

A new packing variant of catena-poly[[aquachlorocopper(II)]- μ -pyrazine-2-carboxylato-O,N:N']

 Karen J. Nordell,^{a*} Dana S. Kass^a and Mark D. Smith^b
^aDepartment of Chemistry, Lawrence University, Appleton, WI 54912, USA, and

^bDepartment of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

Correspondence e-mail: karen.nordell@lawrence.edu

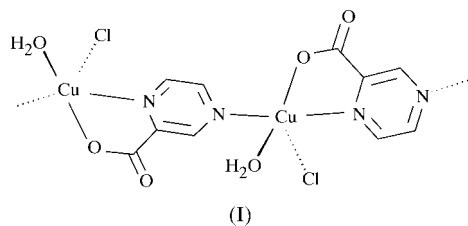
Received 1 August 2001

Accepted 7 September 2001

Single crystals of the title coordination polymer, [CuCl(C₅H₃N₂O₂)(H₂O)], have been prepared by hydrothermal synthesis. The compound is composed of infinite one-dimensional chains of pseudo-square-pyramidal Cu^{II} ions connected *via* pyrazine-2-carboxylate ligands. A network of O—H...O hydrogen bonding between adjacent chains is responsible for a bilayer structure different from the previously reported polymorph.

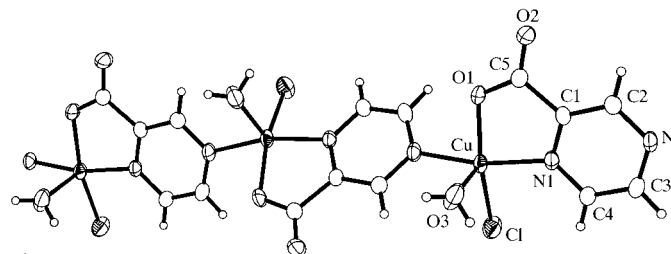
Comment

Pyrazine-2-carboxylate (hereinafter pyzca) complexes of copper(II) (Klein *et al.*, 1982) have recently been used to construct several novel mixed-metal and mixed-valent coordination polymers (Dong *et al.*, 2000; Zheng *et al.*, 2000). The attractiveness of this complex as a 'metal-containing building block' for the construction of novel framework materials of varying dimensionality lies in its donor-acceptor versatility. Chelation of the Cu^{II} center by two pyrazine-2-carboxylate ligands leaves two *para*-N-donors and two free carboxylate O atoms available for intermolecular bonding and supramolecular interactions. Since this complex often forms as a diaqua complex, structural diversity through hydrogen-bonding interactions is also possible. Investigation of the hydrothermal reactivity of [Cu(pyzca)₂] with various metal salts has led to the formation of a new polymorph of [CuCl(pyzca)(H₂O)], (I), the structure of which is reported here.



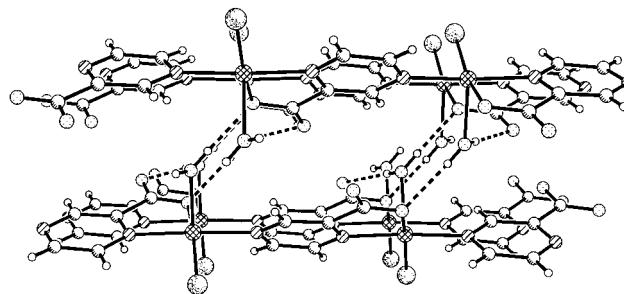
The structure of (I) consists of one-dimensional chains of Cu^{II} centers connected through pyzca ligands (Fig. 1). The Cu²⁺ ion resides in a pseudo-square-pyramidal coordination environment. An O and an N atom from the chelating end of a

pyzca ligand, a *para* N atom from a symmetry-equivalent pyzca ligand (symmetry code: $x, -y, z - \frac{1}{2}$) and a Cl ligand form the base of the pyramid. A water molecule occupies the apical site. The distortion from ideal square-pyramidal geometry is due primarily to the larger size of the Cl ligand.


Figure 1

A view of (I) showing the one-dimensional chains and the atom-numbering scheme in one repeat unit. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Compound (I) is a polymorph of the structure reported by Goher *et al.* (1998). The central structural unit of both compounds, *viz.* the one-dimensional chains, is virtually identical. The two structures differ in the pattern of hydrogen bonding linking the chains. In (I), the chains assemble into bilayers parallel to the crystallographic *bc* plane. The water ligands in (I) point toward the bilayer interior and form a hydrogen-bonding network involving an unchelated carboxylate O atom (O3—H3WA...O2) and a carboxylate O atom bound to Cu (O3—H3WB...O1) (Table 2). Each water molecule is linked to two neighboring chains in this fashion. The Cl ligands protrude outward from the bilayers, which then stack in a centrosymmetric fashion along [001] (Fig. 2).


Figure 2

A view of the packing of the double layers in (I) along [010]. Intralayer hydrogen bonds are shown as dashed lines.

