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A square-planar Ni^{II} complex with an asymmetric coordination of a novel polynucleative 2,6-diacetylpyridine bis{[2-(hydroxyimino)propanoyl]-hydrazone} ligand

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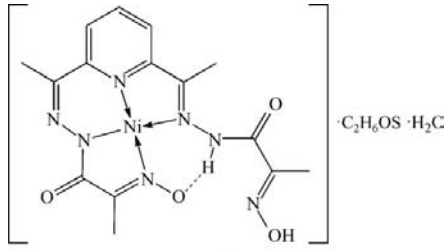
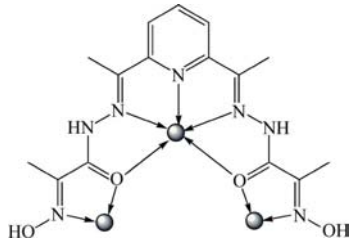
The title compound, (2,6-diacetylpyridine bis{[2-(hydroxyimino)propanoyl]hydrazone}(2−))nickel(II) dimethyl sulfoxide solvate monohydrate, $[Ni(C_{15}H_{17}N_7O_4)]\cdot C_2H_6OS\cdot H_2O$, represents the first example of square-planar N_4 coordination *via* N atoms with four different functions, namely amide, azomethine, hydroxyimino and pyridine. The coordination polyhedron of the central Ni atom has a slightly distorted square-planar geometry. The 2,6-diacetylpyridine bis{[2-(hydroxyimino)propanoyl]hydrazone} ligand forms one six- and two five-membered chelate rings, and a pseudo-chelate ring through an intramolecular hydrogen bond with an amide group as donor and a deprotonated hydroxyimino group as acceptor, resulting in a pseudomacrocyclic arrangement.

Comment

2,6-Diacetylpyridine acylhydrazones and bis(acylhydrazones) are an interesting class of compounds due to their ability to form stable metal complexes, their versatility as chelating agents and their flexibility in assuming different conformations (Wester & Palenik, 1974; Carcelli *et al.*, 1999; Kasuga *et al.*, 2003). Complexes of this type of ligand with 3*d* metals reveal biological activity and can be used in bioinorganic modelling of active sites of redox and hydrolytic enzymes. To date, more than 65 complexes based on 2,6-diacetylpyridine derivatives of different compositions have been characterized by X-ray crystallographic analysis. In almost all cases the ligands are five-coordinated *via* pyridine, two azomethine N atoms and two O or S atoms (Pelizzi *et al.*, 1986). The title compound, (I), is a complex of Ni^{II} with a novel polynucleative derivative of 2,6-diacetylpyridine, namely 2,6-diacetylpyridine bis{[2-(hydroxyimino)propanoyl]hydrazone}, *L*. The presence of three powerful chelate centres in the ligand may be used for obtaining polynuclear metal complexes (see second scheme below).





The structure of (I) consists of the neutral asymmetric complex and dimethyl sulfoxide (DMSO) and water solvent molecules (Fig. 1). Thus, ligand *L* is doubly deprotonated at the amide (N3) and hydroxyimino (O2) groups, which was confirmed by ^{1}H NMR data. Compound (I) represents the first example of square-planar N_4 coordination *via* N atoms of different functions, namely amide (N3), azomethine (N5), hydroxyimino (N4) and pyridine (N1). A structure reported by Simonov *et al.* (1993) contains the NiN_4 chromophore with

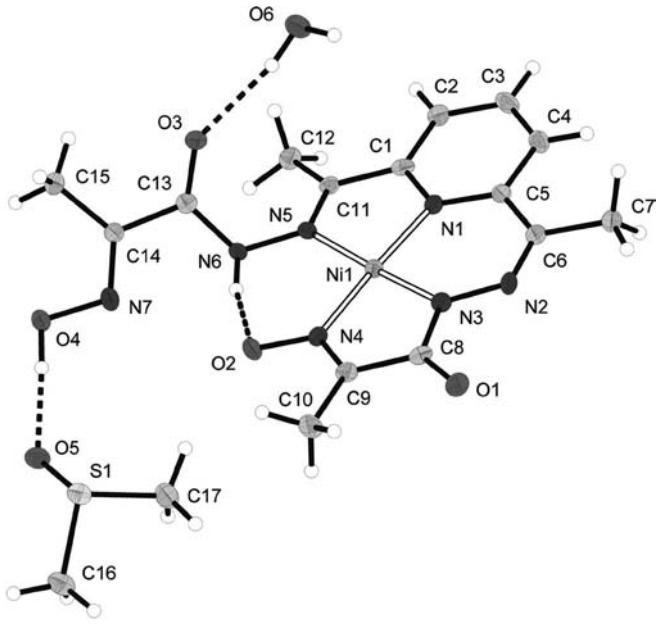


Figure 1
A view of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

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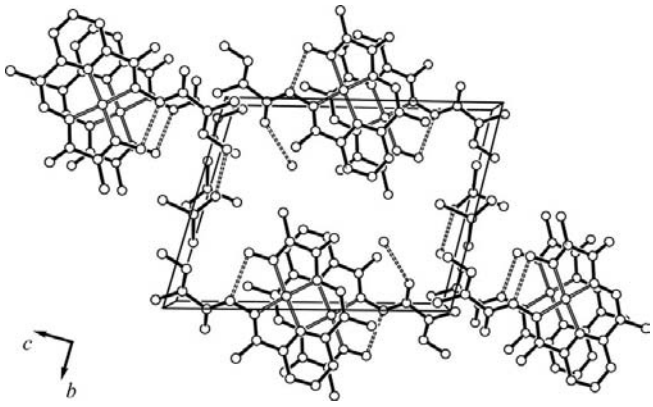

Figure 2
A packing diagram for complex (I), projected along the *a* direction. Hydrogen bonds are indicated by dashed lines and H atoms have been omitted for clarity.

four chemically different N atoms but the groups are the same, *viz*. hydroxyimino and hydrazone.

