Crystal structure of (2,6-pyridinedicarboxylato-κ^3*O,N,O′*)[2,6-bis(benzimidazol-2-yl)pyridine-κ^3*N,N′,N″*]copper(II) — methanol (1:1), $C_{27}H_{20}CuN_6O_5$

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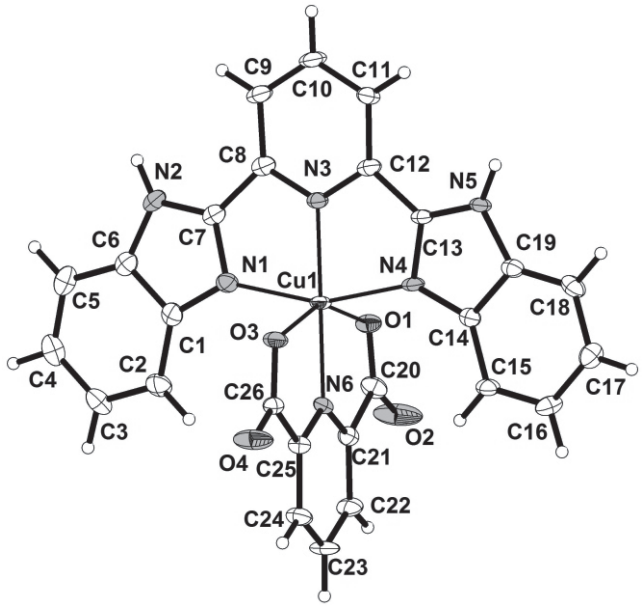

Abstract

$C_{27}H_{20}CuN_6O_5$, triclinic, $P\bar{1}$ (no. 2), a = 10.4231(9) Å, b = 11.8744(11) Å, c = 13.5630(8) Å, α = 96.829(6)°, β = 110.187(7)°, γ = 106.805(8)°, V = 1463.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.0507, $wR_{ref}(F^2)$ = 0.1312, T = 105 K.

Table 1. Data collection and handling.

Crystal:	green needles, size 0.04×0.05×0.70 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	7.91 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, Gemini, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11266, 5739
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4544
$N(param)_{refined}$:	354
Programs:	SHELX [6]

Source of material

2,6-Bis(benzimidazol-2-yl)pyridine (*bbp*) was synthesized by condensation of 2,6-pyridinedicarboxylic acid with *o*-phenylenediamine according to the published procedures [1]. The title complex was synthesized via the solvothermal method. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.048 g, 0.2 mmol), *bbp* (0.062 g, 0.2 mmol), 2,6-pyridinedicarboxylic acid (0.033 g, 0.2 mmol) and NaOH (0.016 g, 0.4 mmol) in methanol (20 ml) was stirred for 30 min. Afterwards it was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 160 °C for 3 days. After being cooled to room temperature at a rate of 2 °C per hour, green needle-shaped crystals were obtained in 65 % yield.

Discussion

2,6-Pyridinedicarboxylate is one of the frequently used aromatic dicarboxylates as the key component of bacterial spores [2]. Metal complexes with 2,6-pyridinedicarboxylate ligands own interesting structural features with various coordination modes and strong H-bonds for self-assembly [3, 4] and the ligand has been used as a coligand in constructing magnetic coupling systems [5]. Till now, no copper complex containing tridentate benzimidazole ligand 2,6-bis(benzimidazol-2-yl)pyridine (*bbp*) and 2,6-pyridinedicarboxylate has been reported. As part of our study on understanding the interactions between metal complexes based on benzimidazole ligands and aromatic dicarboxylates, the copper(II) complex $[Cu(C_{19}H_{13}N_5)(C_7H_3O_4N)]$ has been prepared. Single crystal X-ray diffraction analysis reveals that the title structure consists of one neutral [Cu(*bbp*)(2,6-dipic)] (2,6-dipic = the anion of 2,6-pyridinedicarboxylic acid) unit and one methanol molecule. The Cu(II) center is six-coordinated in a distorted octahedral environment. In the structure, *bbp* and 2,6-dipic both act as tridentate chelating ligands by coordination of N1, N3, N4 and O1, N6, O3 to the copper(II) ion, respectively. *bbp* is nearly coplanar. All the Cu–N bond lengths are nearly identical, ranging from 1.981(2) Å to 2.043(3) Å. The distances between center copper and coordinated oxygen atoms from different carboxylate groups of 2,6-dipic [Cu1–O1, 2.322(2) Å; Cu1–O2, 2.319(3) Å] are also similar. The equatorial plane is defined by four nitrogen atoms of two ligands with the total of bond angles as 360.01° and apical sites are occupied by O1, O3 of 2,6-dipic with the axial bond angle of O1–Cu1–O3 as 151.84(7)°. The title complex is connected by intermolecular H-bonds through the benzimidazole NH group of *bbp* and the adjacent coordinated carboxylate oxygen atoms of 2,6-pyridinedicarboxylate [N2–H2···O1, d(D···A) = 2.738(3) Å; N5–H5···O3, d(D···A) = 2.665(4) Å] to form a 1D chain structure. H-bonds also occur between the [O5–H5B···O4, d(D···A) = 2.747(4) Å] methanol molecule and one of the uncoordinated carboxylate oxygen atoms of 2,6-dipic. The structure is stabilized by two kinds of similar $\pi\cdots\pi$ stacking interactions between pyridine and benzene moieties of adjacent molecules with the shortest distance of 3.5312 Å (center-to-center) (Cg1 = C8-C9-C10-C11-C12-N3, Cg2 = C14-C15-C16-C17–C18-C19) and 3.5315 Å (center-to-center).

