

Two nickel complexes stabilized by nitrate counter-ions

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Received 17 January 2002

Accepted 11 February 2002

Online 12 March 2002

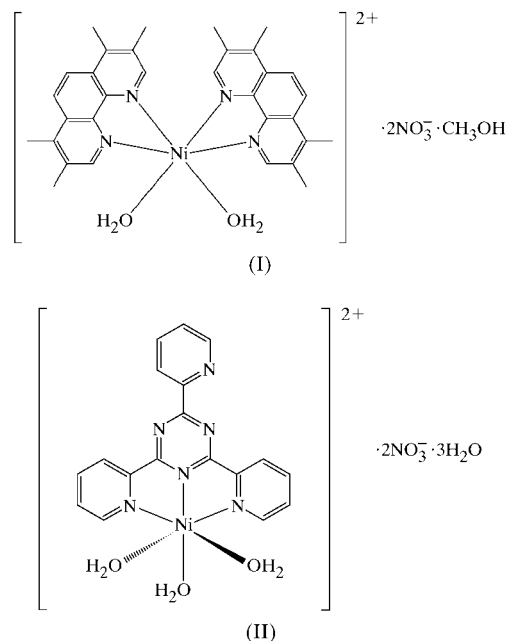
Two new nickel nitrates, diaquabis(3,4,7,8-tetramethyl-1,10-phenanthroline- κ^2N,N')nickel(II) dinitrate methanol solvate, $[\text{Ni}(\text{C}_{16}\text{H}_{16}\text{N}_2)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{O}$, (I), and triaqua[2,4,6-tris(2-pyridyl)-1,3,5-triazine- κ^3N^1,N^2,N^6]nickel(II) dinitrate trihydrate, $[\text{Ni}(\text{C}_{18}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})_3](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, (II), are reported. In both structures, the cation is octahedrally coordinated, to two bidentate 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) and two water molecules in (I), and to one tridentate 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) and three water molecules in (II). Both structures are stabilized by extensive hydrogen-bonding interactions.

Comment

During a long-term project aimed at the synthesis and characterization of sulfur oxoanions complexed to transition metals, a number of sulfur-free compounds have been obtained as unwitting, though nonetheless interesting, by-products. In the present work, we report two such nickel complexes stabilized by nitrate counter-ions, namely diaquabis(3,4,7,8-tetramethyl-1,10-phenanthroline- κ^2N,N')nickel(II) dinitrate methanol solvate, (I), and triaqua[2,4,6-tris(2-pyridyl)-1,3,5-triazine- κ^3N^1,N^2,N^6]nickel(II) dinitrate trihydrate, (II), obtained while attempting to prepare the corresponding thiosulfates. Though nickel(II) structures are rather predictable in their coordination behavior, the simultaneous presence of free NO_3^- ions in conjunction with a number of coordinated and hydration water molecules usually ensures extremely complex hydrogen-bonding schemes, as exemplified by the two structures reported herein.

The structure of (I) is formed by $[\text{Ni}(\text{tmp})_2(\text{H}_2\text{O})_2]^{2+}$ monomers, with two external NO_3^- counter-ions balancing the charge and one disordered methanol molecule solvate molecule (in the specimen studied, this solvate molecule was also slightly depleted; site-occupation factor = 0.88). The Ni coordination polyhedron is octahedral, with the two organic

ligands acting in a bidentate manner and two water molecules completing the coordination sphere (Fig. 1). The coordination distances are quite similar [$\text{Ni}-\text{N}$ 2.055 (3)–2.079 (3) Å and $\text{Ni}-\text{O}$ 2.085 (3)–2.100 (3) Å] and the coordination angles depart slightly from ideal values due to the chelate character



of the ligands. The 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) groups bind to the cation in a *cis* manner, almost orthogonal to one another, with an angle between the mean planes of *ca* 83°. A search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) showed 18 structures where the ligand was complexed to a transition metal (none with Ni), only two of which, *i.e.* bis(3,4,7,8-tetramethyl-1,10-phenanthroline)palladium bis(hexafluorophosphate) bi-

