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{*N*-Anilino-2-[(2-oxidophenyl)methylenehydrazono]-2-sulfidoacetamide}pyridinenickel(II)

Vladimir N. Yarovenko,[a]* Alexander V. Shirokov,[a] Pavel A. Kondrashev,[a] Victor B. Rybakov,[b] Igor V. Zavarzin[a] and Mikhail M. Krayushkin[a]

[a]N.D.Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky ave., 119991 Moscow, Russian Federation, and [b]Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation

Correspondence e-mail: yarov@ioc.ac.ru

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Key indicators

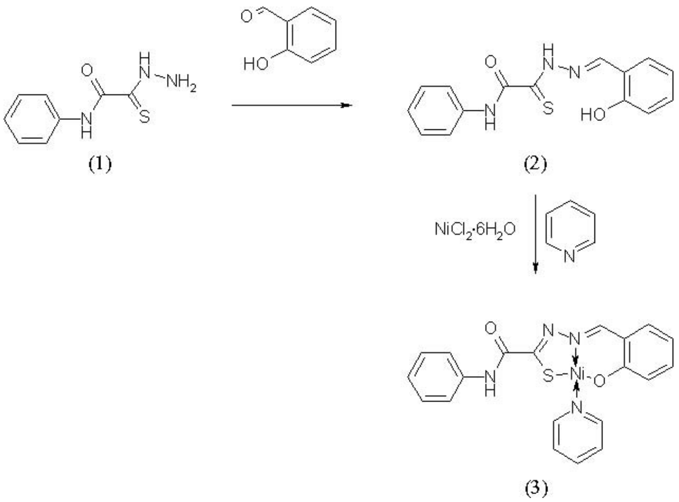
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.044
wR factor = 0.084
Data-to-parameter ratio = 16.1

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

The title compound is a square-planar tetracoordinate Ni complex, [Ni($C_{15}H_{11}N_3O_2S$)(C_5H_5N)]. The coordination of the Ni atom can also be considered to be highly elongated square bipyramidal, this being accomplished by an S and an O atom of adjacent molecules. In this way, polymeric chains are formed extending in the *b* direction

Comment

Thiosemicarbazones are widely used in the synthesis of various pharmaceuticals, and the biological activity of these compounds can be enhanced in the presence of metal cations (Zelenin *et al.* 1992). It seemed worthwhile to use thiohydrazides of oxamic acids, exhibiting various biological activities (Shawali *et al.*, 2004), for the construction of sulfur-containing tridentate hydrazones as ligands for such complexes. It should be noted that the complexation properties of hydrazones of oxamic acid thiohydrazides have not been studied previously. We have developed a procedure for the synthesis of oxamic acid thiohydrazides, and their hydrazones have been prepared and characterized for the first time (Yarovenko *et al.*, 2003*a*,*b*). In the present study, we examined the possibility of preparing complexes based on such hydrazones using hydrazone (2) as an example. Compound (2) was synthesized by the reaction of oxamic acid thiohydrazide, (1), with salicylaldehyde. Reaction of compound (2) with $NiCl_2$, in the presence of pyridine, produced the title complex, (3).



The molecular structure of (3) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The square-planar coordination of the central Ni atom is typical. The deviations of atoms N8, O1, N21 and S from their mean

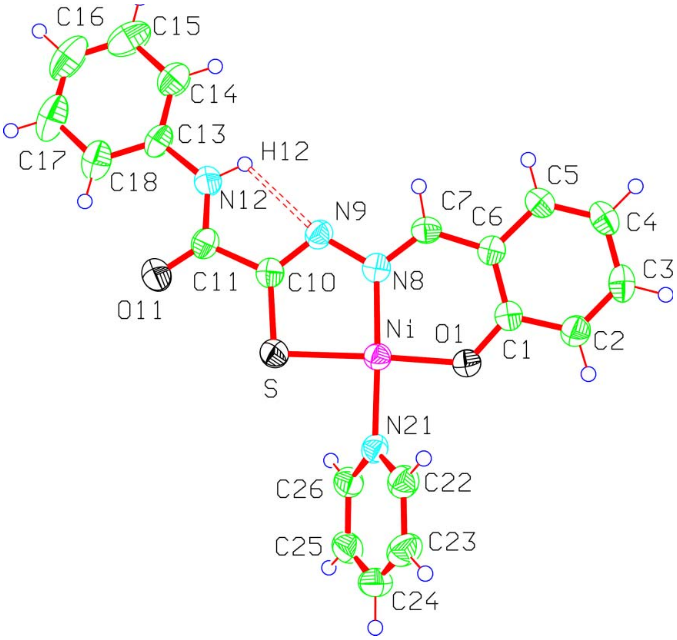


Figure 1
ORTEP-3 (Farrugia, 1997) view of complex (3), showing the numbering scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are presented as spheres with arbitrary radius. The broken lines represent a hydrogen bond.

plane are less than 0.1 Å. The six-membered N21/C22–C26 heterocycle is twisted with respect to the above-mentioned square plane by 58.8 (1)°. All the six-membered rings are planar within 0.02 Å (Fig. 1).

