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Bis[2-hydroxy-*N*′-(3-phenylprop-2-enylidene)benzohydrazidato-κ^2*N*′,*O*]bis(methanol-κ*O*)nickel(II) and bis[2-hydroxy-*N*′-(3-phenylprop-2-enylidene)benzohydrazidato-κ^2*N*′,*O*]bis(pyridine-κ*N*)nickel(II)

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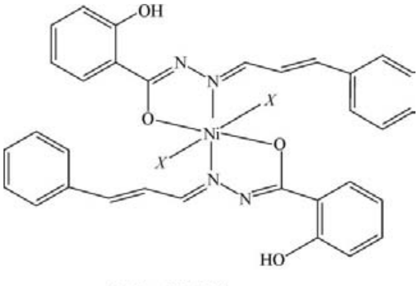
In the two title complexes of cinnamaldehyde salicyloylhydrazone [or 2-hydroxy-*N*′-(3-phenylprop-2-enylidene)benzohydrazide], $[Ni(C_{16}H_{13}N_2O_2)_2(CH_4O)_2]$, (I), and $[Ni(C_{16}H_{13}N_2O_2)_2(C_5H_5N)_2]$, (II), the Ni^{II} atoms lie on crystallographic inversion centres and have distorted octahedral geometries. The equatorial plane is defined by two carbonyl O atoms and two hydrazine N atoms of two bidentate *trans*-oriented salicyloylhydrazone ligands. The axial positions are occupied by two O atoms from two coordinated methanol molecules in (I) and by two N atoms from two coordinated pyridine molecules in (II). There is an extended chain structure in (I) resulting from intermolecular O—H⋯O hydrogen bonds between coordinated methanol molecules and phenol O atoms, while (II) comprises discrete molecules. Complex (I) also exhibits weak π–π stacking interactions, and intramolecular O—H⋯N hydrogen bonds are present in both (I) and (II). The salicyloylhydrazone ligands in (I) and (II) are coordinated to the metal atom through the carbohydrazide O and N^2 atoms, not *via* the phenol O atom. We have established a link between the reagents used and the nuclearity of the complex formed: the ligand produced by condensation between salicylhydrazide and an aldehyde leads to mononuclear complexes, while replacing the aldehyde in the reaction by a ketone leads to multinuclear complexes.

Comment

The design and construction of hydrazone complexes are of great interest due to their intriguing structural topologies and potential applications (Sreekanth *et al.*, 2004; Bai *et al.*, 2006). To date, only a few structures of cinnamaldehyde hydrazone complexes have been reported (Son *et al.*, 2002; Chumakov *et al.*, 2006), although many hydrazone complexes have been synthesized and characterized. We present here the syntheses and structural characterization of the title nickel(II) complexes, $[NiL_2(CH_3OH)_2]$, (I), and $[NiL_2(C_5H_5N)_2]$, (II), where L is monoanionic cinnamaldehyde salicyloylhydrazone or 2-hydroxy-*N*′-(3-phenylprop-2-enylidene)benzohydrazidate. To the best of our knowledge, the title complexes represent the first examples of structurally characterized cinnamaldehyde salicyloylhydrazone complexes.



(I) X = MeOH
(II) $X = C_5H_5N$ (pyridine)

As shown in Fig. 1, compound (I) contains a distorted octahedrally coordinated Ni^{II} ion located on a crystallographic inversion centre, with two L ligands acting in a bidentate manner to form five-membered chelate rings. Two methanol molecules coordinate axially *via* their O atoms. Atoms O2, O2^i, N2 and N2^i [symmetry code: (i) $1 - x, -y, 1 - z$] of the two hydrazone ligands form the equatorial plane, while the two O atoms of the methanol molecules (O3 and O3^i) occupy the two axial positions. The Ni1—N2(hydrazine) bond distance of 2.0845 (15) Å in (I) is longer than the corresponding values of 1.988 (2), 1.995 (2) and 1.983 (2) Å in similar complexes (Table 1). The Ni1—O3(methanol) bond length of 2.0970 (14) Å in (I) falls within the range 2.0661 (7)–2.148 (3) Å found for octahedral nickel complexes containing methanol in axial positions (Table 2).

