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# A nickel(II) complex of an unsymmetrical tetradentate Schiff base

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**Key indicators**

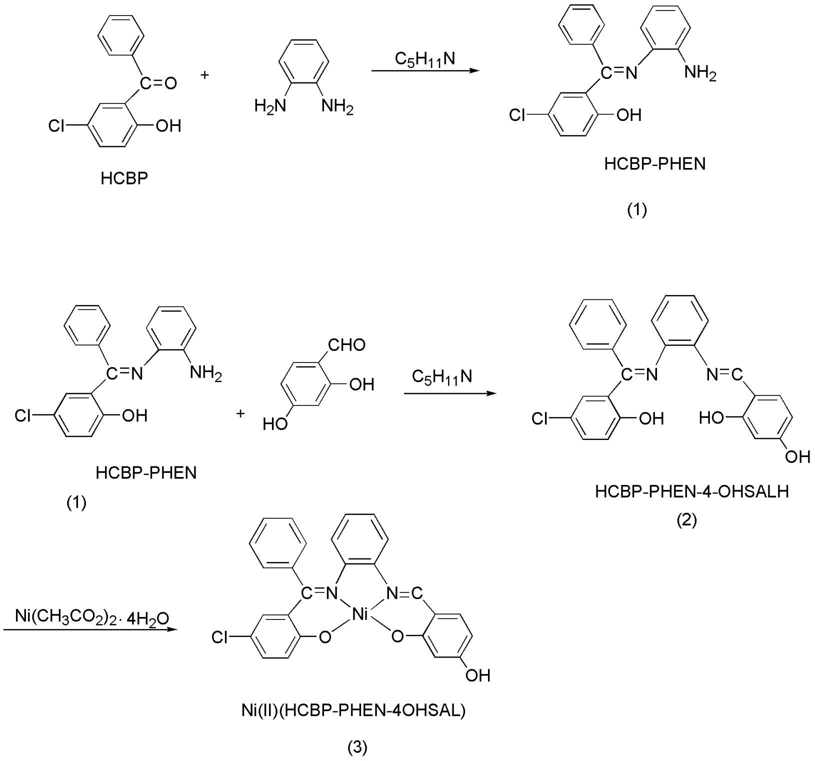
Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.007 Å
$R$ factor = 0.053
$wR$ factor = 0.129
Data-to-parameter ratio = 15.4

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

The structure of the title nickel(II) complex, (2-{2-[$\alpha$-(5-chloro-2-oxidophenyl)benzylideneamino]phenyliminomethyl}-5-hydroxyphenolato)nickel(II) methanol disolvate, $[Ni(C_{26}H_{17}ClN_2O_3)]\cdot 2CH_3OH$, containing an unsymmetrical tetradentate schiff base, comprises two neutral [Ni(CBP-PHEN-4-OHSAL)] complex molecules and four methanol solvent molecules in the asymmetric unit. Each $Ni^{II}$ center exists in a four-coordinate square-planar geometry defined by an $N_2O_2$ donor set.

## Comment

Transition metals occur in metalloenzymes, usually in a distorted coordination environment, bound to a macrocycle, such as a heme ring, or to donor atoms derived from peptide chains, as in hemerythrin ($Fe_2$) or hemocyanin ($Cu_2$) (Co *et al.*, 1981; Stenkamp *et al.*, 1981).



Unsymmetrical tetradentate Schiff base complexes are required to model the irregular binding of peptides (Atkins *et al.*, 1985). In this context, compound (1) (HCBP-PHEN; see scheme) was prepared from the condensation of 5-chloro-2-hydroxybenzophenone (HCBP) and one of the amino groups of 1,2-diaminobenzene. The second amino group can then be reacted with a substituted salicylaldehyde (4-OHSALH) to

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form the unsymmetrical tetradentate Schiff base ligand (HCBP-PHEN-4OHSALH) (2). This can be reacted with nickel(II) acetate to form the title complex, (3).

The structure of (3) contains two independent mononuclear complex molecules and four solvent methanol molecules (see Fig. 1 and Table 1). Each $Ni^{II}$ center has a slightly distorted square-planar geometry defined by two N and two O atoms. The $Ni^{II}$ center deviates from the coordination plane by 0.0137 (1) and 0.0125 (1) Å for atoms Ni1 and Ni2, respectively. All Ni–donor atom bond distances are within the range expected for such bonds (Atkins *et al.*, 1985). With the $Ni^{II}$ atom, the coordinated ligand gives rise to one five- and two six-membered chelate rings. There is some deviation from planarity in the ligand as shown in the dihedral angle between the OCCCN fragments, 13.5 (2) (Ni1) and 14.1 (2)° (Ni2). This distortion results from the steric constraints within the ligand.

The molecular packing is controlled by hydrogen bonds and intermolecular $\pi$–$\pi$ interactions. Thus, O—H···O hydrogen bonds are formed between the OH group of solvent methanol molecules and the ligand-bound OH groups and coordinated O atoms so that there exist eight O—H···O hydrogen bonds, as listed in Table 2. Intermolecular $\pi$–$\pi$ interactions exist between the phenyl rings of two complex molecules with a separation of approximately 3.68 Å between the centroids of the rings and the dihedral angle is approximately 11°.

