

Aqua-1κO-{\mu-1,3-bis[2-(2-oxido-benzylideneamino)ethyl]-2-(2-oxido-phenyl)imidazolidine-1κ⁴O,N,N',O';-2κ⁴O',N'',N''',O'''}(μ-2-formyl-phenolato-1:2κ³O¹:O¹,O²)-dinickel(II) trihydrate: a one-dimensional chain linked by O—H···O hydrogen bonds and C—H···π interactions

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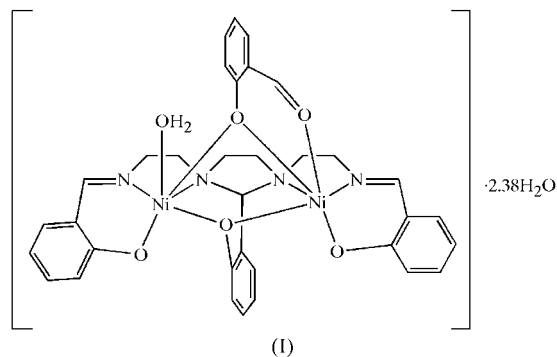
In the title compound, [Ni₂(C₇H₅O₂)(C₂₇H₂₇N₄O₂)(H₂O)]·2.38H₂O, each Ni atom is coordinated by two N atoms and four O atoms from the heptadentate Schiff base ligand and one salicylaldehyde or water molecule, forming an asymmetric molecule with three bridges linking the two Ni^{II} ions, which are separated by 3.081 (1) Å. Hydrogen-bonded water and C—H···π interactions take part in the stabilization of the complex. The complex molecules are connected into a one-dimensional chain along the *c* axis by O—H···O hydrogen bonds between coordinated and solvent water molecules and by C—H···π interactions.

Comment

Multinuclear complexes of the heptadentate Schiff base 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine (H₃L) have attracted much attention because of their various properties, such as fixing atmospheric carbon dioxide (Fondo *et al.*, 2002) or their magnetic properties (Fondo *et al.*, 2004; Prasant Kumar *et al.*, 2006). The title complex, (I), was synthesized in order to study its inhibitory activity on the protein tyrosine phosphatase 1B (PTP1B) and we present its crystal structure here.

The molecular structure of (I) is illustrated in Fig. 1. The compound consists of a binuclear phenolic Schiff base complex and three water molecules. In the binuclear complex, each Ni atom is coordinated by two N atoms and four O atoms

from the heptadentate Schiff base ligand and one salicylaldehyde or water molecule, forming an asymmetric molecule with three bridges. The Ni—N and Ni—O distances and angles



around the two metal ions are in the normal ranges (Table 1; Fondo *et al.*, 2006). A water molecule acts as a hydrogen-bond bridge between atoms O1 and O2. Additionally, a C—H···π interaction, *viz.* C20—H···Cg1 (Cg1 is the centroid of the C13—C18 ring), with a C···Cg distance of 3.510 (5) Å, takes part in stabilization of the structure. All these structural characteristics are in good agreement with those of the compound [Ni₂L(*o*-OC₆H₃BrCHO)(H₂O)]·2.25MeCN·H₂O [*L* is 2-(5-bromo-2-hydroxyphenyl)-1,3-bis[4-(5-bromo-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine; Fondo *et al.*, 2006], (II), indicating that the 5-Br atom in (II) has little effect on the molecular structure.

