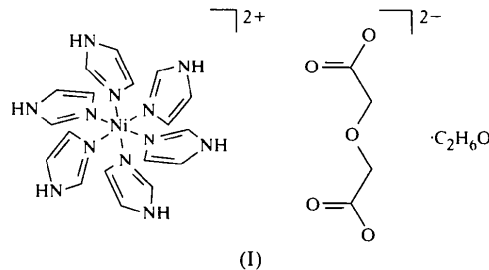


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Hexakis(imidazole-*N*³)nickel(II) oxydiacetate ethanol solvate

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Abstract

The crystal structure of the title complex, [Ni(C₃H₄N₂)₆](C₄H₄O₅)·C₂H₅OH, is a tightly woven three-dimensional network composed of [Ni(Him)₆]²⁺ cations (Him is imidazole) interlinked by the oxydiacetate anion through six different N—H···O bonds, in which all the N—H imidazole groups, as well as all the carboxylate O atoms, take part. This structure is the first to show an [Ni(Him)₆]²⁺ group which does not display any crystallographic symmetry.

Comment

Nickel(II) has a strong affinity for nitrogen-donor ligands and nickel(II)–imidazole (Him) interactions are important in biological processes. We report herein the synthesis and crystal structure of a new salt, (I), containing the [Ni(Him)₆]²⁺ complex cation and the oxydiacetate (oda) anion.

The molecular diagram and the atomic numbering scheme used are shown in Fig. 1. As is usually found in nickel–imidazole compounds, Ni²⁺ is coordinated by

six monodentate imidazole ligands to form a bulky [Ni(Him)₆]²⁺ cation. The present case is unique, however, in the sense that it is the first structure reported where the group does not display crystallographic symmetry; in all the other references in the literature (*viz.* Konopelski *et al.*, 1976; Ivarsson & Forsling, 1979; van Ingen Schenau, 1975; Dev *et al.*, 1991; Tebbe & Nafepour, 1994; Povse *et al.*, 1998, and references therein), the Ni²⁺ cation occupies a site with $\bar{1}$ symmetry or higher. In spite of this formal lack of symmetry, the distortion of the Ni²⁺ coordination polyhedron from a perfect octahedron is quite small, with an Ni—N bond-length range of 2.113 (3)–2.139 (4) Å, and maximum departures from 90 and 180° of ~1.5 (1)°. These values are quite similar to those found in the more symmetric environments in the above references. Perhaps the most significant difference is to be found in the rotation angle

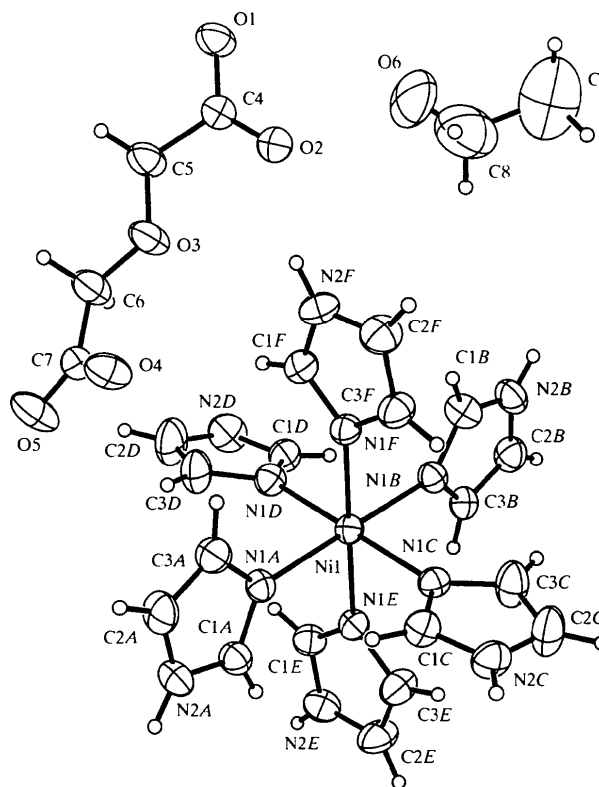


Fig. 1. The molecular diagram, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

of the Him groups around the N—Ni vector away from the similarly oriented NiN₄ coordination planes, which in the present structure ranges from 2.9(1) to 18.2(1)°. Moreover, the pair of opposite Him groups labelled as *E–F* presents an alteration with respect to the rough $\bar{1}$ symmetry displayed by the cation, probably due to the hydrogen-bond interaction described below.

