

Bis[1-(2,6-dimethylanilino)propane-1,2-dione dioximato]nickel(II)

Hümeýra Batı,^a Aýşin Zülfikaroğlu,^a Murat Taş,^a Omer Andac^a and William T. A. Harrison^{b*}

^aDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey, and ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: oandac@omu.edu.tr

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.034

wR factor = 0.093

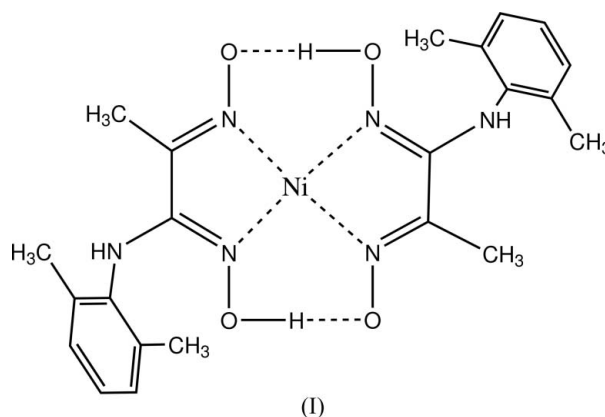
Data-to-parameter ratio = 26.3

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

The structure of the title complex consists of isolated $[\text{Ni}(\text{C}_{11}\text{H}_{14}\text{N}_3\text{O}_2)_2]$ units. The Ni atom is coordinated by four oxime N atoms in distorted square-planar geometry and lies on an inversion centre. The structure is stabilized by strong intramolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and a possible $\text{N}-\text{H}\cdots\pi$ intermolecular interaction.

Comment

This work is part of our ongoing research on the synthesis and characterization of new *vic*-dioximes and their transition metal complexes (Zülfikaroğlu *et al.*, 2003). Metal complexes of various glyoximate ligands have long been of importance in analytical chemistry and medicine (Chakravorty, 1974; Michael *et al.*, 2000).



In the title compound, (I), alternately named bis[*N*-(2,6-dimethylphenyl)aminomethylglyoximato-*N,N'*]nickel(II) (Fig. 1), the Ni atom, which lies on a site of $\bar{1}$ symmetry, is coordinated by four oxime N atoms arising from two bidentate ligand molecules. The local coordination of the NiN_4 chromophore is distorted square planar (D_{2h} symmetry). The Ni—N and $\text{O1}\cdots\text{O2}^i$ distances (Tables 1 and 2; symmetry code as in these tables) are similar to the distances found in the related complexes bis[*N*-(2,6-dimethylphenyl)aminoglyoximato-*N,N'*]nickel(II) (Ülkü *et al.*, 1996), bis[*N*-(4-methylphenyl)aminoglyoximato-*N,N'*]nickel(II) (Isik *et al.*, 2000), bis[*N*-(2,6-dimethylphenyl)aminophenylglyoximato- κ^2N,N']nickel(II) dimethyl sulfoxide solvate (Batı *et al.*, 2004) and bis[*N*-(4-methoxyphenyl)aminomethylglyoximato]nickel(II) (Batı *et al.*, 2005). In these, one Ni—N bond is significantly longer than the other (by between 0.02 and 0.05 Å). This difference can possibly be attributed to the different groups attached to oxime atoms C9 and C10.

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The different N—O bond lengths reflect the chemically distinct O atoms. The oxime group has an *E* configuration with planar O1—N2—C9—C10. The oxime OH group is adjacent to the bridging amine group in all complexes, and in (I) accepts an intraligand N—H···O bond. The benzene and five-membered chelate (NiC₂N₂) rings in (I) are essentially planar, with r.m.s. deviations of only 0.0045 and 0.0159 Å.

Comparison of the bond lengths of the oxime group with those of the free ligand (Hökelek *et al.*, 2001) reveals that, upon complex formation, the N2—O1, N3—O2 and C9—C10 distances are shortened by 0.040, 0.078 and 0.018 Å, respectively, whereas the C9—N2 and C10—N3 distances are increased by 0.013 and 0.028 Å, respectively.

The intramolecular inter-ligand O···O separations in these compounds are all similar, lying between 2.462 (3) and 2.547 (3) Å. Such short O···O separations are often associated with symmetrical O···H···O hydrogen bonds (Chakravorty, 1974). In (I), one of the O-bound acidic H atoms is lost from each ligand during complex formation and the remaining O-bound H atom participates in a very strong intramolecular hydrogen bond to the adjacent O atom (Table 2). The H atom was clearly visible in a difference map and, like the other complexes noted above, the O—H···O bond is not symmetrical.

