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# Bis{1-[(4-methoxyphenyl)amino]-2-methylglyoximato-$\kappa^2N,N'$}nickel(II)

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean $\sigma$(C–C) = 0.004 Å
*R* factor = 0.033
*wR* factor = 0.088
Data-to-parameter ratio = 12.9

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

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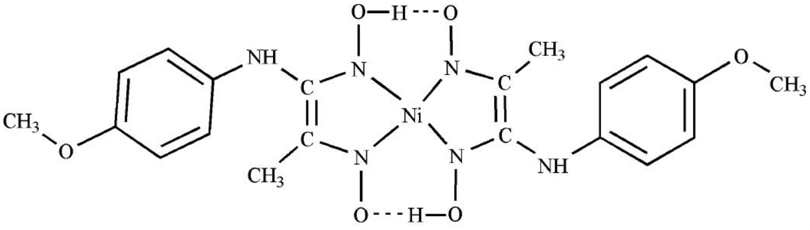
The title molecule, $[\mathrm{Ni(C_{10}H_{12}N_3O_3)_2}]$, possesses a crystallographic centre of symmetry at the $\mathrm{Ni^{II}}$ atom. The coordination geometry around the $\mathrm{Ni^{II}}$ atom is distorted square planar, consisting of four N atoms from two oxime ligands. The crystal packing shows two-dimensional polymeric chains, which are stabilized by a hydrogen-bonded network, and other weak intermolecular interactions.

## Comment

Transition metal complexes of vic dioximes are structurally well known compounds in which metal ions coordinate through N atoms (Chakravorty, 1974). Generally, coordination occurs through deprotonation of two ligands, giving neutral metal complexes which are only soluble in organic solvents. The most common example of a dioxime complex is the dimethylglyoxime–nickel(II) complex, which is also used for the analytical determination of $\mathrm{Ni^{II}}$ ions. Aminoglyoximes and related ligands are of interested because of their free amino substituents, which give them the ability to form new ligand systems or metal complexes.



(I)

The molecule of the title compound, (I), is centrosymetric (Fig. 1). Selected bond lengths and angles are listed in Table 1. Each oxime acts as a bidentate ligand. The coordination around the Ni atom is distorted square planar (Ni lies on the basal plane), involving four oxime N atoms of two chelating 1-[(4-methoxyphenyl)amino]-2-methylglyoximate moieties, with Ni—N distances of 1.848 (2) and 1.864 (2) Å. These distances are typical for Ni–oxime complexes. The difference between the two Ni—N bonds can be attributed to the amino group attached to oxime atom C1.

One of the oxime protons is lost from each ligand in forming the complex; the remaining oxime proton forms a strong intramolecular hydrogen bond between O atoms of the two oximes. The hydrogen bonds between the oxime O atoms are not symmetrical, with an O···O distance of 2.462 (3) Å and O—H···O angles of 171 (4)° (Table 2). The H atoms in complexes with O···O distances of 2.42–2.43 Å are almost

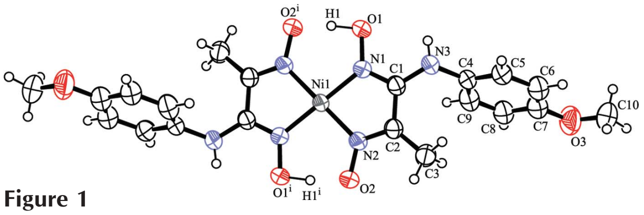


**Figure 1**
An *ORTEP3* drawing (Farrugia, 1997) of the title molecule, with the atom-numbering scheme and displacement ellipsoids for non-H atoms drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, -z$.]

