Crystal structure of monoaquabenzoato-2,5,8-triaza-1,9-di(2-fluorobenzyl)-nonanecopper(II) benzoate dihydrate, $Cu(C_{25}H_{30}F_2N_3O_3)(C_7H_5O_2) \cdot 2H_2O$

H.-L. Zhu*[I,II], S.-C. Shao[I], J.-L. Ma[I], X.-Y. Qiu[I], S. Yang[I] and L. Sun[I]

[I] Fuyang Normal College, Department of Chemistry, Fuyang, Anhui, 236041 P. R. China
[II] Wuhan University of Science and Engineering, Department of Chemistry, Wuhan, 430073 P. R. China

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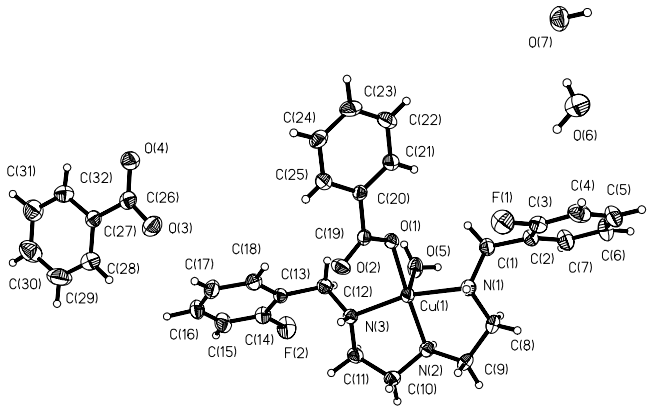

Abstract

$C_{32}H_{39}CuF_2N_3O_7$, triclinic, $P\bar{1}$ (No. 2), a = 7.331(3) Å, b = 8.983(3) Å, c = 26.34(1) Å, α = 95.570(6)°, β = 95.797(6)°, γ = 110.811(5)°, V = 1596.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.103, T = 298 K.

Source of material

Dien and 2-fluorobenzaldehyde were condensed in anhydrous methanol and then reduced to obtain the ligand L, where dien is diethylenetriamine and L is 2,5,8-triaza-1,9-di(2-fluorobenzyl)-nonane. Copper(II) benzoate (1.0 mmol, 306 mg) and L (1.0 mmol, 317 mg) were suspended in water (20 ml), stirring for ca. 1 hour to obtain a clear blue solution. After keeping the resulting solution in air for one week, large blue single crystals were formed on slow evaporation. The crystals were isolated, washed with water three times and dried in a vacuum desiccator using $CaCl_2$ (yield 62%). Elemental analysis: found – C, 56.08%; H, 5.90%; N, 6.11%; calc. for $C_{32}H_{39}CuF_2N_3O_7$ – C, 56.59%; H, 5.79; N, 6.19%.

Experimental details

All the H atoms were located from difference Fourier maps and refined isotropically.

Discussion

Amine complexes with transition metals carboxylate represent an important branch in the field of coordination chemistry. Previously we reported some examples of this kind of complexes [1-4]. The title compound consists of one coordination cation, one benzoate anion, and two lattice water molecules. In the cation, the Cu(1) atom is in a square-pyramidal environment and is five-coordinated by three N atoms from an amine ligand, two O atoms from a benzoate ligand and a water molecule, respectively. N(1), N(2), N(3) and O(1) atoms constitute the basal plane (plane **I**) of the square-pyramid with the average deviation of 0.094 Å, and Cu(1) atom locates 0.094 Å above **I** toward the axial O(5) atom, which occupies the axial position. The average Cu—N bond length (2.023(4) Å) in the title complex is slightly shorter than those found in the similar copper(II) complex with the secondary amines (average d(Cu—N) = 2.10(3) Å [1], = 2.07(1) Å [2]). The Cu(1)—O(1) distance of 1.958(2) Å is much shorter than that 2.259(3)Å found in the copper(II) complex with the carboxylate ligand [3]. The three aromatic rings, C2–C3–C4–C5–C6–C7 (plane **II**), C13–C14–C15–C16–C17–C18 (plane **III**), C20–C21–C22–C23–C24–C25 (plane **IV**) in the coordination cation are all well-defined planes. The dihedral angles between the metal basal plane I and the other three aromatic planes (**II**, **III** and **IV**) are respectively, 52.2°, 39.9°, and 37.6°. The dihedral angle between the two aromatic rings (**II** and **III**) in the same ligand is 13.9°, indicating that these two rings are almost parallel each other. All the oxygen and the nitrogen atoms in the complex contribute to the formation of hydrogen bonds. A great number of hydrogen bonds link the molecules into a two-dimensional network. First, the molecules are interconnected, in columns parallel to a-axis and then in layers parallel to ac-plane, by intermolecular hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.32 × 0.44 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.47 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8478, 5580
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3852
$N(param)_{refined}$:	562
Programs:	SHELXTL [5], SADABS [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	–0.123(5)	0.938(4)	0.338(1)	0.06(1)
H(2)	2*i*	0.056(4)	0.891(4)	0.364(1)	0.05(1)
H(3)	2*i*	0.255(5)	1.201(4)	0.518(1)	0.05(1)
H(4)	2*i*	0.007(6)	1.294(5)	0.532(2)	0.09(1)
H(5)	2*i*	–0.249(6)	1.243(5)	0.468(2)	0.09(1)

