

Bis[*N*-(2-hydroxyethyl)ethylenediamine- $\kappa^3N,N',O$ ]nickel(II) squarate monohydrate

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Key indicators

Single-crystal X-ray study  
 $T = 297\text{ K}$   
 Mean  $\sigma(C-C) = 0.004\text{ \AA}$   
 H-atom completeness 97%  
 Disorder in solvent or counterion  
 $R$  factor = 0.042  
 $wR$  factor = 0.094  
 Data-to-parameter ratio = 16.5

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

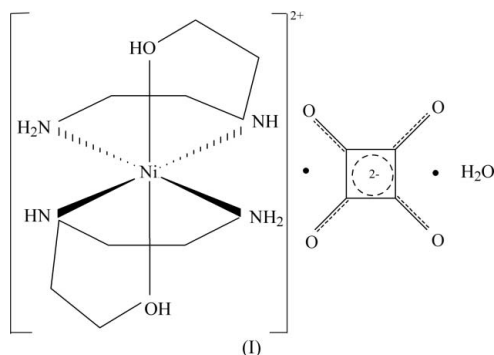
In the title compound,  $[Ni(C_4H_{12}N_2O)_2](C_4O_4)\cdot H_2O$  or  $[Ni(\text{Hydet-en})_2](\text{Sq})\cdot H_2O$ , where Hydet-en is *N*-(2-hydroxyethyl)ethylenediamine and Sq is the squarate dianion, the  $Ni^{II}$  centre has a distorted octahedral coordination geometry comprising four amine N and two hydroxyl O atoms from two tridentate Hydet-en ligands. All the O atoms of the squarate dianion are involved in  $N-H\cdots O$  and  $O-H\cdots O$  hydrogen bonding.

Comment

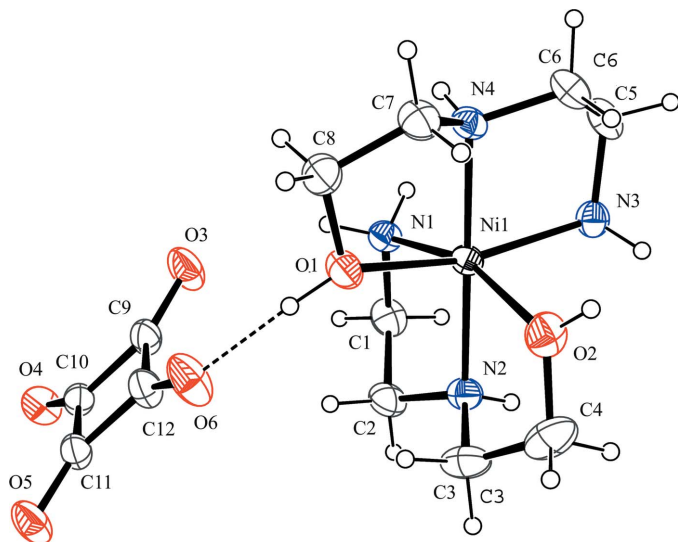
In the last decade, considerable progress has been made in the crystal design and engineering of multidimensional arrays and networks containing metal ions as nodes. Many workers from a variety of scientific disciplines are interested in this field. It has been shown that metal-ion-containing supramolecular structures can be used as zeolite-like materials (Venkataraman *et al.*, 1995; Kepert & Rosseinsky, 1999), catalysts (Fujita *et al.*, 1994) or magnetic materials (Kahn, 1993). There is also intense research on metal-organic materials with functional building blocks, as a result of their attractive new topologies and intriguing structural features (Batten & Robson, 1998; Yaghi *et al.*, 1998).

In this context, squaric acid ( $H_2Sq$ ) and its metal complexes are of potential interest since it is a molecule frequently used to build co-crystals (Bouma *et al.*, 1999; Bertolasi *et al.*, 2001; Bulut *et al.*, 2003). On the other hand, the *N*-(2-hydroxyethyl)ethylenediamine (Hydet-en) ligand, with three donor sites, has been the subject of only a few studies (Karadağ *et al.*, 2004; Paşaoğlu *et al.*, 2005), and its coordination behaviour is, therefore, not well characterized.

