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#### Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
R factor = 0.025  
wR factor = 0.072  
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Diaquabis(pyridine-2-carboxamide- $\kappa^2\text{N}^1, \text{O}^2$ )-copper(II) squarate

The title compound,  $[\text{Cu}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2](\text{C}_4\text{O}_4)$  [or  $\text{Cu}(\text{pia})_2(\text{H}_2\text{O})_2 \cdot \text{Sq}$ , where pia is picolinamide or pyridine-2-carboxamide, and Sq is the squarate dianion,  $(\text{C}_4\text{O}_4)^{2-}$ ], has been synthesized and the crystal structure determination is reported. The  $\text{Cu}^{2+}$  cation, located on a centre of symmetry, is coordinated by two symmetry-related aqua ligands together with a pair of symmetry-related bidentate pia molecules and exhibits elongated octahedral *trans*- $[\text{CuN}_2\text{O}_4]$  coordination geometry. The unligated Sq dianion also lies on a crystallographic inversion centre. The squarate O atoms link the Sq ions to the metal complex *via*  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds. Intermolecular  $\pi-\pi$  and  $\text{C}-\text{H}\cdots\pi$  interactions between the moieties also stabilize the crystal structure.

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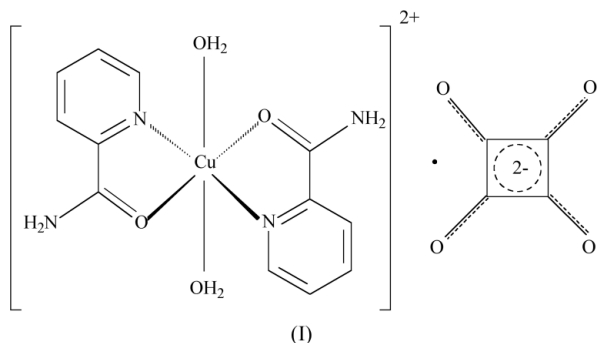
Online 27 November 2004

#### Comment

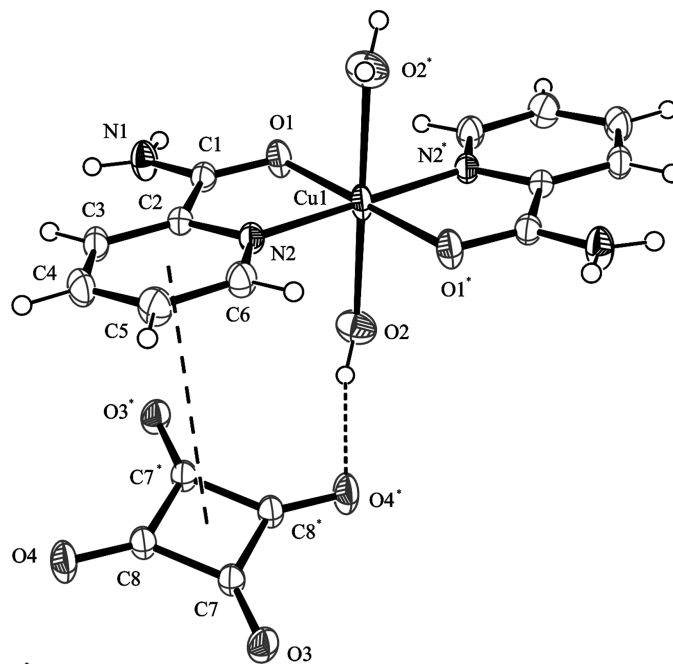
The binding of metal ions by peptides (amides) and proteins is of fundamental interest because of the importance of metal ions in biological systems (Addison *et al.*, 1977). Amides, essential components of living organisms, have strong coordinating ability to various transition metal ions, such as  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Ln}^{\text{III}}$  and  $\text{Re}^{\text{III}}$  (Masuko *et al.*, 1967; Brown *et al.*, 1971; Castro *et al.*, 1990; Sieroń & Strzyzewska, 1997, 1998, 1999; Banerjee *et al.*, 1997; Baaden *et al.*, 2003; Paşaoğlu *et al.*, 2004). Usually, ligands containing an amide group coordinate to a metal through the terminal amine N atom and the O atom of the amide moiety. When amide ligands donate an amide H atom in alkaline solution, metal ion complexation has mainly occurred at the amide N atom, since it is the most basic site. Thus, amide ligands can act as chelating ligands to yield monomeric, dimeric, and polymeric complexes with transition metal ions (Villanueva *et al.*, 1994; Brooker *et al.*, 1998; Jain *et al.*, 2004). Picolinamide (pyridine-2-carboxamide, pia) and its alkylated derivatives exhibit a potential for  $\text{An}^{\text{III}}/\text{Ln}^{\text{III}}$  separation from aqueous solutions of nuclear waste obtained by dissolution of spent fuel in nitric acid (Baaden *et al.*, 2003). The structures of copper(II) complexes with pia have been systematically investigated (Batsanov *et al.*, 1986; Cantarero *et al.*, 1988; Sieroń & Strzyzewska, 1997, 1998, 1999), but very little has been published to date about the structure of mixed-ligand copper(II) complexes of pia (Tosik *et al.*, 1995; Sieroń, 2004). As a part of our ongoing research on squaric acid ( $\text{H}_2\text{Sq}$ ) and its mixed-ligand metal complexes (Uçar *et al.*, 2004; Yeşilel *et al.*, 2004), the title compound, (I), has been synthesized and its crystal structure is reported.

