Crystal structure of bis[2-((2-aminocyclohexylamino)methyl)benzoato]-copper(II) trihydrate, $Cu(C_{14}H_{19}N_2O_2)_2 \cdot 3H_2O$

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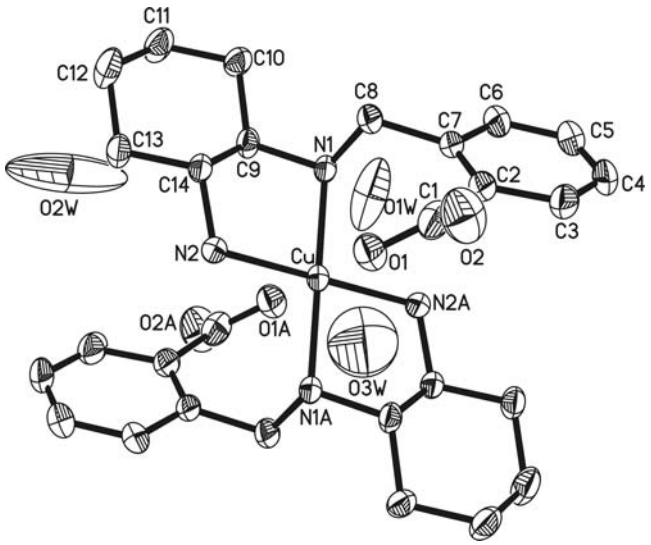

Abstract

$C_{28}H_{44}CuN_4O_7$, monoclinic, *C*12/*c*1 (no. 15), a = 21.796(2) Å, b = 13.4861(9) Å, c = 11.9078(6) Å, β = 107.474(6)°, V = 3338.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.063, $wR_{ref}(F^2)$ = 0.167, T = 293 K.

Source of material

A mixture of 2-formylbenzoic acid (0.03 g, 0.2 mmol), cyclohexane-1,2-diamine (0.023 g, 0.2 mmol) and methanol (15 mL) was stirred and refluxed for an hour. Then the mixture was cooled to room temperature and sodium borohydride (0.015 g, 0.4 mmol) was added. After stirring for an hour, methanol was evaporated and 15 mL water was added, and the mixture was sirred for another hour. Then $Cu(NO_3) \cdot 3H_2O$ (0.024 g, 0.1 mmol) and aqua ammonia was added to the mixture, and a blue precipitate was obtained. Keep on adding aqua ammonia drop by drop until the solution was clear. Suitable blue single crystals were obtained by slow evaporation of the ammonia solution at ambient temperature (yield 47 %).

Experimental details

H atoms on C atoms and N atoms were placed in calculated positions with d(C—H)= 0.93 - 0.98 Å, d(N—H) = 0.9 - 0.91 Å and U_{iso}(H) = 1.2 U_{eq}(C,N). The hydrogen atoms bound to O1W, O2W and O3W could not be located. Non-hydrogen atoms of the complexes were refined with anisotropic temperature parameters except that O3W were refined with isotropic temperature parameters. During refinement, we realized that, owing to inherently poor crystal quality, the $N(hkl)_{gt}/N(param)$ ratio is relatively low and $wR_{ref}(F^2)$ is relatively high. The refinement of occupancies for O1W, O2W and O3W could not be converged, so the occupancies for them were fixed at 0.5. A check of the structure by PLATON did not reveal additional water molecule.

Discussion

The Cu(II) cation is coordinated by four N atoms in the equatorial positions and two O atoms in the apical positions from two different 2-((2-aminocyclohexylamino)methyl)benzoate species in a distorted octahedral CuN_4O_2 manner according to the Jahn-Teller-effect. The bond lengths d(Cu—N) are 2.026, 2.050 Å and d(Cu—O) = 2.455 Å, respectively. The chelating bond angle ∠N2–Cu–N1 = 83.9(1)°, is smaller than 90°. Both carboxylate groups both adopt mono-dentate mode to coordinate Cu(II) cation. The discrete molecules are interlinked by the hydrogen bonds between the lattice water and N, O atoms of 2-((2-aminocyclohexylamino)methyl)benzoate to form a 3D supramolecular framework.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.12 × 0.17 × 0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.99 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	58.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7339, 3774
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1579
$N(param)_{refined}$:	191
Programs:	SHELXS-97, SHELXL-97 [1]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8*f*		0.6383	0.2421	0.3667	0.051
H(2A)	8*f*		0.7375	0.2672	0.6988	0.052
H(2B)	8*f*		0.7628	0.3609	0.6711	0.052
H(9)	8*f*		0.6212	0.2325	0.5378	0.052
H(10A)	8*f*		0.5569	0.4099	0.4434	0.066
H(10B)	8*f*		0.5288	0.3032	0.4083	0.066
H(14)	8*f*		0.6702	0.4262	0.5873	0.052
H(13A)	8*f*		0.6681	0.3976	0.7785	0.063
H(13B)	8*f*		0.6408	0.2903	0.7445	0.063
H(6)	8*f*		0.6033	0.3048	0.1342	0.088
H(8A)	8*f*		0.6698	0.4404	0.3918	0.066
H(8B)	8*f*		0.6042	0.4002	0.3090	0.066
H(11A)	8*f*		0.4865	0.3737	0.5513	0.084
H(11B)	8*f*		0.5236	0.2750	0.5981	0.084
H(12A)	8*f*		0.5554	0.3944	0.7451	0.087
H(12B)	8*f*		0.5736	0.4681	0.6584	0.087