In order to elucidate the properties of these types of crystals, a detailed knowledge of the combining forces that construct the supramolecular structure is needed. The present paper reports the synthesis and crystal structure determination of the title compound,  $[Ni(C_4H_{12}N_2O)_2](C_4O_4)\cdot H_2O$ , (I).



Received 10 November 2005  
 Accepted 24 November 2005  
 Online 30 November 2005



**Figure 1**

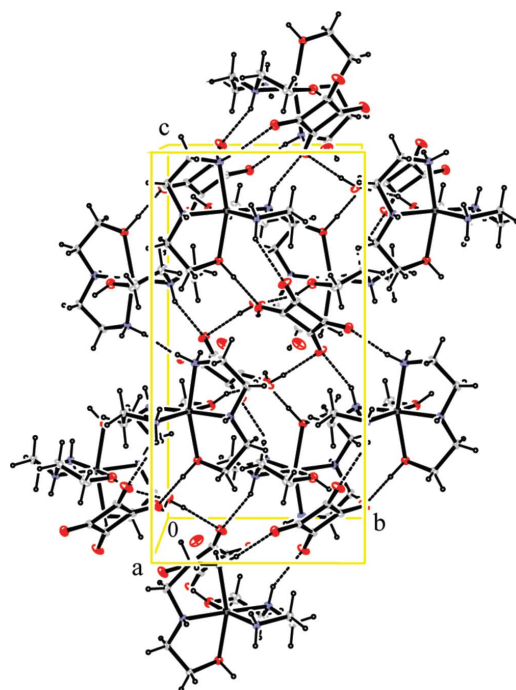
A view of (I), showing the atom-labelling scheme and with 40% probability displacement ellipsoids. The disordered water molecule has been omitted for clarity. The dashed line indicates an O—H...O hydrogen bond.

A view of (I) and its numbering scheme are shown in Fig. 1. The crystal structure consists of a complex cation, one squarate counter-anion, and one solvent water molecule. In the complex cation, the Ni<sup>II</sup> ion is sandwiched by two bulky Hydete-en ligands. Each Hydete-en ligand acts as a tridentate ligand through the two N atoms and the hydroxyl O atom, resulting in a six-coordinate Ni<sup>II</sup> ion. The coordination geometry around the Ni<sup>II</sup> ion is irregular and indicates a distorted octahedral geometry. In the complex, Ni—O distances are in the range 2.142 (2)–2.188 (2) Å and Ni—N distances are in the range 2.039 (2)–2.094 (2) Å, while the bond angles at Ni range from 79.14 (9) to 176.12 (9)°. These bond distances and angles are comparable with those observed for other Ni<sup>II</sup> complexes with the Hydete-en ligand (Karadağ *et al.*, 2004). The squarate counter-anion is planar, and intramolecular bond distances are found to be almost the same as in 8-aminoquinolinium hemisquarate (Bertolasi *et al.*, 2001) and dinicotinamidium squarate (Bulut *et al.*, 2003).

The crystal packing of (I) is stabilized by intermolecular O—H...O and N—H...O hydrogen-bonding interactions (Fig. 2). The solvent water molecule, hydroxyl O and amine N atoms link the complex cation to the squarate dianion *via* hydrogen-bonding interactions (see Table 2 for details). Short O5...O7(1 - x, 1 - y, 1 - z) [2.698 (6) Å] and O6...O7 [2.630 (6) Å] contacts are observed and these are indications for the O—H...O hydrogen bonds involving the H atoms attached to O7, which were not located.

## Experimental

Squaric acid (0.57 g, 5 mmol) was dissolved in water (25 ml), neutralized with NaOH (0.40 g, 10 mmol) and added to a hot solution of nickel(II) chloride (1.19 g, 5 mmol) dissolved in water (100 ml). The mixture was refluxed at 353 K for 12 h and then cooled to room temperature. The blue crystals which formed were filtered off and



**Figure 2**

A view of the packing of (I), showing the hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 10% probability level.

washed with water and ethanol, and dried *in vacuo*. A solution of *N*-(2-hydroxyethyl)ethylenediamine (0.208 g, 2 mmol) in ethanol (50 ml) was added dropwise with stirring to a suspension of NiSq·2H<sub>2</sub>O (0.207 g, 1 mmol) in water (100 ml). The mixture was refluxed at 353 K for 12 h and then cooled to room temperature. After a few days, well formed violet crystals of (I) were selected for X-ray studies.

