Crystal structure of bis[dinitrato-2,5,8-triaza-1,9-di(2-fluorobenzyl-nonanecopper(II)] monohydrate, $Cu(C_{18}H_{22}F_2N_5O_6)_2 \cdot H_2O$

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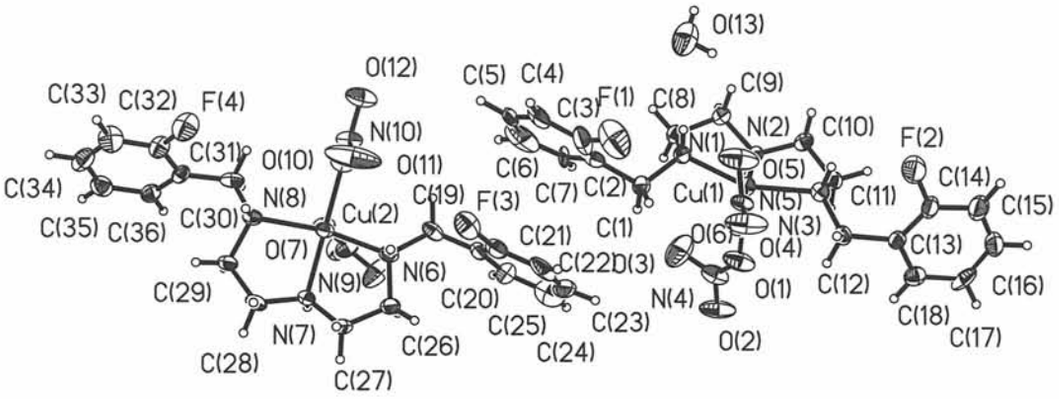

Abstract

$C_{36}H_{48}Cu_2F_4N_{10}O_{13}$, monoclinic, *C*1*c*1 (No. 9), $a = 14.870(8)$ Å, $b = 20.78(1)$ Å, $c = 14.660(7)$ Å, $\beta = 101.308(9)°$, $V = 4441.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.053$, $wR_{ref}(F^2) = 0.147$, $T = 298$ K.

Source of material

$Cu(NO_3) \cdot 6H_2O$ (1.0 mmol, 296 mg) and 2,5,8-triaza-1,9-di(2-fluorobenzyl-nonane (1.0 mmol, 317 mg) were suspended in water (20 ml) and stirred for ca. 0.5 hour to obtain a clear blue solution. After the above solution was kept in air for 3 days large blue crystals were collected, washed with water, and dried in a vacuum desiccator under drying $CaCl_2$ (yield 45%). Elemental analysis: found – C, 42.04%; H, 4.75%; N, 13.46%; calc. for $C_{36}H_{48}Cu_2F_4N_{10}O_{13}$ – C, 41.90%; H, 4.69%; N, 13.57%.

Experimental details

Because they can rotate freely, the two H atoms attached to O(13) atom are added theoretically, and $U_{iso}(H) = 0.08$ Å^2. All the other H atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with N—H and C—H distances of 0.90 Å and 0.96 Å, respectively. Attempts to determine the structure in a higher symmetry space group failed.

Discussion

The structure of the title compound consists of two similar mononuclear copper(II) complexes and one lattice water molecule. In the electronically neutral monocopper(II) units, each of the central metal atoms is coordinated by three nitrogen atoms from one amine ligand and two oxygen atoms from two different nitrate anions, forming a distorted CuN_3O_2 square pyramid. The average Cu—N bond lengths (2.008(8) Å for Cu(1) and 2.014(8) Å for Cu(2) atom) are slightly shorter than that (2.023(4) Å) found in the compound with the same ligand [1]. Four atoms N(1), N(2), N(3) and O(4) around Cu(1) (or N(6), N(7), N(8) and O(7) around Cu(2) form the basal plane of the CuN_3O_2 square pyramid. The distances Cu1—O4 (2.005(7) Å) and Cu2—O10 (1.977(7) Å) are in the normal bond length ranges for copper(II) complexes with nitrate anions. Compared to the basal oxygen atoms, the apical O atoms from the nitrate ligands are weakly coordinated to the central copper(II) atoms with d(Cu1—O1) = 2.40(1) Å and d(Cu2—O7) = 2.366(8) Å. All the nitrogen atoms in the amine ligands contribute to the formation of the hydrogen bonds. A great number of hydrogen bonds link the complexes into a three-dimensional network.

