

# Interactions between dimers of {1,1'-[*o*-phenylenebis(nitrilomethy- ldyne)]di-2-naphtholato- $\kappa^4 O,N,N',O'$ }- nickel(II)}

Anita Blagus<sup>a</sup> and Branko Kaitner<sup>b\*</sup>

<sup>a</sup>Department of Chemistry, J. J. Strossmayer University, Osijek, Franje Kuhača 20, HR-31000 Osijek, Croatia, and <sup>b</sup>Department of Chemistry, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Horvátovac 102a, HR-10002 Zagreb, Croatia  
Correspondence e-mail: kaitner@chem.pmf.hr

Received 25 September 2009

Accepted 26 October 2009

Online 7 November 2009

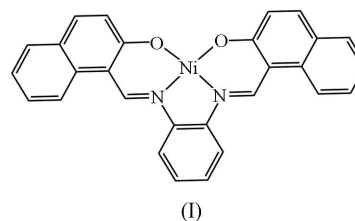
In the title compound, [Ni(C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>)], the Ni<sup>II</sup> centre has a square-planar coordination geometry in which the Schiff base ligand acts as a *cis*-*O,N,N',O'*-tetradentate ligand. The crystal structure is built up of centrosymmetric dimer units stacked into chains along the [010] direction. Adjacent chains associate *via* C—H...O hydrogen bonding only, leading to a two-dimensional sheet-like structure consisting of layers parallel to (10 $\bar{1}$ ). The cofacial dimeric complex contains an Ni...Ni contact of 3.291 (4) Å.

## Comment

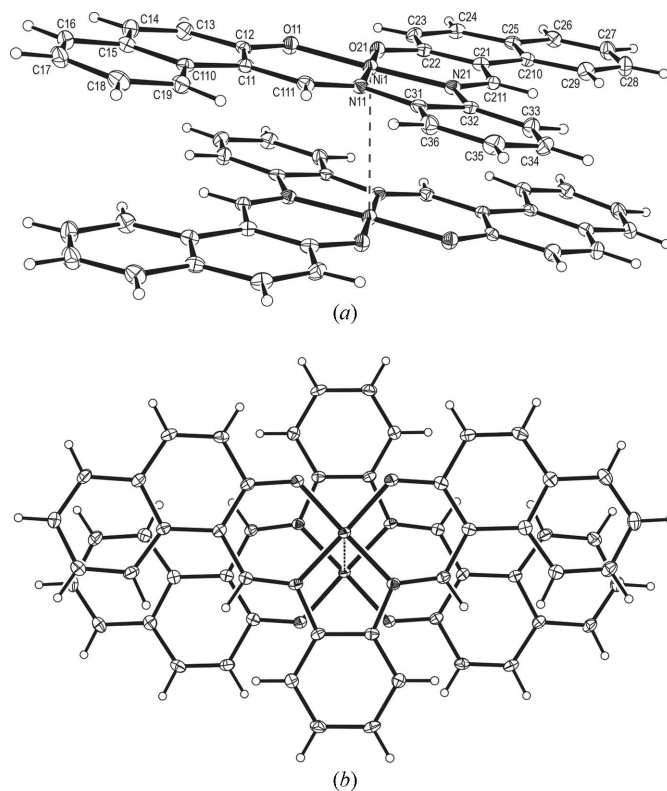
Polydentate Schiff base ligands and their metal complexes have been extensively studied because of their preparative availability and structural variability (Dodziuk, 2002). Compounds of this type having a delocalized system of conjugated  $\pi$  electrons play an important role as building blocks in new materials for nonlinear optical applications (Schalley, 2007). Schiff bases are electronically and sterically tunable, which makes them versatile ligands for investigating the effects of ligand flexibility on the reactivity of complexes containing these ligands (Szlyk *et al.*, 1999). Tetradentate Schiff base metal complexes may form *trans*- or *cis*-planar or tetrahedral structures (Elmali *et al.*, 2000). Nickel(II) complexes of aromatic diamine Schiff bases generally display either square-planar or slightly distorted square-planar coordination (Fun *et al.*, 2008). In comparison with salicylaldimine metal complexes, structural data for naphthaldimines and related complexes are quite rare. So far, the coordination compounds of 2-hydroxy-1-naphthaldimine derivatives of tin (Teoh *et al.*, 1997), iron (Elerman *et al.*, 1997), chromium (Wang *et al.*, 2006), ruthenium (Prabhakaran *et al.*, 2006) and copper (Xue *et al.*, 2007) have been reported.

