Crystal structure of [bis(benzimidazol-2-yl-methyl)amine-κ^3N,N',N''] phthalato-κ^2O,O' copper(II) — methanol — water (1:1:2), $C_{25}H_{27}CuN_5O_7$

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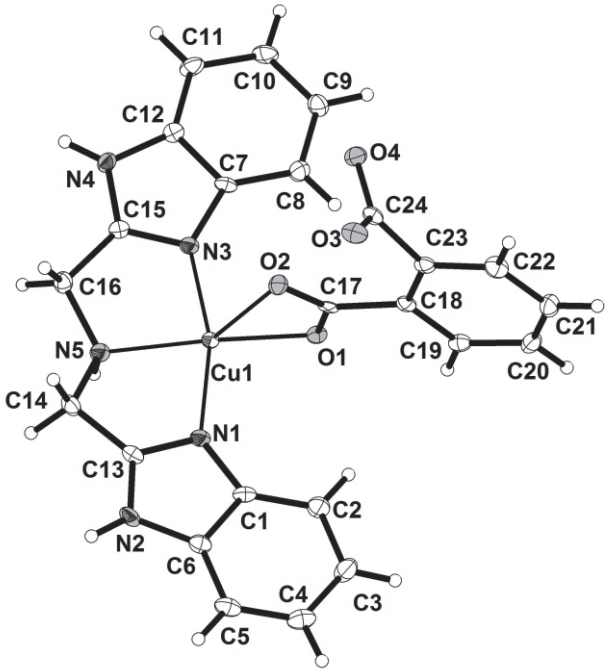

Abstract

$C_{25}H_{27}CuN_5O_7$, triclinic, $P\bar{1}$ (no. 2), a = 9.3812(6) Å, b = 11.3399(6) Å, c = 13.0957(8) Å, α = 81.654(8)°, β = 71.623(6)°, γ = 69.745(6)°, V = 1239.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0361, $wR_{ref}(F^2)$ = 0.0830, T = 99 K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.03×0.10×0.25 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	9.38 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, Gemini, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8922, 4856
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4268
$N(param)_{refined}$:	361
Programs:	SHELX [7]

Source of material

A methanol solution (25 mL) containing of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.075 g, 0.2 mmol) and bis(benzimidazol-2-yl-methyl)amine (*bbma*, 0.058g, 0.2 mmol) was stirred half an hour, then phthalic acid (0.033g, 0.2 mmol) and triethylamine (0.041g, 0.4 mmol) mixed in 5 mL methanol were added dropwise. After refluxing for 3 hours, the solution was filtered and allowed to stand at room temperature for slow evaporation. Blue crystals suitable for X-ray structure determination were formed.

Experimental details

Atom N5 and N6 are disordered with an occupancy ratio of 0.842(4) and 0.158(4) (For clarity the split positions with the lower occupancy are not shown in the figure).