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Table 1. Data collection and handling.

Crystal:	blue block, size 0.28 × 0.34 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.47 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11601, 5555
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3040
$N(param)_{refined}$:	586
Programs:	SHELXTL [2], SADABS [3]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.8078	0.6171	0.3294	0.070
H(2)	4*a*	0.8259	0.4391	0.3137	0.060
H(3)	4*a*	1.0477	0.5080	0.4254	0.072
H(6)	4*a*	0.3016	0.7570	0.4864	0.079
H(7)	4*a*	0.0670	0.7087	0.4989	0.074
H(8)	4*a*	0.0690	0.8698	0.3902	0.069

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(13A)	4*a*	0.8012	0.6946	0.1726	0.080
H(13B)	4*a*	0.9016	0.7019	0.1900	0.080
H(1A)	4*a*	0.6754	0.5659	0.4126	0.082
H(1B)	4*a*	0.7444	0.6176	0.4628	0.082
H(4)	4*a*	0.6223	0.8129	0.3378	0.226
H(5)	4*a*	0.4756	0.7596	0.2478	0.283
H(6A)	4*a*	0.4598	0.6636	0.2717	0.330
H(7A)	4*a*	0.5407	0.5870	0.2816	0.190
H(8A)	4*a*	0.7060	0.5771	0.2156	0.078
H(8B)	4*a*	0.6901	0.5171	0.2759	0.078
H(9A)	4*a*	0.7815	0.4814	0.1746	0.073
H(9B)	4*a*	0.8497	0.5396	0.2001	0.073
H(10A)	4*a*	0.9816	0.4744	0.2592	0.078
H(10B)	4*a*	0.9347	0.4062	0.2493	0.078
H(11A)	4*a*	0.9732	0.3892	0.4069	0.072
H(11B)	4*a*	1.0635	0.4117	0.3756	0.072
H(12A)	4*a*	1.0044	0.4450	0.5711	0.081
H(12B)	4*a*	1.0627	0.5079	0.5748	0.081
H(15)	4*a*	1.3404	0.4292	0.5186	0.130
H(16)	4*a*	1.3461	0.3339	0.5834	0.133
H(17)	4*a*	1.2251	0.2940	0.6424	0.127

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(18)	4*a*	1.0891	0.3518	0.6189	0.093
H(19A)	4*a*	0.2816	0.6499	0.3785	0.091
H(19B)	4*a*	0.3376	0.7110	0.3620	0.091
H(22)	4*a*	0.6114	0.6737	0.5894	0.182
H(23)	4*a*	0.5972	0.5657	0.5752	0.212
H(24)	4*a*	0.4871	0.5082	0.5271	0.248
H(25)	4*a*	0.3588	0.5652	0.4436	0.111
H(26A)	4*a*	0.3029	0.6854	0.5913	0.086
H(26B)	4*a*	0.2236	0.6464	0.5283	0.086
H(27A)	4*a*	0.1549	0.7000	0.6312	0.079
H(27B)	4*a*	0.2057	0.7645	0.6175	0.079
H(28A)	4*a*	0.0762	0.8308	0.5631	0.089
H(28B)	4*a*	0.0010	0.7791	0.5708	0.089
H(29A)	4*a*	–0.0634	0.7880	0.4182	0.089
H(29B)	4*a*	–0.0469	0.8591	0.4539	0.089
H(30A)	4*a*	0.0281	0.8542	0.2400	0.089
H(30B)	4*a*	–0.0394	0.8002	0.2580	0.089
H(33)	4*a*	–0.1148	1.0421	0.2504	0.141
H(34)	4*a*	–0.2639	1.0126	0.2475	0.132
H(35)	4*a*	–0.3049	0.9076	0.2590	0.114
H(36)	4*a*	–0.1911	0.8292	0.2742	0.084

