Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# Poly[[[diaquabis(pyridine-4-carboxamide-$\kappa N^1$)-cobalt(II)]-$\mu_2$-squarato-$\kappa O$:$O'$] dihydrate]

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Received 24 May 2005
Accepted 9 June 2005
Online 17 June 2005

**Key indicators**

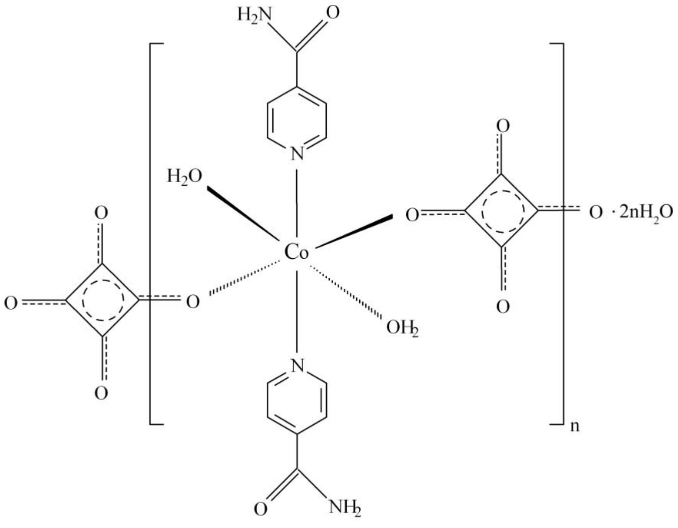
Single-crystal X-ray study
$T$ = 297 K
Mean $\sigma$(C–C) = 0.006 Å
$R$ factor = 0.056
$wR$ factor = 0.164
Data-to-parameter ratio = 13.6

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

The title polymeric compound, $\{[Co(C_4O_4)(C_6H_6N_2O)_2(H_2O)_2]\cdot 2H_2O\}_n$, has two crystallographically independent half-molecules in the asymmetric unit, each Co atom residing on a center of symmetry. The two polymeric chains exhibit similar coordination geometry but display differences with regard to other structural features. Each Co$^{II}$ center is octahedrally coordinated by two mutually *trans* pyridine-4-carboxamide (or isonicotinamide) ligands, two mutually *trans* squarate ligands and two *trans* aqua ligands. The crystal structure contains chains of squarate-1,3-bridged Co$^{II}$ 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

Squaric acid, the dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione, and its metal complexes continue to attract attention, not only because of the various coordination modes of squaric acid, such as singly and multiply monodentate ligands or a bridging ligand between two or more metal atoms (Trombe *et al.*, 2002; Millet *et al.*, 2003), but also because of the potential application of metal complexes to xerographic photoreceptors, organic solar cells and optical recording (Seitz & Imming, 1992; Liebeskind *et al.*, 1993). The squarate (Sq = $C_4O_4^{2-}$) anion does not behave like a chelating ligand but rather as a bridge connecting two or more metal atoms. It is coordinated to Fe$^{II}$, Fe$^{III}$, Ni$^{II}$ and Cu$^{II}$ complexes in a $\mu$-1,3 fashion (as in the title complex) giving binuclear (Bernardinelli *et al.*, 1989) and chain structures (Lee *et al.*, 1996), whereas the $\mu$-1,2 coordination mode has been reported for binuclear and chain complexes of Cu$^{II}$ and Pd$^{II}$ (Castro *et al.*, 1997; Crispini *et al.*, 2000). It is also observed that the squarate anion, with Cu$^{II}$ and Ni$^{II}$, acts as a tetramonodentate ligand and forms polynuclear compounds (Castro *et al.*, 1995). In all the cases reported so far, metal squarate complexes have been found interesting in terms of the structural relationship between their respective solid-state architectures. We have also used isonicotinamide (ina) as a second ligand; this pyridine derivative, with an amide group (–CONH$_2$) in the $\gamma$ position, possesses strong antitubercular, antipyretic, fibrinolytic and antibacterial properties (Ahuja & Prasad, 1976). In inorganic chemistry, isonicotinamide is of interest because it has three donor sites, *viz* (i) the pyrimidine ring N atom, as in the title complex, (ii) the amine N atom and (iii) the carbonyl O atom, acting as monodentate ligand. There are only a few reports of complexes of this ligand with transition metals (Baum *et al.*, 2002). In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal(II) complexes of squaric acid and their structures have been reported (Uçar *et al.*, 2004; Bulut *et al.*, 2004). In our latest study, the squarate dianion acts as bridging ligand between two copper(II) ions, forming one crystallographically independent polymeric $[Cu(H_2O)_2(ina)_2(Sq)]_n$ chain (Uçar *et al.*, 2005). In this study, the title mixed-ligand complex, (I), has two crystallographically independent polymeric $[Co(H_2O)_2(ina)_2(Sq)]_n$ chains.