An analysis of the intermolecular contacts in (I) with *PLATON* (Spek, 2003) revealed a possible weak N—H··· π ($-x, 1 - y, 2 - z$) interaction between the amine H atom and an adjacent benzene ring (atoms C1—C6) with an H··· π distance of 2.965 (16) Å.

Experimental

1-(2,6-Dimethylphenylamino)propane-1,2-dione dioxime (*L*) was prepared according to the method of Hökelek *et al.* (2001). A solution of NiCl₂·6H₂O (0.48 g, 2 mmol) in ethanol–water (1:1) was added dropwise to a solution of *L* (0.882 g, 4 mmol) in ethanol (20 ml). A 1% solution of KOH in water was then dripped slowly into the mixture until the pH reached 5.5. The resulting precipitate was removed by suction filtration, washed and dried *in vacuo*. Recrystallization from a chloroform–ethanol mixture (2:1) gave orange rod crystals of (I).

Crystal data

[Ni(C ₁₁ H ₁₄ N ₃ O ₂) ₂]	$D_x = 1.433 \text{ Mg m}^{-3}$
$M_r = 499.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4650 reflections
$a = 8.1081$ (4) Å	$\theta = 2.5\text{--}32.0^\circ$
$b = 16.0311$ (8) Å	$\mu = 0.88 \text{ mm}^{-1}$
$c = 8.9223$ (4) Å	$T = 293$ (2) K
$\beta = 94.202$ (1)°	Rod, orange
$V = 1156.62$ (10) Å ³	$0.49 \times 0.30 \times 0.24 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	4184 independent reflections
ω scans	2988 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1997)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.736$, $T_{\text{max}} = 0.810$	$\theta_{\text{max}} = 32.5^\circ$
11778 measured reflections	$h = -12 \rightarrow 11$
	$k = -24 \rightarrow 16$
	$l = -13 \rightarrow 13$

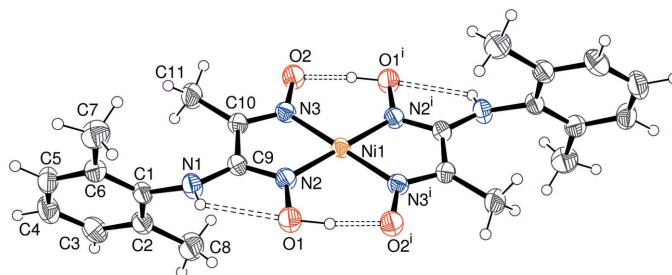


Figure 1

View of (I) showing 40% probability displacement ellipsoids (arbitrary spheres for the H atoms) and hydrogen bonds as dashed lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4184 reflections	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
159 parameters	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—N2	1.8397 (11)	Ni1—N3	1.8779 (11)
N2—Ni1—N3 ⁱ	97.62 (5)	N2—Ni1—N3	82.38 (5)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1—H1O···O2 ⁱ	0.86 (1)	1.65 (1)	2.4972 (14)	171 (2)
N1—H1N···O1	0.82 (1)	2.20 (2)	2.6361 (16)	113 (1)

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

The O- and N-bound H atoms were found in difference maps and were refined with distance restraints [O—H = 0.84 (2) Å and N—H = 0.86 (2) Å] and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$. C-bound H atoms were placed in calculated positions (C—H = 0.93–0.96 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl carrier})$. The —CH₃ groups were rotated to fit the electron density.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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References

- Bati, H., Dağ, C., Soylu, M. S., Taş, M., Çalışkan, N. & Büyükgüngör, O. (2005). *Acta Cryst. E* **61**, m1866–m1868.

- Batı, H., Zülfişkaroglu, A., Taş, M., Çalışkan, N., Soylu, S., Andac, O. & Büyükgüngör, O. (2004). *Acta Cryst.* **E60**, m1334–m1336.
- Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chakravorty, A. (1974). *Coord. Chem. Rev.* **13**, 1–46.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hökelek, T., Zülfişkaroglu, A. & Batı, H. (2001). *Acta Cryst.* **E57**, o1247–o1249.
- Isik, S., Ozturk, S., Erdonmez, A., Macit, M. & Fun, H.-K. (2000). *Anal. Sci.* **16**, 559–560.
- Michael, J. P., Anthony, W. A. & Raymond, J. B. (2000). *Inorg. Chim. Acta*, **300–302**, 992–1003.
- Sheldrick, G. M. (1997). *SADABS*, *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Ülkü, D., Ercan, F., Macit, M. & Gulce, A. (1996). *Acta Cryst.* **C52**, 2680–2682.
- Zülfişkaroglu, A., Taş, M., Batı, H. & Batı, B. (2003). *Synth. React. Inorg. Met.-Org. Chem.* **33**, 625–638.