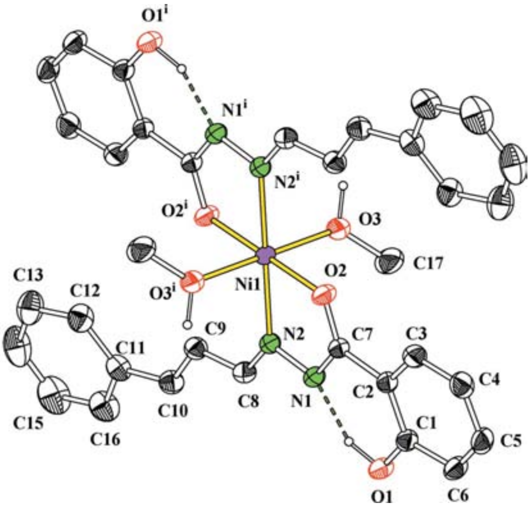


Figure 1
A view of compound (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding. H atoms not involved in the hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

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The $\mathrm{Ni^{II}}$ centre in complex (II) displays a slightly distorted octahedral coordination and lies on an inversion centre. The $\mathrm{Ni^{II}}$ centre is coordinated by two O atoms [O2 and $\mathrm{O2^{i}}$; symmetry code: (i) $-x, 1-y, 1-z$] and two N atoms (N2 and $\mathrm{N2^{i}}$) of two *L* ligands, and by two N atoms (N3 and $\mathrm{N3^{i}}$) of two coordinated pyridine molecules (see Fig. 2). In the equatorial plane, the Ni1—N2(hydrazine) bond distances of 2.082 (2) Å and Ni1—O2(carboxyl) bond distances of 2.0182 (15) Å are similar to the corresponding values in (I). The Ni1—N3(pyridine) bond length of 2.1487 (19) Å lies within the range 2.140 (2)—2.165 (2) Å found for related nickel complexes (Table 3).

The dihedral angles between the two benzene rings (C1–C6 and C11–C16) of the *L* ligand in (I) and (II) are 8.1 (1) and 18.8 (1)°, respectively. These values indicate slightly different degrees of coplanarity for the *L* ligands in the two complexes.

Adjacent complex molecules in (I) are linked by two intermolecular methanol–phenol $\mathrm{O-H\cdots O^{ii}}$ hydrogen bonds [symmetry code: (ii) $x, y-1, z$] to form an extended one-dimensional chain along the *b* axis (see Table 4 and Fig. 3). However, there is no comparable intermolecular hydrogen bonding in (II) and this complex exists as discrete molecules. There are intramolecular phenol–hydrazine $\mathrm{O-H\cdots N}$ hydrogen bonds in (I) and (II), forming a six-membered ring (H1/O1/C1/C2/C7/N1) (Tables 4 and 5).

The structure of (I) also exhibits weak π–π stacking interactions between the C9=C10 double bond and the phenol ring (C1–C6) in adjacent molecules (Fig. 3). The distance between their centroids is 3.467 (1) Å.

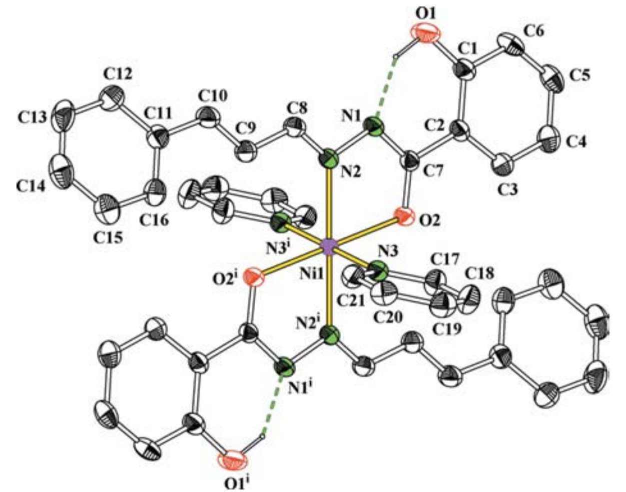


Figure 2
A view of compound (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding. H atoms not involved in the hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $-x, 1-y, 1-z$.]