The crystal structure of (I) consists of a centrosymmetric complex cation and a squarate dianion (Fig. 1). The title complex adopts an elongated octahedral *trans*- $[\text{CuN}_2\text{O}_4]$  coordination geometry, where atom Cu1 is located at a centre of symmetry. The amide O and pyridine ring N atoms of the

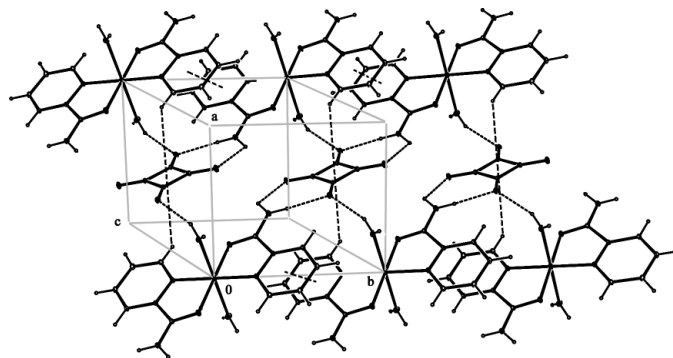
chelating pia ligands form the equatorial plane. The Cu1—O1 [1.9976 (10) Å] and Cu1—N2 [1.9724 (11) Å] bond lengths are distinctly longer than similar bonds in [Cu(H<sub>2</sub>O)<sub>2</sub>(pia)<sub>2</sub>]Cl<sub>2</sub>, [Cu(H<sub>2</sub>O)<sub>2</sub>(pia)<sub>2</sub>]Br<sub>2</sub> (Sieroń & Strzyzewska, 1997), [Cu(ClO<sub>4</sub>)(pia)<sub>2</sub>] (Sieroń & Strzyzewska, 1998) and [Cu(H<sub>2</sub>O)(NO<sub>3</sub>)(pia)<sub>2</sub>]NO<sub>3</sub>·H<sub>2</sub>O (Castro *et al.*, 1990), where their average values are 1.946 (2) Å for Cu1—O1 and 1.967 (1) Å for Cu1—N2. The water molecules occupy the axial positions, forming two long symmetry-related Cu1—O2 bonds [Cu1—O2 = 2.3342 (14) Å]. The Cu1—O1 bond length is significantly shorter than the Cu1—O2 bond distance (see above) owing to the pseudo-Jahn–Teller effect, in this case because the ligands are not all identical. From studies on copper complexes of pia, it has been seen that the elongation of the equatorial Cu—O bond was connected with the shortening of the axial Cu—O bonds [Cu—O<sub>axial</sub> and Cu—O<sub>equatorial</sub>: 2.265 (4)/1.995 (2) Å for Castro *et al.* (1990); 2.418 (2)/1.981 (1), 2.649 (3)/2.937 (2) and 2.317 (12)/1.9639 (12) Å for Sieroń & Strzyzewska (1997, 1998, 1999, respectively)]. In the title complex, the angle subtended at the Cu atom by the pia ligands is 82.17 (4)°, which is in agreement with those previously reported for other pia-containing Cu<sup>II</sup> complexes (see above).