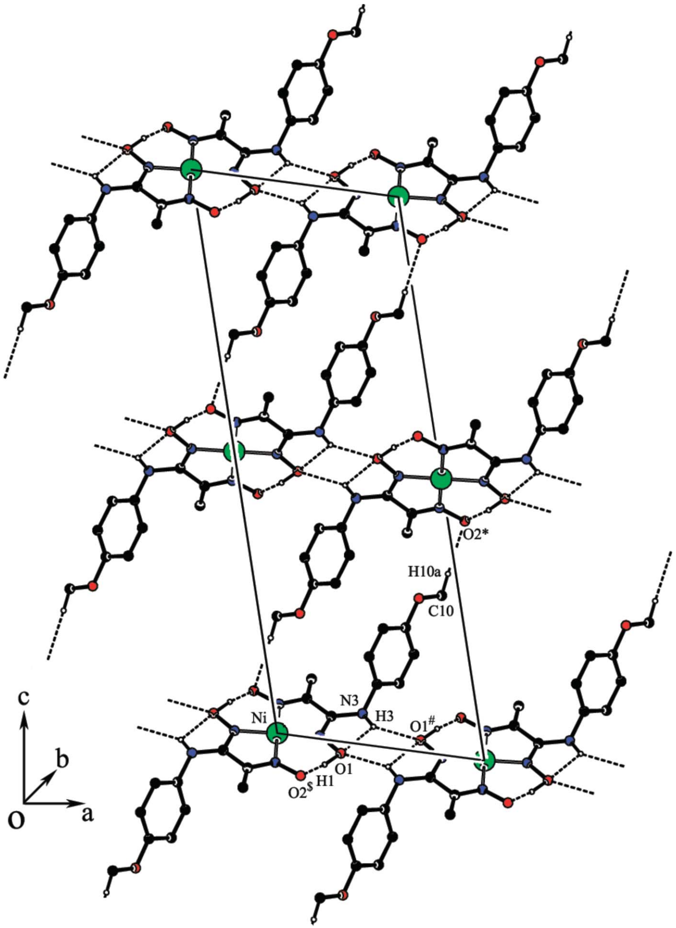


**Figure 2**
A view of the hydrogen-bond interactions (dashed lines) in (I). For clarity, H atoms, except for H1, H3 and H10*A*, have been omitted. [Symmetry codes: (#) $1 - x, -y, -z$; ($) $-x, -y, -z$; (*) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

centred between the O atoms. However, symmetrical hydrogen bonds are only observed in vic dioximes where the two groups attached to the oxime C atoms are identical. The N—Ni—N angle within the $NiC_2N_2$ chelate ring is 82.28 (9)°. The coordination plane around the Ni atom and the plane of the chelating moiety coincide within experimental error. A comparision of the C═N and N—O distances with those of free oximes [N1—O1 = 1.4093 (18) Å and C1═N1 = 1.288 (2) Å; Soylu *et al.*, 2004] shows that at least one of the N—O distances [N1—O1 = 1.376 (3) Å and C1═N1 = 1.295 (3) Å for (I)] is slightly shortened in the complex, while the C═N distance is increased by about 0.01 Å. The oxime moieties in (I) have an *E* configuration with a C2—C1═N1—O1 torsion angle of −178.7 (2)°.

While the hydroxyl H atom is only involved in an intramolecular hydrogen bond [O1$\cdots$O2$^{i}$ = 2.462 (3) Å; symmetry code: (i) $-x, -y, -z$], the amine H atom is involved in both intra- and intermolecular hydrogen bonding [N3$\cdots$O1$^{ii}$ = 2.916 (3) Å and N3$\cdots$O1 = 2.685 (3) Å; symmetry code: (ii) $1 - x, 1 - y, -z$] (Fig. 2). Further analysis by *PLATON* (Spek, 2003) showed that the sum of the three angles about the amine H atom is 357°. Atom C10 of the methyl group behaves as a donor in very weak intermolecular hydrogen bonding with an oxime O atom [C10$\cdots$O2$^{iii}$ = 3.441 (4) Å; symmetry code: (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The crystal packing shows an infinite two-dimensional framework, which is stabilized by the above-mentioned hydrogen-bonded network and other weak intermolecular interactions (Fig. 2). Except for slight deviations in geometric measurements, all the configurations are in accord with transition metal complexes of oximes and related ligands.