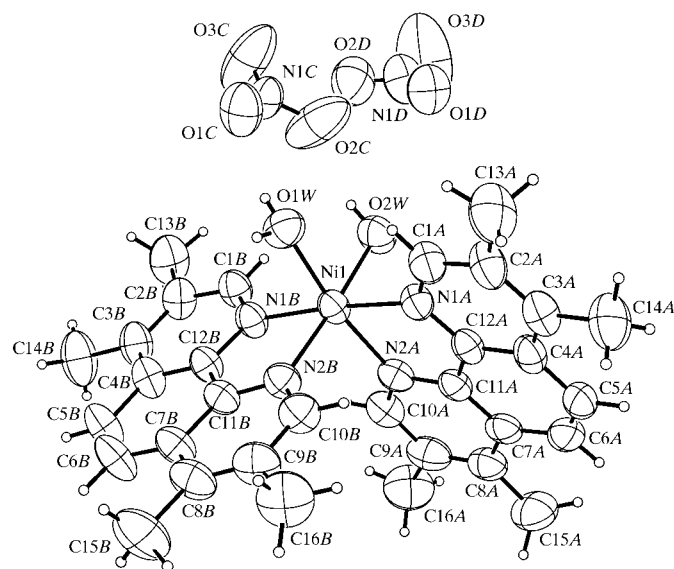


Figure 1

The asymmetric unit of (I) showing the atom-numbering scheme used. For clarity, the disordered methanol solvate is not shown. Displacement ellipsoids are drawn at the 50% probability level.

pyridine solvate (Geremia *et al.*, 1992) and bis(3,4,7,8-tetramethyl-1,10-phenanthroline)copper(I) tetraphenylborate (Cunningham *et al.*, 2000), displayed two coordinated tmp molecules. There is a difference, however, in that the latter are both tetracoordinated complexes (the cobalt complex being distorted square planar and the copper complex being tetrahedral) and the ligands are *trans* to each other. The individual coordination polyhedra in (I) organize in pairs around a symmetry center at $(\frac{1}{2}, 1, \frac{1}{2})$ as 'dimers' held together by hydrogen bonds linking coordinated water molecules and nitrate counter-ions, one of the latter (unit *C*) taking part with all three O atoms and the other (unit *D*) just through O1*D* (Fig. 2 and Table 2). The other two O atoms remain almost free of interactions and, accordingly, their displacement parameters appear rather large. As a result, the packing is governed mainly by weak interactions, *viz.* long C—H...O, van der Waals, *etc.*

Compound (II) is also monomeric, with a tridentate 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) group complexed to an Ni²⁺ ion and three coordinated water molecules completing the octahedral environment of the cation (Fig. 3). Three extra hydration water molecules and two free NO₃⁻ counter-ions complete and stabilize the structure. There is a formally similar compound reported in the literature, *i.e.* [2,4,6-tris(2-pyridyl)-1,3,5-triazine]triaquanickel(II) trinitrate monohydrate (Byers *et al.*, 1996), where the main difference with (II) is that the N atom of the uncoordinated pyridyl ring of the former is protonated, probably as a result of different pH conditions used during the synthesis process. This seemingly minor difference, however, produces noticeable effects in the corresponding crystal structures: first, in the protonated structure, there is one extra nitrate counter-ion, as required by charge balance; secondly, the protonated N atom acts as a donor in a hydrogen bond, which preserves the coplanarity of the pyridyl group with the rest of the ligand, while the unprotonated N atom in (II) acts instead as a hydrogen-bond acceptor, which pushes the ring around its free rotation C—C bond by *ca* 10° out of the plane defined by the remaining three coplanar rings; finally, the protonated structure presents a single hydration water molecule instead of the three water