The pia ligand is essentially planar, with an r.m.s. deviation of 0.0157 Å and a maximum deviation from this plane of 0.0304 (10) Å for atom O1. This deviation in the pia ligand is caused by coordination to the Cu<sup>II</sup> ion. A slight deviation from planarity is also observed arising from the non-zero torsion angle between the carboxamide group and the pyridine ring [C3—C2—C1—N1 = -2.5 (2)°]. Metal coordination also affects the degree of elasticity of the pia molecule. In complexes of pia with Cu (Sieroń & Strzyzewska, 1997, 1998; Sekizaki, 1973) and Ni (Paşaoğlu *et al.*, 2004), the C2—N2—C6 angle is smaller [119.16 (12), 119.1 (2), 119.9 (2), 120.9 (3) and 119.43 (14)°, respectively] than that found in the deprotonated free pia ligand [123.0 (3)°; Uçar *et al.*, 2004]. This narrowing of the C2—N2—C6 angle is due to metal coordination at N1, which causes slight widening of the adjacent N2—C2—C3 and N2—C6—C5 angles to 122.03 (12) and 121.96 (13)°, respectively [119.0 (3) and 120.1 (3)°, respectively; Uçar *et al.*, 2004]. However, the N1—C1 and C1=O1 bond lengths in the carboxamide group do not display variability when the pia ligand coordinates to a Cu<sup>II</sup> ion. The chelate ring is almost planar (r.m.s. deviation is 0.0275 Å) and



**Figure 1**  
An ORTEP (Burnett & Johnson, 1996) view of the constituent ions of (I), showing the atom-numbering scheme and 40% probability displacement ellipsoids. [Symmetry code: (\*)  $-x, -y, 2-z$  (for cation);  $1-x, -y, 1-z$  (for anion)]



**Figure 2**  
A view of the O—H...O, N—H...O, C—H...π and π-π interactions in (I).

the maximum deviation from this plane is 0.0365 (8) Å for atom O1. The pyridine ring and carboxamide group are approximately coplanar with the chelate ring, with dihedral angles of 2.00 (18) and 3.55 (16)°, respectively.

The uncoordinated squarate anion, which also lies on an inversion centre, plays an important role in the supramolecular architecture. This anion exhibits an excellent planarity, with an r.m.s. deviation of 0.0033 Å. The dihedral angle between the squarate anion and pyridine ring is 22.13 (5)°. In the squarate anion, the O—C bond distances are 1.2495 (16) and 1.2523 (16) Å, while the C—C bond distances are 1.4648 (18) and 1.4687 (17) Å. These bond lengths agree with the fact that the squarate anion, which possesses a pronounced degree of electron delocalization, is considered to be aromatic.

The crystal packing is formed by intermolecular hydrogen-bonding, π-π and π-ring interactions. It is seen from Fig. 2

that each squarate anion is surrounded by four  $[\text{Cu}(\text{pia})_2(\text{H}_2\text{O})_2]^{2+}$  cations. The squarate O atoms participate in hydrogen bonds with the amide and the water H atoms (see Table 2 for details). In the crystal structure of (I), there are also weak  $\pi$ - $\pi$  and  $\pi$ -ring interactions. An intermolecular  $\pi$ - $\pi$  contact occurs between the symmetry-related pyridine rings (hereafter ring *A*) of neighbouring molecules. Ring *A* is oriented in such a way that the perpendicular distance from *A* to  $A^{iv}$  is 3.431 Å, the closest interatomic distance being  $\text{C2}\cdots\text{C3}^{iv}$  [3.429 (2) Å; symmetry code: (iv)  $-x, 1-y, 2-z$ ]. The distance between the ring centroids is 4.1207 (10) Å. Another weak  $\pi$ - $\pi$  interaction is observed between ring *A* and squarate ring (ring *B*), with the distance between ring centroids being 4.1550 (11) Å. Ring *B* (centroid  $\text{Cg1}$ ) is also involved in weak intermolecular  $\text{C}-\text{H}\cdots\pi$  interaction with pyridine atom C6 (Table 2). These interactions are responsible for the formation of a three-dimensional network.

