545(4)	0.0383(3)	0.0072(2)	0.097(3)	0.032(2)	0.062(2)	−0.007(2)	0.005(2)	0.006(2)
O(1)	4e	0.2519(3)	0.2603(2)	0.1147(2)	0.088(2)	0.029(1)	0.108(2)	−0.002(1)	0.055(2)	−0.002(1)
O(2)	4e	0.3188(3)	0.4395(2)	0.0991(2)	0.061(2)	0.038(1)	0.070(2)	−0.005(1)	0.029(1)	0.001(1)
O(4)	4e	0.2784(3)	0.6668(2)	0.1897(2)	0.066(2)	0.037(2)	0.089(2)	−0.009(1)	0.017(2)	0.011(1)
O(3)	4e	0.1261(4)	0.6587(2)	0.0925(2)	0.095(2)	0.048(2)	0.067(2)	−0.015(2)	0.018(2)	0.008(1)
C(1)	4e	0.2469(4)	0.3670(3)	0.1251(2)	0.050(2)	0.030(2)	0.053(2)	−0.001(2)	0.013(2)	0.005(2)
C(2)	4e	0.3625(4)	−0.0513(3)	0.1150(2)	0.056(2)	0.029(2)	0.051(2)	−0.002(2)	0.020(2)	−0.002(2)
C(3)	4e	0.2650(4)	−0.0530(3)	0.0514(2)	0.067(2)	0.029(2)	0.055(2)	−0.004(2)	0.021(2)	−0.002(2)
C(4)	4e	0.1441(3)	0.4048(3)	0.1756(2)	0.047(2)	0.032(2)	0.049(2)	0.001(2)	0.012(2)	0.006(2)
C(5)	4e	0.5768(4)	0.3387(3)	0.0121(2)	0.051(2)	0.034(2)	0.064(2)	−0.002(2)	0.025(2)	0.002(2)
C(6)	4e	0.1819(4)	0.6209(3)	0.1526(2)	0.066(3)	0.029(2)	0.067(2)	0.002(2)	0.032(2)	−0.000(2)
C(7)	4e	0.1177(4)	0.5192(3)	0.1874(2)	0.055(2)	0.034(2)	0.066(2)	−0.004(2)	0.026(2)	−0.001(2)
C(8)	4e	0.0763(5)	0.3235(3)	0.2119(3)	0.087(3)	0.034(2)	0.090(3)	0.000(2)	0.044(3)	0.009(2)
C(9)	4e	0.4760(4)	0.3375(3)	−0.0503(2)	0.054(2)	0.032(2)	0.059(2)	−0.001(2)	0.024(2)	0.003(2)
C(10)	4e	−0.0433(5)	0.4656(4)	0.2704(3)	0.083(3)	0.053(3)	0.089(3)	0.003(2)	0.059(3)	0.005(2)
C(11)	4e	0.5230(5)	0.0170(4)	0.1910(3)	0.078(3)	0.051(3)	0.080(3)	−0.014(2)	−0.002(2)	−0.001(2)
C(12)	4e	0.4951(5)	−0.0905(4)	0.2144(3)	0.082(3)	0.056(3)	0.071(3)	−0.009(2)	−0.008(2)	0.008(2)
C(13)	4e	−0.0174(5)	0.3529(4)	0.2586(3)	0.092(3)	0.046(2)	0.100(3)	−0.005(2)	0.058(3)	0.016(2)
C(14)	4e	0.6738(5)	0.2901(4)	0.1186(3)	0.066(3)	0.071(3)	0.074(3)	0.004(2)	0.012(2)	0.022(2)
C(15)	4e	0.7506(5)	0.3738(4)	0.0919(3)	0.064(3)	0.070(3)	0.076(3)	−0.011(2)	0.010(2)	0.007(2)
C(16)	4e	0.1597(7)	0.0077(5)	−0.0503(3)	0.153(5)	0.054(3)	0.079(3)	−0.013(3)	−0.041(4)	0.014(2)
C(17)	4e	0.3549(5)	0.3636(5)	−0.1542(3)	0.086(4)	0.090(4)	0.068(3)	−0.026(3)	0.005(3)	0.016(3)
C(18)	4e	0.0241(6)	0.5470(4)	0.2349(3)	0.123(4)	0.032(2)	0.122(4)	0.001(2)	0.084(4)	−0.003(2)
C(19)	4e	0.1143(6)	−0.0987(4)	−0.0387(3)	0.126(5)	0.051(3)	0.083(3)	−0.017(3)	−0.027(3)	0.005(3)
C(20)	4e	0.2929(6)	0.2874(5)	−0.1148(3)	0.087(4)	0.095(4)	0.072(3)	−0.041(3)	0.005(3)	0.007(3)
OW(1)	4e	0.938(1)	0.5435(9)	0.0066(8)	0.35(2)	0.26(2)	0.33(1)	−0.02(1)	−0.11(1)	0.01(1)

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