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Tris(1,10-phenanthroline)nickel(II) squarate octahydrate

Ibrahim Uçar,[a]* Okan Zafer Yeşilel,[b] Ahmet Bulut,[a] Halis Ölmez[b] and Orhan Büyükgüngör[a]

[a]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayís University, TR-55139, Kurupelit-Samsun, Turkey, and [b]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, TR-55139, Kurupelit-Samsun, Turkey

Correspondence e-mail: iucar@omu.edu.tr

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In the title mononuclear [Ni(phen)$_3$]sq·8H$_2$O complex [phen is 1,10-phenanthroline ($C_{12}H_8N_2$) and sq is squarate ($C_4O_4^{2-}$)], the Ni^{II} ion has a distorted octahedral coordination geometry composed of six N atoms from three bidentate chelating phen ligands. An extensive three-dimensional network of O$_{water}$—H···O, O$_{water}$—H···O$_{water}$ and C—H···O hydrogen-bonding interactions is responsible for crystal stabilization.

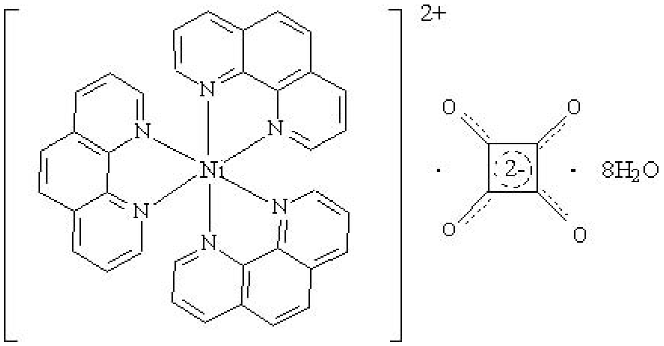
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.083
Data-to-parameter ratio = 15.0

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

Comment

In recent years, considerable progress has been made in the crystal engineering of multidimensional arrays and networks containing metal ions as nodes. From the viewpoint of crystal engineering, squaric acid is a useful tool for constructing crystalline architectures, because of its rigid, planar four-membered ring framework, and its proton donating and accepting capabilities for hydrogen bonding (Reetz *et al.*, 1994; Bertolasi *et al.*, 2001; Zaman *et al.*, 2001; Mathew *et al.*, 2002; Uçar *et al.*, 2004). Squaric acid has also been studied for potential application in xerographic photoreceptors, organic solar cells and optical recording (Seitz & Imming, 1992; Liebeskind *et al.*, 1993). Additionally, mixed-ligand metal complexes of 1,10-phenanthroline (phen) and its substituted derivatives continue to attract attention because this group plays an important role in biological systems, such as binding of small molecules to DNA (Xu *et al.*, 2002; Macias *et al.*, 2003; Sastri *et al.*, 2003). In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal complexes of squaric acid and their structures have been reported (Bulut *et al.*, 2004; Yeşilel *et al.*, 2004). In this context, the title mixed-ligand complex, (I), of nickel squarate with phen has been prepared and its crystal structure is reported here.



(I)

The asymmetric unit of (I) contains an [Ni(phen)$_3$]$^{2+}$ complex cation, an uncoordinated squarate dianion, $C_4O_4^{2-}$, and eight water molecules (Fig. 1). The title complex has

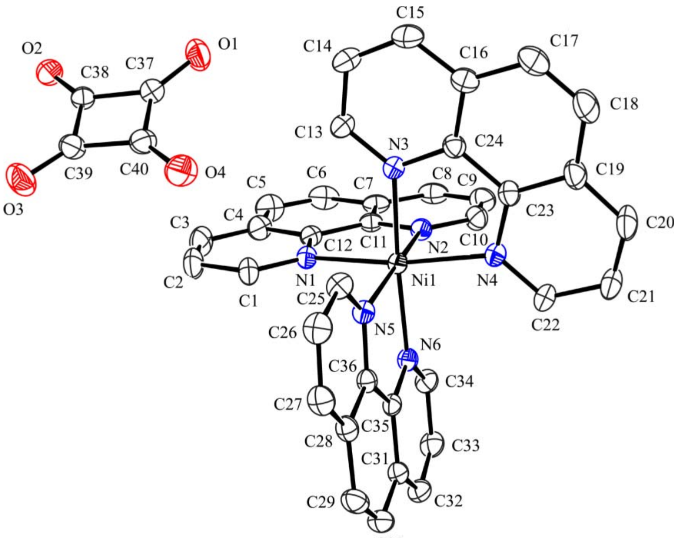


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Water molecules and H atoms have been omitted for clarity.

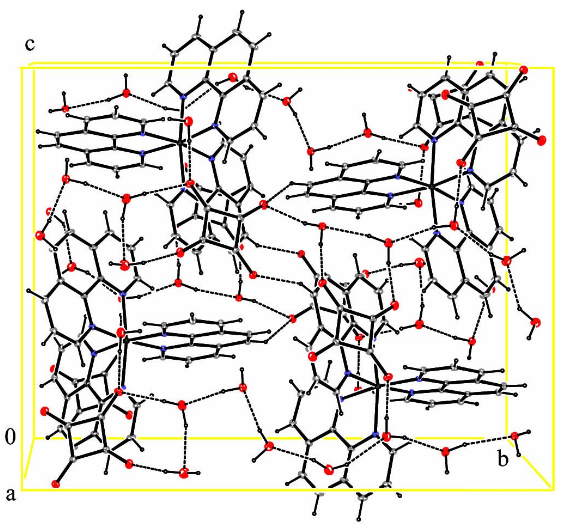


Figure 2

A packing diagram of (I). Dashed lines represent intermolecular hydrogen bonds.

distorted octahedral coordination geometry composed of six N atoms from the chelating phen ligands. The Ni1—N bond distances range from 2.0814 (16) to 2.0954 (17) Å, and are in agreement with those observed in other $[Ni(phen)_3]^{2+}$ complexes (Suescun *et al.*, 1999; Skoulika *et al.*, 1995). The angles subtended at the Ni atom by the phen ligands are 80.01 (7), 79.86 (7) and 79.77 (6)°, which are in agreement with those previously reported for other phen-containing Ni^{II} complexes (Cherni *et al.*, 1999; Lin *et al.*, 2003). All the N—Ni—N bond angles deviate significantly from the ideal values of 90 or 180° because of the constrained geometry of the phen ring systems (Table 1).