Discussion

Nowadays the design and synthesis of coordination complexes based on the N-donor and O-donor mixed ligands have become the focus of current investigation. Phthalic acid (1,2-*BDC*) is a starting material that is widely used for the synthesis of inorganic-organic hybrid materials because of its versatile coordination modes and its potential ability to form H-bond. The ligand bis(benzimidazol-2-yl-methyl)amine (*bbma*), which have proven to be appropriate model compounds of histidine. A number of mono-nuclear copper complexes with the above ligands have been reported [1–6]. To the best of our knowledge, copper(II) complexes of *bbma* by using dianions of the phthalic acid as coligands have never been reported before. The title compound contains the monomeric [Cu(*bbma*)(1,2-*BDC*)] complex, methanol solvent and two water molecules. The Cu1 ion is five-coordinated by three N atoms (N1, N3, N5) of *bbma* and two oxygen atoms (O1, O2) of one carboxylate group, showing a distorted $\{CuN_3O_2\}$ square pyramidal geometry with τ value to be 0.19. The basal plane is formed by two benzimidazole nitrogen atoms (N1, N3), one secondary amine nitrogen atom (N5) of *bbma* and one oxygen atom (O1) from carboxylate group with bond distances to be 1.948(2) Å for Cu1–N1, 1.9451(19) Å for Cu1–N3, 2.053(2) Å for Cu1–N5 and 1.9634(15) Å for Cu1–O1. Another oxygen atom (O2) of the 1,2-*BDC* anion occupies the apical position. The distance between Cu1 and O2 is 2.5598(16) Å, which is longer than the distances of the other atoms in the coordination sphere. The distortion of the coordination environment of [Cu(*bbma*)(1,2-*BDC*)] can be illustrated by the deviation of the angles between O2, Cu1 and other atoms in basal plane. The angles around the Cu(II) ion are also measured. The angles of O2–Cu1–N1, O2–Cu1–N3, O2–Cu1–N5 and O2–Cu1–O1 are 97.17(7)°, 92.98(7)°, 128.49(8)° and 56.88(5)°, respectively. These angles deviate from regular square pyramid. The minimum angle of O2–Cu1–O1 can be explained by chelated coordination style of carboxyl. N4 atom of *bbma* links coordinated O2 atom and uncoordinated O4 atom to form a 2D chain structrue. The 2D chain structure is cross-linked through secondary amine nitrogen atom (N5), oxygen atom (O7) of one water molecule, oxygen atom (O5) of one methanol molecule and uncoordinated oxygen atom (O4).

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(4)	2*i*		0.2979	0.6782	–0.0593	0.017
H(5)	2*i*	0.842(4)	0.4753	0.8543	0.1223	0.016
H(2)	2*i*		0.9403	0.8520	0.1274	0.018
H(2A)	2*i*		0.6989	0.5882	0.4377	0.020
H(11)	2*i*		0.0971	0.5273	0.0093	0.021
H(8)	2*i*		0.3253	0.4349	0.2962	0.020
H(3)	2*i*		0.8635	0.5930	0.5354	0.025
H(20)	2*i*		0.6570	0.2241	0.6092	0.019
H(19)	2*i*		0.5886	0.3937	0.4928	0.017
H(5A)	2*i*		1.0838	0.7935	0.2977	0.021
H(16A)	2*i*	0.842(4)	0.5958	0.7256	–0.0584	0.018
H(16B)	2*i*	0.842(4)	0.4395	0.8410	–0.0257	0.018
H(16C)	2*i*	0.158(4)	0.5492	0.7554	–0.0766	0.018
H(16D)	2*i*	0.158(4)	0.4369	0.8492	0.0151	0.018
H(9)	2*i*		0.1427	0.3424	0.2908	0.021
H(14A)	2*i*	0.842(4)	0.6815	0.9081	0.0428	0.019
H(14B)	2*i*	0.842(4)	0.7780	0.7737	–0.0040	0.019
H(14C)	2*i*	0.158(4)	0.6244	0.9016	0.0679	0.019
H(14D)	2*i*	0.158(4)	0.7870	0.8200	–0.0068	0.019
H(10)	2*i*		0.0247	0.3915	0.1525	0.021
H(21)	2*i*		0.8353	0.0338	0.5417	0.021
H(4A)	2*i*		1.0534	0.6923	0.4669	0.026
H(22)	2*i*		0.9368	0.0116	0.3576	0.021
H(5B)	2*i*		0.5829	0.1218	0.2329	0.064
H(25A)	2*i*		0.5692	–0.0013	0.3796	0.078
H(25B)	2*i*		0.3856	0.0668	0.4086	0.078
H(25C)	2*i*		0.4998	0.1422	0.4038	0.078
H(6A)	2*i*		1.091(5)	0.986(1)	0.075(3)	0.078
H(6B)	2*i*		1.144(5)	0.905(3)	–0.0071(9)	0.078
H(7A)	2*i*		0.368(4)	1.049(3)	0.210(3)	0.078
H(7B)	2*i*		0.231(2)	1.051(3)	0.191(3)	0.078
H(6)	2*i*	0.158(4)	0.7126	0.6655	0.0143	0.016