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)	4*a*	0.88318(8)	0.52491(6)	0.41610(8)	0.0603(8)	0.0561(8)	0.0533(8)	0.0052(7)	0.0067(6)	–0.0110(6)
Cu(2)	4*a*	0.14766(8)	0.76594(6)	0.39760(8)	0.0675(8)	0.0688(8)	0.0534(8)	–0.0041(8)	0.0222(6)	0.0081(7)
F(1)	4*a*	0.754(1)	0.7327(5)	0.409(1)	0.19(1)	0.112(8)	0.31(2)	–0.028(9)	0.11(1)	–0.072(9)
F(2)	4*a*	1.2114(6)	0.5047(5)	0.4899(8)	0.100(6)	0.126(7)	0.23(1)	–0.004(5)	0.042(6)	0.072(7)
F(3)	4*a*	0.4698(5)	0.7558(5)	0.4964(6)	0.090(5)	0.146(8)	0.127(7)	–0.021(5)	0.021(5)	–0.033(6)
F(4)	4*a*	0.0147(6)	0.9711(4)	0.2655(7)	0.111(6)	0.090(6)	0.173(9)	–0.023(5)	0.011(6)	0.014(5)
N(1)	4*a*	0.7813(6)	0.5812(4)	0.3477(5)	0.067(5)	0.056(5)	0.055(6)	0.009(4)	0.019(4)	–0.005(4)
N(2)	4*a*	0.8627(5)	0.4723(4)	0.3034(5)	0.057(5)	0.042(5)	0.049(5)	0.008(4)	0.012(4)	0.000(4)
N(3)	4*a*	1.0084(6)	0.4802(4)	0.4453(6)	0.065(5)	0.047(5)	0.069(6)	0.001(4)	0.015(5)	–0.010(4)
N(4)	4*a*	0.750(1)	0.4205(7)	0.4922(9)	0.11(1)	0.11(1)	0.074(9)	–0.051(9)	0.033(8)	–0.027(7)
N(5)	4*a*	0.9433(6)	0.6232(5)	0.5368(7)	0.072(6)	0.060(6)	0.059(7)	–0.028(5)	0.023(5)	0.001(5)
N(6)	4*a*	0.2641(6)	0.7238(4)	0.4633(6)	0.063(5)	0.085(7)	0.052(6)	–0.001(5)	0.016(4)	0.007(5)
N(7)	4*a*	0.1023(6)	0.7445(4)	0.5124(6)	0.060(5)	0.074(7)	0.058(6)	0.004(5)	0.027(5)	0.014(5)
N(8)	4*a*	0.0420(5)	0.8310(4)	0.3741(6)	0.069(6)	0.054(5)	0.052(6)	–0.017(4)	0.019(5)	0.001(4)
N(9)	4*a*	0.0578(9)	0.6302(6)	0.3193(9)	0.11(1)	0.055(7)	0.097(9)	–0.014(7)	0.010(7)	0.018(6)
N(10)	4*a*	0.2413(8)	0.8235(5)	0.2768(7)	0.106(8)	0.061(6)	0.049(7)	–0.044(6)	0.015(6)	–0.017(5)
O(1)	4*a*	0.8183(8)	0.4460(6)	0.5024(6)	0.140(9)	0.16(1)	0.072(7)	–0.082(8)	0.037(6)	–0.032(6)
O(2)	4*a*	0.7270(9)	0.3760(5)	0.5330(7)	0.22(1)	0.130(9)	0.094(8)	–0.104(9)	0.050(7)	0.009(6)
O(3)	4*a*	0.685(1)	0.4443(6)	0.432(1)	0.19(1)	0.106(9)	0.22(2)	0.02(1)	–0.01(1)	0.04(1)
O(4)	4*a*	0.9041(5)	0.5719(4)	0.5380(5)	0.094(6)	0.053(5)	0.058(5)	–0.014(4)	0.018(4)	–0.011(3)
O(5)	4*a*	0.9487(8)	0.6468(6)	0.4651(7)	0.19(1)	0.20(1)	0.075(7)	–0.13(1)	0.022(7)	–0.010(7)
