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Tris(ethylenediamine)nickel(II) bis[2-cyano-2-(oxidoimino)acetamidato]nickelate(II) monohydrate

Andrey I. Buvaylo,[a] Nikolay M. Dudarenko,[a] Igor O. Fritsky[a]* and Jolanta Świątek-Kozłowska[b]

[a]National Taras Shevchenko University, Department of Chemistry, Volodymyrska str. 64, 01033 Kiev, Ukraine, and [b]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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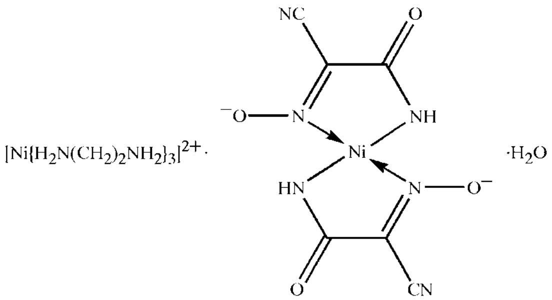
The title compound, $[Ni(C_2H_8N_2)_3][Ni(C_3HN_3O_2)_2]\cdot H_2O$, appears to be a modular associate consisting of two complex counter-ions, containing bivalent nickel as the central atom in both cases, and a solvent water molecule. The Ni^{II} ion in the complex cation lies on the C_2 crystallographic axis. Its coordination environment is formed by six N atoms of three ethylenediamine (en) molecules, representing a distorted octahedral geometry. The Ni^{II} ion in the complex anion occupies a position at the center of inversion. It exhibits a distorted square-planar coordination geometry formed by four N atoms belonging to the deprotonated oxidoimine and amide groups of the two doubly charged 2-cyano-2-(oxidoimino)acetamidate anions, situated in *trans* positions with respect to each other. In the crystal packing, the complex anions are linked by water molecules *via* hydrogen bonds between the amide O atoms and water H atoms, forming chains translated along the *a* direction. The $[Ni(en)_3]^{2+}$ cations fill empty spaces between the translational chains, connecting them by hydrogen bonds between the oxime and amide O atoms of the anions and the amine H atoms of the cations, forming layers along the *ac* plane. The water molecules provide connection between layers through N atoms of the cations, thus forming a three-dimensional modular structure.

Comment

Mononuclear complexes of transition metals containing additional vacant donor sets are of current interest as convenient blocks for the building of polynuclear systems widely used in bioinorganic modeling, electron transfer and molecular magnetism (Kahn, 1993). Polydentate ligands containing oxime groups attract particular attention owing to the possibility that these groups may provide a bridging mode of coordination and mediate very strong magnetic exchange interactions between metal ions (Colacio *et al.*, 1994, and references therein). 2-Cyano-2-(hydroxyimino)acetamide is an efficient chelating ligand for Cu^{II} and Ni^{II} ions (Sliva, Duda *et al.*, 1997). It exhibits either *N*,*O*-chelation [*via* the oxime N atom and amide O atom forming a five-membered chelate ring (Skopenko *et al.*, 1983; Gerasimchuk *et al.*, 1993)] or *N*,*N*-chelation [*via* the oxime and amide N atoms (Sliva, Duda *et al.*, 1997; Mokhir *et al.*, 1998)] forming mononuclear complexes. Bridging coordination modes have been reported by Skopenko *et al.* (1997) (the 2-carbamoylcyanoketoximato *O*,*O*′-bridging mode) and Price *et al.* (2003) (the carbamoyl-μ_2-cyanoketoximato *N*,*O*-bridging mode). In the case of spatial difficulties, the monodentate coordination mode *via* the oxime O atom (Domasevich *et al.*, 1995) and the amide O atom (Domasevitch *et al.*, 1998) is realized. To the best of our knowledge, no structural characterization of modular complexes of the corresponding ligand has been reported to date. We present here the synthesis and X-ray crystal structure of the title modular associate, (I), containing Ni^{II} ions in both complex ions.



