

A new nickel(II) complex, $[\text{NiL}]\cdot\text{CH}_3\text{OH}$, where H_2L is 2-phenyl-3,10,18,21-tetraazatetracyclo-[20.4.0.0^{4,9}.0^{12,17}]hexacos-2,10,12,14,16,22,24,26-octaene-19,20-dionate(2-)

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Key indicators

Single-crystal X-ray study
 $T = 294\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.039
 wR factor = 0.104
Data-to-parameter ratio = 13.4

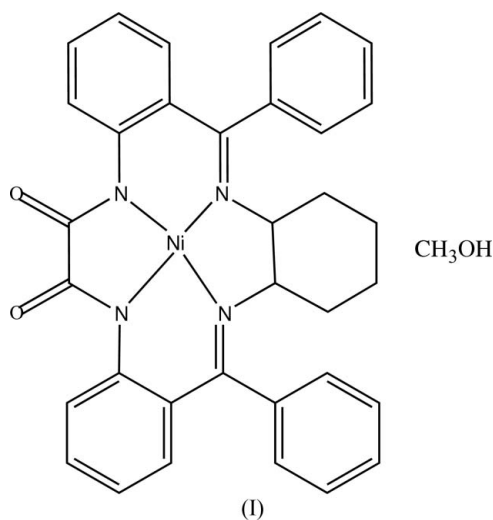
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, [2-phenyl-3,10,18,21-tetraazatetracyclo[20.4.0.0^{4,9}.0^{12,17}]hexacos-2,10,12,14,16,22,24,26-octaene-19,20-dionato(2-)]copper(II) methanol solvate, $[\text{Cu}(\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2)]\cdot\text{CH}_3\text{OH}$, the Ni^{II} atom is coordinated by four N atoms from the doubly deprotonated tetraaza ligand, L^{2-} , in a square-planar coordination geometry. $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the complex to the methanol solvent molecule.

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Comment

Investigation of the structures and properties of macrocyclic transition metal complexes has become a fascinating subject in the field of coordination chemistry, biology and materials science. At the same time, it has been found that oxamide bridges serve as a pathway through which electron spin interaction takes place (Wang *et al.*, 2004). With these facts in mind, we have synthesized the title new complex, $[\text{NiL}]\cdot\text{CH}_3\text{OH}$, (I), and its structure is reported here.



The macrocyclic ligand, L^{2-} , coordinates to the Ni^{II} ion *via* two deprotonated oxamide N atoms and two imine N atoms in a square-planar geometry. The Ni^{II} ion is displaced from the least-squares plane of the four N donor atoms by 0.0336 (12) \AA ; deviations from this mean plane are 0.0801 (11) for atom N1, 0.0777 (11) for atom N2, 0.0765 (11) for atom N3 and -0.0790 (11) \AA for atom N4.

In the crystal structure, $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the complex to the methanol solvent molecule and additional non-classical $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds further stabilize the structure.

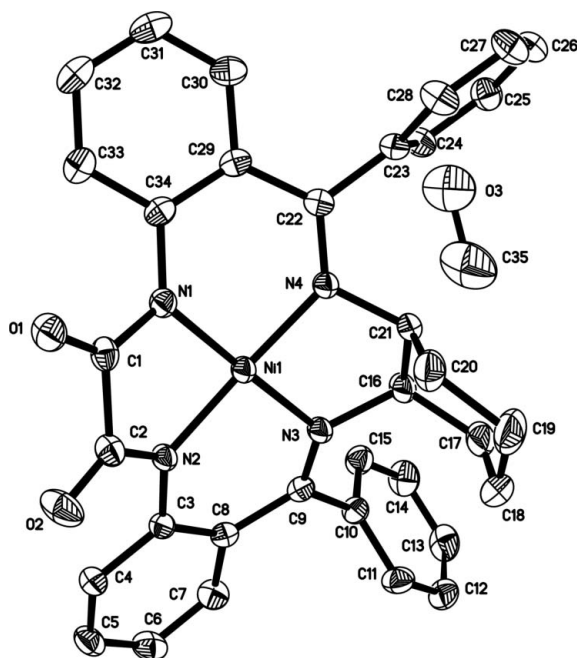


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

Experimental

The synthesis of the ligand L' [$L' = 2,2'-(\text{oxalyldiimino})\text{bis}(\text{benzaldehyde})$] was described previously by Zhang *et al.* (2005). A mixture of L' (0.446 g, 1 mmol), 1,2-diaminocyclohexane (1 mmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.248 g, 1 mmol) was refluxed for 10 h in MeOH (25 ml) in the presence of 2 M NaOH (1 ml). Red crystals of (I) suitable for X-ray analysis were grown at room temperature from an aqueous methanol solution (1:1 *v/v*).