The complex has an intramolecular N—H⋯N hydrogen bond (Table 2) involving atoms H12 and N9, the N12⋯N9 distance being 2.662 (4) Å. The coordination of the Ni atom can also be considered to be highly elongated square bipyramidal. This is accomplished by two additional atoms from adjacent molecules: S^i, with Ni⋯S^i = 3.407 (2) Å, and O^{ii}, with distance Ni⋯O^{ii} = 3.451 (4) Å [symmetry codes: (i) $x, y + 1, z$; (ii) $x, y - 1, z$]. In this way, polymeric chains are formed extending in the *b*-axis direction (Fig. 2).

Experimental

2-[2-(2-Hydroxybenzylidene)hydrazino]-*N*-phenyl-2-thioxoacetamide, (2), was prepared according to a procedure described by Yarovenko *et al.* (2003*a*), from salicylaldehyde and 2-hydrazino-*N*(1)-phenyl-2-thioxoacetamide, (1) (Yarovenko *et al.*, 2003*b*). For the preparation of compound (3), nickel chloride hexahydrate (1.19 g, 0.005 mol) was added to a solution of (2) (1.5 g, 0.005 mol) in pyridine (10 ml). The reaction mixture was refluxed for 3 h and then poured into water (50 ml). The precipitate that formed was filtered off, twice washed with water (50 ml) and recrystallized from acetone (yield 2.18 g, 74%). ^{1}H NMR: δ 6.7 (*t*, 1H, H arom), 6.9 (*d*, 1H, H arom), 7.15 (*t*, 1H, H arom), 7.35 (*m*, 3H, H arom), 7.55 (*m*, 2H, H arom), 7.75 (*m*, 3H, H arom), 8.0 (*t*, 1H, H arom), 9.0 (*m*, 3H), 10.20 (*s*, 1H, NH); ^{13}C NMR: δ 116.1, 117.7, 120.1, 120.9, 124.1, 125.5, 128.7, 133.4, 134.7, 138.3, 139.1, 152.1, 158.7, 161.5, 163.2, 166.8. Analysis found: C 55.09, H 3.82, N 12.89%; calculated for $C_{20}H_{16}N_4NiO_2S$: C 55.20, H 3.71, N 12.88%.

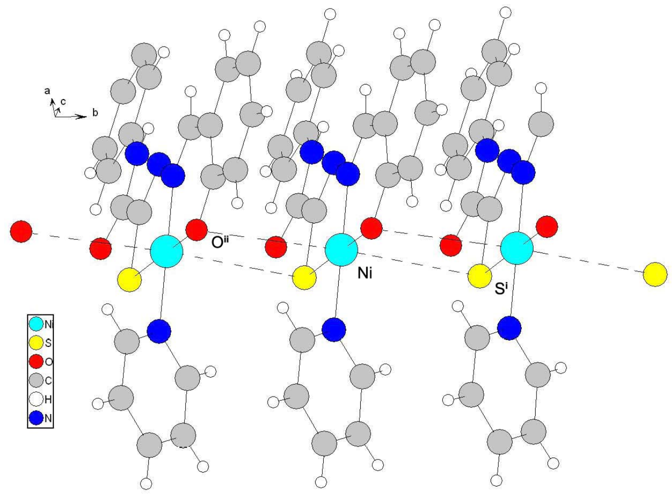


Figure 2
Illustration of the elongated square bipyramidal geometry around the Ni atom, which leads to the formation of the polymeric chains extending in the *b*-axis direction.

Crystal data

$[Ni(C_{15}H_{11}N_3O_2S)(C_5H_5N)]$
M_r = 435.14
Monoclinic, $C2/c$
a = 41.91 (2) Å
b = 3.952 (3) Å
c = 28.840 (13) Å
β = 126.87 (4)°
V = 3821 (4) Å^3
Z = 8

D_x = 1.513 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13–16°
μ = 1.15 mm^{-1}
T = 298 (2) K
Block, dark red
0.3 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.684, $T_{\rm max}$ = 0.708
4228 measured reflections
4134 independent reflections
2393 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.081
$\theta_{\rm max}$ = 27.0°
$h = -52 \rightarrow 42$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 36$
1 standard reflections every 200 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.085
S = 0.97
4134 reflections
257 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.011
$\Delta\rho_{\rm max}$ = 0.28 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N8	1.853 (3)	Ni—N21	1.911 (3)
Ni—O1	1.857 (2)	Ni—S	2.1490 (13)
N8—Ni—O1	94.90 (12)	N8—Ni—S	87.53 (10)
N8—Ni—N21	177.66 (12)	O1—Ni—S	177.30 (8)
O1—Ni—N21	87.42 (11)	N21—Ni—S	90.15 (10)

Acta Cryst. (2005). E**61**, m964–m966 Yarovenko *et al.* • $[Ni(C_{15}H_{11}N_3O_2S)(C_5H_5N)]$ **m965**

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12···N9	0.81 (3)	2.25 (3)	2.662 (4)	112 (3)

The NH H atom was refined isotropically, with the N—H bond length restrained to 0.81 (3) Å. The remainder of the H atoms were included in calculated positions and refined as a riding atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent C atom).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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