(I)

An *ORTEP-3* (Farrugia, 1997) view of (I) and packing diagrams are shown in Figs. 1–3, and geometric and hydrogen-bonding parameters are given in Tables 1 and 2. The title compound consists of two discrete modules, each containing an Ni atom in a different coordination environment.

In the complex cation, the Ni^{II} ion lies on the C_2 crystallographic axis. The coordination environment is formed by six N atoms of three ethylenediamine molecules, providing a distorted octahedral geometry. The axial Ni—N distances [Ni1—N5 = 2.113 (2) Å] are a little shorter than those in the equatorial plane [Ni1—N6 = 2.125 (2) Å and Ni1—N4 = 2.124 (2) Å]. The values of the angles around the central atom deviate slightly from ideal octahedral geometry.

The structure of the anion is analogous to those reported by Sliva, Duda *et al.* (1997) and Mokhir *et al.* (1998). It consists of the central atom and two doubly deprotonated residues of 2-cyano-2-(oxidoimino)acetamidate coordinated *via* four N atoms belonging to the deprotonated oxidoimine and oxime groups, providing a slightly distorted square-planar geometry. The ligands are situated in *trans* positions with respect to each other, while in the case of a related ligand containing the same coordination set [2-(hydroxyimino)propanamide; Sliva, Kowalik-Jankowska *et al.*, 1997], the two molecules of the ligand are situated in *cis* positions owing to the intramolecular hydrogen bond between the two oxime O atoms. This bond is not observed in the case of 2-cyano-2-(oxidoimino)acetamidate owing to the increased acidity of the oxidoimine group (Sliva, Duda *et al.*, 1997). The coordination bond lengths Ni—

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N_{oxime} and Ni—N_{amide} are 1.881 (2) and 1.858 (2) Å, respectively. The fact that the angles around the central atom are slightly distorted from an ideal square-planar configuration [N2—Ni2—N1^{ii} = 96.58 (9)° and N2^{ii}—Ni2—N1^{ii} = 83.42 (9)°] can be explained by the formation of the five-membered chelate rings, which in fact have ill-defined envelope conformations [the deviation of atom Ni2 from the plane defined by atoms N1, N2, C1 and C2 is −0.088 (4) Å].

The N1—O1 and N1—C2 distances are 1.286 (3) and 1.329 (3) Å, respectively, close to those reported for the *N*-coordinated deprotonated oxime group (Fritsky *et al.*, 1993). This indicates the existence of the CNO– grouping in the nitroso form (Domasevich *et al.*, 1995)

It is worth noting the different functions of the solvent water molecules in the previously reported structure of tetramethylammonium bis(2-oximinocyanacetamidato)-nickelate(II) (Sliva, Duda *et al.*, 1997) and in (I). In the former case, the water molecules bind the anion through oxime atom O1 and the amide H atom, forming a closed pseudo-macrocyclic system, while in (I), the water molecule is linked to the anion only *via* amide atom O2, forming translational chains. In both cases, the water molecules provide intermolecular hydrogen-bonding interactions between anions.

In the crystal packing, the anions are connected by the water molecules *via* an O1*W*—H14···O2 hydrogen bond, forming zigzag-like chains translated along the *a* direction (Table 2). The $[Ni(en)_3]^{2+}$ cations occupy empty spaces between the chains and interact with them *via* N—H···O hydrogen bonds through the oxime O1 atom and also the amide O2 atom (Table 2) to form cationic and anionic layers spread along the *ac* plane (Fig. 2). Interaction between layers is realized only *via* N—H···O1*W* hydrogen bonds (Table 2), forming a three-dimensional modular structure (Fig. 3).