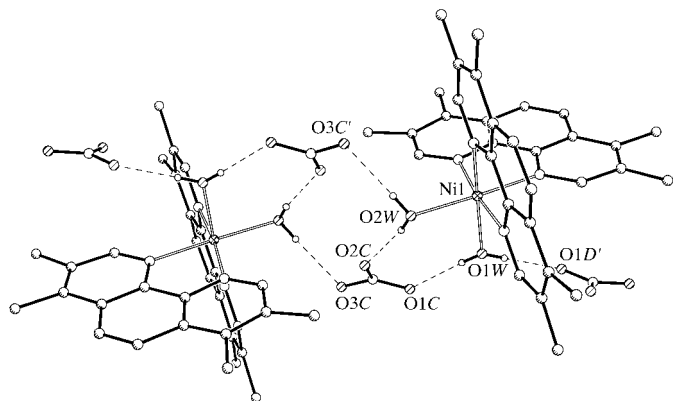


Figure 2
Schematic view of the 'dimeric unit' in (I), formed around the center of symmetry at $(\frac{1}{2}, 1, \frac{1}{2})$. [Symmetry code: (*l*) $1 - x, 2 - y, 1 - z$.]

molecules observed in (II). These environmental differences show that in spite of the similarities of the cationic groups, the structures end up being quite different from a crystallographic point of view.

The availability of hydrogen-bond donors and acceptors in (II) provides a unique medium for hydrogen bonding. All the available water H atoms (both coordinated and hydration), as well as all the nitrate O atoms, take part in these strong interactions. The result is a very intricate, almost impossible to

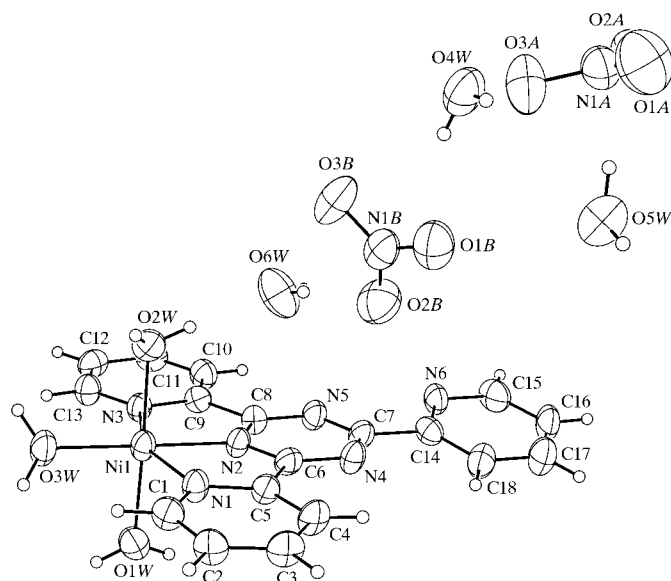


Figure 3
The asymmetric unit of (II), showing the atom-numbering scheme used. Displacement ellipsoids are drawn at the 50% probability level.

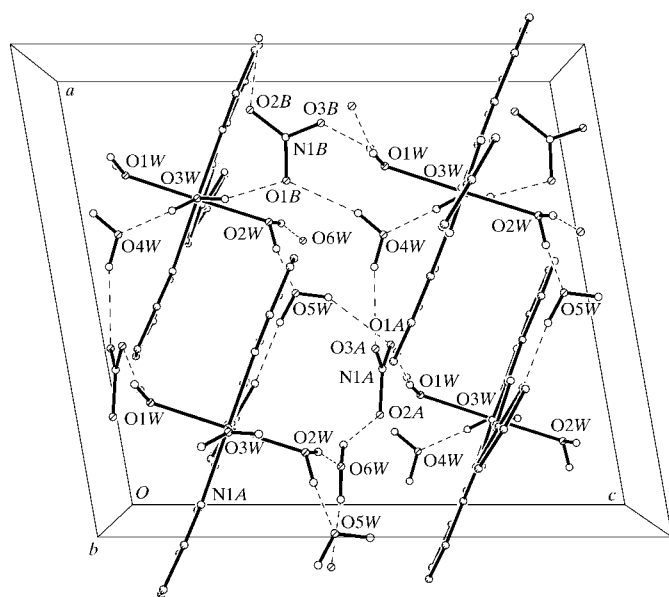


Figure 4
Packing view of (II) showing the intricate three-dimensional hydrogen-bonding scheme.

describe, three-dimensional network (Table 3 and Fig. 4), in which all the constituents of the structure take part.

