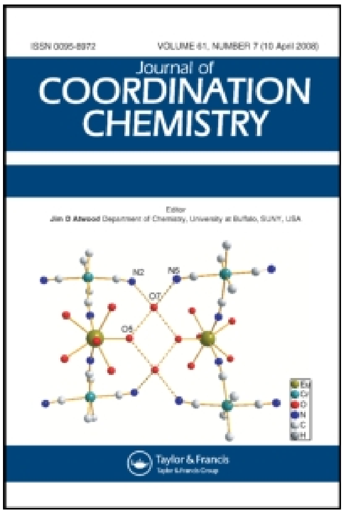

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Synthesis and crystal structure of bis(*m*-hydroxybenzoato(1-))bis(benzimidazole) copper(II) dihydrate

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Synthesis and crystal structure of bis(*m*-hydroxybenzoato(1-))bis(benzimidazole) copper(II) dihydrate

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The crystal structure of the title complex was determined by single-crystal X-ray diffraction methods. The unit cell contains two independent molecules, A and B. B is a mononuclear Cu(II) complex with square-planar coordination geometry formed by two benzimidazole molecules and two hydroxylbenzoate anions. A is a dimer of B, formed by bridging hydroxybenzoate, and copper assumes square-pyramidal geometry. Aromatic π–π stacking is observed between parallel benzimidazole rings of neighboring A molecules. IR spectra of the compound are assigned in line with the crystal structure.

Keywords: Copper(II) complex; *m*-Hydroxybenzoic acid; Benzimidazole; Crystal structure; π–π stacking

1. Introduction

In the past decade, intermolecular interactions have been recognized as the basis of the functional properties of most molecular assembles [1] and a detailed understanding of noncovalent chemistry is therefore fundamental to interpreting and predicting relationships between chemical structure and function. As part of an investigation of π–π stacking between aromatic rings in metal complexes [2], a Cu(II) complex incorporating benzimidazole (BZIM) has been prepared in our laboratory. We present here the X-ray structure of the title complex, which shows π–π stacking between BZIM rings in the title crystal.

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2. Experimental

2.1. *Synthesis*

All reagents were commercially available and of analytical grade. Sodium *m*-hydroxybenzoate (1 mmol), BZIM (2 mmol), NaOH (1 mmol) and $CuCl_2 \cdot 2H_2O$ (1 mmol) were dissolved in a water (16 cm^3)/ethanol (4 cm^3) mixture. The solution was refluxed for 4 h, then cooled to room temperature and filtered. Blue, single crystals of the complex were obtained from the filtrate after 1 week.

2.2. *Physical measurements*

C, H and N contents were determined on a Carlo-Erba 1160 instrument. Anal. Calcd. for $Cu(C_7H_6N_2)_2(C_7H_5O_3)_2 \cdot 2H_2O$(%): C, 55.09; N, 9.18; H, 4.26. Found: C, 54.81; N, 9.51; H, 4.44. The IR spectrum of the title complex was recorded using KBr pellets in the 4000–400 cm^{-1} range using a Nicolet 5DX FTIR spectrophotometer.

2.3. *Crystal structure determination*

X-ray diffraction intensities of a single crystal of the complex were collected on a Rigaku RAXIS-RAPID diffractometer at room temperature. The crystal structure was solved by direct methods [3] followed by Fourier syntheses using Sir92. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on F^2 [4].

One BZIM molecule is disordered in the crystal structure. Three different spatial orientations were found in a difference Fourier map. Occupancy factors were initially refined using the SUMP command and then fixed in final cycles of refinement as 0.40, 0.28 and 0.32, respectively. The disordered non-H atoms were refined isotropically, whereas other non-H atoms were refined anisotropically. H atoms of lattice water molecules were located in a difference Fourier map and included in the structure factors calculation with fixed positional and isotropic displacement parameters of 0.08 $Å^2$. Other H atoms were placed in calculated positions, with C–H = 0.93 Å and N–H = 0.86 Å, and were included in the final cycles of refinement in riding mode with $U_{iso}(H) = 1.2U_{eq}$ of the parent atoms.

