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Bis[ethyl 2-cyano-2-(oxidoimino)acetate]-bis(ethylenediamine)nickel(II) hexahydrate

Mikhail P. Azarkh,[a] Nikolay M. Dudarenko,[a] Igor O. Fritsky,[a]* Turganbay S. Iskenderov[b] and Jolanta Świątek-Kozłowska[c]

[a]National Taras Shevchenko University, Department of Chemistry, Volodymyrska Str. 64, 01033 Kiev, Ukraine, [b]Karakalpakian University, Department of Chemistry, Universitet Keshesi 1, 742012 Nukus, Uzbekistan, and [c]Medical University of Wrocław, Department of Basic Medical Sciences, J. Kochanowskiego Str. 14, 51-601 Wrocław, Poland

Correspondence e-mail: ifritsky@univ.kiev.ua

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The centrosymmetric neutral mononuclear title complex, $[Ni(C_5H_5N_2O_3)_2(C_2H_8N_2)_2]\cdot 6H_2O$, has the Ni centre in a distorted octahedral environment, defined by six N atoms belonging to two chelating ethylenediamine molecules and two cyano N atoms derived from cyanoxime ligands. The O atom of the deprotonated oxime group forms hydrogen bonds with two solvent water molecules.

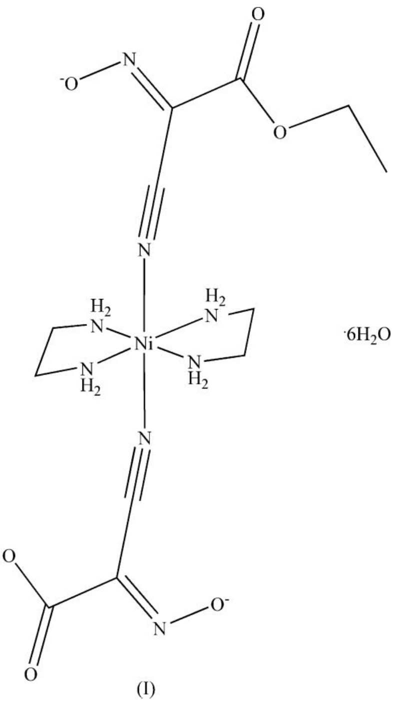
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.114
Data-to-parameter ratio = 16.0

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

Comment

Over the past two decades, much attention has been paid to the chemistry of cyanoximes RC(=NOH)CN, an interesting class of organic ligands (Skopenko *et al.*, 1983), because of their simplicity and coordination versatility. As a general rule, the cyano group of these ligands does not take part in metal ion coordination, with only a few known examples (Domasevich, 1997; Skopenko *et al.*, 1994; Ponomareva, Skopenko *et al.*, 1997). The most typical coordination modes for cyanoximes are O-coordination for p-metals (Domasevich *et al.*, 1996, 2000; Skopenko *et al.*, 1994, 1997) and chelate N(oxime)-coordination for d-metals (Hvastijova *et al.*, 1999; Eddings *et al.*, 2004; Ponomareva, Domasevich *et al.*, 1997; Sliva *et al.*, 1997).



(I)

During a study on different types of coordination of the ligands, the title complex, (I), was obtained, in which the

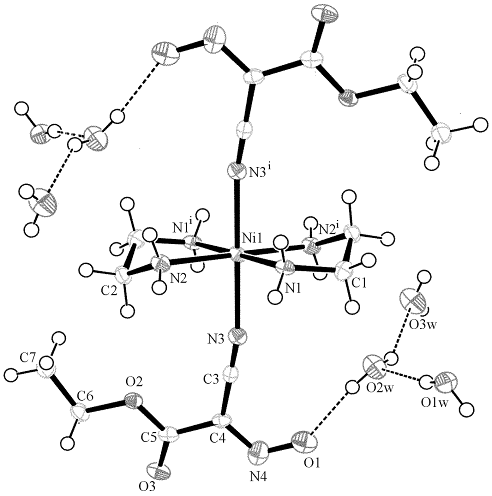


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 60% probability level. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

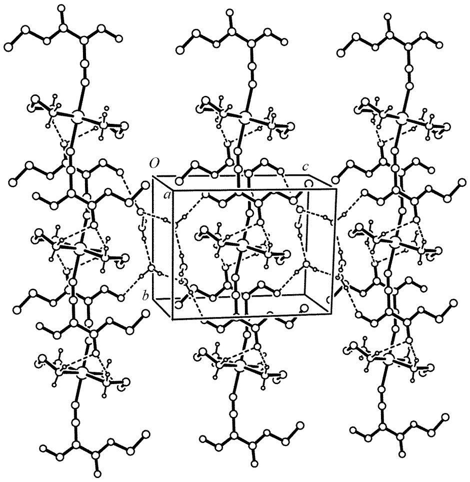


Figure 2
A view of the crystal packing in (I). H atoms not involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

cyanoxime ligand was found to act as a monodentate ligand to Ni, binding *via* the N atom of the cyano group.