(I)

A view of part of the polymeric structure of (I), with the atom-numbering scheme is shown in Fig. 1. In the crystal structure, the squarate dianion adopts a bridging position between the $Co^{II}$ atoms, coordinating *via* two of its O atoms in a $\mu$-1,3 fashion. Both polymeric units form 'zigzag' chains in the direction of the crystallographic *a* axis (Fig. 1). These crystallographically independent chains exhibit similar coordination geometries about the metal center but show differences in other structural features. Each $Co^{II}$ center lies on a center of symmetry and is octahedrally coordinated by two mutually *trans* ina ligands, two mutually *trans* squarate anions and two symmetry-related aqua ligands. In the title complex, there are also two non-symmetry-related solvent water molecules. The ring plane of the ina ligand nearly bisects the adjacent coordination planes, containing the octahedron axis. In each polymeric chain, the coordinated pyridine N atoms of two ina ligands are located in axial positions, while the squarate O atoms and aqua ligands form the equatorial planes. The dihedral angle between the equatorial planes of the Co atoms in the two polymer chains is 15.6 (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 geometrical shapes of the two crystallographically independent chains are similar but not identical. The Co—$O_{squarate}$ bond distance for polymeric chain *A*, containing Co1, is slightly shorter than the corresponding bond length in polymeric chain *B*, containing Co2, while the Co—$O_{water}$ bond for chain *A* is slightly longer than that for chain *B*. Although the squarate ligand is electronegative in character in each chain, the Co—$O_{water}$ bond distances are significantly shorter than the Co—$O_{squarate}$ bond distances (Table 1). Similarly, in each chain, the Co—$N_{ina}$ bond distances are slightly different from each other. However, these bond distances are in agreement with the values reported previously for other squarate-containing $Co^{II}$ complexes (Greve *et al.*, 2003;

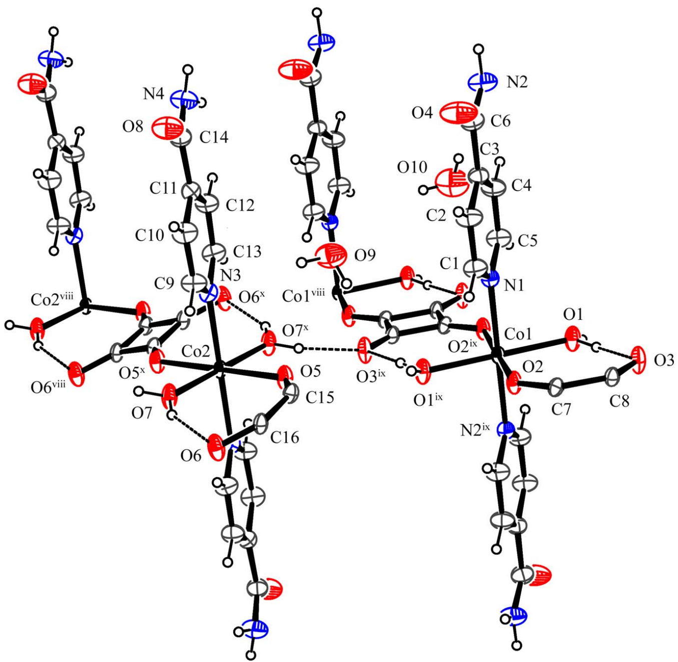


**Figure 1**
Part of the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (viii) $-1 + x, y, z$; (ix) $1 - x, 1 - y, 1 - z$; (*x*) $-x, 1 - y, -z$.]