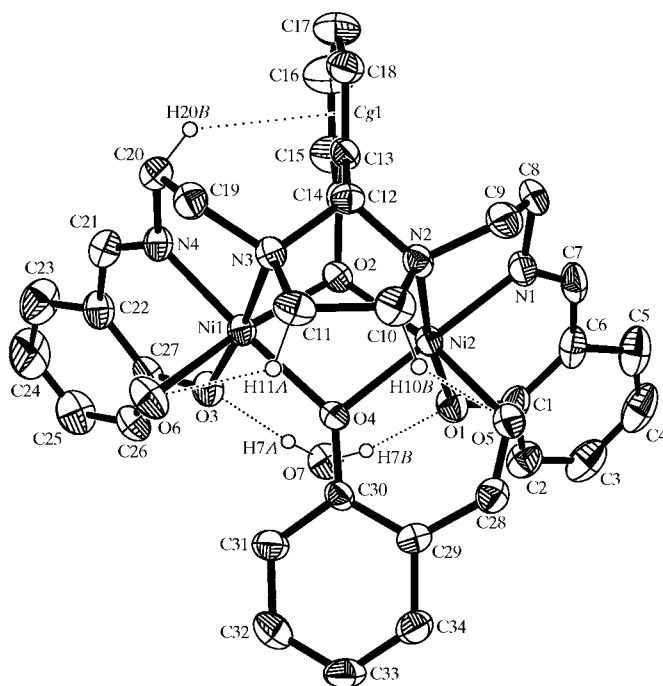
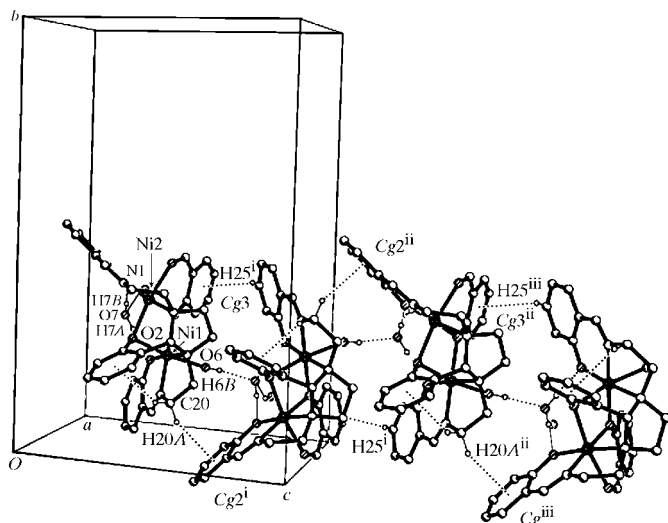


Figure 1
 The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Dotted lines indicate hydrogen bonds and C—H···π interactions. Cg1 is the centroid of the C13—C18 ring. H atoms not involved in hydrogen bonds and the minor components of the disordered O atoms have been omitted.


Figure 2

The one-dimensional chain constructed by O—H...O hydrogen bonds and C—H... π interactions (dotted lines), viewed along the *c* axis. $Cg2$ and $Cg3$ are the centroids of the C1—C6 and C29—C34 rings, respectively. The minor components of the disordered O atoms have been omitted. [Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, y, 1 + z$; (iii) $x, \frac{1}{2} - y, \frac{3}{2} + z$.]

Complex molecules of (I) are linked to form a one-dimensional chain along the *c* axis by an O—H...O hydrogen bond between coordinated and solvent water molecules (Fig. 2). This is similar to what is observed in the (II) and $[Ni_2L(OAc)(H_2O)_2] \cdot 3MeCN \cdot 2H_2O$, (III) (Fondo *et al.*, 2006), especially the latter, where the coordinated *o*-OC₆H₃BrCHO ligand is replaced by an acetate group, but this hydrogen bond still exists and connects the complexes to form a one-dimensional chain. Thus, this hydrogen bond is very important in the packing of this kind of compound.

In addition to this hydrogen bond, there are a further two C—H... π interactions contributing to the stabilization of the one-dimensional chain, *viz.* C20... $Cg2^i$ and C25... $Cg3^{iii}$ [$Cg2$ is the centroid of the C1—C6 ring and $Cg3$ is the centroid of the C29—C34 ring; symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$], with C... Cg distances of 3.577 (5) and 3.550 (6) Å, respectively (Fig. 2). This can be compared with (II), where the corresponding C20—H... π interaction is retained but another is changed, possibly because of the repulsive interaction between the 5-bromo-2-hydroxyphenyl groups. Therefore, although the 5-Br atom of the ligand has little effect on the molecular structure, it can influence crystal packing. Because of these C—H... π interactions, the closest Ni...Ni distance between neighbouring complexes of (I) is 7.248 Å, 0.152 Å longer than that in (II).

Experimental

The heptadentate Schiff base was prepared following a modified literature procedure (Sarma & Bailar, 1955). The ligand was collected by filtration and recrystallized from warm ethanol. For the preparation of the title compound, (I), NiSO₄·6H₂O (0.1314 g) in water (10 ml) was added to a solution of H₃L (0.1770 g) in methanol (15 ml) with stirring. The resulting solution was refluxed for 1 h and the

cooled solution was filtered. Deep-green crystals were obtained from the filtrate after 10 d on slow evaporation. The presence of the salicylaldehyde ligand in the structure of (I) demonstrates that the heptadentate Schiff base is unstable in solution over a long period, undergoing hydrolysis.