### Crystal data

[Ni(C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>](C<sub>4</sub>O<sub>4</sub>)·H<sub>2</sub>O  
*M<sub>r</sub>* = 397.08  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 11.9740 (8) Å  
*b* = 8.7618 (4) Å  
*c* = 16.9051 (12) Å  
 $\beta$  = 97.454 (6)°  
*V* = 1758.59 (19) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.500 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5487 reflections  
 $\theta$  = 2.3–28.0°  
 $\mu$  = 1.14 mm<sup>-1</sup>  
*T* = 297 (2) K  
 Prism, violet  
 0.30 × 0.28 × 0.16 mm

### Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)  
 $T_{\min}$  = 0.659,  $T_{\max}$  = 0.763  
 28256 measured reflections  
 4128 independent reflections

3478 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.084  
 $\theta_{\text{max}}$  = 27.8°  
 $h$  = -15 → 15  
 $k$  = -11 → 11  
 $l$  = -22 → 22

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.042  
 $wR(F^2)$  = 0.095  
 $S$  = 1.06  
 4128 reflections  
 250 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 1.2308P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}}$  = 0.004  
 $\Delta\rho_{\text{max}}$  = 0.48 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.65 e Å<sup>-3</sup>

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

N1—Ni1	2.084 (2)	N4—Ni1	2.051 (2)
N2—Ni1	2.039 (2)	O1—Ni1	2.1422 (19)
N3—Ni1	2.097 (2)	O2—Ni1	2.188 (2)
N2—Ni1—N4	176.12 (9)	N1—Ni1—O1	92.71 (8)
N2—Ni1—N1	84.03 (9)	N3—Ni1—O1	161.81 (8)
N4—Ni1—N1	99.04 (9)	N2—Ni1—O2	79.14 (9)
N2—Ni1—N3	98.52 (9)	N4—Ni1—O2	97.54 (9)
N4—Ni1—N3	83.48 (9)	N1—Ni1—O2	162.13 (9)
N1—Ni1—N3	97.34 (9)	N3—Ni1—O2	91.11 (9)
N2—Ni1—O1	97.57 (8)	O1—Ni1—O2	83.64 (8)
N4—Ni1—O1	79.99 (8)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1C...O3	0.90	2.24	3.007 (3)	143
N1—H1D...O4 <sup>i</sup>	0.90	2.10	2.994 (3)	170
N3—H3C...O7 <sup>ii</sup>	0.90	2.24	3.087 (6)	157
N3—H3D...O4 <sup>iii</sup>	0.90	2.07	2.965 (3)	170
O8—H8C...O6	0.84 (1)	1.97 (5)	2.659 (5)	139 (7)
O8—H8C...O7	0.84 (1)	2.02 (6)	2.488 (7)	115 (5)
O8—H8D...O5 <sup>iv</sup>	0.84 (1)	2.08 (1)	2.910 (5)	174 (6)
N4—H4...O3 <sup>i</sup>	0.82 (3)	2.04 (3)	2.820 (3)	159 (3)
O1—H1...O6	0.93 (4)	1.71 (4)	2.633 (3)	172 (4)
O2—H2...O8 <sup>v</sup>	0.87 (4)	1.91 (4)	2.735 (5)	158 (4)
O2—H2...O7 <sup>ii</sup>	0.87 (4)	2.14 (4)	2.711 (6)	123 (3)
N2—H3...O5 <sup>iii</sup>	0.85 (3)	2.05 (3)	2.842 (3)	154 (3)

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

The water O atom was found to be disordered over two positions, O7 and O8. The occupancy factors for these positions were initially refined to 0.452 (6) and 0.548 (6), respectively, and later fixed at 0.50 each. The H atoms attached to atom O8 were located in a difference map and were refined with the O—H and H...H distances restrained

to 0.84 (1) and 1.37 (2) Å, respectively, while those attached to atom O7 were not located. The H atoms attached to —NH and —OH groups were located in a difference map and were refined freely. The remaining H atoms were placed in calculated positions, with N—H = 0.90 Å and C—H = 0.97 Å, and were allowed to ride on their parent atom, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

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 for Windows* (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 TAPF020.

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