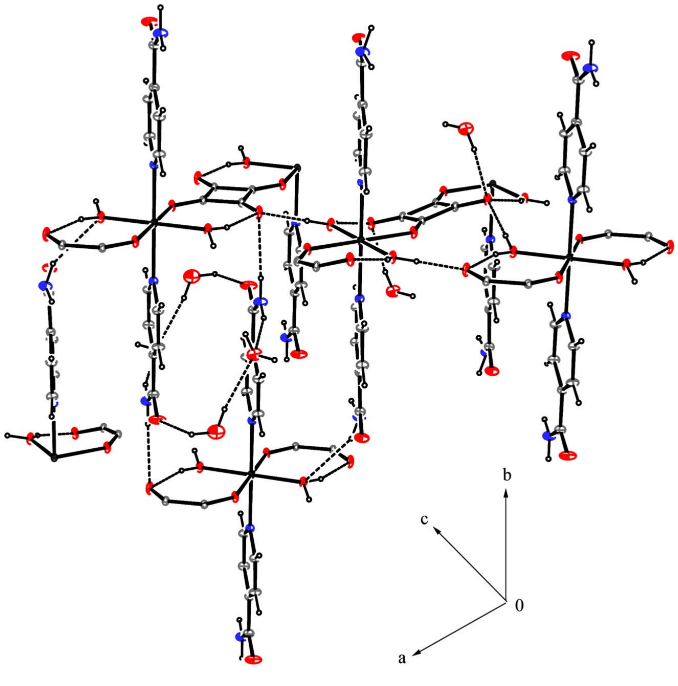


**Figure 2**
The zigzag chain structure of the cobalt(II) complex, with intra- and interchain interactions shown as dashed lines.

Kirchmaier *et al.*, 2003). The bonding angles also show some differences with each other in both polymeric chains (Table 1). All the N—Co—N, N—Co—O and O—Co—O bond angles deviate slightly from 90 or 180°, presumably as a result of steric constraints arising from the shape of the ligands. The dihedral angle between the two squarate dianions in chains *A* and *B* is 20.90 (6)°. In polymeric chain *A*, the dihedral angle between the equatorial plane and the squarate dianion is 4.10 (10)°, with a torsion angle (Co1–O2–C7–C8) of 1.3 (7)°, while in polymeric chain *B*, this angle is 30.75 (16)°, with a torsion angle (Co2–O5–C15–C16) of 18.1 (7)°. Similarly, the dihedral angle between the two pyridine rings in chains *A* and *B* is 7.4 (3)°.

We assume that the hydrogen bonds influence the observed geometrical shape of both chains. The hydrogen bonds may be responsible for the different orientations of the squarate and pyridine planes. The $NH_2$ and CO groups of the ina ligand, the aqua ligand, the solvent water molecules and the uncoordinated squarate O atoms are involved in interchain hydrogen bonding. These interactions are also effective in forming a layered structure; the geometry of the interactions is given in Table 2. In both polymeric chains, the shortest intrachain Co1···Co1($-1+x, y, z$) and Co2···Co2($-1+x, y, z$) distances are equal [8.1578 (9) Å], whereas the interchain equivalent, Co1···Co2($x, y, z+1$), is 7.3058 (8) Å.

## Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and was added to a hot solution of $CoCl_2\cdot H_2O$ (0.74 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 pink crystals that formed were filtered off and washed with water and methanol, 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 $CoSq\cdot 2H_2O$ (0.20 g, 1 mmol) in water (50 ml). The light-pink solution was refluxed for about 2 h and then cooled to room temperature. A few days later, well formed pink crystals were selected for X-ray studies.

