

Poly[copper(II)- μ -pyrazine- μ_3 -squarato]

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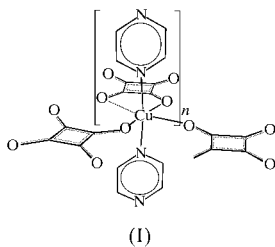
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In the structure of the title compound, $[\text{Cu}(\text{C}_4\text{O}_4)(\text{C}_4\text{H}_4\text{N}_2)]_n$, each copper cation is surrounded by three squarate (3,4-dihydroxy-3-cyclobutene-1,2-dioate) anions and two pyrazine ligands, all of which are located in special positions. The copper cation and all atoms of the squarate anion are located on a mirror plane, whereas the pyrazine ligand is located around a mirror plane which is perpendicular to the ring plane. The cations are connected *via* the squarate anions and the pyrazine ligands, forming sheets parallel to (001).

Comment

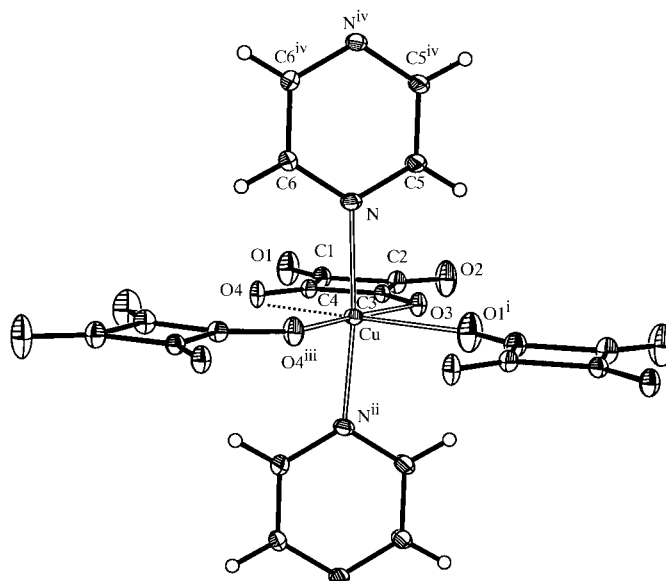
The structure determination of the title compound, (I), is part of a project on the synthesis and characterization of new coordination polymers based on squaric acid derivatives and aromatic diamines using solvothermal methods. There are some copper(II) squarate diamine compounds reported in the literature, but most of them contain additional water molecules coordinated to the copper cations (Bernardinelli *et al.*, 1989; Castro *et al.*, 1990, 1995; Solans *et al.*, 1990; Yaghi *et al.*, 1995).



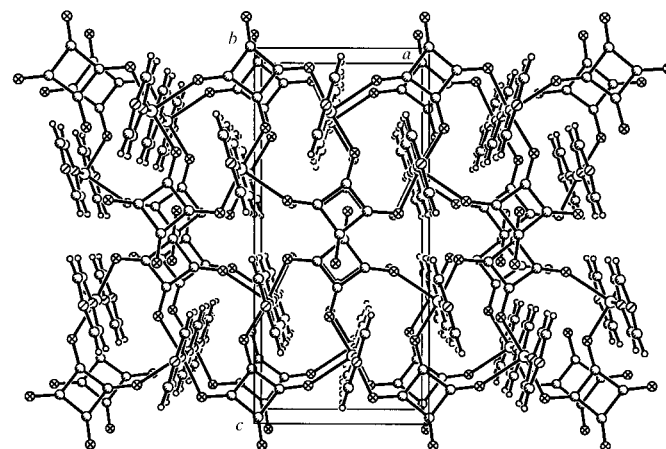
In the crystal structure of (I), the copper cations are coordinated by three O atoms of three squarate anions and two N atoms of two pyrazine molecules within a slightly distorted tetragonal pyramid, with one O atom at the apex of the pyramid (Figs. 1 and 2). The Cu—O distances to the O atoms within the quadratic plane are similar, whereas the Cu—O distance to the apical O atom, O1, is elongated. The angles around the copper cation within the quadratic plane deviate only slightly from ideal values, whereas larger deviations are found for the angles in which the O1 atom is involved. There is

one additional, but extremely long, Cu—O contact to O4 of 2.732 (3) Å, which should represent only a very weak interaction. However, if this contact is considered in the Cu coordination, the coordination polyhedron around the copper cation is a slightly distorted octahedron.

The copper cations are connected *via* the pyrazine ligands, which sit across mirror planes, forming nearly linear chains in the direction of the crystallographic *b* axis. The copper cation is located in the plane of the six-membered ring and the C5—N—Cu and C6—N—Cu angles are about 120°, which shows that the cations are oriented in the direction of the nitrogen lone pair. In the squarate anion, only three of the four O atoms are involved in copper coordination. Each anion is surrounded by three copper cations and all lie on the one mirror plane. From this arrangement, double chains are


Figure 1

View of the copper coordination with labelling and displacement ellipsoids drawn at the 50% probability level (the long Cu...O contact is shown with dotted lines). [Symmetry codes: (i) $x - 1, y, z$; (ii) $x, -y + \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (iv) $x, \frac{1}{2} - y, z$.]