Experimental

Both title compounds, (I) and (II), were prepared while trying to obtain single crystals of the corresponding thiosulfate complexes. They were obtained by diffusion of methanolic solutions of the corresponding organic ligand and an aqueous solution of nickel nitrate and sodium thiosulfate, in a 1:1:3 molar ratio, as the original aim was to produce the thiosulfate compound. On standing, crystals suitable for X-ray diffraction analysis were obtained for compound (II), while in the case of (I), slow evaporation produced a crop of pale-violet crystals.

Compound (I)

Crystal data

[Ni(C₁₆H₁₆N₂)₂(H₂O)₂]
(NO₃)₂·CH₄O
M_r = 723.42
Monoclinic, P₂₁/n
a = 11.803 (1) Å
b = 25.951 (2) Å
c = 12.310 (1) Å
β = 115.31 (1)°
V = 3408.6 (6) Å³
Z = 4

D_x = 1.410 Mg m⁻³
Mo Kα radiation
Cell parameters from 16 736 reflections
θ = 1.6–28.1°
μ = 0.63 mm⁻¹
T = 298 (2) K
Plate, pale violet
0.40 × 0.30 × 0.12 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (SADABS in SAINT-NT; Bruker, 2000)
T_{min} = 0.84, T_{max} = 0.93
16 404 measured reflections

7275 independent reflections
4648 reflections with I > 2σ(I)
R_{int} = 0.033
θ_{max} = 27.0°
h = -14 → 14
k = -31 → 32
l = -11 → 15

Table 1

Selected geometric parameters (Å, °) for (I).

Ni1–N1A	2.054 (3)	Ni1–N2A	2.079 (3)
Ni1–N2B	2.067 (3)	Ni1–O2W	2.085 (3)
Ni1–N1B	2.071 (3)	Ni1–O1W	2.100 (3)
N1A–Ni1–N2B	94.88 (10)	N1B–Ni1–O2W	96.06 (10)
N1A–Ni1–N1B	174.33 (10)	N2A–Ni1–O2W	88.41 (12)
N2B–Ni1–N1B	79.67 (10)	N1A–Ni1–O1W	90.83 (11)
N1A–Ni1–N2A	79.39 (11)	N2B–Ni1–O1W	90.36 (11)
N2B–Ni1–N2A	93.21 (10)	N1B–Ni1–O1W	90.78 (11)
N1B–Ni1–N2A	99.21 (11)	N2A–Ni1–O1W	169.84 (11)
N1A–Ni1–O2W	89.41 (11)	O2W–Ni1–O1W	88.72 (13)
N2B–Ni1–O2W	175.63 (11)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

D–H...A	D–H	H...A	D...A	D–H...A
O1W–H1WA...O1C	0.81 (3)	2.05 (3)	2.842 (5)	166 (7)
O1W–H1WB...O1D ⁱ	0.84 (3)	1.92 (3)	2.746 (5)	169 (5)
O2W–H2WA...O3C ⁱⁱ	0.79 (3)	2.12 (3)	2.907 (6)	173 (5)
O2W–H2WB...O2C	0.79 (3)	1.88 (3)	2.638 (5)	160 (4)

Symmetry codes: (i) 1 – x, 1 – y, 1 – z; (ii) 1 – x, 2 – y, 1 – z.

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.056
wR(F²) = 0.163
S = 0.95
7275 reflections
472 parameters

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F_o²) + (0.104P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.006
Δρ_{max} = 0.70 e Å⁻³
Δρ_{min} = -0.52 e Å⁻³

Compound (II)

Crystal data

[Ni(C₁₈H₁₂N₆)(H₂O)₃](NO₃)₂·3H₂O
M_r = 603.16
Monoclinic, Cc
a = 12.328 (2) Å
b = 14.851 (3) Å
c = 14.124 (3) Å
β = 100.06 (3)°
V = 2546.1 (9) Å³
Z = 4

D_x = 1.574 Mg m⁻³
Mo Kα radiation
Cell parameters from 7432 reflections
θ = 2.2–28.1°
μ = 0.84 mm⁻¹
T = 298 (2) K
Block, green
0.38 × 0.26 × 0.18 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (SADABS in SAINT-NT; Bruker, 2000)
T_{min} = 0.76, T_{max} = 0.83
7312 measured reflections

3955 independent reflections
3550 reflections with I > 2σ(I)
R_{int} = 0.027
θ_{max} = 27.0°
h = -8 → 15
k = -18 → 18
l = -17 → 17

Table 3

Selected geometric parameters (Å, °) for (II).