The six independent imidazole groups display geometries closely similar to each other; they are all planar within a confidence level of 95% (maximum deviations from the mean plane of ~ 0.006 Å) and homologous parameters present a very small dispersion, as shown by the s.u.'s of the mean values obtained by averaging over the six independent moieties, viz. N1—C1 1.322(4), N1—C3 1.374(4), N2—C1 1.337(8), N2—C2 1.351(6) and C2—C3 1.352(5) Å, and C1—N1—C3 104.5(5), C1—N2—C2 107.3(3), N1—C1—N2 111.9(4), N2—C2—C3 106.5(5) and C2—C3—N1 109.9(4)°.

The internal dimensions of the oxydiacetate (oda) anion are comparable to those found in polymeric [Zn(Him)₂oda]_n, which contains an extended oda anion (Baggio *et al.*, 1999). The structure is completed by a loosely bound ethanol solvate molecule which, in the specimen under study, presented an occupation of *ca* 50%.

Details of the complex hydrogen-bonding scheme, which links ions into a compact three-dimensional network, are shown in Fig. 2. In the process, each

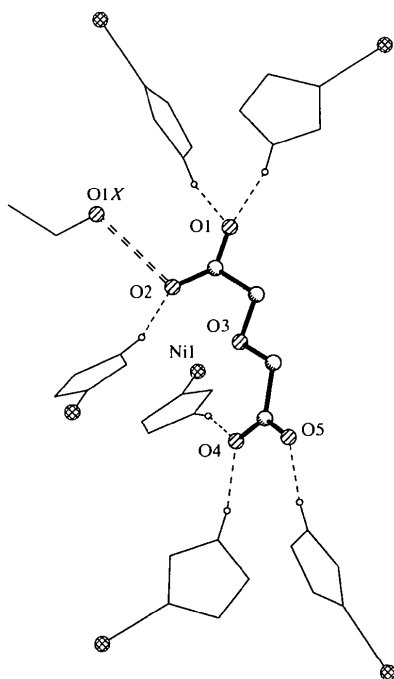


Fig. 2. A highly simplified packing diagram showing details of the intermolecular interactions. Each Ni(Him)₆ group has been represented schematically as the metal centre and the Him group involved in the interaction. Non-interacting H atoms have been omitted.

of the six independent Him groups is involved as a donor and the oda anion acts as an acceptor of these six different hydrogen interactions through its four carboxylate groups (Table 2). Besides these interactions, there are a number of much weaker contacts (not shown) involving the ether O3 atom. The strong hydrogen bonds described clamp the otherwise free rotation of the Him groups. In the process, two opposite pairs (*A–B* and *C–D*) adopt a nearly 'anti' conformation, with the third pair (*E–F*) being almost 'cis' and thus departing from the pseudo- $\bar{1}$ symmetry roughly displayed by the rest of the [Ni(Him)₆]²⁺ group.

Experimental

To a 1:1 water–ethanol solution (50 ml) of nickel nitrate hexahydrate (0.50 g, 1.7 mmol) at room temperature was added oxydiacetic acid (0.25 g, 1.9 mmol). After heating to 353 K for 2 h, imidazole (0.70 g, 10.3 mmol) was added with stirring and a violet–blue solution formed. After a week, thin violet crystals were collected, washed with cold ethanol and carefully dried under vacuum (yield: 0.75 g, 70%). Analysis calculated (found) for unsolvated C₂₂H₂₈N₁₂NiO₅: C 44.10 (43.9), H 4.71 (4.8), N 28.05% (28.2%); IR (KBr disc, cm⁻¹): 3129 (s), 3029 (s), 2928 (s), 2851 (s), 2704 (m), 2629 (m), 1593 (vs), 1545 (s), 1489 (m), 1441 (m), 1408 (m), 1327 (m), 1306 (m), 1125 (m), 1067 (vs), 941 (s), 831 (l), 756 (m), 667 (vs). Specimens recrystallized from ethanol–water showed a fraction of a solvate ethanol molecule. The reactants (Aldrich Chemical Co.) were used without further purification. The elemental analyses (CHN) were performed on a Carlo Erba EA 1108 instrument, the IR spectra were recorded with a Nicolet 510P FT-IR spectrophotometer and the single-crystal data were gathered with graphite-monochromated Mo K α radiation on a Siemens R3m four-circle diffractometer.

