

Poly[[diaqua(μ_4 -squarato-*O,O',O'',O'''*)-nickel(II)] 0.71-hydrate]

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

Disorder in solvent or counterion

R factor = 0.024

wR factor = 0.077

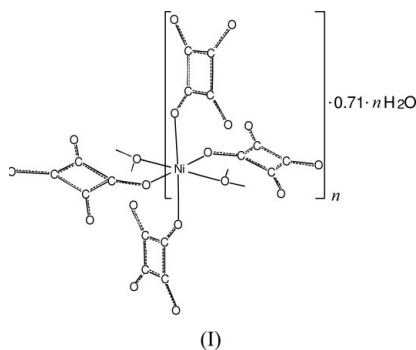
Data-to-parameter ratio = 11.9

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

In the title compound, $\{[\text{Ni}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_2] \cdot 0.71\text{H}_2\text{O}\}_n$, each Ni atom is coordinated by four squarate dianions and two water molecules within a slightly distorted octahedron. The water molecules occupy general positions and the Ni atom, as well as the two crystallographically independent squarate dianions, are located in special positions. Hydrogen bonding is found between the O atoms of the squarate dianions and the water molecules. In the crystal structure, voids are found that are filled with disordered clathrate water molecules. The compound is isotypic with the previously reported Mn, Fe and Co compounds.

Comment

Recently, we have been interested in the preparation of new coordination polymers based on transition-metal squarates and *N*-donor ligands, such as 4,4'-bipyridine (Näther *et al.*, 2002*a*; Greve, 2000) or pyrazine (Greve, 2000; Näther & Jeß, 2001; Näther *et al.*, 2002*b*). During the preparation of these compounds, mixtures are sometimes obtained that contain the pure metal squarate dihydrates. This is the case for the reaction of nickel chloride with squaric acid and 4,4'-bipyridine, in which crystals of the title compound, (I), are obtained as the minor phase.



The structure of (I) is isotypic with the previously reported Mn (Greve & Näther, 2002), Fe (Näther *et al.*, 2002*c*) and Co compounds (Lee *et al.*, 1996). The asymmetric unit contains half an Ni atom, quarters of two separate dianions which are located in special positions and one water molecule in a general position. One of the two crystallographically independent squarate dianions is located around a fourfold axis, whereas the second is located around a fourfold rotoinversion axis. The geometry of these two dianions is comparable. Between the water molecules and the squarate O atoms strong O—H···O hydrogen bonding is found. The Ni atoms are coordinated by four O atoms of squarate dianions and two water molecules within a slightly distorted octahedron. Each

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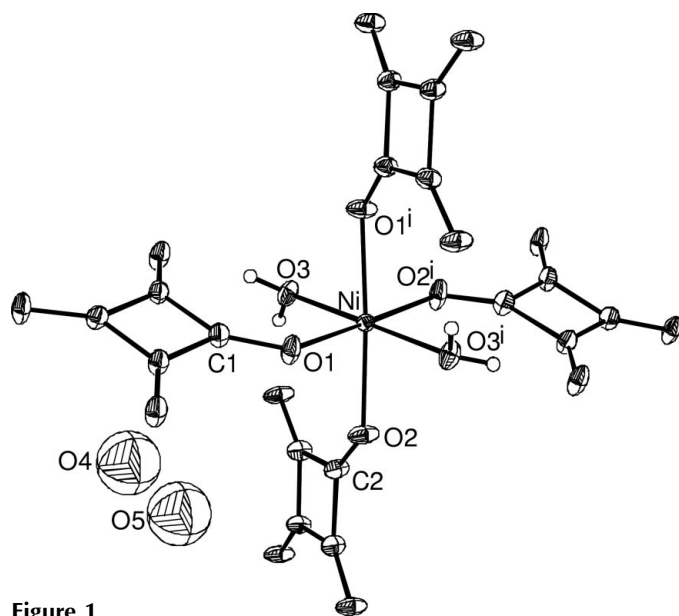


Figure 1
The crystal structure of the title compound, with a view of the Ni coordination, the atom labelling and displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $y, x, -z + \frac{1}{2}$].