The molecular packing in (I) is controlled by intermolecular hydrogen bonding interactions (Fig. 2). The eight solvent water molecules link the squarate dianions to each other through hydrogen-bonding interactions (see Table 2 for details). The complex cation and squarate dianion are also linked to each other *via* C—H···O hydrogen bonding. These interactions are responsible for constructing a three-dimensional network in the crystal structure of (I).

Experimental

Squaric acid (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 $NiCl_2 \cdot H_2O$ (0.73 g, 5 mmol) dissolved in water (50 ml). The mixture was refluxed at 333 K for 12 h and then cooled to room temperature. The light blue crystals that formed were filtered off and washed with water and ethanol, and dried in a vacuum. A solution of 1,10-phenanthroline (0.54 g, 3 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of $Ni(sq) \cdot 2H_2O$ (0.20 g, 1 mmol) in water (50 ml). The resulting red solution was refluxed for 2 h and then cooled to room temperature. After a few days, well formed red crystals were selected for X-ray studies.

Crystal data

$[Ni(C_{12}H_8N_2)_3](C_4O_4) \cdot 8H_2O$
$M_r = 855.47$
Monoclinic, $P2_1/c$
$a = 10.9746$ (4) Å
$b = 21.4090$ (11) Å
$c = 17.0115$ (6) Å
$\beta = 98.468$ (3)°
$V = 3953.4$ (3) Å^3
$Z = 4$

$D_x = 1.437$ Mg m$^{-3$}
Mo *K*α radiation
Cell parameters from 12 345 reflections
$\theta = 1.5$–27.2°
$\mu = 0.56$ mm^{-1}
$T = 297$ (2) K
Prism, red
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.737$, $T_{max} = 0.900$
56 939 measured reflections
8678 independent reflections

5074 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.1°$
$h = -13 \rightarrow 14$
$k = -27 \rightarrow 27$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.083$
$S = 0.84$
8678 reflections
580 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

N1—Ni1	2.0814 (15)	N4—Ni1	2.0913 (16)
N2—Ni1	2.0823 (17)	N5—Ni1	2.0829 (16)
N3—Ni1	2.0886 (17)	N6—Ni1	2.0954 (17)
N1—Ni1—N2	80.02 (7)	N5—Ni1—N4	93.21 (6)
N1—Ni1—N5	94.31 (6)	N3—Ni1—N4	79.85 (7)
N2—Ni1—N5	170.69 (7)	N1—Ni1—N6	91.68 (6)
N1—Ni1—N3	94.59 (6)	N2—Ni1—N6	92.96 (6)
N2—Ni1—N3	93.26 (6)	N5—Ni1—N6	79.75 (6)
N5—Ni1—N3	94.56 (6)	N3—Ni1—N6	171.84 (6)
N1—Ni1—N4	170.99 (6)	N4—Ni1—N6	94.54 (6)
N2—Ni1—N4	93.13 (7)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O10	0.84 (3)	1.98 (3)	2.804 (3)	166 (4)
O5—H5*B*···O4$^{\rm i}$	0.84 (2)	1.88 (2)	2.723 (3)	178 (3)
O6—H6*A*···O5	0.85 (3)	1.99 (3)	2.788 (3)	155 (4)
O6—H6*B*···O7$^{\rm ii}$	0.85 (3)	1.96 (3)	2.776 (3)	160 (3)
O7—H7*A*···O6$^{\rm iii}$	0.84 (3)	2.18 (3)	2.886 (3)	141 (3)
O7—H7*B*···O8$^{\rm iv}$	0.84 (3)	1.93 (3)	2.747 (3)	163 (3)
O8—H8*A*···O9$^{\rm iii}$	0.85 (2)	2.02 (2)	2.843 (3)	162 (3)
O8—H8*B*···O11	0.86 (2)	1.85 (2)	2.698 (3)	171 (3)
O9—H9*A*···O1$^{\rm v}$	0.83 (2)	2.02 (2)	2.825 (3)	164 (3)
O9—H9*B*···O2$^{\rm vi}$	0.84 (2)	1.90 (2)	2.735 (2)	173 (3)
O10—H10*A*···O9	0.84 (2)	2.04 (2)	2.848 (2)	163 (3)
O10—H10*B*···O3$^{\rm vi}$	0.84 (2)	1.88 (2)	2.716 (3)	170 (3)
O11—H11*A*···O12	0.84 (2)	1.97 (2)	2.797 (4)	167 (3)
O11—H11*B*···O4	0.85 (2)	1.92 (2)	2.746 (3)	163 (3)
O12—H12*B*···O3	0.86 (3)	1.92 (3)	2.765 (4)	167 (3)
C6—H6···O2$^{\rm vii}$	0.93	2.58	3.464 (3)	159
C30—H30···O1$^{\rm v}$	0.93	2.51	3.306 (4)	144

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

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed to ride on the parent atom [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The water H atoms were located in a difference map and were refined with the O—H and H···H distances restrained to 0.84 (1) and 1.34 (2) Å, respectively, and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

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: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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