We report here the structure of a nickel(II) complex with a naphthaldimine-type ligand (Fig. 1) in which  $\pi$ - $\pi$  stacking

interactions and C—H...O hydrogen bonding lead to a two-dimensional supramolecular network. Upon coordination to the metal centre, the ligand undergoes a substantial stereochemical change from significantly nonplanar to an almost planar configuration. It has been found that the free ligand in the solid state exists in both enol-imine and keto-amine forms (Popović *et al.*, 2001; Blagus, 2005), while in complex (I), the two chelating rings apparently contain delocalized electrons.



Comparison of the bond lengths observed in free (Popović *et al.*, 2001) and Ni-coordinated ligands (Table 1) shows no significant differences except in the case of the C<sub>ar</sub>—O and C=N imine bond distances. In complex (I), the C<sub>N11</sub>—N<sub>N1</sub> distances are slightly longer than the standard imine C=N double bond (1.28 Å; Allen *et al.*, 1987), and the C<sub>N2</sub>—O<sub>N1</sub> bond lengths are shorter than the typical C—O single bond (1.34 Å; *n* = 1 or 2). Both the C—N and C—O bond distances



**Figure 1**  
(a) The molecular structure of the dimeric nickel(II) complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. (b) A perpendicular projection of the dimer complex molecule, showing the offset arrangement of the monomeric units.

in the coordinated ligand are intermediate between single- and double-bond values. The remaining bond lengths and angles are all typical of their types (Allen *et al.*, 1987).

The coordination of the Ni<sup>II</sup> ion is square planar, with a *cis*-O,N,N',O' donor set. The Ni—N and Ni—O bond lengths are within the ranges expected for square-planar Schiff base Ni complexes (Sztyk *et al.*, 1999; de Castro *et al.*, 2001). Similar coordination geometry has been observed in analogous nickel complexes with Schiff bases derived from *o*-phenylenediamine and salicylaldehyde (Wang *et al.*, 1994, 2003). The Ni—N distances are longer than the Ni—O distances for complexes with ligands in which the diimine bridge is aromatic, whereas for those with two aliphatic C atoms the opposite is observed (Azevedo *et al.*, 1994). The Ni—N bond distances in Ni(salen) complexes are slightly longer than those in Ni(naphthen) complexes (Wojtczak *et al.*, 1997).

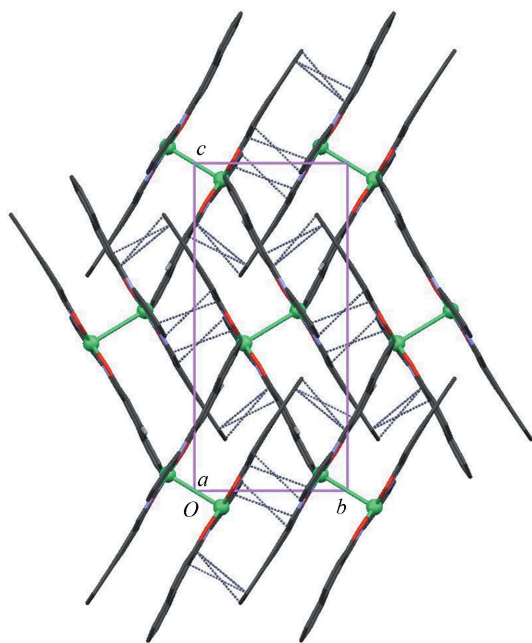
In the title compound, the Ni atom is displaced from the least-squares plane through the N and O atoms by only 0.0082 (3) Å, and this planarity permits extensive  $\pi$ -electron delocalization. In spite of that, the terminal naphthalene moieties retained the genuine quinoidal bond-length arrangement [*Cn*3—*Cn*4 = 1.352 (3) and 1.359 (3) Å, respectively, for *n* = 1 and 2; Allen *et al.*, 1987]. The dihedral angle between the two six-membered chelate rings is 1.25 (8)°.