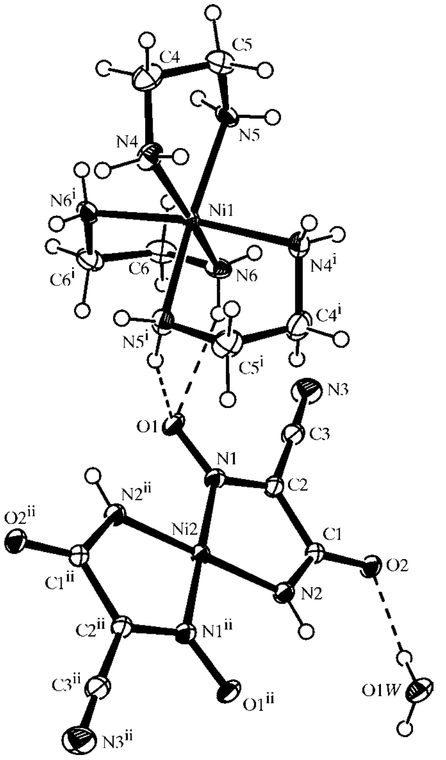

Figure 1
A view of compound (I), with displacement ellipsoids shown at the 40% probability level. H atoms are drawn as spheres of arbitrary radii. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x, -y + 1, -z$.]

Experimental

$[N(CH_3)_4]_2[Ni(C_3HN_3O_2)_2]\cdot 2H_2O$ (0.928 g, 0.2 mmol), prepared according to the method described by Sliva, Duda *et al.* (1997), was dissolved in water, and then solutions of $Ni(NO_3)_2\cdot H_2O$ (0.058 g, 0.2 mmol) and ethylenediamine (0.040 ml, 0.036 g, 0.6 mmol) in ethanol were added. Red crystals were obtained after evaporation of

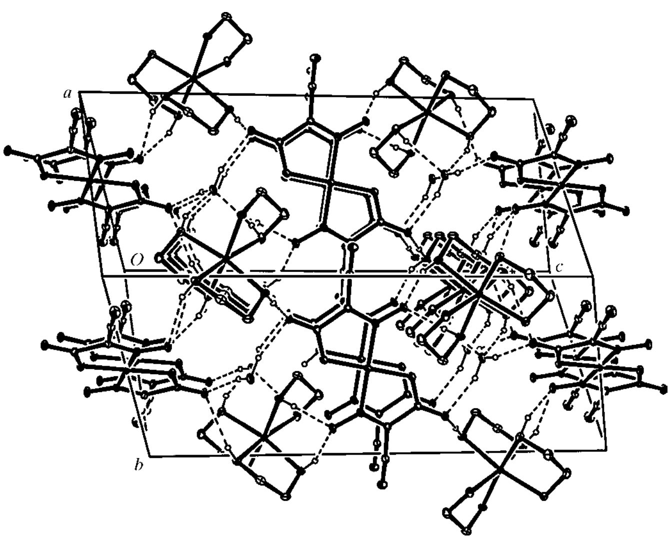

Figure 2
A packing diagram for (I). Hydrogen bonds are indicated by dashed lines. All H atoms not involved in hydrogen bonding have been omitted for clarity.

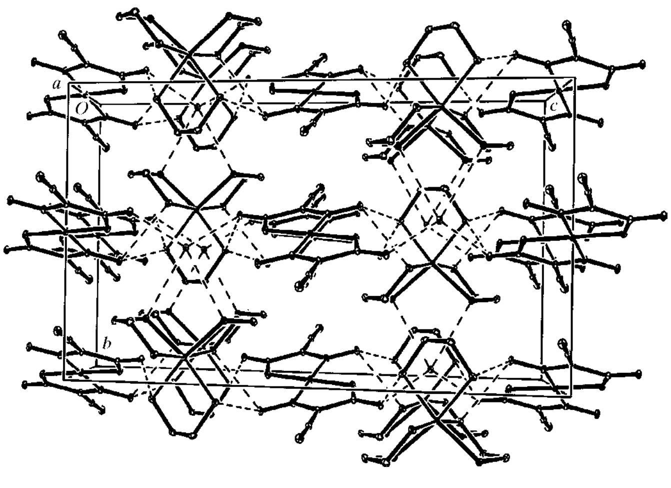

Figure 3
A view of the packing for (I), shown along the *ac* plane to represent connection between layers. All H atoms not involved in hydrogen bonding have been omitted for clarity.