O(6)	4*a*	0.9743(9)	0.6524(5)	0.6081(7)	0.25(1)	0.137(9)	0.059(6)	–0.119(9)	0.036(7)	–0.036(6)
O(7)	4*a*	0.0552(6)	0.6874(4)	0.3068(6)	0.116(7)	0.050(5)	0.078(6)	–0.015(5)	0.019(5)	0.005(4)
O(8)	4*a*	–0.0003(8)	0.5935(5)	0.2747(8)	0.144(9)	0.074(7)	0.16(1)	–0.040(7)	–0.013(7)	–0.005(6)
O(9)	4*a*	0.1151(8)	0.6051(6)	0.380(1)	0.15(1)	0.103(8)	0.21(1)	–0.023(7)	–0.05(1)	0.056(9)
O(10)	4*a*	0.1856(6)	0.7811(4)	0.2774(6)	0.095(6)	0.094(7)	0.076(6)	–0.022(6)	0.035(5)	0.005(5)
O(11)	4*a*	0.280(2)	0.8439(7)	0.342(1)	0.48(3)	0.21(2)	0.14(1)	–0.25(2)	0.16(2)	–0.08(1)
O(12)	4*a*	0.2706(7)	0.8354(5)	0.2053(7)	0.126(8)	0.17(1)	0.087(7)	–0.061(7)	0.039(6)	0.009(6)
O(13)	4*a*	0.8541(7)	0.6833(5)	0.202(1)	0.106(8)	0.118(9)	0.28(2)	0.006(7)	–0.002(9)	0.01(1)
C(1)	4*a*	0.7124(7)	0.6027(5)	0.4024(7)	0.076(8)	0.063(8)	0.068(8)	0.015(6)	0.020(6)	0.000(6)
C(2)	4*a*	0.6504(9)	0.6549(6)	0.3583(8)	0.09(1)	0.045(7)	0.081(9)	0.016(7)	0.047(8)	0.013(6)
C(3)	4*a*	0.672(1)	0.7200(9)	0.369(1)	0.08(1)	0.13(2)	0.13(1)	–0.01(1)	0.033(9)	–0.03(1)
C(4)	4*a*	0.611(2)	0.7689(7)	0.332(2)	0.31(3)	0.053(9)	0.28(3)	0.10(1)	0.26(3)	0.09(1)
C(5)	4*a*	0.523(2)	0.735(2)	0.281(1)	0.12(2)	0.54(6)	0.07(1)	0.22(3)	0.07(1)	0.15(2)
C(6)	4*a*	0.522(3)	0.674(2)	0.287(2)	0.35(5)	0.39(6)	0.13(3)	–0.20(4)	0.15(3)	–0.20(4)
C(7)	4*a*	0.558(1)	0.629(1)	0.299(2)	0.09(1)	0.27(3)	0.13(2)	0.13(2)	0.05(1)	0.09(2)
C(8)	4*a*	0.7360(7)	0.5466(5)	0.2617(7)	0.060(7)	0.071(7)	0.060(7)	0.010(6)	0.002(5)	–0.001(6)
C(9)	4*a*	0.8096(7)	0.5100(5)	0.2243(7)	0.075(7)	0.054(7)	0.051(7)	0.000(6)	0.006(5)	–0.004(5)
C(10)	4*a*	0.9475(7)	0.4437(5)	0.2890(7)	0.088(9)	0.043(6)	0.063(8)	0.004(6)	0.013(6)	0.001(5)
C(11)	4*a*	1.0025(7)	0.4250(5)	0.3819(7)	0.057(6)	0.058(7)	0.065(8)	0.003(5)	0.013(6)	–0.001(6)
C(12)	4*a*	1.0494(7)	0.4671(6)	0.5428(7)	0.063(7)	0.091(9)	0.050(7)	0.017(7)	0.012(6)	–0.007(6)
C(13)	4*a*	1.1365(7)	0.4276(5)	0.5587(7)	0.055(7)	0.063(7)	0.056(7)	0.001(6)	0.004(5)	0.003(5)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(14)	4*a*	1.2137(9)	0.4480(7)	0.5316(9)	0.057(8)	0.078(9)	0.10(1)	0.010(7)	0.002(7)	0.024(7)
