metal-organic compounds

catena-Poly[[[diaquabis(pyridine-4-carboxamide-*κN*)copper(II)]-*μ₂*-squarato-*κO¹:O³*] dihydrate]

Ibrahim Uçar,* Ahmet Bulut and Orhan Büyükgüngör

Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayís University, TR-55139 Kurupelit Samsun, Turkey
Correspondence e-mail: iucar@omu.edu.tr

The asymmetric unit of the title compound, $\{[Cu(C_4O_4)(C_6H_6N_2O)_2(H_2O)_2]\cdot 2H_2O\}_n$, consists of one pyridine-4-carboxamide (isonicotinamide or ina) ligand, one-half of a squarate dianion, a coordinated aqua ligand and a solvent water molecule. Both the Cu^{II} and the squarate ions are located on inversion centers. The Cu^{II} ions are octahedrally surrounded by four O atoms of two water molecules and two squarate anions, and by two N atoms of the isonicotinamide ligands. The crystal structure contains chains of squarate-1,3-bridged Cu^{II} ions. These chains are held together by N—H···O and O—H···O intermolecular hydrogen-bond interactions, forming an extensive three-dimensional network.

Comment

The coordination chemistry of the squarate (Sq) anion has attracted increasing attention because it gives rise to a wide variety of complexes and adopts mono- or polydentate coordination modes when acting as a ligand towards first-row transition metal ions. The squarate anion does not behave like a chelating ligand but rather like a bridge between two or more metal atoms, as a singly or multiply monodentate ligand (Bernardinelli *et al.*, 1989; Castro *et al.*, 1999; Crispini *et al.*, 2000). In all the cases reported so far, each coordination site of squaric acid is coordinated to a different metal atom, and either a one-dimensional chain or a three-dimensional polymer is obtained (Hilberts *et al.*, 1996; Greve & Nather, 2002; Greve *et al.*, 2003). The exchange interactions, between transition metal ions through extended bridging squarate groups, in such polymer complexes have been studied by both inorganic and bioinorganic chemists in recent years (Van Ooijen *et al.*, 1978; Reinprecht *et al.*, 1980; Yufit *et al.*, 1999; Trombe *et al.*, 2002). We have also used isonicotinamide (ina) as a second ligand; this pyridine derivative, with an amide group (–CONH₂) in the γ-position, possesses strong antitubercular, antipyretic, fibrinolytic and antibacterial properties. Because of their strong pharmacological effects, mixed salts of isonicotinamide find extensive use as drugs in various

biological and medicinal processes (Ahuja & Prasad, 1976). Isonicotinamide is also of interest in inorganic chemistry, since the ligand has three donor sites, *viz.* (i) the pyridine ring N atom, as in the title complex, (ii) the amine N atom and (iii) the carbonyl O atom, acting as a monodentate ligand. To our knowledge, there are only a few reports of complexes of this ligand with transition metals (Baum *et al.*, 2002). Despite the structural and magnetic interest, only a few crystal structures containing copper(II) squarate and geometrically demanding N-atom donor ligands have been investigated (Solans *et al.*, 1990; Graf *et al.*, 1997; Bernardinelli *et al.*, 1989). In our ongoing research on squaric acid, we have synthesized some mixed ligand–copper(II) complexes of squaric acid and their structures have been reported. In these compounds, squaric acid behaves as a counter-anion or monodentate ligand (Uçar *et al.*, 2004; Bulut *et al.*, 2004), while in the title compound, (I), squaric acid acts as a bridging ligand between the copper(II) ions.
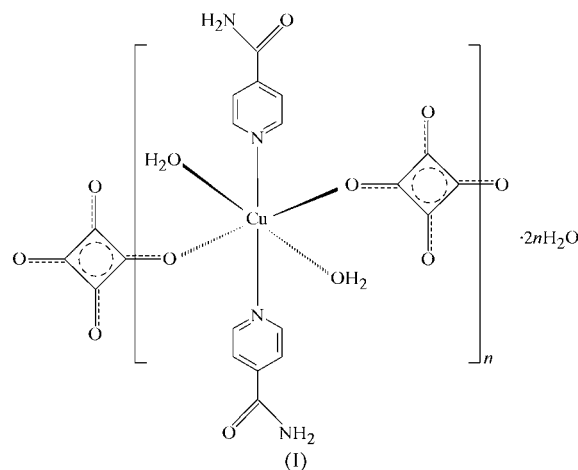
The coordination polyhedron of copper in (I) is best described as a distorted octahedron (Fig. 1). Each Cu atom is *trans*-connected to two molecules of ina, two aqua ligands and two squarate O atoms (Table 1). In the title complex, there are also two solvent water molecules. The metal atoms are connected by the squarate dianions *via* μ-*O:O* coordination, forming 'zigzag' chains in the direction of the crystallographic *b* axis (Fig. 2). Only one O atom of each squarate dianion is involved in metal coordination, and the mode of direct coordination in which two neighboring O atoms are involved is not found. The Cu atoms are located nearly in the molecular plane of the squarate dianions and are oriented in the direction of the oxygen lone pair.