the solvent and these were filtered off and washed with cool water. Finally, red cubic crystals suitable for X-ray analysis were obtained by diffusion of 2-propanol into a methanol solution of the product at room temperature. Analysis calculated for $C_{12}H_{28}N_{12}Ni_2O_5$: C 26.80, H 5.25, N 31.25%; found: C 26.40, H 5.32, N 31.09%. IR (KBr pellet, cm^{-1}): ν(C≡N) 2220, ν(C=N) 1665, ν(N—O) 1305.

Crystal data

$[Ni(C_2H_8N_2)_3][Ni(C_3HN_3O_2)_2]\cdot H_2O$
M_r = 537.88
Monoclinic, $C2/c$
a = 10.119 (2) Å
b = 11.212 (2) Å
c = 19.170 (4) Å
β = 105.26 (3)°
V = 2098.2 (8) Å^3
Z = 4
D_x = 1.703 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.85 mm^{-1}
T = 100 K
Prism, red
0.27 × 0.16 × 0.11 mm

Data collection

Sapphire KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.696, $T_{\max}$ = 0.820
6962 measured reflections
2655 independent reflections
2202 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.038
$\theta_{\max}$ = 28.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.082
S = 1.08
2655 reflections
175 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 6.5482P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 1.08 e Å^{-3}
$\Delta\rho_{\min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N5^{i}	2.113 (2)	Ni2—N1	1.881 (2)
Ni1—N4^{i}	2.124 (2)	O1—N1	1.286 (3)
Ni1—N6^{i}	2.125 (2)	N1—C2	1.329 (3)
Ni2—N2	1.858 (2)	N3—C3	1.146 (3)
N5^{i}—Ni1—N5	170.18 (13)	N5—Ni1—N6^{i}	94.88 (9)
N5^{i}—Ni1—N4^{i}	82.60 (9)	N4^{i}—Ni1—N6^{i}	170.31 (9)
N5—Ni1—N4^{i}	90.95 (9)	N4—Ni1—N6^{i}	90.44 (9)
N5—Ni1—N4	82.60 (9)	N6^{i}—Ni1—N6	81.58 (13)
N4^{i}—Ni1—N4	98.00 (13)	N2—Ni2—N1	83.42 (9)
N5^{i}—Ni1—N6^{i}	92.56 (8)	N2^{ii}—Ni2—N1	96.58 (9)
N2^{ii}—Ni2—N1—C2	176.27 (19)	O1—N1—C2—C3	2.3 (4)
N1^{ii}—Ni2—N2—C1	−176.2 (2)	N2—C1—C2—N1	−0.2 (3)
Ni2—N2—C1—C2	−2.9 (3)		

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

C-bound H atoms were placed in calculated positions, with C—H = 0.97 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C), and treated using the riding-model approximation. Other H atoms were observed in a difference Fourier map and were refined freely.

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H1···O2^{iii}	0.78 (4)	2.47 (4)	3.214 (3)	161 (4)
N4—H3···O1W^{iv}	0.88 (3)	2.28 (3)	3.113 (4)	160 (3)
N5—H5···O1^{i}	0.96 (4)	2.00 (4)	2.929 (3)	160 (3)
N6—H7···O1	0.85 (3)	2.28 (3)	3.077 (3)	156 (3)
O1W—H14···O2	0.86 (4)	1.96 (4)	2.777 (2)	158 (3)

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

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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3007). Services for accessing these data are described at the back of the journal.

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