Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(triethanolamine-$\kappa^3 N,O,O'$)nickel(II) squarate

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

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

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

Received 5 January 2004
Accepted 20 January 2004
Online 30 January 2004

The crystal structure determination of the title compound, $[Ni(C_6H_{15}NO_3)_2](C_4O_4)$, is reported; the squarate dianion is located on an inversion centre and a supramolecular architecture is formed. All the O atoms of the squarate dianion are involved in hydrogen bonding and connect two centrosymmetric nickel triethanolamine complex cations through two symmetry-related hydrogen bonds. There is also a hydrogen-bond interaction between the free hydroxyl O atom of the complex cation and one of the O atoms of the squarate dianion. All these hydrogen bonds link the molecular units in chains. The inter-chain packing is formed by van der Waals forces.

Key indicators

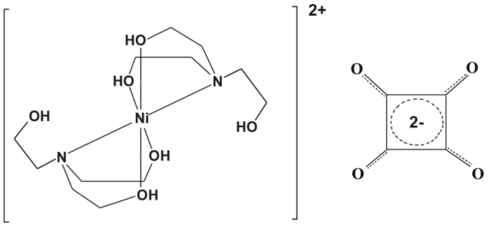
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.089
Data-to-parameter ratio = 24.3

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

© 2004 International Union of Crystallography
Printed in Great Britain – all rights reserved

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).



(I)

In this context, squaric acid (H_2Sq) and its metal complexes are of potential interest since it is a molecule frequently used to build cocrystals (Bouma *et al.*, 1999; Bertolasi *et al.*, 2001; Bulut *et al.*, 2003). Furthermore, the triethhanolamine (TEA) ligand, having a number of potential donor sites which are high in electronegativity, and a diversity of coordination modes, is also conducive to the construction of supramolecular structures. Although TEA usually acts as an N,O,O'-tridentate ligand in transition metal complexes (Sen & Dotson, 1970; Icbudak *et al.*, 1995; Topcu *et al.*, 2001), an N,O,O',O''-tetradentate ligand behaviour has also been observed, especially towards metal ions having large ionic radii (Chiswell *et al.*,

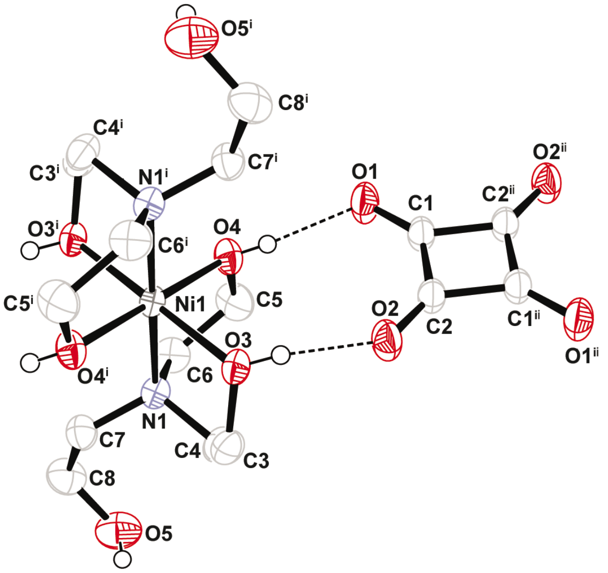


Figure 1
An *ORTEP*III (Burnett & Johnson, 1996) view of (I). The atom-numbering scheme is shown and displacement ellipsoids are drawn at the 50% level. H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$.]

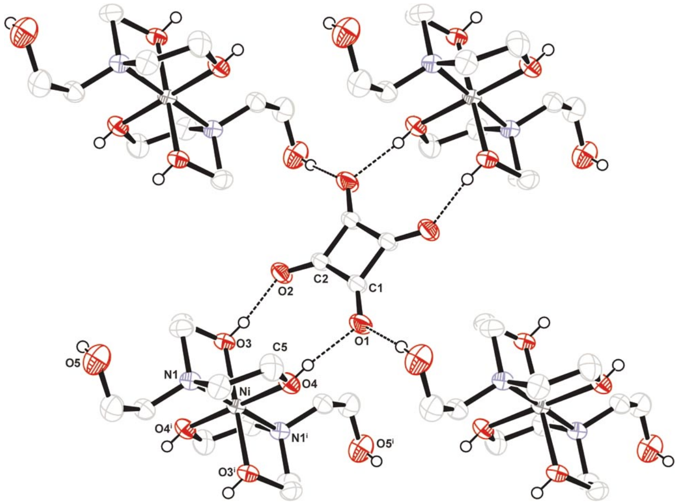


Figure 2
An *ORTEP*III (Burnett & Johnson, 1996) drawing of the hydrogen-bonding, shown as dashed lines.