Crystal data

[Ni(C₃H₄N₂)₆](C₄H₄O₅)·
C₂H₆O
M_r = 645.34
Triclinic
 $\bar{1}$
a = 8.9510(18) Å
b = 10.8181(16) Å
c = 16.585(3) Å
 α = 77.735(14)°
 β = 81.298(16)°
 γ = 73.906(15)°
V = 1500.5(5) Å³
Z = 2
D_x = 1.428 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
Cell parameters from 30
reflections
 θ = 7.5–12.5°
 μ = 0.71 mm⁻¹
T = 293(2) K
Plate
0.30 × 0.25 × 0.12 mm
Violet

Data collection

Siemens R3m diffractometer
 $\omega/2\theta$ scans
Absorption correction:
 ψ scan (XEMP in
SHELXTLPC; Sheldrick,
1994)
T_{min} = 0.82, *T_{max}* = 0.90

3533 reflections with
I > 2 σ (*I*)
R_{int} = 0.022
 θ_{\max} = 25.05°
h = -1 → 8
k = -12 → 12
l = -19 → 19

5958 measured reflections
4849 independent reflections

2 standard reflections
every 98 reflections
intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.147$
 $S = 1.077$
4849 reflections
408 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 1.148P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

Ni1—N1B	2.113 (3)	Ni1—N1A	2.129 (3)
Ni1—N1E	2.118 (3)	Ni1—N1C	2.134 (3)
Ni1—N1F	2.121 (3)	Ni1—N1D	2.139 (4)

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

D—H...A	D—H	H...A	D...A	D—H...A
N2A—H2AA...O5 ⁱ	0.88 (5)	1.82 (5)	2.690 (6)	172 (4)
N2B—H2BA...O1 ⁱⁱ	0.85 (5)	1.93 (6)	2.749 (6)	163 (4)
N2C—H2CA...O4 ⁱⁱⁱ	0.87 (4)	1.87 (3)	2.723 (5)	168 (3)
N2D—H2DA...O1 ^{iv}	0.83 (4)	1.99 (4)	2.812 (5)	169 (4)
N2E—H2EA...O4 ^v	0.88 (5)	1.93 (5)	2.768 (6)	160 (4)
N2F—H2FA...O2	0.86 (4)	1.98 (5)	2.801 (5)	163 (4)

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

H atoms were initially idealized and those relevant for the description of the hydrogen bonding were subsequently refined with a unique refinable N—H distance [final value 0.85 (2) Å], while those attached to carbon were allowed to ride. The ethanol solvate molecule could only be worked out with restrained C—O and C—C distances, and a fractional occupation factor which refined to a final value of 0.52 (4). Only the five H atoms attached to carbon were included; the hydroxy H atom was not found and was thus disregarded. During refinement, the terminal methyl group was allowed to rotate. The rather large displacement parameters exhibited by the solvate and the concentration of the largest residual electron-density peaks around it (range 0.67–0.35 e Å⁻³) suggested some kind of disorder. Outside this zone, the final ΔF map showed no relevant features, with extreme values below 0.35 e Å⁻³.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1429). Services for accessing these data are described at the back of the journal.

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μ_3 -Iodo-2:3:4 κ^3 I-tri- μ_3 -sulfido-1:2:3 κ^3 S; 1:2:4 κ^3 S;1:3:4 κ^3 S-sulfido-1 κ S-tris- (triphenylphosphine)-2 κ P,3 κ P,4 κ P- trisilvertungsten-triphenylphosphine sulfide (1/1)

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Abstract

The crystal structure of [Ag₃WS₄I{P(C₆H₅)₃}₃]₃·SP(C₆H₅)₃ comprises discrete neutral [Ag₃WS₄I{P(C₆H₅)₃}₃] and SP(C₆H₅)₃ molecules. The [Ag₃WS₄I{P(C₆H₅)₃}₃] skeleton is cubane-like and the phosphorus environment of the SP(C₆H₅)₃ molecule is a distorted tetrahedron.