## Experimental

The title complex, (3), was synthesized in methanol solution as described earlier and indicated in the scheme (Atkins *et al.*, 1985). Single crystals suitable for X-ray crystallography were obtained from an ethanol–$CH_2Cl_2$ mixture by slow evaporation at room temperature.

### Crystal data

$[Ni(C_{26}H_{17}ClN_2O_3)]\cdot 2CH_4O$
$M_r = 563.66$
Triclinic, $P\overline{1}$
$a = 13.856$ (10) Å
$b = 14.172$ (10) Å
$c = 15.863$ (11) Å
$\alpha = 95.181$ (12)°
$\beta = 101.862$ (12)°
$\gamma = 119.151$ (11)°
$V = 2595$ (3) Å$^3$

$Z = 4$
$D_x = 1.443$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 870 reflections
$\theta = 3.0$–25.9°
$\mu = 0.89$ mm$^{-1}$
$T = 293$ (2) K
Prism, yellow
0.34 × 0.22 × 0.20 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.779$, $T_{max} = 1$
14885 measured reflections

10432 independent reflections
6469 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 26.4$°
$h = -17 \rightarrow 9$
$k = -15 \rightarrow 17$
$l = -17 \rightarrow 19$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.129$
$S = 1.03$
10432 reflections
677 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.9807P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$

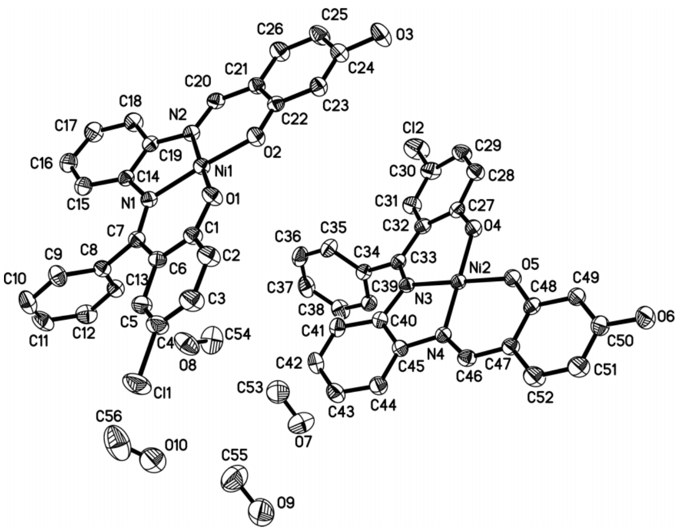

**Figure 1**
The molecular structure of (3). H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

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

| | | | |
|---|---|---|---|
| Ni1—O1 | 1.833 (3) | Ni2—O4 | 1.840 (3) |
| Ni1—O2 | 1.841 (3) | Ni2—O5 | 1.841 (3) |
| Ni1—N1 | 1.876 (3) | Ni2—N3 | 1.884 (3) |
| Ni1—N2 | 1.845 (3) | Ni2—N4 | 1.854 (3) |
| | | | |
| O1—Ni1—O2 | 82.80 (11) | O4—Ni2—O5 | 82.60 (11) |
| O1—Ni1—N1 | 95.33 (12) | O4—Ni2—N3 | 95.83 (12) |
| O1—Ni1—N2 | 174.72 (13) | O4—Ni2—N4 | 174.85 (13) |
| O2—Ni1—N1 | 176.63 (13) | O5—Ni2—N3 | 176.74 (12) |
| O2—Ni1—N2 | 94.50 (13) | O5—Ni2—N4 | 94.78 (12) |
| N1—Ni1—N2 | 87.59 (13) | N3—Ni2—N4 | 87.01 (13) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3···O7$^{i}$ | 0.82 | 1.82 | 2.638 (5) | 173 |
| O6—H6···O8$^{ii}$ | 0.82 | 1.86 | 2.661 (5) | 167 |
| O7—H7···O1$^{iii}$ | 0.82 | 1.96 | 2.773 (4) | 169 |
| O7—H7···O2$^{iii}$ | 0.82 | 2.53 | 3.051 (5) | 123 |
| O8—H8···O4$^{i}$ | 0.82 | 2.06 | 2.856 (4) | 165 |
| O8—H8···O5$^{i}$ | 0.82 | 2.52 | 3.092 (5) | 128 |
| O9—H9a···O3$^{i}$ | 0.82 | 2.13 | 2.927 (5) | 164 |
| O10—H10*a*···O6$^{iv}$ | 0.82 | 1.98 | 2.789 (5) | 168 |

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, 1+z$; (iii) $1+x, 1+y, z$; (iv) $x, y, z-1$.

C-bound H atoms were included in the riding-model approximation, with C—H distances of 0.93 Å (0.96 Å for methyl groups), and $U_{iso}$(aromatic H) = $1.2U_{eq}$(C) and $U_{iso}$(methyl H) = $1.5U_{eq}$(C). The hydroxy H atoms were located in a difference map and refined with O—H distances fixed at 0.82 Å and $U_{iso} = 1.5U_{eq}$(O).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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