## Experimental

Squaric acid ( $\text{H}_2\text{Sq}$ ; 0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and added to a hot solution of copper(II) chloride dihydrate (0.853 g, 5 mmol) dissolved in water (50 ml). The mixture was refluxed at 353 K for 12 h and then cooled to room temperature. The green crystals which formed were filtered off and washed with water, and dried in a vacuum. A solution of pyridine-2-carboxamide (0.244 g, 2 mmol) in ethanol (20 ml) was added dropwise with stirring to a suspension of  $\text{CuSq}\cdot 2\text{H}_2\text{O}$  (0.212 g, 1 mmol) in water (50 ml). The mixture was stirred at 323 K for 12 h and then cooled to room temperature. After a few days, well formed crystals were selected for X-ray studies.

### Crystal data

$[\text{Cu}(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2](\text{C}_4\text{O}_4)$	$Z = 1$
$M_r = 455.87$	$D_x = 1.784 \text{ Mg m}^{-3}$
Triclinic, $\overline{P}1$	Mo $K\alpha$ radiation
$a = 7.1240$ (9) Å	Cell parameters from 7374 reflections
$b = 7.7627$ (9) Å	$\theta = 2.7$ – $29.7^\circ$
$c = 8.1191$ (9) Å	$\mu = 1.35 \text{ mm}^{-1}$
$\alpha = 108.150$ (9)°	$T = 293$ (2) K
$\beta = 92.225$ (10)°	Prism, green
$\gamma = 94.531$ (10)°	$0.42 \times 0.27 \times 0.18 \text{ mm}$
$V = 424.37$ (9) Å <sup>3</sup>	

### Data collection

Stoe IPDS-2 diffractometer	2361 independent reflections
$\omega$ scans	2241 reflections with $I > 2\sigma(I)$
Absorption correction: by integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)	$R_{\text{int}} = 0.070$
$T_{\text{min}} = 0.656$ , $T_{\text{max}} = 0.803$	$\theta_{\text{max}} = 29.6^\circ$
8483 measured reflections	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 10$
	$l = -11 \rightarrow 11$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.1621P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
2361 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
149 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

C1—O1	1.2489 (16)	C7—C8	1.4687 (17)
C1—N1	1.3104 (18)	C8—O4	1.2495 (16)
C2—N2	1.3438 (16)	N2—Cu1	1.9724 (11)
C6—N2	1.3314 (18)	O1—Cu1	1.9976 (10)
C7—O3	1.2523 (16)	O2—Cu1	2.3342 (14)
N2—C2—C3	122.03 (12)	N2—Cu1—O1	82.17 (4)
N2—C6—C5	121.96 (13)	N2—Cu1—O2	89.46 (5)
C6—N2—C2	119.16 (12)	O1—Cu1—O2	85.19 (5)
O1—C1—C2—N2	−1.74 (19)	O3—C7—C8—O4	−1.3 (3)
N1—C1—C2—C3	−2.5 (2)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1A $\cdots$ O3 <sup>i</sup>	0.858 (15)	1.987 (16)	2.8324 (16)	168 (2)
N1—H1B $\cdots$ O4 <sup>ii</sup>	0.853 (16)	2.53 (2)	3.0678 (19)	122 (2)
O2—H2A $\cdots$ O4 <sup>iii</sup>	0.808 (16)	1.977 (17)	2.7659 (17)	165 (3)
O2—H2B $\cdots$ O3 <sup>ii</sup>	0.816 (16)	2.053 (17)	2.8264 (16)	158 (2)
C6—H6 $\cdots$ Cg1 <sup>iv</sup>	0.93	3.13	3.8251 (17)	133

Symmetry codes: (i)  $x, 1+y, 1+z$ ; (ii)  $x, y, 1+z$ ; (iii)  $1-x, -y, 1-z$ ; (iv)  $-x, -y, 1-z$ . Cg1 is the centroid of the squarate ring *B*.

H atoms attached to C atoms were placed at calculated positions ( $\text{C}-\text{H} = 0.93$  Å) and were allowed to ride on the parent atom [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. The other H atoms were located in a difference map and were refined with the O—H and N—H distances restrained to 0.85 (2) and 0.87 (2) Å, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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