The Ni—N coordination bond lengths (Table 1) fall in the range 1.828 (3)–1.888 (3) Å and are typical for square-planar Ni^{II} complexes with deprotonated amide ligands (Leininger *et al.*, 2000; Leovac *et al.*, 2000; Hlavica & Lewis, 2001; Moroz *et al.*, 2006). The azomethine double-bond distances N2═C6 and N5═C11 [1.295 (5) and 1.301 (4) Å, respectively] are about the same. On the other hand, the N2—N3 [1.355 (4) Å] and N4—O2 [1.320 (4) Å] bonds are shorter than the N5—N6 [1.394 (4) Å] and N7—O4 [1.392 (4) Å] bonds. The differences can be explained by the deprotonation of atoms N3 and O2. As a result of the formation of five- and six-membered chelate rings, the bite angles around Ni1 deviate from ideal square-planar values (Table 1). The chelate rings are essentially planar. A pseudo-chelate ring is formed *via* the presence of an intramolecular hydrogen bond with amide atom N6 as donor and the deprotonated hydroxyimino group (O2) as acceptor (Table 2), resulting in a pseudomacrocyclic arrangement. The noncoordinated part of *L* is not planar, because of the tendency to reduce repulsion between the CO and CH_3 groups and also because of the presence of an intermolecular hydrogen bond with hydroxyimino atom O4 as donor and DMSO as acceptor. The C11—N5—N6—C13 torsion angle is 60.5 (4)°.

The elements of the structure are connected through a system of hydrogen bonds and π–π stacking interactions. The solvent water molecules and protonated hydroxyimino groups (O4) act as donors, and amide (O3) and DMSO O atoms act as acceptors (Table 2). An extensive three-dimensional system of hydrogen bonds is formed (Fig. 2). The π–π stacking (3.45 Å) is realized between neighbouring molecules of the complex along the crystallographic *a* direction. Slabs of (I) form columns, with DMSO and water molecules between them.

Table 1
Selected geometric parameters (Å, °).

Ni1—N3	1.828 (3)	Ni1—N4	1.879 (3)
Ni1—N1	1.873 (3)	Ni1—N5	1.888 (3)
N3—Ni1—N1	94.01 (13)	N1—Ni1—N5	83.41 (13)
N3—Ni1—N4	83.99 (13)	N4—Ni1—N5	98.61 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4O···O5	0.95	1.73	2.661 (4)	165
O6—H6O···O3	0.90	2.07	2.948 (4)	162
O6—H6*P*···O1^{i}	0.91	1.98	2.819 (4)	151
N6—H6N···O2	0.89	1.70	2.555 (4)	162

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

Experimental

For the synthesis of the ligand *L*, 2,6-diacetylpyridine (3.4 g, 0.021 mol) was added to 2-(hydroxyimino)propanohydrazide (5 g, 0.043 mol; Fritsky *et al.*, 1998) dissolved in EtOH (20 ml). The resulting mixture was heated for 1 h. After cooling, a white precipitate was separated by filtration and recrystallized from dimethylformamide (yield 6.95 g, 91%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.986 (6H, *s*, CH_3), 2.432 (6H, *s*, CH_3), 7.929 (1H, *t*, pyH), 8.086 (2H, *d*, pyH), 10.27 (2H, *s*, NH), 12.148 (2H, *s*, OH).

For the preparation of crystals of (I), $NiCl_2$ $6H_2O$ (0.0291 g, 0.1 mmol) and *L* (0.0361 g, 0.1 mmol) were dissolved in DMSO (20 ml) and aqueous NaOH (1 ml, 0.1 mmol) was added. The mixture was heated for 40 min, filtered and left in a desiccator for crystallization. After one week, red crystals of (I) suitable for X-ray analysis were obtained (yield 0.0544 g, 45%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.792 (3H, *s*, CH_3), 1.979 (3H, *s*, CH_3), 2.28 (3H, *s*, CH_3), 2.518 (3H, *s*, CH_3), 8.1 (1H, *d*, pyH), 8.171 (1H, *d*, pyH), 8.375 (1H, *t*, pyH), 12.332 (1H, *s*, NH), 15.485 (1H, *s*, OH).

Crystal data

$[Ni(C_{15}H_{17}N_7O_4)]\cdot C_2H_6OS\cdot H_2O$
M_r = 514.21
Triclinic, $P\overline{1}$
a = 7.3076 (2) Å
b = 11.1899 (5) Å
c = 13.9875 (6) Å
α = 74.652 (2)°
β = 84.472 (2)°
γ = 73.641 (2)°
V = 1058.04 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 120 (2) K
0.19 × 0.05 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*, Version 2.10; Sheldrick, 2003)
T_{min} = 0.822, T_{max} = 0.965
18361 measured reflections
4128 independent reflections
3008 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.109
S = 1.06
4128 reflections
296 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

OH and NH hydrogens were located in a difference Fourier map but were constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(parent atom). Other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95–0.98 Å and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). The highest peak is

located 1.10 Å from atom H16*B* and the deepest hole is located 0.61 Å from atom S1.

Data collection: *COLLECT* (Bruker–Nonius, 2004); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3126). Services for accessing these data are described at the back of the journal.

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