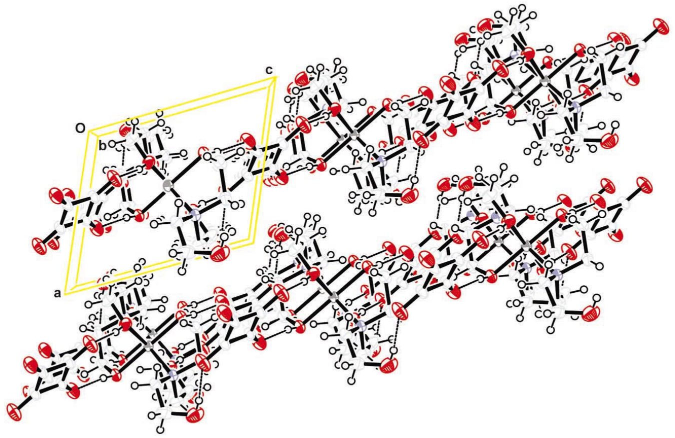


Figure 3
The three-dimensional structure of the cocrystal. Dashed lines indicate the hydrogen bonds. Adjacent layers interlock in a square-wave pattern.

1987). The present study reports the crystal structure of bis(triethanolamine-κ^3N,O,O')nickel(II) squarate, (I).

A view of (I) and its numbering scheme are shown in Fig. 1. The crystal structure consists of a complex cation and one squarate anion. In the complex cation, the Ni$^{\rm II}$ ion lies on a centre of symmetry, sandwiched by two bulky TEA ligands. Each TEA acts as a tridentate ligand through two of the three hydroxyl O atoms and the amine N atom, resulting in a six-coordinate Ni$^{\rm II}$ ion similar to those observed for the Ni complex of TEA with chloride (Icbudak *et al.*, 1995), saccharine (Topcu *et al.*, 2001) and acetate (Krabbes *et al.*, 2000). The coordination geometry around the Ni$^{\rm II}$ ion is irregular and indicates a distorted octahedral geometry, whereas the squarate counter-anion is planar and centrosymmetric, 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 hydroxyl O atoms of two TEA ligands form the equatorial plane of the octahedral geometry, while atoms N1 and N1$^{\rm i}$ are placed in axial positions (symmetry code as in Fig. 1). In the complex, Ni—O distances are in the range 2.0581 (11)–2.0708 (11) Å and the Ni—N distance is 2.0992 (12) Å, while the bond angles at Ni range from 81.63 (4) to 95.64 (4)°. The dihedral angle between the squarate plane (O1/C1/C2/O2) and the equatorial plane (O3/O4/Ni1) of the complex is 17.92 (12)°.

The Sq^{2-} anions lie on centres of symmetry and form a quite simple supramolecular architecture. Each squarate anion is surrounded by four centrosymmetric [Ni(TEA)$_2$]$^{2+}$ cations. Two are connected to each other by two hydrogen bonds involving squarate O atoms [O3···O2 = 2.5579 (14) Å and O4···O1 = 2.5976 (14) Å], while the other two cations are connected by a hydrogen bond interaction between the free hydroxyl O5 of TEA and O1 of the squarate dianion [O5···O1 = 2.8000 (19) Å], as shown in Fig. 2. These hydrogen bonds are responsible for linking the ions in chains. There are also weak van der Waals interactions, which are responsible for the inter-chain packing (Fig. 3).

Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in 25 ml water was 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 100 ml water. 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 washed with water and alcohol and dried in vacuum. A solution of triethanolamine (0.298 g, 2 mmol) in ethanol (50 ml) was added dropwise with stirring to a suspension of NiSq·2H$_2$O (0.207 g, 1 mmol) in water (100 ml). The mixture was refluxed at 323 K for 12 h and then cooled to room temperature. A few days later, well formed crystals were selected for X-ray studies.