C(15)	4*a*	1.290(1)	0.4136(9)	0.540(1)	0.08(1)	0.12(1)	0.13(1)	0.01(1)	–0.002(9)	0.03(1)
C(16)	4*a*	1.293(1)	0.358(1)	0.578(1)	0.07(1)	0.16(2)	0.10(1)	0.04(1)	0.016(9)	0.00(1)
C(17)	4*a*	1.220(1)	0.3334(6)	0.6117(9)	0.17(2)	0.063(8)	0.08(1)	0.04(1)	–0.01(1)	0.022(7)
C(18)	4*a*	1.1404(8)	0.3684(6)	0.5996(7)	0.084(9)	0.081(9)	0.061(8)	–0.011(8)	0.003(6)	0.005(6)
C(19)	4*a*	0.3206(9)	0.6839(6)	0.4098(8)	0.082(8)	0.093(9)	0.060(8)	–0.004(8)	0.033(7)	–0.017(7)
C(20)	4*a*	0.4042(8)	0.6539(7)	0.4627(8)	0.055(8)	0.10(1)	0.064(8)	0.015(8)	0.023(6)	0.009(7)
C(21)	4*a*	0.480(1)	0.6917(7)	0.508(1)	0.11(1)	0.08(1)	0.10(1)	–0.014(9)	0.06(1)	–0.006(8)
C(22)	4*a*	0.5580(9)	0.655(1)	0.5567(9)	0.048(9)	0.37(3)	0.034(8)	0.00(2)	0.009(6)	–0.03(1)
C(23)	4*a*	0.544(2)	0.588(1)	0.550(2)	0.27(4)	0.16(2)	0.15(2)	0.14(3)	0.14(3)	0.09(2)
C(24)	4*a*	0.485(2)	0.553(2)	0.520(3)	0.21(3)	0.24(4)	0.19(3)	–0.04(3)	0.08(2)	0.01(3)
C(25)	4*a*	0.410(1)	0.5887(8)	0.472(1)	0.09(1)	0.10(1)	0.09(1)	0.020(9)	0.010(8)	0.014(8)
C(26)	4*a*	0.2464(8)	0.6893(6)	0.5455(8)	0.070(8)	0.090(9)	0.054(7)	–0.003(7)	0.011(6)	0.015(6)
C(27)	4*a*	0.1775(7)	0.7264(6)	0.5860(7)	0.061(7)	0.091(8)	0.045(7)	–0.011(6)	0.007(6)	0.015(6)
C(28)	4*a*	0.0405(8)	0.7956(5)	0.5308(8)	0.096(9)	0.078(8)	0.059(8)	–0.006(7)	0.042(7)	0.000(6)
C(29)	4*a*	–0.0166(7)	0.8195(6)	0.4424(7)	0.078(8)	0.100(9)	0.049(7)	0.006(7)	0.026(6)	0.017(6)
C(30)	4*a*	–0.0129(9)	0.8412(6)	0.2806(8)	0.10(1)	0.078(9)	0.044(8)	–0.024(8)	0.019(6)	0.001(6)
C(31)	4*a*	–0.0865(8)	0.8878(5)	0.2717(7)	0.067(8)	0.059(8)	0.049(7)	0.007(7)	–0.005(5)	0.001(5)
C(32)	4*a*	–0.067(1)	0.9521(6)	0.2642(9)	0.07(1)	0.056(9)	0.10(1)	–0.009(8)	0.005(7)	0.001(7)
C(33)	4*a*	–0.130(1)	0.9990(9)	0.255(1)	0.11(1)	0.10(1)	0.15(2)	–0.02(1)	0.03(1)	–0.01(1)
C(34)	4*a*	–0.219(1)	0.9809(8)	0.253(1)	0.17(2)	0.07(1)	0.08(1)	0.03(1)	0.01(1)	0.006(8)
C(35)	4*a*	–0.244(1)	0.9190(9)	0.2605(9)	0.09(1)	0.13(1)	0.068(9)	0.01(1)	0.016(7)	0.000(9)
C(36)	4*a*	–0.1755(9)	0.8723(6)	0.2696(7)	0.067(8)	0.074(8)	0.064(8)	0.000(7)	0.000(6)	0.008(6)

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