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Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(3)	8*f*		0.8005	0.4336	0.1513	0.088
H(5)	8*f*		0.6425	0.2897	–0.0235	0.106
H(4)	8*f*		0.7406	0.3572	–0.0149	0.100
O(3W)	8*f*	0.50	0.9090(9)	0.531(1)	0.566(2)	0.214(7)

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	4*c*		¾	¼	½	0.0408(5)	0.0599(6)	0.0300(4)	0.0051(5)	0.0138(3)	0.0018(5)
N(1)	8*f*		0.6573(2)	0.2925(3)	0.4156(3)	0.040(2)	0.059(3)	0.031(2)	0.003(2)	0.015(2)	–0.001(2)
O(1)	8*f*		0.7890(2)	0.4117(3)	0.4557(3)	0.076(3)	0.071(3)	0.055(2)	0.003(2)	0.020(2)	0.009(2)
N(2)	8*f*		0.7333(2)	0.3133(3)	0.6424(3)	0.038(2)	0.055(3)	0.036(2)	0.006(2)	0.011(2)	–0.001(2)
C(9)	8*f*		0.6243(2)	0.3000(4)	0.5096(3)	0.041(3)	0.059(3)	0.035(2)	–0.008(3)	0.019(2)	–0.002(2)
C(10)	8*f*		0.5560(2)	0.3427(4)	0.4719(4)	0.036(3)	0.081(4)	0.049(3)	0.003(3)	0.014(2)	–0.008(3)
C(14)	8*f*		0.6678(2)	0.3574(4)	0.6123(3)	0.041(3)	0.056(3)	0.034(2)	0.002(3)	0.014(2)	–0.003(2)
C(7)	8*f*		0.6796(3)	0.3729(4)	0.2433(4)	0.057(4)	0.068(4)	0.042(3)	0.025(3)	0.025(3)	0.019(3)
C(13)	8*f*		0.6409(2)	0.3575(4)	0.7154(4)	0.052(3)	0.072(4)	0.038(2)	–0.006(3)	0.020(2)	–0.008(3)
O(2)	8*f*		0.8113(3)	0.5350(4)	0.3486(4)	0.120(4)	0.103(4)	0.102(3)	–0.035(3)	0.038(3)	0.015(3)
C(6)	8*f*		0.6439(3)	0.3295(5)	0.1398(4)	0.060(4)	0.120(6)	0.038(3)	0.020(4)	0.013(3)	0.010(3)
C(2)	8*f*		0.7390(3)	0.4107(4)	0.2502(4)	0.068(4)	0.068(4)	0.050(3)	0.024(3)	0.029(3)	0.021(3)
C(8)	8*f*		0.6495(3)	0.3852(4)	0.3422(4)	0.066(4)	0.061(4)	0.045(3)	0.018(3)	0.027(3)	0.018(3)
C(11)	8*f*		0.5286(3)	0.3428(5)	0.5750(4)	0.043(3)	0.109(5)	0.063(3)	–0.003(3)	0.025(3)	–0.018(3)
C(12)	8*f*		0.5726(3)	0.3987(5)	0.6790(5)	0.064(4)	0.102(5)	0.063(3)	–0.011(4)	0.035(3)	–0.028(3)
C(1)	8*f*		0.7828(3)	0.4564(5)	0.3598(5)	0.072(4)	0.069(5)	0.074(4)	0.000(4)	0.039(3)	0.000(3)
C(3)	8*f*		0.7611(3)	0.4057(5)	0.1488(5)	0.085(5)	0.080(5)	0.069(4)	0.027(4)	0.046(4)	0.027(3)
C(5)	8*f*		0.6668(4)	0.3217(6)	0.0445(5)	0.090(5)	0.135(7)	0.042(3)	0.035(5)	0.023(3)	0.018(3)
C(4)	8*f*		0.7254(4)	0.3612(6)	0.0501(5)	0.105(6)	0.114(6)	0.041(3)	0.042(5)	0.036(4)	0.018(3)
O(1W)	8*f*	0.50	0.6111(6)	0.093(1)	0.303(1)	0.18(1)	0.22(2)	0.16(1)	–0.16(1)	0.12(1)	–0.14(1)
O(2W)	8*f*	0.50	0.5657(7)	0.134(2)	0.769(3)	0.08(1)	0.30(3)	0.87(6)	0.01(1)	0.06(2)	0.37(4)

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