* Correspondence author (e-mail: hlzhu@wist.edu.cn)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(6)	2*i*	–0.240(5)	1.103(4)	0.389(1)	0.05(1)
H(7)	2*i*	0.263(4)	1.102(3)	0.337(1)	0.024(8)
H(8)	2*i*	0.142(4)	1.293(4)	0.329(1)	0.05(1)
H(9)	2*i*	–0.036(5)	1.160(3)	0.296(1)	0.042(9)
H(10)	2*i*	0.144(4)	1.322(3)	0.239(1)	0.049(9)
H(11)	2*i*	0.335(5)	1.294(4)	0.264(1)	0.05(1)
H(12)	2*i*	0.020(5)	1.064(3)	0.209(1)	0.040(9)
H(13)	2*i*	0.208(4)	1.161(3)	0.150(1)	0.040(8)
H(14)	2*i*	0.386(5)	1.165(3)	0.188(1)	0.044(9)
H(15)	2*i*	0.079(4)	0.879(3)	0.135(1)	0.032(8)
H(16)	2*i*	0.293(5)	0.937(4)	0.124(1)	0.06(1)
H(17)	2*i*	0.370(4)	0.874(3)	0.200(1)	0.020(8)
H(18)	2*i*	0.171(4)	0.619(3)	0.208(1)	0.046(9)
H(19)	2*i*	0.029(5)	0.641(3)	0.164(1)	0.047(9)
H(20)	2*i*	0.210(5)	0.478(4)	0.017(1)	0.06(1)
H(21)	2*i*	0.495(5)	0.408(4)	0.043(1)	0.07(1)
H(22)	2*i*	0.600(5)	0.458(4)	0.131(1)	0.06(1)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(23)	2*i*	0.456(4)	0.567(3)	0.190(1)	0.027(7)
H(24)	2*i*	0.203(4)	0.671(3)	0.386(1)	0.042(9)
H(25)	2*i*	0.244(5)	0.517(4)	0.447(1)	0.06(1)
H(26)	2*i*	0.488(5)	0.411(4)	0.449(1)	0.06(1)
H(27)	2*i*	0.679(5)	0.461(4)	0.383(1)	0.05(1)
H(28)	2*i*	0.630(4)	0.609(3)	0.327(1)	0.029(9)
H(29)	2*i*	0.816(5)	0.303(4)	0.087(1)	0.07(1)
H(30)	2*i*	0.815(6)	0.196(5)	0.004(2)	0.09(1)
H(31)	2*i*	0.749(6)	–0.065(5)	–0.019(2)	0.10(2)
H(32)	2*i*	0.702(6)	–0.236(5)	0.042(2)	0.09(1)
H(33)	2*i*	0.689(4)	–0.126(4)	0.126(1)	0.05(1)
H(34)	2*i*	–0.185(7)	0.671(3)	0.242(2)	0.10(1)
H(35)	2*i*	–0.247(4)	0.801(4)	0.244(2)	0.09(2)
H(36)	2*i*	0.47(2)	0.858(7)	0.673(2)	0.10(2)
H(37)	2*i*	0.348(5)	0.744(2)	0.704(2)	0.09(2)
H(38)	2*i*	0.040(2)	0.474(6)	0.718(2)	0.09(1)
H(39)	2*i*	0.183(5)	0.590(4)	0.7568(9)	0.08(1)

