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Crystal structure of aqua(1,10-phenanthroline)(2-amino-1,4-benzenedicarboxylato)copper(II) dimethylformamide solvate, $Cu(H_2O)(C_{12}H_8N_2)(C_8H_5NO_4) \cdot (CH_3)_2NCHO$

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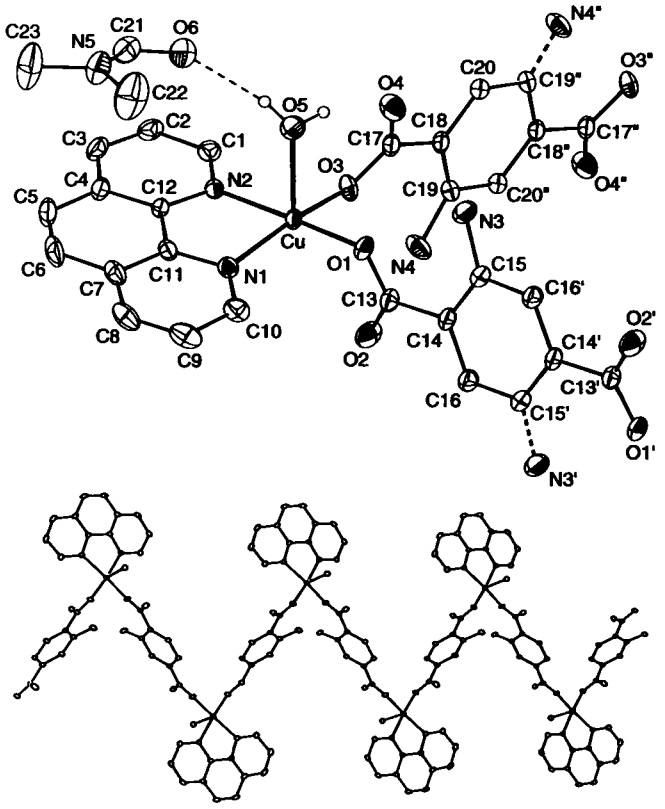

Abstract

$C_{23}H_{22}CuN_4O_6$, triclinic, $P\bar{1}$ (no. 2), $a = 8.9752(7)$ Å, $b = 10.3522(9)$ Å, $c = 12.017(1)$ Å, $\alpha = 95.275(1)°$, $\beta = 94.078(2)°$, $\gamma = 93.317(2)°$, $V = 1106.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.108$, $T = 298$ K.

Source of material

The title complex was synthesized by mixed solution method. $Cu(ClO_4)_2 \cdot 6H_2O$ (0.214 g, 0.58 mmol), 2-amino-1,4-benzenedicarboxylic acid (0.090 g, 0.5 mmol), and 1,10-phenanthroline (0.098 g, 0.5 mmol) were dissolved in 20 ml of *N,N'*-dimethylformamide. After three months, green crystals were obtained.

Experimental details

The methyl H atoms were allowed to be rotated to fit the electron density with d(C—H) = 0.96 Å and $U_{iso} = 1.5U_{eq}$(C); the other carbon-bound H atoms were generated geometrically (d(C—H$_{aromatic}$) = 0.93 Å, U_{iso}(H) = $1.2U_{eq}$(C)). These were included in the refinement in the riding model approximation. The water H atoms were located from difference Fourier maps and refined with restraints for O—H distances at 0.85(1) Å and with U_{iso}(H) = 0.05 Å^2. The structure has some disorder in the two amino groups which was treated as half occupancy for each amino group.

Discussion

The modification of 1,4-benzenedicarboxylates is valuable for the assembly of networks and the tuning of functional properties [1]. In this study, we chose 2-amino-1,4-benzenedicarboxylic acid (H_2abdc) as a building block to obtain one-dimensional coordination polymer of the title compound.

The crystal structure consists of a five-coordinated Cu(II) center in a square pyramidal CuN_2O_2+O chromophoric environment with the basal plane being formed by two nitrogen atoms of 1,10-phenanthroline and two oxygen atoms of two abdc^{2-} ligands. The coordination of copper ion is completed by one large apical Cu–O distance from the water molecule (figure, top). In our previous study of 1,4-benzenedicarboxylate complexes [2], a similar complex was reported, $[Cu(bdc)(phen)(H_2O)](H_2O)(DMF)$, in which the copper center adopts a perfect square pyramidal coordination. The bond lengths of Cu—O(carboxyl) and Cu—N are basically similar in both crystal structures, however, the bond length of Cu—O(aqua) is significantly longer in the title complex. Each carboxyl group of the abdc^{2-} ligand is coordinated as a bis(monodentate) mode, therefore the structure is a one-dimensional chain (figure, bottom). The separation of Cu···Cu bridged by abdc^{2-} ligand is 11.107 Å, which is slightly longer than that of the complex with the unsubstituted benzenedicarboxylato ligand. It is worth noting that there are four intermolecular hydrogen bonds among amino groups, coordination water and oxygen atoms of carboxylate anions. Hydrogen bonds between amino groups and uncoordinated carboxyl oxygen atoms provide the basis of the two-dimensional hydrogen-bonding architecture parallel to the a,b plane. Considering O···O–H and N–H···N bonds to the DMF molecule, a 3D network is formed.