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*		0.56244(3)	0.64060(3)	0.20254(2)	0.0143(2)	0.0139(2)	0.0119(1)	–0.0083(1)	–0.0054(1)	0.0015(1)
O(1)	2*i*		0.5582(2)	0.5135(1)	0.3215(1)	0.0121(8)	0.0130(9)	0.0135(7)	–0.0035(7)	–0.0046(6)	–0.0018(6)
O(4)	2*i*		0.7792(2)	0.1498(2)	0.1525(1)	0.0171(8)	0.0173(9)	0.0148(8)	–0.0062(7)	–0.0052(6)	–0.0023(6)
O(2)	2*i*		0.7457(2)	0.4124(2)	0.1824(1)	0.0150(8)	0.0169(9)	0.0106(8)	–0.0070(7)	–0.0019(6)	–0.0004(6)
O(3)	2*i*		1.0241(2)	0.1374(2)	0.1483(1)	0.0145(8)	0.0188(9)	0.0190(8)	–0.0065(7)	0.0003(7)	–0.0066(7)
N(4)	2*i*		0.3158(2)	0.6479(2)	0.0012(1)	0.014(1)	0.018(1)	0.0121(9)	–0.0065(8)	–0.0061(7)	0.0018(7)
N(5)	2*i*	0.842(4)	0.5535(3)	0.7863(2)	0.0890(2)	0.014(1)	0.015(1)	0.013(1)	–0.006(1)	–0.004(1)	–0.0006(9)
N(3)	2*i*		0.4172(2)	0.6116(2)	0.1383(1)	0.013(1)	0.013(1)	0.0128(9)	–0.0060(8)	–0.0038(7)	–0.0007(7)
N(1)	2*i*		0.7069(2)	0.7094(2)	0.2340(1)	0.014(1)	0.016(1)	0.0141(9)	–0.0081(8)	–0.0044(7)	–0.0008(7)
C(15)	2*i*		0.4104(3)	0.6747(2)	0.0459(2)	0.010(1)	0.013(1)	0.013(1)	–0.0025(9)	–0.0035(8)	–0.0025(8)
N(2)	2*i*		0.8857(2)	0.8081(2)	0.1703(2)	0.015(1)	0.014(1)	0.020(1)	–0.0097(8)	–0.0044(8)	0.0018(8)
C(2)	2*i*		0.7737(3)	0.6298(2)	0.4102(2)	0.015(1)	0.021(1)	0.018(1)	–0.009(1)	–0.0050(9)	0.0003(9)
C(24)	2*i*		0.8794(3)	0.1591(2)	0.1948(2)	0.017(1)	0.007(1)	0.017(1)	–0.0034(9)	–0.0049(9)	–0.0019(8)
C(11)	2*i*		0.1415(3)	0.5093(2)	0.0663(2)	0.014(1)	0.026(1)	0.016(1)	–0.009(1)	–0.0071(9)	–0.0019(9)
C(6)	2*i*		0.9036(3)	0.7537(2)	0.2691(2)	0.015(1)	0.012(1)	0.018(1)	–0.004(1)	–0.0044(9)	–0.0032(9)
C(8)	2*i*		0.2795(3)	0.4539(2)	0.2399(2)	0.017(1)	0.019(1)	0.015(1)	–0.008(1)	–0.0059(9)	0.0009(9)
C(3)	2*i*		0.8729(3)	0.6325(2)	0.4673(2)	0.021(1)	0.029(2)	0.014(1)	–0.010(1)	–0.007(1)	0.000(1)
C(20)	2*i*		0.6993(3)	0.2152(2)	0.5352(2)	0.016(1)	0.023(1)	0.012(1)	–0.009(1)	–0.0052(9)	0.0011(9)
C(17)	2*i*		0.6709(3)	0.4157(2)	0.2797(2)	0.010(1)	0.015(1)	0.016(1)	–0.0098(9)	–0.0049(9)	–0.0015(9)