The molecules of (I) form centrosymmetric dimers through a weak metal–metal interaction with an Ni···Ni distance of 3.291 (4) Å. This contact is out of the range for bond-length values usually accepted for the Ni—Ni bond distance (2.38–2.81 Å; Peng & Goedken, 1976, and references therein). The bond between two Ni atoms was first proposed in 1953 to

explain the seemingly anomalous insolubility of nickel(II) bis(dimethylglyoxime) as compared with its copper analogue (Godycki & Rundle, 1953). This interaction is not common, occurring only rarely in the numerous Ni structures in the Cambridge Structural Database (CSD; Allen, 2002). The reported Ni—Ni distances in the CSD, based on a search for bonded Ni atoms in tetracoordinated complexes with a set of either N<sub>4</sub> or N<sub>2</sub>O<sub>2</sub> nonbridging donor atoms, range from 2.808 to 3.336 Å. The shorter Ni—Ni distances are observed in structures for which nonbonding repulsions of the ligands are minimal (Berry *et al.*, 2006). In the present case, the *d*<sup>8</sup>–*d*<sup>8</sup> Ni···Ni interaction is weak, being a consequence of other types of stronger intermolecular interactions. Such Ni···Ni interactions are weaker than most covalent or ionic bonds, but they are stronger than other van der Waals interactions, and are roughly comparable in strength to typical hydrogen bonds (Pyykkö, 1997). Similar Ni···Ni distances [Ni···Ni = 3.3244 (4) Å] are found in a naphthaldimine nickel(II) complex with an aliphatic bridging diamine unit (Akhtar, 1981) and in a range of analogous nickel Schiff base complexes [3.201 (1)–3.582 (1) Å] with metal–metal interactions (Chakraborty *et al.*, 2004).

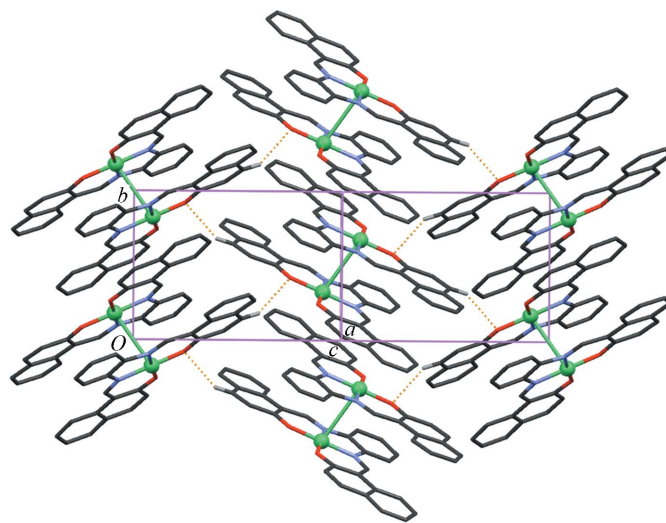
The aromatic rings within the dimer complexes are arranged face-to-face and there are indeed net repulsive interactions between the  $\pi$  systems. If the adjacent dimer molecules are laterally offset with regard to each other this offset geometry increases the attractive forces between the  $\pi$  systems to the extent that they can become more significant than the repulsive forces (Hunter & Sanders, 1990).

In our case, the only attraction within the dimer is the metal–metal interaction, whereas the peripheral atoms show significantly larger separation than those more centrally located, *e.g.* the four donor atoms. The interplanar distance between the least-squares planes defined by the N and O atoms (3.163 Å) is in the repulsive range for nonbonding



**Figure 2**

A projection of the crystal packing along the *a* axis, showing the herringbone arrangement of the complex molecules. The dimers stack by weak  $\pi$ – $\pi$  interactions in columns spreading along the *b* axis. The shortest dimer-to-dimer contacts are represented as dotted lines.