Crystal data and refinement conditions are summarized in table 1. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 2. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 245370.

3. Results and discussion

3.1. *Crystal structure*

The unit cell contains a dimeric complex [A] and a mononuclear complex [B]. Molecular structures of A and B are illustrated in figure 1. The centrosymmetric complex A is a dimer of B. A contains one Cu(II) ion, two *m*-hydroxylbenzoate (HBA) anions and two BZIM molecules. BZIM ligands coordinate *trans* to the Cu1 atom and monodentate carboxyl groups complete the basal plane. A hydroxyl oxygen atom

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{28}H_{26}N_4O_7Cu$
Formula weight	610.1
Crystal size (mm)	$0.14 \times 0.12 \times 0.10$
Temperature (K)	295
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 10.0079(8)$
	$b = 12.8837(7)$
	$c = 17.1062(13)$
	$\alpha = 100.158(3)$
	$\beta = 104.725(1)$
	$\gamma = 101.513(1)$
Volume (Å^3)	2029.4(2)
Z	3
Density (calculated) (g cm^{-3})	1.498
Absorption coefficient (mm^{-1})	0.866
$F(000)$	945
θ range for data collection (°)	1.27 to 25.02
Reflections collected	13356
Independent reflections	6798
Parameters	586
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0523$, $wR_2 = 0.1188$
R indices (all data)	$R_1 = 0.0817$, $wR_2 = 0.1295$
Largest diff. peak and hole (e Å^{-3})	0.57 and −0.50

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}
Cu(1)	5657(1)	6781(1)	3470(1)	33(1)
Cu(2)	0	0	0	41(1)
O(21)	5062(3)	7086(2)	2369(2)	38(1)
O(22)	2726(3)	6274(2)	1866(2)	51(1)
O(23)	1211(3)	8096(3)	−503(2)	80(1)
O(31)	6335(3)	6548(2)	4593(2)	47(1)
O(32)	8403(3)	7833(2)	5081(2)	48(1)
O(33)	6485(3)	4590(2)	6874(2)	57(1)
O(41)	10144(3)	9464(3)	985(2)	50(1)
O(42)	8655(3)	10334(3)	1426(2)	50(1)
O(43)	8181(3)	8901(3)	3913(2)	51(1)
O(1W)	1483(3)	8742(3)	5656(2)	66(1)
O(2W)	9866(4)	5135(4)	1163(3)	101(1)
O(3W)	7010(5)	11419(5)	2242(3)	137(2)
N(11)	4677(3)	7817(3)	3929(2)	39(1)
N(13)	3283(4)	8413(3)	4627(2)	56(1)
N(51)	8105(4)	8942(3)	−585(2)	47(1)
N(53)	5863(4)	8364(4)	−1405(2)	77(1)
C(12)	3937(5)	7631(4)	4452(3)	49(1)
C(14)	3249(5)	10153(4)	4159(4)	68(2)
C(15)	3792(6)	10741(4)	3669(4)	81(2)
C(16)	4677(6)	10383(4)	3231(4)	68(2)
C(17)	5045(5)	9404(3)	3261(3)	48(1)
C(18)	4497(4)	8804(3)	3759(2)	39(1)

(*continued*)

Table 2. Continued.