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

Atom	Site	x	y	z	U_{iso}
H(5)	2*i*	0.6643	1.0519	0.4138	0.022
H(2)	2*i*	0.2399	0.3889	0.4379	0.025

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	2*i*	0.5202	0.6082	0.8384	0.034
H(10)	2*i*	0.3098	0.6493	0.1887	0.033
H(18)	2*i*	0.8685	1.2827	0.5427	0.028
H(15)	2*i*	0.8648	1.0777	0.8191	0.025
H(4)	2*i*	0.2687	0.2555	0.7671	0.037
H(11)	2*i*	0.4756	0.8446	0.2767	0.030
H(5B)	2*i*	0.2637	1.0087	0.7528	0.054
H(22)	2*i*	0.9481	0.8315	1.0062	0.028
H(9)	2*i*	0.2573	0.5096	0.2889	0.030

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(23)	2*i*	0.8462	0.9226	1.1046	0.032
H(5A)	2*i*	0.1937	0.2399	0.5825	0.034
H(24)	2*i*	0.6364	0.9643	1.0120	0.029
H(27A)	2*i*	–0.0013	0.9704	0.6142	0.063
H(27B)	2*i*	0.0388	0.8924	0.6975	0.063
H(27C)	2*i*	0.0863	0.8869	0.5998	0.063
H(3)	2*i*	0.4269	0.4349	0.8922	0.034
H(16)	2*i*	1.0119	1.2805	0.8595	0.030
H(17)	2*i*	1.0142	1.3815	0.7233	0.030