## Experimental

A solution of 1 mmol of $NiCl_2\cdot 6H_2O$ in absolute ethanol (10 ml) was added to 2 mmol of the ligand *N*-(4-methoxphenyl)aminomethylglyoxime dissolved in absolute ethanol (20 ml). The mixture was stirred for 3–4 h at room temperature. The original color of the solution which is pale-yellow changed immediately to red and the pH value decreased from 6 to 2, which was then adjusted to about 5–5.5 with 1% KOH solution. The turbid mixture was stirred in a water bath at 313–323 K for one h in order to completely precipitate the complex. The precipitated complex was filtered off, washed with ethanol and diethyl ether and dried *in vacuo* at room temperature. Elemental analyses (found): C 47.74 (47.56), H 4.77 (4.25), N 16.70% (16.52%). IR (KBr, cm$^{-1}$): 3326 (N—H), 1600 (C═N), 1741 (O—H$\cdots$O), 980 (N—O). $^1$H NMR (DMSO-$d_6$): $\delta$ 16.0 (O—H$\cdots$O), 6.8–7.0 (H$_{ar}$), 7.8 (N—H), 3.8 (O—$CH_3$).

### *Crystal data*

$[Ni(C_{10}H_{12}N_3O_3)_2]$
$M_r$ = 503.16
Monoclinic, $P2_1/c$
$a$ = 8.8819 (7) Å
$b$ = 5.2497 (3) Å
$c$ = 24.216 (2) Å
$\beta$ = 106.165 (7)°
$V$ = 1084.49 (14) Å$^3$
$Z$ = 2

$D_x$ = 1.541 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 8326 reflections
$\theta$ = 1.8–26.1°
$\mu$ = 0.95 mm$^{-1}$
$T$ = 293 (2) K
Block, red
0.35 × 0.30 × 0.28 mm

### *Data collection*

Stoe IPDS-2 diffractometer
$\omega$ scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min}$ = 0.559, $T_{max}$ = 0.928
13231 measured reflections
1916 independent reflections

1525 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.048
$\theta_{max}$ = 25.0°
$h = -10 \rightarrow 10$
$k = -6 \rightarrow 6$
$l = -28 \rightarrow 28$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
$S$ = 1.06
1916 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.1755P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

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**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—N1 | 1.848 (2) | N1—C1 | 1.295 (3) |
| Ni1—N2 | 1.864 (2) | N2—C2 | 1.300 (3) |
| O2—N2 | 1.332 (3) | N3—C1 | 1.356 (3) |
| O1—N1 | 1.376 (3) | N3—C4 | 1.433 (3) |
| O3—C7 | 1.383 (4) | C1—C2 | 1.468 (4) |
| O3—C10 | 1.395 (4) | C2—C3 | 1.480 (4) |
| | | | |
| N1$^{i}$—Ni1—N1 | 180 | C7—O3—C10 | 118.4 (3) |
| N1$^{i}$—Ni1—N2 | 97.73 (9) | C1—N1—O1 | 117.9 (2) |
| N1—Ni1—N2 | 82.27 (9) | C1—N1—Ni1 | 116.30 (17) |
| N2—Ni1—N2$^{i}$ | 180. | O1—N1—Ni1 | 125.04 (15) |
| | | | |
| O1—N1—C1—C2 | −178.7 (2) | | |

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

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O2$^{i}$ | 1.07 (4) | 1.39 (5) | 2.462 (3) | 171 (4) |
| N3—H3···O1$^{ii}$ | 0.81 (4) | 2.19 (4) | 2.916 (3) | 148 (3) |
| C10—H10*A*···O2$^{iii}$ | 0.96 | 2.51 | 3.441 (4) | 165 |
| N3—H3···O1 | 0.81 (4) | 2.34 (4) | 2.685 (3) | 106 (3) |
| C3—H3*A*···O2 | 0.96 | 2.42 | 2.775 (3) | 102 |

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

C-bound H atoms were positioned geometrically, with C—H = 0.93–0.96 Å and $U_{\rm iso}$(H) = 1.2 or 1.5 of the parent atom. H1 on O1 and H3 on N3 were obtained from a difference map and refined freely.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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