In the title complex, the Cu1—O1 bond is considerably shorter than the Cu1—O4 bond because of the electronegative character of the $C_4O_4^{2-}$ ligand. The Cu1—O1 bond distance is nearly identical to that observed in $[Cu_2(C_4O_4)(phen)_4](CF_3SO_3)_2\cdot 3H_2O$ [1.995 (7) Å; phen is 1,10-phenanthroline; Castro *et al.*, 1999], whereas this bond is longer that in $[Cu(C_4O_4)(phen)(H_2O)_2]\cdot 2H_2O$ [1.967 (2) Å; Solans *et al.*, 1990]. This difference is clearly due to the fact that the squarate ligand is coordinated to the Cu atom in a monodentate fashion (Solans *et al.*, 1990; Bulut *et al.*, 2004) and

therefore most of the negative charge is located on the coordinated O atom.

The squarate dianion is planar, with an r.m.s. deviation of 0.002 Å, and the largest deviation from the mean plane is 0.0035 (16) Å for atom C7. The dihedral angle between the equatorial plane of the copper coordination polyhedron and
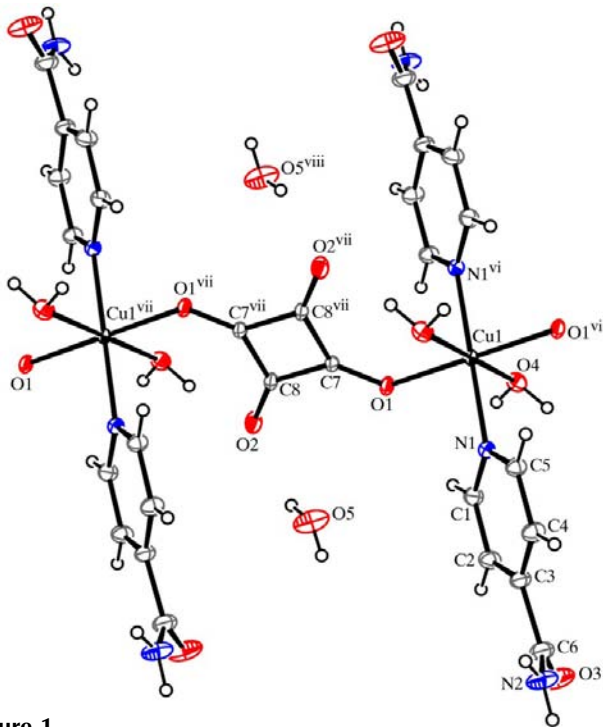

