Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

μ-Oxalato-bis[(1,4,8,11-tetraazacyclotetradecane)nickel(II)] bis(perchlorate) hemihydrate

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Received 1 September 2006
Accepted 17 September 2006

The title compound, $[Ni_2(C_2O_4)(C_{20}H_{48}N_8)](ClO_4)_2\cdot 0.5H_2O$, contains dinuclear $[Ni_2(C_2O_4)(cyclam)_2]^{2+}$ cations (cyclam is 1,4,8,11-tetraazacyclotetradecane) lying on centres of inversion. The geometry of the complex is comparable to that in a previously reported nitrate salt.

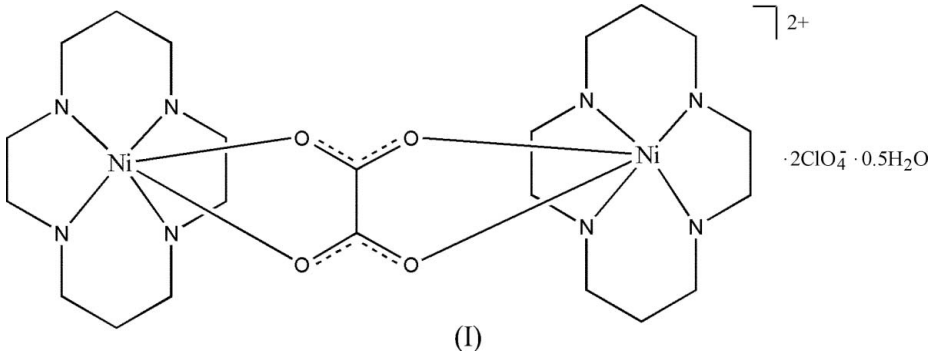
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.047
wR factor = 0.128
Data-to-parameter ratio = 14.1

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

Comment

The 14-membered macrocyle cyclam (1,4,8,11-tetraazacyclotetradecane) has been studied extensively (Melson, 1979; Ciampolini *et al.*, 1992), and its complexes find application in various areas (for example, Konig *et al.*, 1996). The dinuclear cation $[Ni_2(C_2O_4)(cyclam)_2]^{2+}$ has been reported previously, with the nitrate counter-anion (Battaglia *et al.*, 1988). The title compound, (I) (Fig. 1), contains $[Ni_2(C_2O_4)(cyclam)_2]^{2+}$ together with perchlorate anions and water molecules.



(I)

In (I), each Ni atom adopts a distorted octahedral geometry. The bond distances and angles (Table 1) are in general agreement with those reported previously (Battaglia *et al.*, 1988), although the Ni—O distances in (I) are slightly longer. The uncoordinated water molecules lie in suitable positions to form hydrogen bonds to the perchlorate anions. They are included with partial occupancy to provide acceptable displacement parameters, and the designation of the compound as a hemihydrate is therefore approximate.

Experimental

The compound $[Ni(cyclam)(ClO_4)_2]$ was prepared according to a literature method (Ferreira *et al.*, 2003). The title compound was then prepared by adding a 5 ml methanol solution of $Na_2C_2O_4$ (0.12 mmol) to a 10 ml methanol solution of $[Ni(cyclam)(ClO_4)_2]$ (0.2 mmol). The mixture was stirred and refluxed for 2 h, then cooled and filtered. The filtrate was kept at room temperature for several days, providing purple crystals of (I). Elemental analysis found: C 32.54, H 6.12, N 13.69%; calculated: C 32.46, H 6.07, N 13.77%.

Crystal data

$[Ni_2(C_2O_4)(C_{20}H_{48}N_8)](ClO_4)_2\cdot 0.5H_2O$	$V = 1744.5\ (7)$ Å^3
$M_r = 814.01$	$Z = 2$
Monoclinic, $P2_1/n$	$D_x = 1.550$ Mg m^{-3}
$a = 8.854\ (2)$ Å	Mo $K\alpha$ radiation
$b = 13.350\ (3)$ Å	$\mu = 1.30$ mm^{-1}
$c = 15.245\ (4)$ Å	$T = 293\ (2)$ K
$\beta = 104.513\ (4)^\circ$	Block, purple
	0.24 × 0.16 × 0.10 mm

Data collection

Bruker SMART APEXII CCD diffractometer	8405 measured reflections
φ and ω scans	3067 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1951 reflections with $I > 2\sigma(I)$
$T_{min} = 0.627$, $T_{max} = 0.878$	$R_{int} = 0.054$
	$\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.2902P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$(\Delta/\sigma)_{max} = 0.005$
$wR(F^2) = 0.128$	$\Delta\rho_{max} = 0.52$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
3067 reflections	
217 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.086 (2)	Ni1—O2^{i}	2.101 (2)
Ni1—N4	2.089 (3)	Ni1—N2	2.103 (3)
Ni1—N3	2.093 (3)	Ni1—N1	2.109 (3)
O1—Ni1—N4	167.83 (10)	N3—Ni1—N2	83.13 (12)
O1—Ni1—N3	92.15 (11)	O2^{i}—Ni1—N2	170.81 (10)
N4—Ni1—N3	92.16 (12)	O1—Ni1—N1	93.96 (11)
O1—Ni1—O2^{i}	79.68 (8)	N4—Ni1—N1	83.02 (12)
N4—Ni1—O2^{i}	88.65 (10)	N3—Ni1—N1	171.58 (12)
N3—Ni1—O2^{i}	94.39 (11)	O2^{i}—Ni1—N1	92.40 (11)
O1—Ni1—N2	91.55 (10)	N2—Ni1—N1	90.91 (12)
N4—Ni1—N2	100.26 (11)		

Symmetry code: (i) $-x+2, -y+1, -z+2$.

H atoms were included in calculated positions and allowed to ride during subsequent refinement with C—H = 0.97 Å, N—H = 0.91 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$. Restraints were applied to the Cl—O and O···O distances of the perchlorate anion to ensure a reasonable tetrahedral geometry. Atom O7 is included with partial occupancy to provide an acceptable displacement parameter; the description of (I) as a hemihydrate is therefore approximate. H atoms were not included on this solvent water molecule.

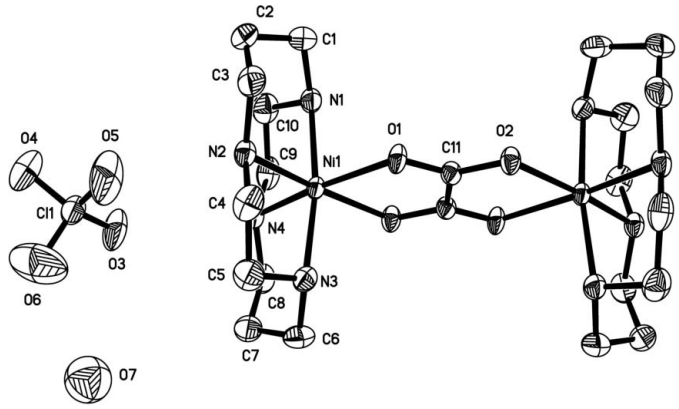


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted. Unlabelled atoms are related to labelled atoms by $2-x, 1-y, 2-z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China.

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