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*	0.17881(6)	0.92881(4)	0.25892(2)	0.0459(3)	0.0444(2)	0.0393(2)	0.0255(2)	0.0107(2)	0.0087(2)
F(1)	2*i*	0.3133(3)	1.0625(3)	0.43937(9)	0.065(2)	0.101(2)	0.088(2)	0.040(1)	0.008(1)	0.017(1)
F(2)	2*i*	0.0346(3)	0.6045(3)	0.06964(8)	0.079(2)	0.105(2)	0.058(1)	0.050(1)	–0.007(1)	0.003(1)
N(1)	2*i*	0.1511(4)	1.0677(3)	0.3218(1)	0.036(2)	0.044(2)	0.043(2)	0.017(1)	0.005(1)	0.006(1)
N(2)	2*i*	0.1409(4)	1.0963(3)	0.2197(1)	0.036(2)	0.044(2)	0.046(2)	0.020(1)	0.005(1)	0.007(1)
N(3)	2*i*	0.2517(4)	0.8446(3)	0.1925(1)	0.034(2)	0.043(2)	0.040(2)	0.017(1)	0.006(1)	0.008(1)
O(1)	2*i*	0.2270(3)	0.7773(2)	0.30212(8)	0.049(1)	0.057(1)	0.047(1)	0.034(1)	0.018(1)	0.020(1)
O(2)	2*i*	0.5206(3)	0.8062(3)	0.27984(9)	0.049(2)	0.078(2)	0.061(2)	0.034(1)	0.025(1)	0.036(1)
O(3)	2*i*	0.7977(4)	0.3079(3)	0.1808(1)	0.087(2)	0.054(2)	0.078(2)	0.031(2)	0.012(2)	0.007(1)
O(4)	2*i*	0.7047(3)	0.0614(3)	0.20213(9)	0.060(2)	0.065(2)	0.062(2)	0.026(1)	0.011(1)	0.015(1)
O(5)	2*i*	–0.1528(3)	0.7705(3)	0.2364(1)	0.040(2)	0.061(2)	0.077(2)	0.020(1)	0.012(1)	–0.005(1)
O(6)	2*i*	0.4199(4)	0.8424(3)	0.7024(1)	0.052(2)	0.075(2)	0.097(2)	0.024(2)	0.017(2)	0.025(2)
O(7)	2*i*	0.1663(5)	0.5244(4)	0.7282(1)	0.080(2)	0.071(2)	0.091(2)	0.031(2)	0.039(2)	0.007(2)
C(1)	2*i*	0.0150(6)	0.9793(4)	0.3560(1)	0.053(2)	0.049(2)	0.051(2)	0.020(2)	0.015(2)	0.003(2)
C(2)	2*i*	0.0129(5)	1.0744(4)	0.4061(1)	0.050(2)	0.049(2)	0.045(2)	0.019(2)	0.014(2)	0.007(2)
C(3)	2*i*	0.1601(5)	1.1104(4)	0.4467(1)	0.057(2)	0.053(2)	0.057(2)	0.018(2)	0.017(2)	0.013(2)
C(4)	2*i*	0.1615(8)	1.1904(5)	0.4940(2)	0.077(3)	0.069(3)	0.047(3)	0.010(2)	0.001(2)	0.012(2)
C(5)	2*i*	0.0075(9)	1.2387(6)	0.5009(2)	0.108(4)	0.075(3)	0.057(3)	0.030(3)	0.034(3)	0.001(2)
C(6)	2*i*	–0.1421(8)	1.2057(6)	0.4617(2)	0.092(4)	0.086(3)	0.072(3)	0.049(3)	0.035(3)	0.003(3)
C(7)	2*i*	–0.1403(7)	1.1251(5)	0.4146(2)	0.068(3)	0.087(3)	0.051(3)	0.042(2)	0.014(2)	0.007(2)
C(8)	2*i*	0.1013(6)	1.2026(4)	0.3035(1)	0.051(2)	0.043(2)	0.054(2)	0.025(2)	0.007(2)	–0.002(2)
C(9)	2*i*	0.1938(6)	1.2466(4)	0.2559(1)	0.054(2)	0.037(2)	0.061(2)	0.024(2)	0.005(2)	0.006(2)
C(10)	2*i*	0.2472(6)	1.1045(4)	0.1749(1)	0.052(2)	0.051(2)	0.050(2)	0.026(2)	0.010(2)	0.018(2)