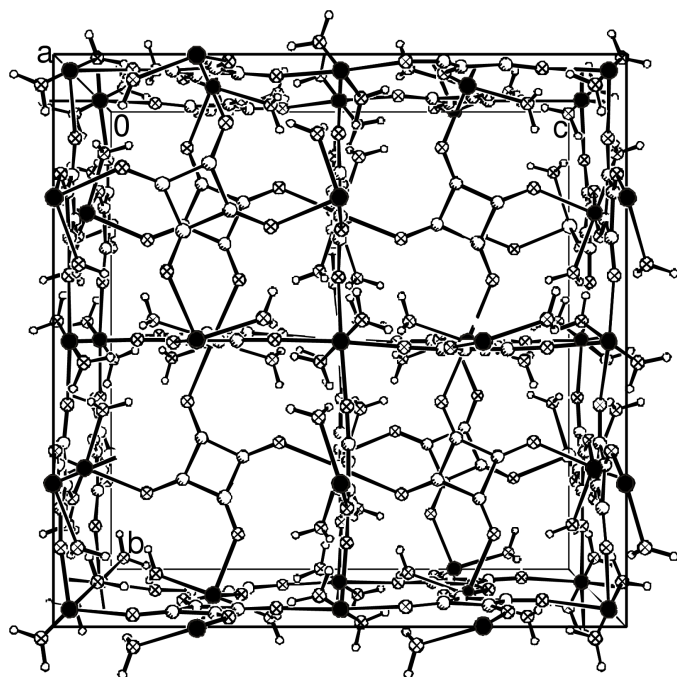


Figure 2
The crystal structure of the title compound, viewed along the crystallographic a axis. The disordered water molecules have been omitted for clarity.

squarate dianion is connected to four Ni atoms, forming a three-dimensional coordination network, which contains cubic voids surrounded by six squarate dianions. Within these voids, additional disordered water molecules are found.

Experimental

The title compound was prepared by the reaction of 0.5 mmol nickel(II) chloride, 0.5 mmol squaric acid and 0.5 mmol 4,4'-bipyridine in

5 ml of water in a Teflon-lined steel autoclave at 423 K under hydrothermal conditions. After 5 d, the reaction mixture was cooled to room temperature, filtered and the resulting precipitate washed with water. The precipitate consists of a mixture of colourless crystals of the 4,4'-bipyridine compound poly[[diaqua(μ_2 -squarato- O, O')(μ_2 -4,4'-bipyridine)nickel(II)] hydrate] (Greve, 2000) and light-green crystals of (I). The composition of the precipitate was determined by X-ray powder diffraction.

Crystal data

[Ni(C₄O₄)(H₂O)₂] \cdot 0.71H₂O
 $M_r = 218.12$
 Cubic, $Pn\bar{3}n$
 $a = 16.1467(8) \text{ \AA}$
 $V = 4209.7(4) \text{ \AA}^3$
 $Z = 24$
 $D_x = 2.065 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation

Cell parameters from 8000 reflections
 $\theta = 2.5\text{--}26.5^\circ$
 $\mu = 2.76 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, light green
 $0.2 \times 0.2 \times 0.2 \text{ mm}$

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: none
 7475 measured reflections
 704 independent reflections
 508 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 26.5^\circ$
 $h = -8 \rightarrow 20$
 $k = -16 \rightarrow 20$
 $l = -14 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.077$
 $S = 1.07$
 704 reflections
 59 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 5.3938P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00045 (9)

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|--------------------------|-------------|--------------------------------------|-------------|
| Ni—O3 | 2.0206 (15) | C1—C1 ⁱ | 1.460 (3) |
| Ni—O1 | 2.0593 (16) | C2—O2 | 1.253 (3) |
| Ni—O2 | 2.0826 (17) | C2—C2 ⁱⁱ | 1.466 (4) |
| C1—O1 | 1.255 (3) | | |
| O3 ⁱⁱⁱ —Ni—O3 | 179.14 (10) | O1—C1—C1 ⁱ | 133.8 (2) |
| O3 ⁱⁱⁱ —Ni—O1 | 83.50 (6) | O1—C1—C1 ^{iv} | 136.0 (2) |
| O3—Ni—O1 | 97.11 (7) | C1 ⁱ —C1—C1 ^{iv} | 90.000 (1) |
| O1—Ni—O1 ⁱⁱⁱ | 90.23 (10) | C1—O1—Ni | 134.56 (15) |
| O3 ⁱⁱⁱ —Ni—O2 | 84.80 (7) | O2—C2—C2 ⁱⁱ | 133.4 (2) |
| O3—Ni—O2 | 94.62 (7) | O2—C2—C2 ^v | 136.6 (2) |
| O1—Ni—O2 | 87.86 (7) | C2 ⁱⁱ —C2—C2 ^v | 89.986 (6) |
| O1 ⁱⁱⁱ —Ni—O2 | 177.14 (7) | C2—O2—Ni | 136.03 (15) |
| O2—Ni—O2 ⁱⁱⁱ | 94.12 (10) | | |

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

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D\text{---}H\cdots A$ | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|----------------------------------|----------------|-------------|-------------|------------------------|
| O3—H1 \cdots O1 ⁱⁱⁱ | 0.82 | 1.92 | 2.724 (2) | 167 |
| O3—H2 \cdots O2 ^{iv} | 0.82 | 1.93 | 2.730 (2) | 164 |

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

The H atoms of the coordinated water molecules were located in a difference Fourier map, and these molecules were refined as rigid groups, with idealized O—H bond lengths of 0.82 \AA and fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The two

clathrate O atoms of clathrate water molecules were refined isotropically with variable site-occupation factors and a common displacement parameter. The site-occupation factors were refined to 0.38 (2) for atom O4 and 0.26 (1) for atom O5. The H atoms of these water molecules could not be located.

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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