	x/a	y/b	z/c	U_{eq}
C(19)	3622(4)	9181(4)	4205(3)	50(1)
C(21)	3843(4)	6893(3)	1840(2)	35(1)
C(22)	3798(4)	7487(3)	1154(2)	35(1)
C(23)	2508(4)	7477(4)	605(2)	45(1)
C(24)	2501(4)	8071(4)	1(3)	48(1)
C(25)	3767(5)	8643(4)	−66(3)	51(1)
C(26)	5042(5)	8648(4)	478(3)	51(1)
C(27)	5062(4)	8080(3)	1089(2)	43(1)
C(31)	7461(4)	7102(3)	5165(2)	37(1)
C(32)	7641(4)	6854(3)	6002(2)	34(1)
C(33)	6932(4)	5847(3)	6071(2)	38(1)
C(34)	7121(4)	5620(3)	6851(2)	38(1)
C(35)	7921(4)	6406(3)	7558(2)	43(1)
C(36)	8607(5)	7411(3)	7490(3)	47(1)
C(37)	8502(4)	7623(3)	6714(2)	42(1)
C(41)	9423(4)	9694(3)	1478(2)	40(1)
C(42)	9576(4)	9097(3)	2172(2)	37(1)
C(43)	8833(4)	9256(3)	2743(2)	37(1)
C(44)	8953(4)	8715(3)	3374(2)	36(1)
C(45)	9829(4)	8005(3)	3444(2)	37(1)
C(46)	10572(4)	7845(3)	2874(2)	42(1)
C(47)	10450(4)	8385(3)	2242(2)	43(1)
C(52)	7073(5)	9181(5)	−1110(3)	59(1)
C(54)	5261(8)	6515(6)	−1143(4)	98(2)
C(55)	5868(9)	5851(6)	−714(5)	110(3)
C(56)	7289(8)	6175(5)	−175(4)	90(2)
C(57)	8141(6)	7212(4)	−82(3)	65(1)
C(58)	7530(5)	7885(4)	−532(3)	53(1)
C(59)	6132(5)	7530(5)	−1049(3)	66(2)
N(1)	6700(20)	5860(20)	3058(17)	47(8)
N(3)	8124(15)	5498(11)	2235(11)	37(4)
C(2)	7380(20)	5970(20)	2390(20)	34(7)
C(4)	8986(15)	4031(11)	2972(9)	53(4)
C(5)	8839(17)	3542(13)	3616(10)	68(4)
C(6)	7867(16)	3766(12)	4074(10)	65(4)
C(7)	7075(15)	4530(11)	3931(9)	41(3)
C(8)	7395(17)	5169(14)	3323(12)	32(4)
C(9)	8248(19)	4830(16)	2849(13)	41(5)
N(1B)	6750(20)	5761(18)	2906(11)	20(5)
N(3B)	7973(18)	5207(15)	2065(11)	41(5)
C(2B)	7240(30)	6010(50)	2462(19)	44(13)
C(4B)	8047(19)	3428(14)	2398(11)	62(5)
C(5B)	7560(20)	2804(16)	2890(12)	68(5)
C(6B)	6784(19)	3083(14)	3386(11)	59(4)
C(7B)	6490(17)	4104(13)	3483(11)	44(4)
C(8B)	6997(14)	4778(12)	3007(9)	26(3)
C(9B)	7759(17)	4432(14)	2466(11)	42(4)
N(1C)	6880(20)	5960(17)	3053(18)	25(6)
N(3C)	8302(12)	5343(13)	2418(9)	33(4)
C(2C)	7290(30)	6120(20)	2360(20)	36(9)
C(4C)	9288(16)	4195(12)	3297(10)	40(4)
C(5C)	9118(17)	3818(13)	3966(11)	50(4)
C(6C)	8255(17)	4080(13)	4371(10)	47(4)
C(7C)	7443(17)	4791(13)	4151(10)	41(4)
C(8C)	7420(20)	5060(20)	3466(14)	46(7)
C(9C)	8410(20)	4844(17)	3034(12)	40(7)