Crystal data

$[Ni_2(C_7H_5O_2)(C_{27}H_{27}N_4O_2)(H_2O)] \cdot 2.38H_2O$
 $M_r = 766.12$
 Monoclinic, $P2_1/c$
 $a = 11.4361$ (8) Å
 $b = 21.5977$ (16) Å
 $c = 14.7334$ (11) Å

$\beta = 101.4660$ (10)^o
 $V = 3566.4$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.11$ mm⁻¹
 $T = 298$ (2) K
 $0.28 \times 0.13 \times 0.02$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{min} = 0.746$, $T_{max} = 0.978$

14776 measured reflections
 6165 independent reflections
 4665 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.168$
 $S = 1.07$
 6165 reflections
 451 parameters

24 restraints
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.95$ e Å⁻³
 $\Delta\rho_{min} = -0.38$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—O3	1.991 (3)	Ni2—N1	2.000 (4)
Ni1—N4	2.011 (4)	Ni2—O1	2.008 (3)
Ni1—O4	2.083 (3)	Ni2—O4	2.019 (3)
Ni1—O2	2.090 (3)	Ni2—O2	2.072 (3)
Ni1—O6	2.167 (3)	Ni2—O5	2.111 (3)
Ni1—N3	2.171 (4)	Ni2—N2	2.184 (4)
Ni1—Ni2	3.081 (1)		
O3—Ni1—N4	91.85 (15)	N1—Ni2—O1	90.57 (16)
O3—Ni1—O4	92.06 (13)	N1—Ni2—O4	176.90 (16)
N4—Ni1—O4	175.87 (14)	O1—Ni2—O4	91.73 (13)
O3—Ni1—O2	93.56 (12)	N1—Ni2—O2	100.26 (14)
N4—Ni1—O2	98.74 (14)	O1—Ni2—O2	95.23 (13)
O4—Ni1—O2	79.67 (12)	O4—Ni2—O2	81.59 (12)
O3—Ni1—O6	90.17 (13)	N1—Ni2—O5	90.10 (15)
N4—Ni1—O6	88.22 (15)	O1—Ni2—O5	88.80 (14)
O4—Ni1—O6	93.12 (13)	O4—Ni2—O5	87.87 (12)
O2—Ni1—O6	171.98 (13)	O2—Ni2—O5	168.82 (13)
O3—Ni1—N3	174.56 (14)	N1—Ni2—N2	83.39 (16)
N4—Ni1—N3	82.87 (15)	O1—Ni2—N2	173.16 (13)
O4—Ni1—N3	93.26 (13)	O4—Ni2—N2	94.19 (13)
O2—Ni1—N3	88.54 (12)	O2—Ni2—N2	89.03 (13)
O6—Ni1—N3	88.38 (13)	O5—Ni2—N2	88.00 (14)

Table 2

Hydrogen-bond geometry (Å, °).

$Cg1$, $Cg2$ and $Cg3$ are the centroids of the C13—C18, C1—C6 and C29—C34 rings, respectively.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O6—H6A...O9B	0.85	2.12	2.859 (15)	145
O7—H7B...O1	0.85	1.85	2.688 (5)	168
O7—H7A...O3	0.85	1.89	2.741 (5)	175
O6—H6B...O7 ⁱ	0.85	1.97	2.795 (5)	164
C20—H20A... $Cg2^i$	0.97	2.68	3.582 (5)	154
C20—H20B... $Cg1$	0.97	2.73	3.510 (5)	138
C25—H25... $Cg3^{iii}$	0.93	2.87	3.552 (6)	131

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

H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^2-H = 0.93 \text{ \AA}$, $Csp^3-H = 0.97 \text{ \AA}$ and $Csp^3-H = 0.98 \text{ \AA}$, and refined with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to O atoms were located from difference Fourier maps and refined as riding in their as-found positions, with $U_{iso}(H) = 1.5U_{eq}(O)$. The O-H distances are in the range 0.850–0.851 Å. Atom O8 was found to be disordered; the final occupancies from the refinement were O8A = 0.59 and O8B = 0.41. Fourier maps also showed that there is only less density for the O9A and O9B sites, which would correspond with oxygen occupancies of 0.125 at O9A and 0.250 at O9B, and with these small occupancies it is not worth refining the positions anisotropically. There is a lack of hydrogen-bonding interactions involving these water molecules (O8, O9A and O9B), which are simply occluded in holes in the structure. For these reasons, the water (O8, O9A and O9B) H atoms were not considered.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3086). Services for accessing these data are described at the back of the journal.

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