Table 1. Data collection and handling.

Crystal:	green block, size 0.21 × 0.31 × 0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.36 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, φ/ω
$2\theta_{max}$:	53°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6280, 4469
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3969
$N(param)_{refined}$:	324
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-3 [5], WinGX [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3A)	2i	0.5	0.1603	−0.0751	0.8775	0.063
H(3B)	2i	0.5	0.2099	0.0383	0.8184	0.063
H(4A)	2i	0.5	0.3522	0.5983	0.9969	0.062
H(4B)	2i	0.5	0.3320	0.5053	0.8940	0.062
H(1)	2i		0.1461	0.5301	0.5945	0.044
H(2)	2i		0.1137	0.6426	0.4371	0.053
H(3)	2i		0.2471	0.5931	0.2847	0.056
H(5)	2i		0.4384	0.4486	0.1935	0.065
H(6)	2i		0.5946	0.2879	0.2070	0.070
H(8)	2i		0.7186	0.1216	0.3290	0.065
H(9)	2i		0.7412	0.0387	0.4989	0.067
H(10)	2i		0.5882	0.1048	0.6380	0.053
H(16)	2i		0.3170	−0.1619	1.0130	0.046
H(20)	2i		−0.1632	0.3494	0.8939	0.041
H(21)	2i		0.0021	0.3325	0.2385	0.070
H(22A)	2i		0.1359	0.0612	0.3319	0.173
H(22B)	2i		0.2557	0.0543	0.2430	0.173
H(22C)	2i		0.0968	−0.0170	0.2144	0.173
H(23A)	2i		0.1141	0.2836	0.0817	0.169
H(23B)	2i		0.0724	0.1366	0.0421	0.169
H(23C)	2i		0.2372	0.1824	0.0867	0.169
H(5A)	2i		0.066(3)	0.172(3)	0.621(2)	0.050
H(5B)	2i		0.076(3)	0.178(3)	0.516(2)	0.050
H(15)	2i	0.5	0.2763	−0.0101	0.8866	0.060
H(19)	2i	0.5	0.2432	0.5258	0.9450	0.060