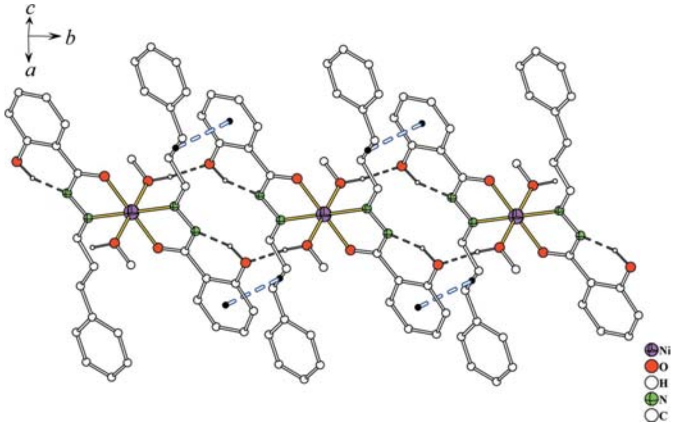
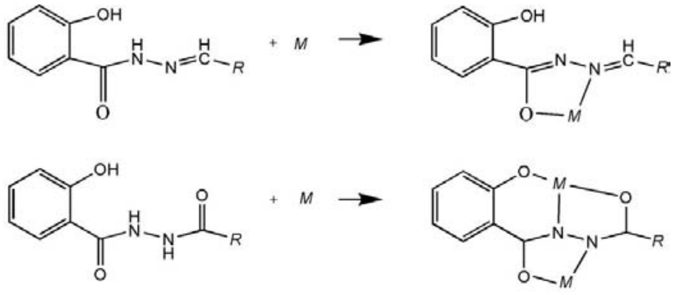


Figure 3
A packing diagram for (I), with hydrogen bonds shown as dashed lines and π–π stacking shown as double-dashed lines. H atoms not involved in hydrogen bonding have been omitted.



Important structural conclusions can be drawn from the synthetic reactions and structural characterization of known salicyloylhydrazone complexes and the salicyloylhydrazone complexes synthesized by our group. Firstly, the salicyloylhydrazone product of the condensation between salicylhydrazide and an aldehyde coordinates to a metal atom through its carboxyl O and hydrazine N atoms, not *via* its phenol O atom. Therefore, the salicyloylhydrazone complexes formed between a metal and this type of hydrazone are usually mononuclear (Bonardi *et al.*, 1991; Bermejo *et al.*, 2000; Dang *et al.*, 2006) (see top of second scheme). Secondly, when a salicyloylhydrazone is synthesized by condensation between salicylhydrazide and a ketone, the salicyloylhydrazone is coordinated through its carboxyl O, hydrazine N and phenol O atom. Therefore, this type of hydrazone ligand is trianionic, and the salicyloylhydrazone complexes formed between a metal and this type of hydrazone are usually linear multinuclear or cyclic multinuclear complexes (Liu *et al.*, 2001; John *et al.*, 2005; Moon *et al.*, 2006) (see bottom of second scheme).

Experimental

The ligand H*L* was prepared by the reaction of salicylhydrazide and cinnamaldehyde in a 1:1 molar ratio under reflux in ethanol for 2 h. The yellow product obtained on cooling was washed first with anhydrous ethanol and then with ethoxyethane. For the preparation of (I), H*L* (0.1 mmol, 27 mg) and $\mathrm{NiCl_2\cdot 6H_2O}$ (0.1 mmol, 24 mg) were dissolved in a mixture of $\mathrm{CH_3OH}$ (8 ml) and $\mathrm{CH_2Cl_2}$ (8 ml). The mixed solution was stirred for 1 h and filtered. Yellow block-like crystals of complex (I) were obtained after 4 d. For the preparation of (II), H*L* (0.1 mmol, 27 mg) and $\mathrm{NiCl_2\cdot 6H_2O}$ (0.1 mmol, 24 mg) were dissolved in a mixture of $\mathrm{CH_3OH}$ (8 ml) and $\mathrm{CH_2Cl_2}$ (8 ml). After stirring for 5 min, one drop of pyridine was added to the mixed solution, which was then stirred for another 1 h and filtered. Yellow prismatic crystals of complex (II) were formed after 3 d. The band at

3255 cm^{-1} in the IR spectrum of the free cinnamaldehyde salicyloylhydrazone ligand was assigned to ν(NH) (Casabó *et al.*, 1989). This absorption of ν(NH) is absent in the IR spectra of the two title nickel complexes, suggesting that the diazine N atom in the two complexes is coordinated to an Ni^{II} centre and that the hydrazone ligand is monoanionic. The bands at 3051 cm^{-1} in (I) and 3055 cm^{-1} in (II) are due to ν(OH) of the phenol (Ding *et al.*, 2006). Two bands at 1521 and 1563 cm^{-1} in the spectrum of (II) are assigned to ν[C=N—N=C(O$^-$)] of the hydrazone and the coordinated pyridine N atom (Hu *et al.*, 2006). The thermogravimetric and differential thermal analysis curves of complex (II) show that the decomposition of the mixed-ligand complex occurs in two regions. Loss of two pyridine molecules takes place in the first region between 436 and 531 K with a mass loss of 21.96% (calculated 21.14%). The second stage between 556 and 773 K corresponds to decomposition of the ligands with a mass loss of 68.43% (calculated 70.90%). The complex finally degraded completely to NiO with a mass of 9.01% (calculated 9.99%).