Ni1–N2	1.968 (2)	Ni1–O2W	2.067 (4)
Ni1–O3W	2.006 (2)	Ni1–N3	2.116 (4)
Ni1–O1W	2.088 (4)	Ni1–N1	2.151 (4)
N2–Ni1–O3W	179.5 (2)	O1W–Ni1–N3	91.08 (16)
N2–Ni1–O1W	90.75 (16)	O2W–Ni1–N3	88.13 (14)
O3W–Ni1–O1W	89.53 (17)	N2–Ni1–N1	77.83 (18)
N2–Ni1–O2W	91.00 (16)	O3W–Ni1–N1	102.60 (18)
O3W–Ni1–O2W	88.71 (16)	O1W–Ni1–N1	89.37 (16)
O1W–Ni1–O2W	177.87 (15)	O2W–Ni1–N1	92.19 (15)
N2–Ni1–N3	76.90 (18)	N3–Ni1–N1	154.73 (8)
O3W–Ni1–N3	102.67 (18)		

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

D–H...A	D–H	H...A	D...A	D–H...A
O1W–H1WA...O1A ⁱ	0.89 (3)	1.93 (3)	2.801 (6)	163 (4)
O1W–H1WB...O3B ⁱⁱ	0.90 (3)	1.94 (3)	2.821 (5)	165 (4)
O2W–H2WA...O6W	0.90 (4)	1.86 (4)	2.744 (5)	170 (7)
O2W–H2WB...O5W ⁱⁱⁱ	0.90 (4)	1.76 (5)	2.647 (5)	168 (7)
O3W–H3WA...O4W ⁱⁱⁱ	0.90 (3)	1.79 (3)	2.689 (6)	176 (4)
O3W–H3WB...O1B ⁱⁱⁱ	0.90 (4)	2.02 (4)	2.842 (6)	152 (7)
O4W–H4WA...O1B	0.90 (4)	2.10 (4)	2.957 (8)	161 (5)
O4W–H4WB...O3A	0.89 (3)	2.20 (3)	3.062 (8)	162 (7)
O5W–H5WA...N6 ^{iv}	0.90 (3)	2.01 (3)	2.832 (6)	152 (5)
O5W–H5WB...O1A	0.90 (3)	2.12 (4)	2.933 (6)	150 (6)
O6W–H6WA...O2A ^v	0.90 (3)	2.14 (3)	2.953 (7)	151 (4)
O6W–H6WB...O2B	0.90 (4)	2.05 (4)	2.926 (7)	165 (7)

Symmetry codes: (i) 1 + x, 1 – y, z – ½; (ii) ½ + x, ½ – y, z – ½; (iii) ½ + x, ½ + y, z; (iv) x – 1, y, z; (v) 1 + x, y, z.

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.092$

$S = 0.92$

3955 reflections

402 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.008$$

$$\Delta\rho_{\max} = 0.54 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack (1983)

Flack parameter = 0.087 (16)

Water H atoms were found in the final ΔF synthesis, and were refined with isotropic displacement parameters and similarity restraints (see Tables 2 and 4). H atoms attached to C atoms were included at expected positions and allowed to ride, with C–H distances in the range 0.93–0.96 Å. Terminal methyl groups were allowed to rotate. A disordered depleted methanol solvate molecule in (I) was refined split over three different sites; similarity restraints were applied to the O–C distances and the refinement led to an overall occupancy of 0.88. No methanol H atoms were included in the model.

For both compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINTE-NT* (Bruker, 2000); data reduction: *SAINTE-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

We acknowledge Fundacion Andes-C13575 and CONICYT-FONDAP 11980002 for the purchase of a CCD detector. We also thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD. EF and JCM are grateful recipients of two scholarships from CONICET and the Deutscher Akademischer Austauschdienst, respectively.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1640). Services for accessing these data are described at the back of the journal.

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