**Figure 3**

A view of the crystal packing, showing the interconnection of the parallel (010) columns into (101) layers through the C24—H24···O21( $-x + \frac{3}{2}$ ,  $y - \frac{1}{2}$ ,  $-z + \frac{3}{2}$ ) hydrogen bonds (shown as dotted lines).

interactions (Williams *et al.*, 1968). The apparent nonbonding repulsion of the peripheral naphthalene rings is observed, as indicated by the C17...C28<sup>ii</sup> [symmetry code: (ii)  $-x, -y, -z + 1$ ] separation of *ca* 3.677 Å and the C18...C27<sup>ii</sup> separation of *ca* 3.582 Å. The influence of the reciprocally repulsive interactions of the peripheral naphthalene rings leads to a slightly saddle-shaped conformation of particular dimeric molecules. The adjacent dimers have a staggered arrangement that minimizes repulsive interactions. The later is shown by an interplanar separation shorter than that in graphite (3.35 Å), amounting to *ca* 3.251 Å. These interactions (clearly visible in Fig. 2) could be recognized as offset  $\pi$ - $\pi$  attractive forces existing between the dimer molecules exclusively and linking the dimers into parallel columns spreading along [010].

The crystals are built up of parallel (10 $\bar{1}$ ) layers formed by [010] columns linked by the C—H...O hydrogen bond (Fig. 3 and Table 2). The apparent herringbone packing pattern typical for arrays of fused aromatic rings (Desiraju & Gavezzotti, 1989) is shown in Fig. 2.

## Experimental

The title nickel complex was synthesized by template synthesis. A solution of nickel(II) chloride hexahydrate (1 mmol) and 2-hydroxy-1-naphthaldehyde (2 mmol) in absolute ethanol and an ethanol solution of *o*-phenylenediamine (1 mmol) were allowed to mix by slow diffusion through chloroform. After one week, red crystals had formed.

### Crystal data

[Ni(C <sub>28</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> )]	$V = 1953.23 (5) \text{ \AA}^3$
$M_r = 473.15$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 15.8669 (3) \text{ \AA}$	$\mu = 1.03 \text{ mm}^{-1}$
$b = 7.5765 (1) \text{ \AA}$	$T = 100 \text{ K}$
$c = 16.4065 (2) \text{ \AA}$	$0.6 \times 0.2 \times 0.02 \text{ mm}$
$\beta = 97.9769 (13)^\circ$	

### Data collection

Oxford Diffraction Xcalibur CCD diffractometer	11136 measured reflections
Absorption correction: analytical (Alcock, 1970)	4227 independent reflections
$T_{\min} = 0.667, T_{\max} = 0.936$	3694 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	298 parameters
$wR(F^2) = 0.094$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
4227 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1—O11	1.8385 (17)	O11—C12	1.298 (3)
Ni1—O21	1.8266 (17)	O21—C22	1.301 (3)
Ni1—N11	1.846 (2)	N11—C111	1.315 (3)
Ni1—N21	1.851 (2)	N21—C211	1.313 (3)
O11—Ni1—O21	84.04 (7)	O21—Ni1—N11	178.60 (8)
O11—Ni1—N11	94.60 (8)	O21—Ni1—N21	94.32 (8)
O11—Ni1—N21	177.87 (8)	N11—Ni1—N21	87.05 (9)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C24—H24...O21 <sup>i</sup>	0.95	2.46	3.298 (3)	147

Symmetry code: (i)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .

All H atoms were located in a difference map and then treated as riding in geometrically idealized positions, with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST97* (Nardelli, 1996) and *Mercury* (Version 1.4; Macrae *et al.*, 2006).

Financial support by the Ministry of Science, Education and Sport of the Republic of Croatia is gratefully acknowledged (grant No. 119-1193079-3069).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3313). Services for accessing these data are described at the back of the journal.

