Crystal structure of diaqua-bis(pyridine-2,6-dicarboxylato-*O,N,O'*)-(μ₂-pyrazino)dicopper(II) dihydrate, [Cu₂(C₄H₄N₂)(C₇H₃NO₄)₂(H₂O)₂] · 2H₂O

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Abstract

C₁₈H₁₈Cu₂N₄O₁₂, monoclinic, *P*12₁/*n*1 (no. 14), *a* = 5.808(1) Å, *b* = 15.541(3) Å, *c* = 11.962(3) Å, *β* = 92.79(3)°, *V* = 1078.3 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.028, *wR*_{ref}(*F*²) = 0.079, *T* = 293 K.

Source of material

The blue needle-shaped single crystals of the title compound were obtained with the sol gel method. Hereby a solution of 10 ml copper nitrate (0.5 M) was mixed with the same volume of sodium metasilicate (1.06 g/ml, pH = 6). After the gelling process has finished, a solution containing 0.5 M pyrazine and 0.2 M sodium pyridine-2,6-dicarboxylate (pH = 10) was placed over the gel.

Experimental details

During the structure refinement, H atoms bound to the water molecules O5 and O6 were localized directly from the difference Fourier synthesis and refined isotropically. The remaining H atoms (pyrazine and pyridine-2,6-dicarboxylate) are geometrically located as idealized aromatic C–H groups using a riding model.

Discussion

The dipicolinate ion is an excellent tridentate ligand. Various structures of transition metal complexes containing pyridine-2,6-dicarboxylate and aromatic *N*-ligands have been published [1–3]. In the crystal structure of diaqua-bis(pyridine-2,6-dicarboxylato-*O,N,O'*)-(μ₂-pyrazino)copper(II) dihydrate, the coordination polyhedron is best described as a distorted pyramid. Each cop-

per atom is *trans*-connected to the tridentate picolinate ion (*d*(Cu1–O1) = 2.034 Å, *d*(Cu1–O3) = 2.014 Å, *d*(Cu1–N1) = 1.894 Å) and to the pyrazine ligand (*d*(Cu1–N2) = 1.970 Å, ∠N1–Cu1–N2 = 167.33°). The copper ion obtains the coordination number CN = 5 by binding a water molecule (*d*(Cu1–O5) = 2.215 Å), which forms the top of the pyramid (∠O5–Cu1–N1 = 95.28°, ∠O5–Cu1–N2 = 97.34°).

Due to the pyrazine molecule as a bridging ligand, the structure can also be described as a dinuclear complex, including two pyridine-2,6-dicarboxylic units, two copper atoms, one pyrazine and two water ligands. Regarding the unit cell, the obtained units are bonded to each other with a complex framework of hydrogen bonds between the water molecules and the carboxylic O atoms, which are not coordinated to the copper ion.

Table 1. Data collection and handling.

Crystal:	blue needle fragment, size 0.12 × 0.27 × 0.35 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
<i>μ</i> :	20.41 cm ^{−1}
Diffractometer, scan mode:	Stoe IPDS, <i>φ</i>
2 <i>θ</i> _{max} :	51.8°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	10375, 1988
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 <i>σ</i> (<i>I</i> _{obs}), 1633
<i>N</i> (<i>param</i>) _{refined} :	167
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4)	4 <i>e</i>	0.6673	1.0614	0.9342	0.036
H(5)	4 <i>e</i>	1.1398	0.8843	0.9110	0.036
H(3)	4 <i>e</i>	0.1452	0.9394	0.4726	0.033
H(1)	4 <i>e</i>	0.6615	0.7725	0.4193	0.032
H(2)	4 <i>e</i>	0.3256	0.8423	0.3562	0.033