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (vi) $1 - x, 1 - y, 1 - z$; (vii) $1 - x, -y, 1 - z$; (viii) $1 - x, -y, 1 - z$.]
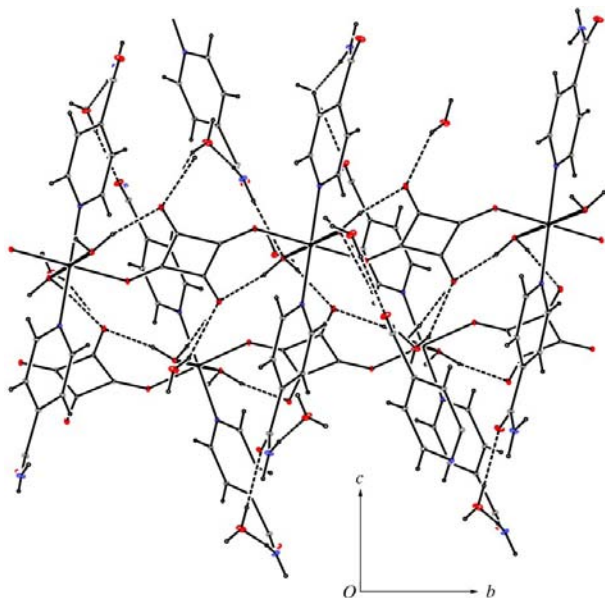

Figure 2
The zigzag chain structure of the title copper(II) complex, with intra- and interchain interactions indicated by dashed lines.

the squarate plane is 36.86 (8)°. The pyridine ring of the isonicotinamide ligand is essentially planar (the r.m.s. deviation is 0.0087 Å) and the largest deviation from the mean plane is −0.0125 Å for atom C1. The dihedral angle between the plane of the pyridine ring and the squarate mean plane is 59.45 (5)°, while that between the pyridine and copper equatorial planes is 85.12 (5)°.

In the extended structure, the NH_2 and CO groups of the ina ligand, the aqua ligand, the solvent water molecule and the uncoordinated squarate O atoms are involved in interchain hydrogen bonding; the polymer chains are connected by interchain $N2—H2A\cdots O5(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $N2—H2B\cdots O4(\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, $O5—H5A\cdots O3(1 - x, 1 - y, -z)$ and $O5—H5B\cdots O2$ interactions (Fig. 2). These interactions are also effective in forming a layered structure; the geometry of the interactions is given in Table 2. The shortest interchain $Cu1\cdots Cu1(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ of 7.4251 (6) Å, whereas the intrachain equavalent is $Cu1\cdots Cu1(x, -1 + y, z)$ of 7.7824 (7) Å.

Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol), and the mixture was added to a hot solution of $CuCl_2\cdot H_2O$ (0.77 g, 5 mmol) dissolved in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The yellow crystals that formed were filtered off, washed with water and alcohol, and dried in a vacuum. A solution of isonicotinamide (0.24 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of $CuSq\cdot 2H_2O$ (0.21 g, 1 mmol) in water (50 ml). The green solution was refluxed for about 2 h and then cooled to room temperature. A few days later, well formed dark-green crystals were selected for X-ray studies.

Crystal data

$[Cu(C_4O_4)(C_6H_6N_2O)_2$ $(H_2O)_2]\cdot 2H_2O$	$D_x = 1.641$ Mg m^{-3}
$M_r = 491.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5487
$a = 11.3221$ (9) Å	reflections
$b = 7.7824$ (4) Å	$\theta = 1.8–27.9°$
$c = 12.6314$ (11) Å	$\mu = 1.16$ mm^{-1}
$\beta = 116.535$ (6)°	$T = 297$ (2) K
$V = 995.75$ (13) Å^3	Prism, dark green
$Z = 2$	$0.23 \times 0.21 \times 0.16$ mm

Data collection

Stoe IPDS-II diffractometer	1755 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.058$
Absorption correction: integration	$\theta_{max} = 27.8°$
(*X-RED32*; Stoe & Cie, 2002)	$h = -14 \rightarrow 14$
$T_{min} = 0.768, T_{max} = 0.843$	$k = -10 \rightarrow 10$
11 948 measured reflections	$l = -16 \rightarrow 16$
2363 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.89$	$\Delta\rho_{max} = 0.44$ e Å^{-3}
2363 reflections	$\Delta\rho_{min} = -0.47$ e Å^{-3}
167 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.089 (3)

Table 1
Selected geometric parameters (Å, °).