Acta Cryst. (2004). E**60**, m228–m230 Okan Zafer Yeşilel *et al.* • [Ni(C$_6$H$_{15}$NO$_3$)$_2$](C$_4$O$_4$) **m229**

Crystal data

$[Ni(C_6H_{15}NO_3)_2](C_4O_4)$
$M_r = 469.13$
Triclinic, $P\overline{1}$
$a = 7.5058\ (7)$ Å
$b = 8.5766\ (8)$ Å
$c = 8.9156\ (8)$ Å
$\alpha = 102.551\ (7)^\circ$
$\beta = 110.398\ (7)^\circ$
$\gamma = 99.698\ (7)^\circ$
$V = 506.04\ (9)$ Å^3

$Z = 1$
$D_x = 1.539$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15818 reflections
$\theta = 1.2$–32.1°
$\mu = 1.02$ mm^{-1}
$T = 293\ (2)$ K
Prism, violet
0.45 × 0.43 × 0.28 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{min} = 0.516$, $T_{max} = 0.772$
6624 measured reflections

3549 independent reflections
3346 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 32.2^\circ$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.08$
3549 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.108 (7)

Table 1
Selected geometric parameters (Å, °).

Ni1—O3	2.0581 (9)	O1—C1	1.2537 (15)
Ni1—O4	2.0707 (10)	O2—C2	1.2437 (16)
Ni1—N1	2.0992 (11)	C1—C2	1.4604 (18)
O3—Ni1—O4	95.64 (4)	O4—Ni1—N1	81.63 (4)
O3—Ni1—N1	84.26 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O1^{iii}	0.81 (3)	2.00 (3)	2.8000 (19)	172 (3)
O3—H3···O2	0.78 (2)	1.79 (2)	2.5579 (14)	169 (2)
O4—H4···O1	0.75 (2)	1.86 (2)	2.5976 (14)	168 (3)

Symmetry code: (iii) $x, y - 1, z$.

H atoms of the hydroxyl groups were found in a difference map and the parameters were freely refined. O—H bond distances were in the range 0.75 (2)–0.81 (3) Å and U_{iso}(H) values in the range 0.047 (5)–0.067 (8) Å^2. Other H atoms were introduced at idealized positions (C—H = 0.97 Å) and were allowed to ride on the parent atom [$U_{iso}(H) = 1.2U(C)$].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1461–1494.

Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (2001). *Acta Cryst.* B**57**, 591–598.

Bouma, B., Kooijman, H., Kroon, J., Grech, E. & Brzezinski, B. (1999). *Acta Cryst.* C**55**, 1824–1826.

Bulut, A., Yeşilel, O. Z., Dege, N., İçbudak, H., Ölmez, H. & Büyükgüngör, O. (2003). *Acta Cryst.* C**59**, o727–o729.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Chiswell, B., McKenzie, E. D. & Lindoy, L. F. (1987). *Comprehensive Coordination Chemistry*, Vol. 4, edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty, pp. 1–122. Oxford: Pergamon Press.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.

Icbudak, H., Yılmaz, V. T., Howie, R. A., Andac, O. & Olmez, H. (1995). *Acta Cryst.* C**51**, 1759–1761.

Kahn, O. (1993). *Molecular Magnetism*. New York: VCH.

Kepert, C. J. & Rosseinsky, M. J. (1999). *Chem. Commun.* **1**, 31–32.

Krabbes, I., Seichter, W. & Gloe, K. (2000). *Acta Cryst.* C**56**, e178-e178.

Sen, B. & Dotson, R. L. (1970). *J. Inorg. Nucl. Chem.* **32**, 2707–2716.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany, 1997.

Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Topcu, Y., Andac, O., Yılmaz, V. T. & Harrison, W. T. A. (2001). *Acta Cryst.* E**57**, m82–m84.

Venkataraman, D., Gardner, G. B., Lee, S. & Moore, J. S. (1995). *J. Am. Chem. Soc.* **117**, 11600–11601.

Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.

m230 Okan Zafer Yeşilel *et al.* • $[Ni(C_6H_{15}NO_3)_2](C_4O_4)$ *Acta Cryst.* (2004). E**60**, m228–m230