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(9)	4 <i>e</i>	0.0972	0.1334	0.7772	0.06(1)
H(8)	4 <i>e</i>	0.2149	0.1982	0.8060	0.06(1)
H(6)	4 <i>e</i>	0.4931	0.7687	0.8223	0.06(1)
H(7)	4 <i>e</i>	0.5251	0.7884	0.9205	0.07(2)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu(1)	4 <i>e</i>	0.71037(5)	0.91560(2)	0.77705(3)	0.0225(2)	0.0272(2)	0.0174(2)	0.0040(1)	−0.0063(1)	−0.0048(1)
O(3)	4 <i>e</i>	0.4453(3)	0.9992(1)	0.7737(2)	0.0313(9)	0.032(1)	0.024(1)	0.0076(8)	−0.0109(8)	−0.0065(8)
O(1)	4 <i>e</i>	0.9463(3)	0.8286(1)	0.7274(2)	0.0240(9)	0.037(1)	0.021(1)	0.0058(7)	−0.0057(8)	−0.0060(8)
O(2)	4 <i>e</i>	1.0088(3)	0.7365(1)	0.5889(2)	0.036(1)	0.040(1)	0.027(1)	0.0138(9)	−0.0009(9)	−0.0061(8)
O(4)	4 <i>e</i>	0.1152(3)	1.0270(1)	0.6760(2)	0.033(1)	0.039(1)	0.039(1)	0.0153(8)	−0.0117(9)	−0.0078(9)
O(5)	4 <i>e</i>	0.5233(3)	0.8157(1)	0.8685(2)	0.043(1)	0.034(1)	0.029(1)	−0.0054(8)	0.005(1)	0.0072(9)
O(6)	4 <i>e</i>	0.0769(4)	0.1871(1)	0.7844(2)	0.039(1)	0.036(1)	0.046(2)	0.0055(9)	−0.007(1)	−0.0058(9)
N(1)	4 <i>e</i>	0.5754(3)	0.8875(1)	0.6344(2)	0.020(1)	0.023(1)	0.020(1)	−0.0009(8)	−0.0020(9)	0.0013(8)
N(2)	4 <i>e</i>	0.8806(3)	0.9661(1)	0.9076(2)	0.021(1)	0.027(1)	0.018(1)	0.0004(8)	−0.0029(9)	−0.0036(8)
C(6)	4 <i>e</i>	0.3798(4)	0.9276(2)	0.6005(2)	0.024(1)	0.023(1)	0.019(2)	−0.0004(9)	−0.003(1)	0.0039(9)
C(2)	4 <i>e</i>	0.6804(4)	0.8301(1)	0.5712(2)	0.022(1)	0.023(1)	0.017(1)	−0.0040(9)	0.001(1)	−0.0002(9)
C(8)	4 <i>e</i>	0.8034(4)	1.0352(2)	0.9606(2)	0.024(1)	0.035(2)	0.031(2)	0.008(1)	−0.011(1)	−0.010(1)
C(9)	4 <i>e</i>	1.0798(5)	0.9317(2)	0.9471(3)	0.028(1)	0.031(1)	0.031(2)	0.009(1)	−0.006(1)	−0.011(1)
C(5)	4 <i>e</i>	0.2809(4)	0.9119(2)	0.4968(2)	0.023(1)	0.032(1)	0.026(2)	−0.002(1)	−0.006(1)	0.003(1)
C(3)	4 <i>e</i>	0.5896(4)	0.8118(2)	0.4648(2)	0.027(1)	0.031(1)	0.022(2)	−0.002(1)	0.002(1)	−0.005(1)
C(4)	4 <i>e</i>	0.3889(4)	0.8534(2)	0.4277(2)	0.029(1)	0.038(1)	0.015(1)	−0.009(1)	−0.006(1)	−0.001(1)
C(1)	4 <i>e</i>	0.8968(4)	0.7943(2)	0.6326(2)	0.022(1)	0.027(1)	0.021(2)	0.000(1)	0.000(1)	−0.001(1)
C(7)	4 <i>e</i>	0.3031(4)	0.9899(2)	0.6899(2)	0.027(1)	0.022(1)	0.024(2)	0.001(1)	−0.003(1)	0.001(1)

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