Crystal data

$[\text{Ni}(\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2)] \cdot \text{CH}_4\text{O}$	$Z = 2$
$M_r = 615.36$	$D_x = 1.370 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.1790$ (15) Å	Cell parameters from 2957 reflections
$b = 12.5659$ (18) Å	$\theta = 2.5\text{--}25.6^\circ$
$c = 12.8305$ (19) Å	$\mu = 0.69 \text{ mm}^{-1}$
$\alpha = 71.764$ (2)°	$T = 294$ (2) K
$\beta = 83.782$ (3)°	Block, red
$\gamma = 73.156$ (2)°	$0.26 \times 0.20 \times 0.14 \text{ mm}$
$V = 1491.5$ (4) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	5216 independent reflections
φ and ω scans	3953 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.750$, $T_{\text{max}} = 0.908$	$\theta_{\text{max}} = 25.0^\circ$
7640 measured reflections	$h = -11 \rightarrow 12$
	$k = -14 \rightarrow 14$
	$l = -15 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.1888P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
5216 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
390 parameters	
H-atom parameters constrained	

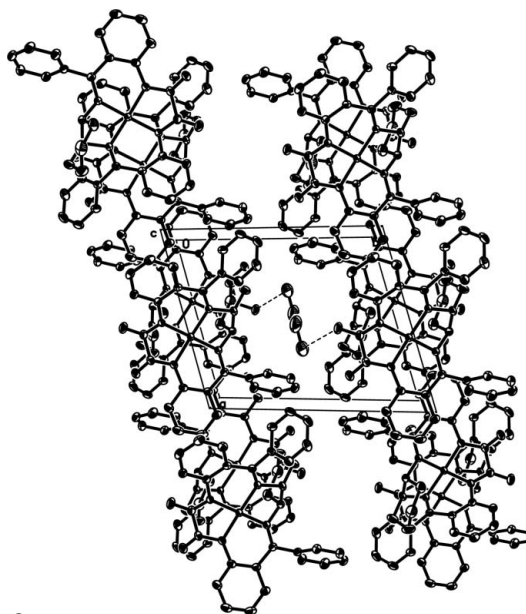


Figure 2
A packing diagram for (I), with hydrogen bonds drawn as dashed lines. H atoms have been omitted.

Table 1

Selected geometric parameters (Å, °).

Ni1—Ni1	1.855 (2)	Ni1—N3	1.887 (2)
Ni1—N2	1.854 (2)	Ni1—N4	1.854 (2)
N1—Ni1—N3	177.07 (10)	N2—Ni1—N4	172.89 (10)
N2—Ni1—N1	86.88 (9)	N4—Ni1—N1	91.56 (9)
N2—Ni1—N3	94.35 (9)	N4—Ni1—N3	87.55 (9)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O3—H3···O2 ⁱ	0.82	2.17	2.862 (3)	143
O3—H3···O1 ⁱ	0.82	2.46	3.169 (4)	145
C5—H5···O3 ⁱⁱ	0.93	2.88	3.675 (5)	144
C15—H15···N2 ⁱⁱ	0.93	2.94	3.558 (4)	125
C12—H12···O3 ⁱⁱⁱ	0.93	2.65	3.556 (5)	164
C13—H13···O1 ^{iv}	0.93	2.55	3.349 (4)	145
C19—H19A···O3 ^v	0.97	2.99	3.865 (5)	151
C27—H27···O1 ^{vi}	0.93	2.55	3.409 (4)	153
C35—H35C···O2 ⁱ	0.96	2.48	3.074 (5)	120

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, -y, -z + 2$; (iii) $x - 1, y, z$; (iv) $x - 1, y + 1, z$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $-x + 2, -y, -z + 1$.

All H atoms were positioned geometrically and refined using a riding model, with $\text{C—H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H, $\text{C—H} = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH_2 and $\text{C—H} = 0.96 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH_3 , and with $\text{O—H} = 0.82 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for the OH group.

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

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