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	2i		0.32320(3)	0.29133(3)	0.65716(2)	0.0322(2)	0.0368(2)	0.0215(2)	0.0082(1)	0.0066(1)	0.0097(1)
O(1)	2i		0.3585(2)	0.1631(2)	0.7603(1)	0.047(1)	0.048(1)	0.0304(9)	0.0035(8)	−0.0026(8)	0.0180(8)
O(2)	2i		0.5470(2)	0.2901(2)	0.8473(2)	0.064(1)	0.059(1)	0.060(1)	−0.017(1)	−0.016(1)	0.035(1)
O(3)	2i		0.2107(2)	0.3938(2)	0.7611(1)	0.048(1)	0.047(1)	0.0307(9)	0.0040(8)	0.0198(8)	0.0014(8)
O(4)	2i		0.0080(2)	0.2585(2)	0.7586(2)	0.052(1)	0.058(1)	0.043(1)	−0.005(1)	0.0141(9)	−0.013(1)
O(5)	2i		0.1218(2)	0.1496(2)	0.5701(2)	0.044(1)	0.050(1)	0.041(1)	0.0114(9)	0.0040(8)	0.0005(9)
O(6)	2i		0.0062(3)	0.2552(3)	0.3700(2)	0.067(2)	0.088(2)	0.051(1)	0.006(1)	0.008(1)	0.007(1)
N(1)	2i		0.4791(2)	0.2278(2)	0.5549(2)	0.032(1)	0.034(1)	0.034(1)	0.0060(8)	0.0066(8)	0.0055(8)
N(2)	2i		0.2915(2)	0.4127(2)	0.5369(2)	0.029(1)	0.034(1)	0.028(1)	0.0050(8)	0.0049(8)	0.0070(8)
N(3)	2i	0.5	0.2276(5)	−0.0158(5)	0.8671(4)	0.046(3)	0.065(3)	0.045(3)	−0.011(2)	−0.012(2)	0.021(2)
N(4)	2i	0.5	0.2957(5)	0.5446(5)	0.9511(4)	0.038(2)	0.071(3)	0.043(3)	−0.013(2)	0.018(2)	−0.017(2)
N(5)	2i		0.0977(3)	0.1730(3)	0.2099(2)	0.089(2)	0.060(2)	0.047(2)	0.020(2)	0.008(1)	0.012(1)
C(1)	2i		0.1994(3)	0.5081(2)	0.5327(2)	0.033(1)	0.037(1)	0.042(1)	0.006(1)	0.003(1)	0.008(1)
C(2)	2i		0.1800(3)	0.5769(3)	0.4380(2)	0.039(1)	0.042(2)	0.053(2)	0.007(1)	−0.008(1)	0.018(1)
C(3)	2i		0.2587(3)	0.5470(3)	0.3474(2)	0.051(2)	0.052(2)	0.038(1)	−0.005(1)	−0.011(1)	0.022(1)
C(4)	2i		0.3572(3)	0.4469(3)	0.3484(2)	0.043(1)	0.049(2)	0.026(1)	−0.008(1)	−0.002(1)	0.011(1)
C(5)	2i		0.4459(4)	0.4073(3)	0.2591(2)	0.065(2)	0.071(2)	0.027(1)	−0.009(2)	0.010(1)	0.013(1)
C(6)	2i		0.5397(4)	0.3120(3)	0.2674(2)	0.068(2)	0.075(2)	0.032(1)	−0.007(2)	0.027(1)	−0.001(1)
C(7)	2i		0.5580(3)	0.2458(3)	0.3676(2)	0.042(2)	0.048(2)	0.039(1)	−0.004(1)	0.016(1)	−0.006(1)
C(8)	2i		0.6596(3)	0.1503(3)	0.3858(3)	0.047(2)	0.050(2)	0.065(2)	0.002(1)	0.029(1)	−0.011(2)
C(9)	2i		0.6717(3)	0.0999(3)	0.4859(3)	0.041(2)	0.041(2)	0.088(2)	0.016(1)	0.017(2)	0.003(2)
C(10)	2i		0.5792(3)	0.1404(3)	0.5698(3)	0.040(1)	0.039(1)	0.057(2)	0.010(1)	0.008(1)	0.011(1)
C(11)	2i		0.4706(3)	0.2815(2)	0.4560(2)	0.031(1)	0.036(1)	0.028(1)	−0.002(1)	0.0076(9)	0.001(1)
C(12)	2i		0.3695(2)	0.3822(2)	0.4465(2)	0.030(1)	0.037(1)	0.022(1)	−0.0022(9)	0.0010(9)	0.0057(9)
C(13)	2i		0.4620(3)	0.1912(3)	0.8392(2)	0.042(1)	0.047(2)	0.028(1)	0.007(1)	0.004(1)	0.014(1)
C(14)	2i		0.4785(3)	0.0914(2)	0.9219(2)	0.041(1)	0.038(1)	0.023(1)	0.004(1)	0.0014(9)	0.010(1)
C(15)	2i		0.3675(3)	−0.0072(3)	0.9303(2)	0.038(1)	0.044(1)	0.028(1)	0.002(1)	−0.003(1)	0.009(1)
C(16)	2i		0.3910(3)	−0.0965(3)	1.0078(2)	0.040(1)	0.043(1)	0.033(1)	−0.003(1)	−0.001(1)	0.013(1)
C(17)	2i		0.0892(3)	0.3524(3)	0.8002(2)	0.039(1)	0.044(2)	0.024(1)	0.012(1)	0.008(1)	0.010(1)
C(18)	2i		0.0470(3)	0.4312(2)	0.9038(2)	0.035(1)	0.042(1)	0.022(1)	0.008(1)	0.0067(9)	0.008(1)
C(19)	2i		0.1473(3)	0.5219(3)	0.9692(2)	0.033(1)	0.050(2)	0.028(1)	0.003(1)	0.009(1)	0.008(1)
C(20)	2i		−0.0975(3)	0.4106(2)	0.9366(2)	0.032(1)	0.043(1)	0.027(1)	0.001(1)	0.0030(9)	0.006(1)
C(21)	2i		0.0320(4)	0.2599(3)	0.2723(3)	0.061(2)	0.059(2)	0.055(2)	0.005(2)	−0.005(2)	0.011(2)
C(22)	2i		0.1509(7)	0.0584(5)	0.2534(4)	0.183(5)	0.080(3)	0.094(3)	0.057(3)	0.019(3)	0.028(3)
C(23)	2i		0.1335(7)	0.1959(5)	0.0951(3)	0.177(5)	0.121(4)	0.052(2)	0.048(4)	0.033(3)	0.023(2)

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