### *Crystal data*

$[Co(C_4O_4)(C_6H_6N_2O)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 487.29$
Triclinic, $P\overline{1}$
$a = 8.1578\ (8)$ Å
$b = 10.8246\ (12)$ Å
$c = 12.1665\ (11)$ Å
$\alpha = 75.445\ (8)^\circ$
$\beta = 89.690\ (8)^\circ$
$\gamma = 74.082\ (8)^\circ$
$V = 997.68\ (17)$ Å$^3$
$Z = 2$
$D_x = 1.622$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5876 reflections
$\theta = 2.3$–$27.3^\circ$
$\mu = 0.92$ mm$^{-1}$
$T = 297\ (2)$ K
Prism, pink
0.3 × 0.2 × 0.1 mm

### *Data collection*

Stoe IPDS-II diffractometer
$\omega$ scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.710$, $T_{max} = 0.899$
20174 measured reflections
4333 independent reflections
3003 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.0^\circ$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.164$
$S = 1.05$
4333 reflections
319 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1027P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 1.12$ e Å$^{-3}$
$\Delta\rho_{min} = -0.81$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Co1—O1 | 2.058 (2) | Co2—O7 | 2.042 (3) |
| Co1—O2 | 2.128 (2) | Co2—O5 | 2.141 (2) |
| Co1—N1 | 2.158 (3) | Co2—N3 | 2.169 (3) |
| O1—Co1—O2 | 95.67 (10) | O7—Co2—O5 | 92.92 (10) |
| O1—Co1—N1 | 88.96 (12) | O7—Co2—N3 | 89.31 (13) |
| O2—Co1—N1 | 88.80 (11) | O5—Co2—N3 | 89.46 (11) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···O3 | 0.86 (3) | 1.80 (3) | 2.635 (4) | 165 (5) |
| O1—H1*B*···O6$^{i}$ | 0.87 (3) | 1.85 (3) | 2.723 (4) | 174 (5) |
| N2—H2*A*···O9$^{ii}$ | 0.89 (3) | 2.15 (3) | 3.015 (6) | 164 (6) |
| N2—H2*B*···O3$^{iii}$ | 0.91 (3) | 2.35 (3) | 3.214 (5) | 158 (5) |
| N4—H4*A*···O10$^{iv}$ | 0.88 (3) | 2.15 (4) | 2.973 (7) | 155 (6) |
| N4—H4*B*···O1$^{ii}$ | 0.88 (3) | 2.50 (4) | 3.316 (5) | 155 (5) |
| O7—H7*A*···O6 | 0.86 (3) | 1.91 (3) | 2.684 (4) | 149 (5) |
| O7—H7*B*···O3$^{v}$ | 0.88 (3) | 1.75 (3) | 2.613 (3) | 166 (5) |
| O9—H9*A*···O8$^{vi}$ | 0.83 (4) | 1.98 (5) | 2.779 (6) | 159 (8) |
| O9—H9*B*···O6$^{vii}$ | 0.84 (4) | 2.16 (4) | 2.984 (6) | 170 (8) |
| O10—H10*A*···O4$^{ii}$ | 0.87 (4) | 2.21 (9) | 2.829 (7) | 128 (9) |
| O10—H10*B*···O9$^{ii}$ | 0.85 (4) | 2.24 (4) | 3.083 (8) | 169 (10) |

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x, y-1, z$; (iv) $-x, -y, -z+1$; (v) $x-1, y, z-1$; (vi) $-x+1, -y, -z$; (vii) $-x+1, -y+1, -z$.

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed to ride on the parent atom [$U_{iso}(H) = 1.2U_{eq}(C)$]. The water and amide H atoms were located in a difference map and were refined with O—H, N—H, $H_{water}\cdots H_{water}$ and $H_{amide}\cdots H_{amide}$ distances restrained to 0.85 (4), 0.90 (3), 1.35 (4) and 1.40 (3) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O,N)$. The highest peak is located on the Co1 atom.

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).

The authors thank the Prime Minister's State Planning Organization of Turkey for financial support to project TAPF-020.

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