Figure 2

Packing diagram of (I) viewed along the *b* axis.

formed in the direction of the crystallographic *a* axis. Within these chains, the copper cations are located in the direction of the oxygen lone pairs. For the O1 atom, which participates in the elongated Cu—O bond, no preferred orientation of the cations in the direction of the oxygen lone pairs is found, which indicates that this must be a weak interaction.

The connection of the copper cations *via* the pyrazine ligands and the squarate anions leads to sheets parallel to (001). No pronounced interactions could be found between the sheets.

Experimental

Squaric acid (Acros), copper(I) oxide and pyrazine (Acros) (molar ratio 1:1:1) were reacted in water (10 ml) in teflon-lined steel autoclaves at 400 K for 7 d and afterwards cooled at 3 K min⁻¹. The product was filtered off and washed with deionized water. The precipitate consisted of yellow–green needles of the title compound.

Crystal data

[Cu(C ₄ O ₄)(C ₄ H ₄ N ₂)]	Mo <i>K</i> α radiation
<i>M_r</i> = 255.67	Cell parameters from 8000 reflections
Orthorhombic, <i>Pnma</i>	<i>θ</i> = 3–30°
<i>a</i> = 7.3003 (4) Å	<i>μ</i> = 2.805 mm ⁻¹
<i>b</i> = 6.8114 (4) Å	<i>T</i> = 293 (2) K
<i>c</i> = 15.6135 (11) Å	Needle, orange
<i>V</i> = 776.39 (8) Å ³	0.10 × 0.04 × 0.04 mm
<i>Z</i> = 4	
<i>D_x</i> = 2.187 Mg m ⁻³	

Data collection

Stoe Imaging Plate Diffraction System	<i>R</i> _{int} = 0.030
<i>φ</i> scans	<i>θ</i> _{max} = 30.41°
8519 measured reflections	<i>h</i> = -9 → 10
1231 independent reflections	<i>k</i> = -9 → 9
1119 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = -22 → 22

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 1.4395P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.064	$\Delta\rho_{\text{max}} = 1.54 \text{ e } \text{Å}^{-3}$
1231 reflections	$\Delta\rho_{\text{min}} = -0.74 \text{ e } \text{Å}^{-3}$
82 parameters	
H-atom parameters constrained	

The H atoms were positioned with idealized geometry and refined using a riding model. In the difference map, the maximum electron-density peak is located 1.07 Å from the Cu atom. This peak cannot be

Table 1

Selected geometric parameters (Å, °).

Cu—O4 ⁱ	1.935 (2)	Cu—N	2.022 (2)
Cu—O3	1.976 (2)	Cu—O1 ⁱⁱⁱ	2.290 (3)
Cu—N ⁱⁱⁱ	2.022 (2)		
O4 ⁱ —Cu—O3	174.48 (10)	O4 ⁱ —Cu—O1 ⁱⁱⁱ	92.59 (11)
O4 ⁱ —Cu—N	90.65 (5)	O3—Cu—O1 ⁱⁱⁱ	81.89 (10)
O3—Cu—N	89.74 (5)	N—Cu—O1 ⁱⁱⁱ	93.94 (6)
N ⁱⁱⁱ —Cu—N	171.96 (12)		

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (ii) $x, \frac{3}{2} - y, z$; (iii) $x - 1, y, z$.

attributed to absorption effects and always appears even if data from different crystals are used. Careful inspection of reciprocal space plots shows clearly that both the selected cell and the selected symmetry are correct.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1113). Services for accessing these data are described at the back of the journal.

References

- Bernardinelli, G., Deguenon, D., Soules, R. & Castan, P. (1989). *Can. J. Chem.* **67**, 1158–1165.
- Castro, I., Faus, J., Julve, M., Verdaguer, M., Monge, A. & Gutierrez-Puebla, E. (1990). *Inorg. Chim. Acta*, **170**, 251–257.
- Castro, I., Sletten, J., Glaerum, L. K., Cano, J., Lloret, F., Faus, J. & Julve, M. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3207–3213.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1990). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Solans, X., Aguiló, M., Gleizes, A., Faus, J., Julve, M. & Verdaguer, M. (1990). *Inorg. Chem.* **29**, 775–784.
- Stoe & Cie (1998). *IPDS Program Package*. Stoe & Cie, Darmstadt, Germany.
- Yaghi, O. M., Guangming, L. & Groy, T. L. (1995). *J. Solid State Chem.* **117**, 256–260.