N1—Cu1	2.0029 (14)	O4—Cu1	2.4698 (18)
O1—Cu1	1.9921 (11)		
O1—Cu1—N1	87.85 (5)	O4—Cu1—N1	89.90 (6)
O1—Cu1—O4	88.08 (6)		
C1—C2—C3—C4	0.1 (3)	O1—C7—C8—O2	0.4 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O5[i]	0.83 (3)	2.04 (3)	2.871 (3)	176 (2)
N2—H2B$\cdots$O4[ii]	0.81 (3)	2.23 (3)	3.036 (2)	174 (3)
O4—H4A$\cdots$O2[iii]	0.88 (3)	1.90 (3)	2.750 (2)	163 (3)
O4—H4B$\cdots$O2[iv]	0.72 (3)	2.07 (3)	2.790 (2)	175 (3)
O5—H5A$\cdots$O3[v]	0.76 (4)	1.97 (4)	2.720 (3)	172 (4)
O5—H5B$\cdots$O2	0.78 (5)	2.59 (5)	3.330 (3)	160 (5)

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

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed to ride on their parent atoms [U_{iso}(H) = $1.2U_{eq}$(C)]. The remaining H atoms were located in a difference map and their parameters were refined.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Ahuja, I. S. & Prasad, I. (1976). *Inorg. Nucl. Chem. Lett.* **12**, 777–784.
Baum, G., Blake, A. J., Hubberstey, P., Julio, C. & Withersby, M. A. (2002). *Acta Cryst.* C**58**, m542–m544.
Bernardinelli, G., Deguenon, D., Soules, R. & Castan, P. (1989). *Can. J. Chem.* **67**, 1158–1165.
Bulut, B., Uçar, I., Yeşilel, O. Z., Içbudak, H., Ölmez, H. & Büyükgüngör, O. (2004). *Acta Cryst.* C**60**, m526–m528.
Castro, I., Calatayud, M. L., Sletten, J., Lloret, F. & Julve, M. (1999). *Inorg. Chim. Acta*, **287**, 173–180.
Crispini, A., Pucci, D., Aiello, I. & Ghedini, M. (2000). *Inorg. Chim. Acta*, **304**, 219–223.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Graf, M., Stoeckli-Evans, H. & Escuer, A. (1997). *Inorg. Chim. Acta*, **257**, 89–97.
Greve, J., Jess, I. & Nather, C. (2003). *J. Solid State Chem.* **175**, 328–340.
Greve, J. & Nather, C. (2002). *Acta Cryst.* E**58**, m653–m655.
Hilberts, M., Meiwald, M. & Mattes. R. (1996). *Z. Naturforsch. Teil B*, **51**, 57–67.
Reinprecht, J. T., Miller, J. G., Vogel, G. C., Haddad, M. S. & Hendrikson, D. N. (1980). *Inorg. Chem.* **19**, 927–931.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Solans, X., Aguilo, M., Gleizes, A., Faus, J., Julve, M. & Verdaguer, M. (1990). *Inorg. Chem.* **29**, 775–784.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Trombe, J. C., Sabadie, L. & Milet, P. (2002). *Solid State Sci.* **4**, 1209–1212.
Uçar, I., Yeşilel, O. Z., Bulut, A., Ölmez, H. & Büyükgüngör, O. (2004). *Acta Cryst.* E**60**, m1025–m1027.
Van Ooijen, J. A. C., Reedijk, J. & Spek, A. L. (1978). *Inorg. Chem.* **18**, 1184–1189.
Yufit, D. S., Price, D. J., Howard, J. A. K., Gutchke, S. O. H., Powell, A. K. & Wood, P. T. (1999). *Chem. Commun.* pp. 1561–1562.