C(7)	2*i*		0.3180(3)	0.5383(2)	0.1561(2)	0.009(1)	0.011(1)	0.018(1)	–0.0036(9)	–0.0042(8)	–0.0035(8)
C(19)	2*i*		0.6565(3)	0.3164(2)	0.4653(2)	0.012(1)	0.017(1)	0.015(1)	–0.006(1)	–0.0035(9)	–0.0036(9)
C(12)	2*i*		0.2521(3)	0.5626(2)	0.0702(2)	0.011(1)	0.015(1)	0.013(1)	–0.0037(9)	–0.0030(8)	–0.0019(9)
C(18)	2*i*		0.7144(3)	0.3034(2)	0.3540(2)	0.010(1)	0.014(1)	0.014(1)	–0.0071(9)	–0.0038(8)	–0.0005(8)
C(5)	2*i*		1.0067(3)	0.7542(2)	0.3258(2)	0.014(1)	0.016(1)	0.026(1)	–0.005(1)	–0.007(1)	–0.0043(9)
C(16)	2*i*		0.5041(3)	0.7630(2)	0.0006(2)	0.014(1)	0.016(1)	0.016(1)	–0.006(1)	–0.0058(9)	0.0029(9)
C(9)	2*i*		0.1703(3)	0.3994(2)	0.2360(2)	0.019(1)	0.019(1)	0.015(1)	–0.010(1)	–0.0019(9)	0.0006(9)
C(14)	2*i*		0.7028(3)	0.8185(2)	0.0589(2)	0.017(1)	0.016(1)	0.019(1)	–0.010(1)	–0.0060(9)	0.0036(9)
C(1)	2*i*		0.7897(3)	0.6917(2)	0.3096(2)	0.012(1)	0.015(1)	0.017(1)	–0.0047(9)	–0.0056(9)	–0.0043(9)
C(10)	2*i*		0.1001(3)	0.4279(2)	0.1514(2)	0.013(1)	0.024(1)	0.020(1)	–0.011(1)	–0.0032(9)	–0.004(1)
C(21)	2*i*		0.8048(3)	0.1013(2)	0.4949(2)	0.019(1)	0.019(1)	0.018(1)	–0.008(1)	–0.010(1)	0.0048(9)
C(13)	2*i*		0.7678(3)	0.7798(2)	0.1538(2)	0.014(1)	0.011(1)	0.017(1)	–0.0049(9)	–0.0029(9)	–0.0022(9)
C(23)	2*i*		0.8193(3)	0.1874(2)	0.3133(2)	0.011(1)	0.016(1)	0.015(1)	–0.0078(9)	–0.0033(9)	–0.0016(9)
C(4)	2*i*		0.9882(3)	0.6932(2)	0.4259(2)	0.019(1)	0.025(2)	0.025(1)	–0.007(1)	–0.010(1)	–0.006(1)
C(22)	2*i*		0.8649(3)	0.0880(2)	0.3845(2)	0.016(1)	0.014(1)	0.021(1)	–0.003(1)	–0.0053(9)	–0.0023(9)
O(6)	2*i*		1.1172(2)	0.9096(2)	0.0608(1)	0.0187(9)	0.0175(9)	0.0156(8)	–0.0075(7)	–0.0024(7)	–0.0024(7)
O(5)	2*i*		0.4998(3)	0.1065(2)	0.2626(2)	0.040(1)	0.079(2)	0.028(1)	–0.043(1)	–0.0166(9)	0.014(1)
O(7)	2*i*		0.3248(3)	1.0063(2)	0.1895(2)	0.029(1)	0.037(1)	0.060(1)	0.003(1)	–0.025(1)	–0.024(1)
C(25)	2*i*		0.4876(4)	0.0762(4)	0.3723(2)	0.056(2)	0.094(3)	0.030(2)	–0.059(2)	–0.015(2)	0.014(2)
N(6)	2*i*	0.158(4)	0.632(2)	0.727(1)	0.055(1)	0.014(1)	0.015(1)	0.013(1)	–0.006(1)	–0.004(1)	–0.0006(9)

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