The structure reported by Goher *et al.* (1998) was crystallized in low (15%) yield by the ambient-temperature evaporation of a 2:1 ethanol-water solution. Due to the non-centrosymmetric stacking of individual chains, each water ligand forms hydrogen bonds to two neighboring chains through a Cl ligand and an unchelated carboxylate O atom of a pyzca ligand, rather than through an exclusively O—H...O network, as in (I). Interestingly, although much harsher hydrothermal reaction conditions in pure water produced (I) rather than the previous structure, (I) is in fact isostructural with the azide analog [Cu^{II}(N₃)(pyrazine-2-carboxylato)(H₂O)], also obtained by Goher *et al.* (1998) by evaporation at room temperature.

Experimental

The title compound was prepared by the hydrothermal reaction of Cu^{II}(pyrazine-2-carboxylate)₂ (0.0276 g, 0.1 mmol) with CuCl₂·2H₂O (0.0275 g, 0.2 mmol) in water (0.8 ml) in an evacuated sealed Pyrex tube. The mixture was heated to 403 K at 1 K min⁻¹ and held at that temperature for 24 h before cooling slowly (0.5 K min⁻¹) to room temperature. The reaction yielded abundant dark-blue-green crystals of (I).

Crystal data

[CuCl(C ₅ H ₃ N ₂ O ₂)(H ₂ O)]	<i>D</i> _x = 2.111 Mg m ⁻³
<i>M</i> _r = 240.10	Mo <i>K</i> α radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 3228 reflections
<i>a</i> = 18.8435 (17) Å	<i>θ</i> = 3.2–26.3°
<i>b</i> = 6.2038 (6) Å	<i>μ</i> = 3.21 mm ⁻¹
<i>c</i> = 13.4129 (12) Å	<i>T</i> = 293 (2) K
<i>β</i> = 105.534 (2)°	Fragment, blue green
<i>V</i> = 1510.7 (2) Å ³	0.30 × 0.22 × 0.16 mm
<i>Z</i> = 8	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1547 independent reflections
<i>ω</i> scans	1323 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1999)	<i>R</i> _{int} = 0.025
<i>T</i> _{min} = 0.449, <i>T</i> _{max} = 0.599	<i>θ</i> _{max} = 26.4°
4831 measured reflections	<i>h</i> = -23 → 22
	<i>k</i> = -7 → 7
	<i>l</i> = -16 → 16

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.025	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0358 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.063	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.00	(Δ/σ) _{max} < 0.001
1547 reflections	Δρ _{max} = 0.42 e Å ⁻³
117 parameters	Δρ _{min} = -0.41 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—O1	1.9762 (17)	Cu—Cl	2.2245 (7)
Cu—N1	2.0095 (19)	Cu—O3	2.192 (2)
Cu—N2 ⁱ	2.0151 (19)		
O1—Cu—N1	81.81 (7)	N2 ⁱ —Cu—O3	96.06 (8)
O1—Cu—N2 ⁱ	88.54 (8)	O1—Cu—Cl	164.09 (6)
N1—Cu—N2 ⁱ	167.67 (9)	N1—Cu—Cl	95.19 (6)
O1—Cu—O3	91.54 (9)	N2 ⁱ —Cu—Cl	92.00 (6)
N1—Cu—O3	91.87 (8)	O3—Cu—Cl	104.20 (7)

Symmetry code: (i) *x*, 1 - *y*, *z* - ½.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3WA...O2 ⁱⁱ	0.79 (2)	1.98 (2)	2.752 (3)	166 (3)
O3—H3WB...O1 ⁱⁱⁱ	0.79 (2)	2.03 (2)	2.821 (3)	174 (3)

Symmetry codes: (ii) *x*, 1 + *y*, *z*; (iii) ½ - *x*, ½ + *y*, ½ - *z*.

All H atoms could be located in the Fourier difference maps. Those bound to C atoms were placed in calculated positions (C—H = 0.93 Å) and given *U*_{iso} values 1.2 times those of the parent C atom. Water H atoms were refined isotropically, subject to a distance restraint of O—H = 0.8 Å.

Data collection: SMART-NT (Bruker, 1999); cell refinement: SAINT-Plus-NT (Bruker, 1999); data reduction: SAINT-Plus-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

Funding was provided by Lawrence University and by the National Science Foundation through grant DMR:9873570. The Bruker SMART APEX diffractometer was purchased using funds provided by the NSF IMR Program through grant DMR:9975623.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1345). Services for accessing these data are described at the back of the journal.

References

Bruker (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (1999). SMART-NT (Version 5.624), SAINT-Plus-NT (Version 6.02a) and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Dong, Y.-B., Smith, M. D. & zur Loye, H.-C. (2000). *Solid State Sci.* **2**, 335–341.
 Goher, M. A. S., Abu-Youssef, M. A. M. & Mautner, F. A. (1998). *Polyhedron*, **17**, 3305–3314.
 Klein, C. L., Majeste, R. J., Trefonas, L. M. & O'Connor, C. J. (1982). *Inorg. Chem.* **21**, 1891–1897.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Zheng, L.-M., Wang, X. & Jacobson, A. J. (2000). *J. Solid State Chem.* **152**, 174–201.