Crystal structure of bis(benzoato-κO)bis(2,2′-biimidazole-$\kappa^2 N,N'$)copper(II), $Cu(C_6H_6N_4)_2(C_7H_5O_2)_2$

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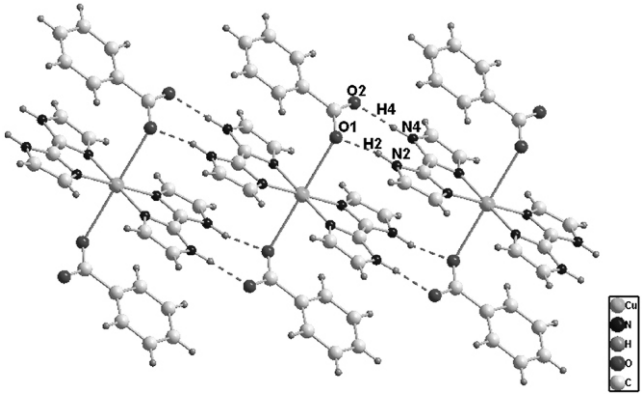

Abstract

$C_{26}H_{22}CuN_8O_4$, monoclinic, $P2_1/n$ (no. 14), a = 12.441(1) Å, b = 7.0747(6) Å, c = 14.072(1) Å, β = 90.609(1)°, V = 1238.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.191, T = 298 K.

Source of material

An aqueous solution (2 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.0729 g, 0.3 mmol) was added into a mixture of benzoic acid (0.0374 g, 0.3 mmol) dissolved in 5 ml ethanol and sodium hydroxide (0.0125 g, 0.3 mmol) dissolved in 3 ml water. The mixture was stirred for 30 min, then H_2biim (H_2biim=2,2′-biimidazole, 0.0408 g, 0.3 mmol) was added under continuous stirring. The mixture was refluxed for 6 h and filtered. The filtrate was allowed to evaporate slowly at room temperature to yield green block-shaped crystals of the title complex. Crystals suitable for single crystal X-ray diffraction were selected directly from the product as prepared.

Discussion

Hydrogen bonds are a powerful assembling force in constructing supramolecular compounds and provide useful information to understand a complicated process in biological systems. Supramolecular assemblies built up from hydrogen-bonding interactions have provided numerous materials with very attractive properties. The neutral 2,2′-biimidazole (H_2biim) is an excellent candidate for construction of hybrid materials via supramolecular interactions. It not only can coordinate to metal ion but also can provide two N–H hydrogen-bond donating sites for multi-dimensional network assembly. Furthermore, it can form robust heteromeric hydrogen-bonded synthons such as $R_2^2(9)$, $R_2^1(7)$ and $R_1^2(4)$ with counter anions [1] or carboxylates [2,3]. Hydrogen-bonded synthons based on H_2biim and carboxylates should be particularly strong, since the N–H···O unit is nearly linear and the N···O separation is close to the lower limit of the accepted range. In previous contributions, our research group discussed the synthesis and crystal structures of metal complexes with 2,2′-biimidazole [4-6].

In the centro-symmetric molecular structure of the title complex, each copper atom is in the center of a distorted octahedron, which is similar to the metal atoms in $[Cd(H_2biim)_2(HBDC)_2]$ (H_2BDC = terephthalic acid) [7] and $[Cu(C_8H_7O_2)_2(C_6H_6N_4)_2]$ [8]. The two axial positions are occupied by the monodentated benzoic acid. The four equatorial positions are occupied by the two chelating H_2biim. The Cu—N(H_2biim) distances (average 2.012(9) Å) are shorter than the Cu—O(benzoic acid) bond lengths (2.6784(4) Å), which agrees with the corresponding distances in [7] and [8]. The two imidazole rings are almost coplanar with a dihedral angle of 5.060°. The molecules $[Cu(C_6H_6N_4)_2(C_7H_5O_2)_2]$ form an extended ribbon along (010), through heteromeric hydrogen-bonded synthon $R_2^2(9)$ between the carboxylate groups and the uncoordinated nitrogen atoms of H_2biim. This type of hydrogen bond can also be found in $[Zn(H_2biim)_2(H_2O)_2](Hbdc)_2 \cdot (H_2biim)_2 \cdot H_2O$ and $[Zn(H_2biim)_2(H_2O)](bdc) \cdot CH_3OH$ (where bdc = 1,3-benzenedicarboxylate) [2], in which carboxylates are uncoordinated as counter anions.