## References

- Akhtar, F. (1981). *Acta Cryst.* **B37**, 84–88.
- Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). *J. Chem. Soc. Perkin Trans 2*, pp. S1–19.
- Azevedo, F., Carrondo, M. A. A. F. de C. T., de Castro, B., Convery, M., Domingues, D., Freire, C., Duarte, M. T., Nielsen, K. & Santos, I. C. (1994). *Inorg. Chim. Acta*, **219**, 43–54.
- Berry, J. F., Bothe, E., Cotton, F. A., Ibragimov, S. A., Murillo, C. A., Villagrán, D. & Wang, X. (2006). *Inorg. Chem.* **45**, 4396–4406.
- Blagus, A. (2005). MSc thesis, The University of Zagreb, Croatia.
- Castro, B. de, Freire, C., Duarte, M. T., Minas da Piedade, M. F. & Santos, I. C. (2001). *Acta Cryst.* **C57**, 370–372.
- Chakraborty, S., Samanta, B., Chowdhury, C. R., Mitra, S. & Mukherjee, A. K. (2004). *Acta Cryst.* **C60**, m578–m580.
- Desiraju, G. R. & Gavezzotti, A. (1989). *J. Chem. Soc. Chem. Commun.* pp. 621–623.
- Dodziuk, H. (2002). *Introduction to Supramolecular Chemistry*. Dordrecht: Kluwer Academic Publishers.
- Elerman, Y., Kabak, M. & Ülkü, D. (1997). *Acta Cryst.* **C53**, 712–714.
- Elmali, A., Elerman, Y. & Svoboda, I. (2000). *Acta Cryst.* **C56**, 423–424.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fun, H.-K., Kia, R., Mirkhani, V. & Zargoshi, H. (2008). *Acta Cryst.* **E64**, m1181–m1182.
- Godycki, L. E. & Rundle, R. E. (1953). *Acta Cryst.* **6**, 487–495.
- Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 8500–8510.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nardelli, M. (1996). *J. Appl. Cryst.* **29**, 296–300.
- Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.170. Oxford Diffraction Ltd, Wroclaw, Poland.
- Peng, S.-M. & Goedken, V. L. (1976). *J. Am. Chem. Soc.* **98**, 8500–8504.
- Popović, P., Roje, V., Pavlović, G., Matković-Čalogović, D. & Giester, G. (2001). *J. Mol. Struct.* **597**, 39–47.
- Prabhakaran, R., Huang, R. & Natarajan, K. (2006). *Inorg. Chim. Acta*, **359**, 3359–3362.

- Pyykkö, P. (1997). *Chem. Rev.* **97**, 597–636.
- Schalley, C. A. (2007). *Analytical Methods in Supramolecular Chemistry*. New York: Wiley–VCH.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Szlyk, E., Wojtczak, A., Larsen, E., Surdykowski, A. & Neumann, J. (1999). *Inorg. Chim. Acta*, **293**, 239–244.
- Teoh, S.-G., Yeap, G.-Y., Loh, C.-C., Foong, L.-W., Teo, S.-B. & Fun, H.-K. (1997). *Polyhedron*, **16**, 2213–2221.
- Wang, J., Bei, F.-L., Xu, X.-Y., Yang, X.-J. & Wang, X. (2003). *J. Chem. Crystallogr.* **33**, 845–849.
- Wang, S., Day, P., Wallis, J. D., Horton, P. N. & Hursthouse, M. B. (2006). *Polyhedron*, **25**, 2583–2592.
- Wang, H., Li, S.-L., Liu, D.-X., Cui, X.-G., Li, X.-Y. & Yang, Z.-H. (1994). *Huaxue Xuebao (Acta Chim. Sin.)*, **52**, 676.
- Williams, J., Stang, P. & Schleyer, P. (1968). *Annu. Rev. Phys. Chem.* **19**, 531–558.
- Wojtczak, A., Szlyk, E., Jaskólski, M. & Larsen, E. (1997). *Acta Chem. Scand.* **51**, 274–278.
- Xue, R.-T., Niu, M.-J., Dou, J.-M. & Wang, D.-Q. (2007). *Acta Cryst.* **E63**, m2111.