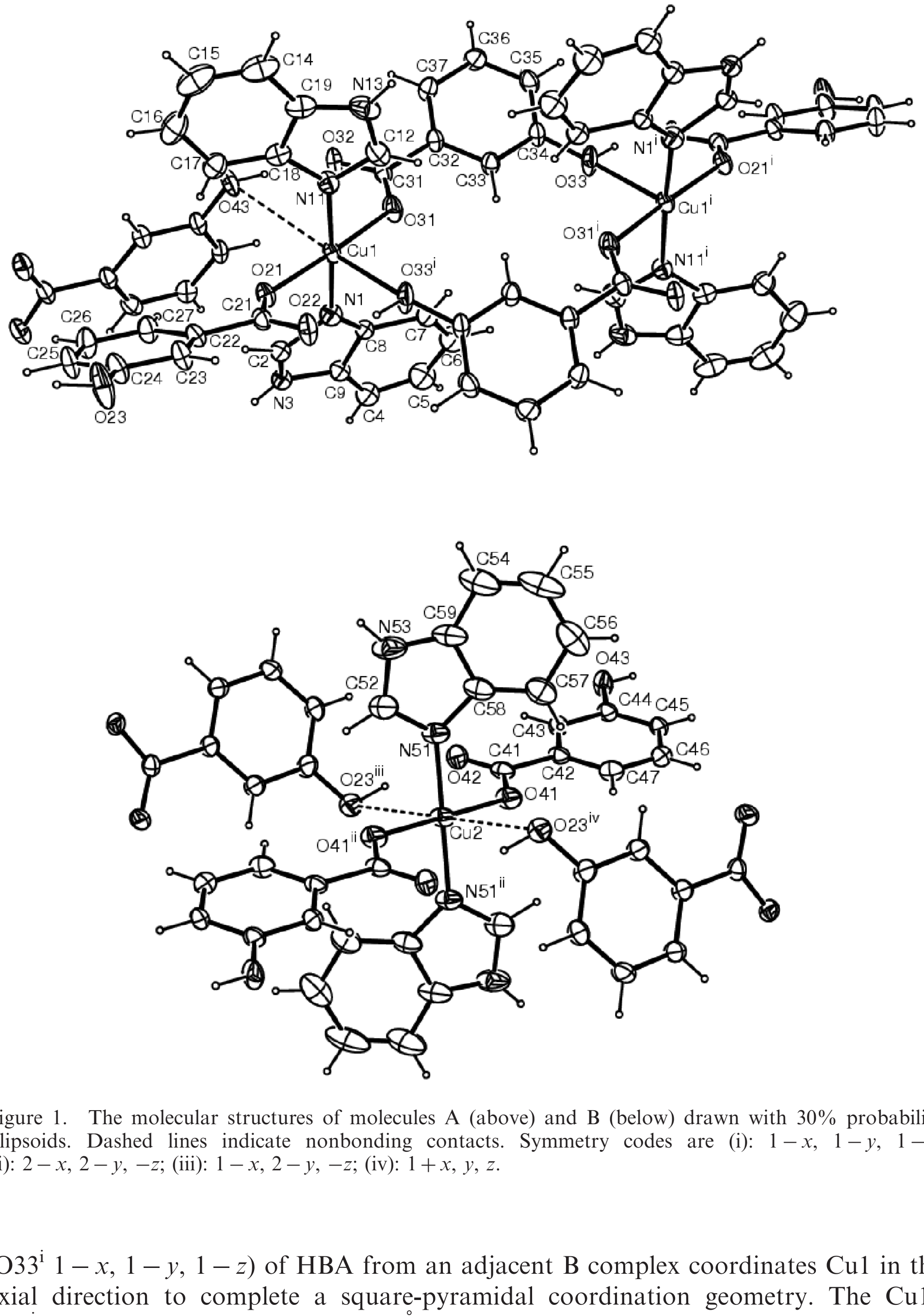

Figure 1. The molecular structures of molecules A (above) and B (below) drawn with 30% probability ellipsoids. Dashed lines indicate nonbonding contacts. Symmetry codes are (i): $1-x$, $1-y$, $1-z$; (ii): $2-x$, $2-y$, $-z$; (iii): $1-x$, $2-y$, $-z$; (iv): $1+x$, y, z.