Compound (I)

Crystal data

$[Ni(C_{16}H_{13}N_2O_2)_2(CH_4O)_2]$
M_r = 653.36
Orthorhombic, *Pbca*
a = 17.536 (5) Å
b = 8.016 (2) Å
c = 22.814 (8) Å
V = 3207.2 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.66 mm^{-1}
T = 293 (2) K
0.31 × 0.25 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
Absorption correction: multi-scan (*TEXRAY*; Molecular Structure Corporation, 1999)
$T_{\min}$ = 0.721, $T_{\max}$ = 0.906
27936 measured reflections
3677 independent reflections
2696 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.102
S = 1.06
3677 reflections
206 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}

Compound (II)

Crystal data

$[Ni(C_{16}H_{13}N_2O_2)_2(C_5H_5N)_2]$
M_r = 747.48
Triclinic, $P\overline{1}$
a = 7.699 (6) Å
b = 9.814 (5) Å
c = 12.412 (7) Å
α = 78.02 (2)°
β = 82.59 (3)°
γ = 79.00 (3)°
V = 896.6 (10) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 293 (2) K
0.20 × 0.20 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
8839 measured reflections
4060 independent reflections
3177 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.100
S = 1.00
4060 reflections
241 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.55 e Å^{-3}
$\Delta\rho_{\min}$ = −0.37 e Å^{-3}

Table 1
Comparative Ni—N(hydrazine) bond lengths (Å) in nickel complexes.

Complex	Ni—N(hydrazine)
(I)^a	2.0845 (15)
(II)^a	2.082 (2)
$Ni(C_{12}H_{14}N_3O_3)(C_2H_3O_2)(C_5H_5N)_2{}^b$	1.988 (2)
$[Ni(C_5H_5N)_3(C_{14}H_{10}N_2O_3)]\cdot1.5C_5H_5N^c$	1.995 (2)
$Ni(C_{14}H_{12}N_3O_2)_2{}^d$	1.983 (2)

References: (*a*) this work; (*b*) Gao *et al.* (2005); (*c*) Hu *et al.* (2005); (*d*) Dang *et al.* (2006).

Table 2
Comparative Ni—O(methanol) bond lengths (Å) in nickel complexes.

Complex	Ni—O(methanol)
(I)^a	2.0970 (14)
$[Ni(C_3H_4NO_3)_2(CH_3OH)_2]\cdot2CH_3OH^e$	2.0661 (7)
$Ni(C_{14}H_9N_2O_2)_2(CH_3OH)_2{}^f$	2.112 (2)
$Ni(C_{24}H_{18}N_4O_3)(C_{10}H_8N_2)(CH_3OH)^g$	2.148 (3)

References: (*a*) this work; (*e*) Lampeka *et al.* (1994); (*f*) Angulo-Cornejo *et al.* (2000); (*g*) Hu *et al.* (2006).

Table 3
Comparative Ni—N(pyridine) bond lengths (Å) in nickel complexes.

Complex	Ni—N(pyridine)
(II)^a	2.1487 (19)
$Ni(C_{12}H_{14}N_3O_3)(C_2H_3O_2)(C_5H_5N)_2{}^b$	2.140 (2), 2.154 (2)
$Ni_3(C_{11}H_{11}N_2O_3)_2(C_5H_5N)_4{}^h$	2.149 (3)
$Ni(C_7H_7N_4O_3)_2(C_5H_5N)_2{}^i$	2.1652 (18)

References: (*a*) this work; (*b*) Gao *et al.* (2005); (*h*) Yang *et al.* (2003); (*i*) Hörner *et al.* (2002).

Table 4
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.95	1.61	2.496 (2)	154
O3—H18···O1$^{\rm i}$	0.95	1.73	2.657 (2)	165

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

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.97	1.71	2.573 (3)	146

The H atom of the phenol OH group in (I) and (II) and the H atom of the methanol OH group in (I) were located in difference Fourier maps and then allowed to ride on their parent O atoms, with $U_{\rm eq}$(H) = 1.5$U_{\rm eq}$(O) and an O—H distance between 0.948 and 0.975 Å. The other H atoms in (I) and (II) were placed in idealized positions and treated as riding, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic, and C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl groups.

For both compounds, data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3048). Services for accessing these data are described at the back of the journal.

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