In the title crystal structure, the N–H···O hydrogen bonds (d(N2—O1) = 2.671 Å; d(N4—O2) = 2.672 Å) have different angles (∠N2–H2···O1 = 165.43°; ∠N4–H4···O2 = 176.76°) because of steric requirement. The bond distance d(O1—C7) = 1.270(6) Å is slightly longer than d(O2—C7) = 1.228(6) Å. This may be attributed to the formation of the hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	green block, size 0.23 × 0.42 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.33 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6039, 2176
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1658
$N(param)_{refined}$:	178
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*e*	0.3814	1.0961	0.3815	0.048
H(4)	4*e*	0.5866	1.0267	0.3048	0.052
H(2A)	4*e*	0.2146	1.0169	0.4623	0.057
H(3)	4*e*	0.2460	0.7085	0.5369	0.055
H(5)	4*e*	0.7569	0.8629	0.2811	0.058
H(6)	4*e*	0.7475	0.5761	0.3779	0.056
H(9)	4*e*	0.6668	0.3755	0.7170	0.056
H(10)	4*e*	0.6979	0.1083	0.8085	0.071
H(11)	4*e*	0.5889	0.0485	0.9373	0.084
H(12)	4*e*	0.4545	0.2544	0.9769	0.082
H(13)	4*e*	0.4220	0.5163	0.8840	0.071

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*a*	½	½	½	0.0393(5)	0.0258(5)	0.0509(6)	0.0047(3)	0.0063(4)	0.0095(4)
N(1)	4*e*	0.3971(3)	0.7138(5)	0.4788(3)	0.038(2)	0.030(2)	0.048(2)	0.001(2)	0.002(2)	0.009(2)
N(2)	4*e*	0.3699(3)	0.9937(5)	0.4127(3)	0.047(2)	0.027(2)	0.045(2)	0.003(2)	–0.001(2)	0.007(2)
N(3)	4*e*	0.5959(3)	0.6635(5)	0.4189(3)	0.043(2)	0.031(2)	0.044(2)	0.002(2)	0.000(2)	0.004(2)
N(4)	4*e*	0.6047(3)	0.9215(6)	0.3311(3)	0.047(2)	0.031(2)	0.051(3)	0.001(2)	0.004(2)	0.010(2)
O(1)	4*e*	0.5758(3)	0.6690(5)	0.6573(3)	0.066(3)	0.039(2)	0.061(2)	0.002(2)	0.011(2)	0.014(2)
O(2)	4*e*	0.4467(3)	0.7551(6)	0.7562(3)	0.072(3)	0.046(2)	0.084(3)	0.020(2)	0.026(2)	0.030(2)
C(1)	4*e*	0.4390(4)	0.8496(6)	0.4252(3)	0.043(3)	0.027(2)	0.035(2)	0.002(2)	–0.003(2)	0.000(2)
C(2)	4*e*	0.2773(4)	0.9458(8)	0.4593(4)	0.047(3)	0.039(3)	0.055(3)	0.010(2)	0.003(3)	0.006(2)
C(3)	4*e*	0.2951(4)	0.7744(8)	0.5002(4)	0.042(3)	0.043(3)	0.054(3)	0.005(2)	0.009(2)	0.010(3)
C(4)	4*e*	0.5463(4)	0.8214(6)	0.3909(3)	0.044(3)	0.028(2)	0.037(3)	0.000(2)	0.002(2)	0.001(2)
C(5)	4*e*	0.6997(4)	0.8259(8)	0.3190(4)	0.045(3)	0.047(3)	0.053(3)	0.000(2)	0.008(2)	0.009(3)
C(6)	4*e*	0.6941(4)	0.6677(7)	0.3727(4)	0.044(3)	0.041(3)	0.054(3)	0.008(2)	0.006(2)	0.002(2)
C(7)	4*e*	0.5188(4)	0.6484(7)	0.7309(4)	0.048(3)	0.031(3)	0.049(3)	–0.001(2)	0.005(2)	0.007(2)
C(8)	4*e*	0.5401(4)	0.4737(7)	0.7902(4)	0.048(3)	0.032(3)	0.045(3)	–0.002(2)	–0.005(2)	0.004(2)
C(9)	4*e*	0.6233(4)	0.3504(7)	0.7688(4)	0.049(3)	0.036(3)	0.054(3)	–0.002(2)	–0.004(2)	–0.001(2)
C(10)	4*e*	0.6424(5)	0.1908(8)	0.8234(5)	0.064(4)	0.039(3)	0.074(4)	0.005(3)	–0.015(3)	0.002(3)
C(11)	4*e*	0.5773(6)	0.1562(9)	0.9007(5)	0.076(4)	0.044(3)	0.091(5)	–0.004(3)	–0.019(4)	0.031(3)
C(12)	4*e*	0.4966(5)	0.278(1)	0.9240(5)	0.065(4)	0.069(4)	0.072(4)	0.003(3)	0.007(3)	0.032(4)
C(13)	4*e*	0.4778(5)	0.4348(9)	0.8685(4)	0.057(4)	0.057(3)	0.065(4)	0.007(3)	0.012(3)	0.019(3)

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