(O33^{i} $1-x$, $1-y$, $1-z$) of HBA from an adjacent B complex coordinates Cu1 in the axial direction to complete a square-pyramidal coordination geometry. The Cu1–O33^{i} bond distance (table 3) is 0.391 Å longer than the average Cu1–O bond distance [1.963(2) Å] in the basal plane, showing typical Jahn–Teller distortion for the Cu(II) complex. The hydroxyl O43 atom of another adjacent B complex is located *trans* to O33^{i} bond, but the Cu1$\cdots$O43 separation of 3.155(3) Å suggests no bonding interaction. In the HBA bridge, the C34–O33–Cu1^{i} bond angle of 147.0(3)° is much larger than any other C–O–Cu angle (table 3).

Table 3. Selected bond lengths (Å) and angles (°) for the complex.

Cu(1)–N(1)	1.89(3)	Cu(1)–N(1B)	2.12(2)
Cu(1)–N(1C)	1.95(3)	Cu(1)–N(11)	1.976(3)
Cu(1)–O(21)	1.960(2)	Cu(1)–O(31)	1.965(2)
Cu(1)–O(33)$^{\mathrm{i}}$	2.354(3)	Cu(2)–O(41)	1.914(3)
Cu(2)–N(51)	1.995(3)		
N(1)–Cu(1)–N(11)	176.5(8)	N(1)–Cu(1)–O(21)	89.0(7)
N(1)–Cu(1)–O(31)	91.4(7)	N(1)–Cu(1)–O(33)$^{\mathrm{i}}$	95.6(7)
N(11)–Cu(1)–O(21)	91.5(1)	N(11)–Cu(1)–O(31)	88.0(1)
N(11)–Cu(1)–O(33)$^{\mathrm{i}}$	87.9(1)	O(21)–Cu(1)–O(31)	177.0(1)
O(21)–Cu(1)–O(33)$^{\mathrm{i}}$	90.1(1)	O(31)–Cu(1)–O(33)$^{\mathrm{i}}$	92.8(1)
O(41)–Cu(2)–N(51)	91.6(1)	C(41)–O(41)–Cu(2)	122.1(3)
C(21)–O(21)–Cu(1)	131.9(2)	C(31)–O(31)–Cu(1)	126.7(2)
C(34)–O(33)–Cu(1)	147.0(3)$^{\mathrm{i}}$		

Symmetry code for (i): $1-x$, $1-y$, $1-z$.

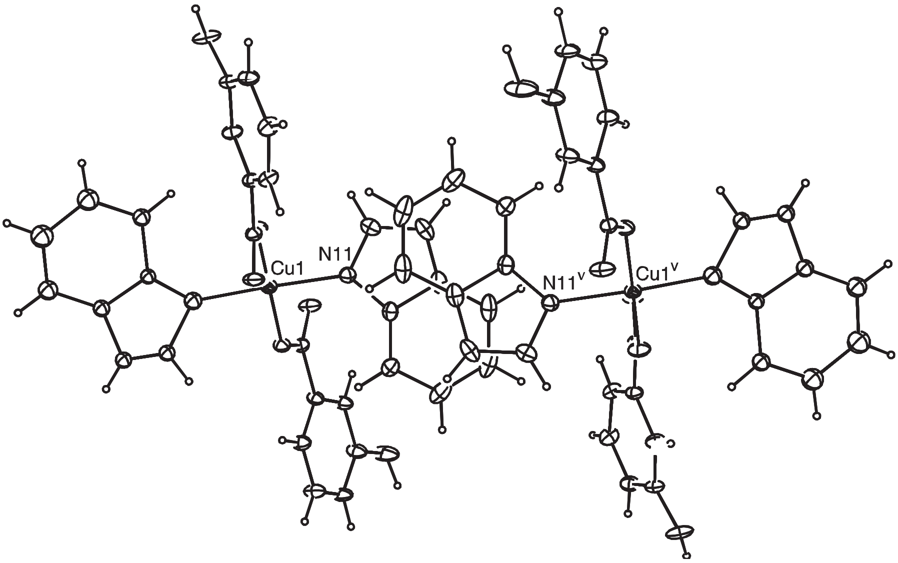

Figure 2. Aromatic stacking between parallel benzimidazole rings. Symmetry code for (v): $1-x$, $2-y$, $1-z$.