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.58197(4)	0.78747(3)	0.64489(3)	0.0188(2)	0.0212(2)	0.0079(2)	0.0058(2)	0.0044(2)	–0.0002(2)
N(3)	2*i*	0.4872(3)	0.7384(2)	0.4846(2)	0.014(1)	0.027(2)	0.011(1)	0.007(1)	0.003(1)	0.002(1)
N(5)	2*i*	0.6842(2)	1.0391(2)	0.4775(2)	0.017(1)	0.028(2)	0.009(1)	0.007(1)	0.004(1)	0.003(1)
N(6)	2*i*	0.6757(3)	0.8378(2)	0.8060(2)	0.020(1)	0.016(1)	0.012(1)	0.007(1)	0.008(1)	0.005(1)
C(12)	2*i*	0.5190(3)	0.8198(3)	0.4284(2)	0.018(2)	0.026(2)	0.013(2)	0.009(1)	0.004(1)	–0.001(1)
N(1)	2*i*	0.4485(3)	0.6136(2)	0.6211(2)	0.020(1)	0.024(2)	0.017(1)	0.008(1)	0.009(1)	0.001(1)
O(4)	2*i*	0.4272(3)	0.9705(2)	0.8429(2)	0.037(1)	0.057(2)	0.016(1)	0.033(1)	0.008(1)	–0.000(1)
O(3)	2*i*	0.4360(2)	0.8787(2)	0.6928(2)	0.020(1)	0.026(1)	0.010(1)	0.009(1)	0.0051(9)	0.0022(9)
C(1)	2*i*	0.4116(3)	0.5265(3)	0.6757(3)	0.018(2)	0.022(2)	0.025(2)	0.009(1)	0.012(1)	0.003(1)
N(2)	2*i*	0.2944(3)	0.4398(2)	0.4995(2)	0.015(1)	0.020(2)	0.021(1)	0.005(1)	0.004(1)	–0.003(1)
C(7)	2*i*	0.3757(3)	0.5569(3)	0.5162(2)	0.015(2)	0.022(2)	0.019(2)	0.010(1)	0.006(1)	–0.001(1)
C(2)	2*i*	0.4562(4)	0.5359(3)	0.7878(3)	0.037(2)	0.026(2)	0.024(2)	0.009(2)	0.018(2)	0.001(2)
C(14)	2*i*	0.7788(3)	1.0596(3)	0.6557(2)	0.017(2)	0.023(2)	0.016(2)	0.010(1)	0.007(1)	0.006(1)
C(10)	2*i*	0.3549(3)	0.6718(3)	0.2639(2)	0.023(2)	0.038(2)	0.011(2)	0.007(2)	0.001(1)	–0.003(2)
N(4)	2*i*	0.6814(2)	0.9415(2)	0.6084(2)	0.014(1)	0.027(2)	0.008(1)	0.008(1)	0.001(1)	0.000(1)
C(18)	2*i*	0.8679(3)	1.2424(3)	0.5974(3)	0.027(2)	0.032(2)	0.020(2)	0.015(2)	0.012(1)	0.014(2)
C(15)	2*i*	0.8655(3)	1.1181(3)	0.7644(2)	0.020(2)	0.027(2)	0.012(1)	0.009(1)	0.003(1)	0.005(1)
C(4)	2*i*	0.3034(4)	0.3230(3)	0.7425(3)	0.032(2)	0.030(2)	0.042(2)	0.014(2)	0.024(2)	0.016(2)
C(8)	2*i*	0.3919(3)	0.6258(3)	0.4353(2)	0.015(2)	0.026(2)	0.017(2)	0.011(1)	0.006(1)	–0.001(1)
C(11)	2*i*	0.4536(3)	0.7885(3)	0.3161(2)	0.021(2)	0.037(2)	0.012(2)	0.006(2)	0.007(1)	0.004(1)
O(1)	2*i*	0.7830(2)	0.7264(2)	0.6883(2)	0.022(1)	0.022(1)	0.014(1)	0.0104(9)	0.0059(9)	0.0006(9)
O(2)	2*i*	0.9685(3)	0.7316(3)	0.8367(2)	0.053(2)	0.085(2)	0.018(1)	0.056(2)	0.008(1)	0.010(1)
O(5)	2*i*	0.2045(3)	1.0354(2)	0.7156(2)	0.037(1)	0.030(2)	0.033(1)	0.015(1)	0.003(1)	0.006(1)
C(19)	2*i*	0.7809(3)	1.1227(3)	0.5743(2)	0.015(2)	0.030(2)	0.014(2)	0.011(1)	0.006(1)	0.005(1)
C(25)	2*i*	0.6177(3)	0.8919(3)	0.8624(2)	0.021(2)	0.020(2)	0.014(1)	0.008(1)	0.006(1)	0.003(1)
C(6)	2*i*	0.3155(3)	0.4169(3)	0.6007(3)	0.016(2)	0.023(2)	0.025(2)	0.010(1)	0.008(1)	0.003(1)
C(21)	2*i*	0.7976(3)	0.8154(3)	0.8595(2)	0.019(2)	0.021(2)	0.016(2)	0.007(1)	0.008(1)	0.004(1)
C(22)	2*i*	0.8636(3)	0.8470(3)	0.9707(2)	0.019(2)	0.034(2)	0.014(2)	0.013(2)	0.001(1)	0.006(1)
C(13)	2*i*	0.6275(3)	0.9347(3)	0.5014(2)	0.013(1)	0.025(2)	0.009(1)	0.009(1)	0.003(1)	0.001(1)
C(20)	2*i*	0.8557(4)	0.7519(3)	0.7892(3)	0.030(2)	0.025(2)	0.021(2)	0.016(2)	0.014(2)	0.007(1)
C(26)	2*i*	0.4816(3)	0.9163(3)	0.7949(2)	0.017(2)	0.022(2)	0.013(2)	0.006(1)	0.004(1)	0.005(1)
C(9)	2*i*	0.3229(3)	0.5883(3)	0.3232(2)	0.016(2)	0.037(2)	0.015(2)	0.008(2)	0.003(1)	–0.005(1)
C(23)	2*i*	0.8034(3)	0.9020(3)	1.0293(2)	0.030(2)	0.039(2)	0.008(1)	0.016(2)	0.003(1)	0.001(1)
C(5)	2*i*	0.2583(3)	0.3123(3)	0.6326(3)	0.020(2)	0.023(2)	0.038(2)	0.006(2)	0.010(2)	0.004(2)
C(24)	2*i*	0.6782(3)	0.9262(3)	0.9745(2)	0.025(2)	0.035(2)	0.014(2)	0.014(2)	0.009(1)	0.004(1)
C(27)	2*i*	0.0713(4)	0.9385(4)	0.6516(3)	0.030(2)	0.046(3)	0.047(2)	0.011(2)	0.018(2)	0.000(2)
C(3)	2*i*	0.4000(4)	0.4323(3)	0.8188(3)	0.038(2)	0.031(2)	0.029(2)	0.016(2)	0.022(2)	0.013(2)
C(16)	2*i*	0.9529(3)	1.2391(3)	0.7878(3)	0.025(2)	0.026(2)	0.017(2)	0.009(2)	0.001(1)	0.002(1)
C(17)	2*i*	0.9543(3)	1.3005(3)	0.7051(3)	0.025(2)	0.019(2)	0.028(2)	0.008(1)	0.007(2)	0.006(2)

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