A distorted octahedral coordination geometry is found in (I) with the Ni atom lying on a center of inversion (Fig. 1). Four N atoms of two chelating ethylenediamine ligands define the equatorial plane, each ligand forming a five-membered ring with an envelope conformation, and the two *trans*-coordinated cyanoxime ligands complete the octahedral coordination geometry. The Ni—N bond lengths in the equatorial plane (Table 1) are somewhat longer than the Ni—N distances in centrosymmetric bis(ethylenediamine)-nickel(II) dinitrate of 2.017 (2) and 2.002 (2) Å (Krause Bauer *et al.*, 2005).

A view of the crystal packing in (I) is shown in Fig. 2, and the parameters defining the hydrogen bonds are listed in Table 2. Molecules of (I) form chains along the *b* axis owing to hydrogen bonds formed between the amino H atoms and the carboxylate atom O3, and between the solvent water molecules and the oxime atom O1. Further π–π interaction between the axial ligands of translationally related complexes is observed with the shortest intermolecular separations $O2\cdots N4^{v} = 3.406\ (3)$ Å and $C5\cdots C4^{v} = 3.384\ (4)$ Å.

Experimental

Ethyl 2-cyano-2-(hydroxyimino)acetate was prepared according to the method reported by Conrad & Schulze (1909). Complex (I) was synthesized by adding a mixture of nickel(II) chloride (0.1 mmol, 0.013 g) and sodium hydroxide (0.2 mmol, 0.2 ml of 1 *M* aqueous solution) to a mixture of 0.013 ml of ethylenediamine (0.2 mmol, 0.012 g), 0.1 ml of H_2SO_4 (0.1 mmol, 1 *M* aqueous solution) and the cyanoxime ligand (0.2 mmol, 0.028 g) in a mixture of water and methanol (1:1, 3 ml) with boiling over 15 min. The resulting solution was filtered and the blue filtrate was left to stand at room temperature. Slow evaporation of the solvent yielded dark-blue crystals of (I). Elemental analysis calculated for $C_{14}H_{38}N_8NiO_{12}$: C 29.54, H 6.73, N 19.60 9%; found: C 29.42, H 6.55, N 19.60%. IR (KBr pellet, cm^{-1}): ν(C≡N) 2225, ν(C=N) 1630, ν(N–O) 1380.

Crystal data

$[Ni(C_5H_5N_2O_3)_2(C_2H_8N_2)_2]\cdot 6H_2O$
$M_r = 569.23$
Triclinic, $P\overline{1}$
$a = 6.690\ (1)$ Å
$b = 8.833\ (2)$ Å
$c = 11.044\ (2)$ Å
$\alpha = 83.11\ (3)^\circ$
$\beta = 81.19\ (3)^\circ$
$\gamma = 75.69\ (3)^\circ$

$V = 622.6\ (2)$ Å^3
$Z = 1$
$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.85$ mm^{-1}
$T = 100\ (2)$ K
Prism, blue
0.25 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.802$, $T_{\max} = 0.905$

4325 measured reflections
2742 independent reflections
2332 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 28.3^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.114$
$S = 1.05$
2742 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.4591P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.90$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.084 (2)	O1—N4	1.250 (3)
Ni1—N2	2.090 (2)	N4—C4	1.329 (4)
Ni1—N3	2.156 (2)		
N1—Ni1—N2^{i}	83.25 (9)	N2—Ni1—N3	89.98 (9)
N1—Ni1—N3	87.58 (9)	N3^{i}—Ni1—N3	180
N1—Ni1—N3^{i}	92.42 (9)	O1—N4—C4	116.6 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O1$^{\rm ii}$	0.87	1.92	2.788 (3)	171
O1*W*—H12*W*···O2*W*	0.81	1.95	2.744 (3)	167
O2*W*—H21*W*···O1	0.86	1.98	2.833 (3)	173
O2*W*—H22*W*···O3*W*	0.83	2.00	2.724 (3)	146
O3*W*—H31*W*···O1*W*$^{\rm iii}$	0.87	1.97	2.823 (3)	167
O3*W*—H32*W*···O1*W*$^{\rm iv}$	0.81	2.00	2.797 (3)	171
N1—H11*N*···O3$^{\rm v}$	0.90	2.21	3.055 (3)	155
N1—H12*N*···O3$^{\rm vi}$	0.90	2.27	3.050 (3)	145
N2—H22*N*···O3$^{\rm v}$	0.90	2.51	3.316 (3)	149

Symmetry codes: (ii) $-x+1, -y, -z+2$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+2$; (v) $x, y+1, z$; (vi) $-x+2, -y, -z+1$.

The H atoms of the water molecules were located in a difference Fourier map and fixed in these positions with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. Other H atoms were included in the riding-model approximation with C—H = 0.96–0.97 Å and N—H = 0.90 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$ and $1.5U_{\rm eq}$(methyl C).

Data collection: *KM-4-CCD Software* (Kuma, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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).

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