A partially overlapped arrangement between neighboring, parallel N11-BZIM (BZIM containing the N11 atom) rings is observed in the crystal structure (figure 2) and the interplanar distance of 3.33(2) Å suggests the existence of aromatic π–π stacking. This is in accordance with the situation found in other reported BZIM complexes [5,6]. The N1-BZIM ligand is disordered in the crystal, displaying three different spatial orientations as shown in figure 3. No aromatic stacking occurs between N1-BZIM rings.

Molecule B is also centrosymmetric. The Cu2 atom lies on an inversion center at the origin and is surrounded by two HBA and two BZIM ligands to give *trans* square-planar coordination geometry. Two hydroxyl oxygen atoms are located on both sides of the coordination plane, as shown in figure 1 (lower diagram), but the Cu2$\cdots$O23$^{\mathrm{iii}}$/O23$^{\mathrm{iv}}$ separation of 3.033(4) Å suggests no bonding.

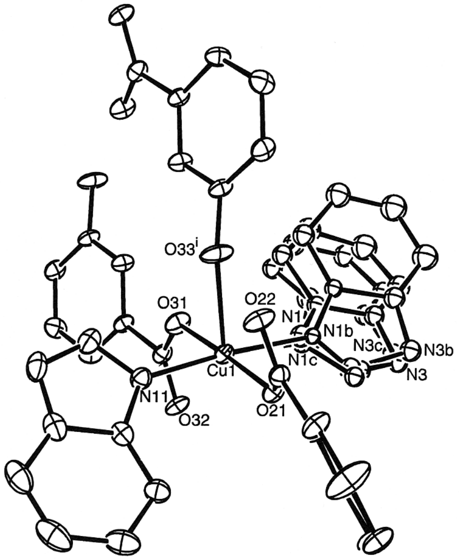

Figure 3. Different spatial orientations of the disordered benzimidazole ligand coordinated to the Cu1 ion.

Table 4. Hydrogen bonding parameters (Å, °) for the complex.

D–H···A	D–H	H···A	D···A	D–H–A
O(1W)–H(1E)···O(32)^a	0.917	1.992	2.907(5)	175.7
O(1W)–H(1F)···O(43)^b	0.846	2.081	2.925(5)	175.7
O(2W)–H(2F)···O(22)^c	0.933	1.852	2.783(5)	174.9
O(3W)–H(3E)···O(42)	0.845	2.029	2.830(7)	158.2
N(3)–H(3)···O(2W)	0.860	2.063	2.88(2)	157.0
N(13)–H(13)···O(1W)	0.861	2.009	2.860(5)	169.3
N(53)–H(53)···O(3W)^d	0.861	2.132	2.961(7)	161.5
O(23)–H(24)···O(42)^d	0.921	1.863	2.780(6)	173.1
O(33)–H(34)···O(22)^e	0.891	1.748	2.616(4)	164.1
O(43)–H(44)···O(32)	0.861	1.748	2.608(4)	176.6

Symmetry codes used are (a): $-1+x, y, z$; (b): $1-x, 2-y, 1-z$; (c): $1+x, y, z$; (d): $1-x, 2-y, -z$; (e): $1-x, 1-y, 1-z$.

An extensive hydrogen-bonding network exists in the lattice (table 4). Uncoordinated carboxyl oxygen atoms link with hydroxyl groups of adjacent complexes through O–H···O interactions. Lattice water molecules link with HBA and BZIM through O–H···O and N–H···O interactions, respectively.

3.2. *IR spectra*

The IR spectrum of the title complex was assigned based on the crystal structure. Stretching vibrations of the carboxyl group were observed at 1561 [ν_{as}(coo)] and 1392 cm^{-1} [ν_s(coo)]. The $\Delta\nu$ value of 169 cm^{-1} agrees with the monodentate coordination mode of the carboxyl group [7]. The water stretch at 3412 cm^{-1} compared to

3650–3600 cm^{-1} found for the "free" hydroxyl group is due to the participation of the hydroxyl groups in hydrogen bonding.

Acknowledgments

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