C(11)	2*i*	0.2112(6)	0.9353(4)	0.1514(1)	0.051(2)	0.056(2)	0.040(2)	0.025(2)	0.008(2)	0.013(2)
C(12)	2*i*	0.1604(6)	0.6672(4)	0.1780(1)	0.046(2)	0.043(2)	0.044(2)	0.014(2)	0.009(2)	0.006(2)
C(13)	2*i*	0.2553(5)	0.5966(3)	0.1394(1)	0.043(2)	0.036(2)	0.039(2)	0.013(2)	0.010(2)	0.002(1)
C(14)	2*i*	0.1901(5)	0.5650(4)	0.0873(1)	0.049(2)	0.055(2)	0.048(2)	0.022(2)	0.003(2)	0.005(2)
C(15)	2*i*	0.2713(7)	0.4958(5)	0.0516(2)	0.080(3)	0.074(3)	0.040(2)	0.029(2)	0.007(2)	–0.007(2)
C(16)	2*i*	0.4263(6)	0.4525(5)	0.0688(2)	0.075(3)	0.059(2)	0.062(3)	0.029(2)	0.027(2)	–0.002(2)
C(17)	2*i*	0.4973(6)	0.4814(4)	0.1203(2)	0.058(3)	0.054(2)	0.072(3)	0.029(2)	0.016(2)	0.006(2)
C(18)	2*i*	0.4119(5)	0.5516(4)	0.1552(1)	0.055(2)	0.046(2)	0.043(2)	0.018(2)	0.005(2)	0.004(2)
C(19)	2*i*	0.3909(5)	0.7559(4)	0.3069(1)	0.045(2)	0.039(2)	0.038(2)	0.020(2)	0.008(2)	0.003(1)
C(20)	2*i*	0.4176(4)	0.6573(3)	0.3482(1)	0.043(2)	0.036(2)	0.035(2)	0.018(2)	0.004(1)	0.003(1)
C(21)	2*i*	0.3001(6)	0.6293(4)	0.3864(1)	0.059(2)	0.057(2)	0.047(2)	0.031(2)	0.015(2)	0.015(2)
C(22)	2*i*	0.3279(7)	0.5390(5)	0.4244(2)	0.073(3)	0.072(3)	0.047(2)	0.028(2)	0.019(2)	0.022(2)
C(23)	2*i*	0.4706(6)	0.4751(4)	0.4236(2)	0.077(3)	0.054(2)	0.050(2)	0.022(2)	–0.004(2)	0.019(2)
C(24)	2*i*	0.5885(6)	0.5017(4)	0.3858(2)	0.061(3)	0.053(2)	0.060(3)	0.033(2)	0.003(2)	0.013(2)
C(25)	2*i*	0.5622(6)	0.5927(4)	0.3484(2)	0.052(2)	0.053(2)	0.045(2)	0.023(2)	0.012(2)	0.011(2)
C(26)	2*i*	0.7482(5)	0.1590(5)	0.1704(1)	0.035(2)	0.055(2)	0.064(2)	0.021(2)	0.004(2)	0.013(2)
C(27)	2*i*	0.7478(5)	0.0933(4)	0.1154(1)	0.037(2)	0.046(2)	0.060(2)	0.016(2)	0.009(2)	0.010(2)
C(28)	2*i*	0.7841(6)	0.1916(5)	0.0777(2)	0.086(3)	0.060(3)	0.075(3)	0.031(2)	0.023(2)	0.019(2)
C(29)	2*i*	0.7885(8)	0.1322(7)	0.0283(2)	0.127(5)	0.090(4)	0.076(4)	0.032(3)	0.036(3)	0.039(3)
C(30)	2*i*	0.7576(8)	–0.0277(7)	0.0151(2)	0.104(4)	0.094(4)	0.065(3)	0.021(3)	0.024(3)	0.002(3)
C(31)	2*i*	0.7199(7)	–0.1261(6)	0.0516(2)	0.090(3)	0.062(3)	0.079(3)	0.020(2)	0.019(3)	–0.005(3)
C(32)	2*i*	0.7137(6)	–0.0677(5)	0.1010(2)	0.064(3)	0.053(3)	0.066(3)	0.016(2)	0.012(2)	0.014(2)

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