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Key indicators

Single-crystal X-ray study
 T = 295 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.033
 wR factor = 0.082
 Data-to-parameter ratio = 14.7

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

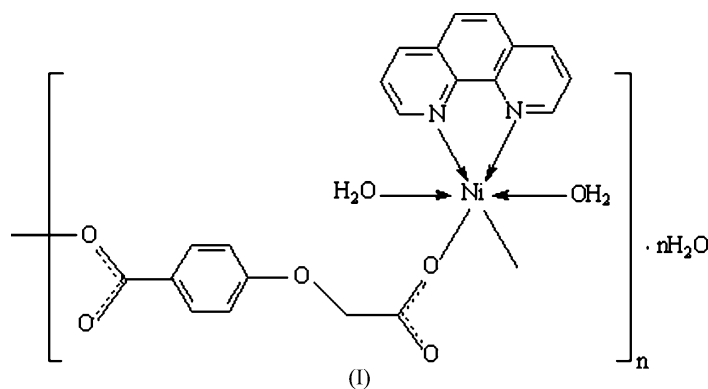
catena-Poly[[[diaqua(1,10-phenanthroline- κ^2N,N')nickel(II)]- μ -4-carboxylato-phenoxyacetato- $\kappa^2O:O'$] monohydrate]

In the title coordination polymer, $\{[\text{Ni}(4\text{-CPOA})(\text{phen})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (phen is 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$; 4-CPOA is the 4-carboxyphenoxyacetate dianion, $\text{C}_9\text{H}_6\text{O}_5$), each Ni^{II} ion displays a distorted octahedral geometry, defined by two carboxyl O atoms from two different 4-CPOA ligands, two N atoms from one phen molecule and two coordinated water molecules. The Ni^{II} ions are bridged by carboxylate groups of 4-CPOA to form a chain structure. Adjacent polymeric chains are connected *via* hydrogen bonds and π - π stacking to construct a three-dimensional supramolecular network.

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Comment

Supramolecular architectures constructed from the deliberate selection of metals and multifunctional organic carboxylate ligands have aroused considerable interest in recent decades (Groeneman *et al.*, 1998; Adams *et al.*, 2004). 4-Carboxyphenoxyacetic acid (4-CPOAH₂) is a multidentate ligand with both rigid and flexible parts, which not only has multiple coordination possibilities but can also form regular hydrogen bonds by functioning as both a hydrogen-bond donor and acceptor. Thus, 4-CPOAH₂ may be considered an excellent candidate for the construction of supramolecular complexes. Recently, we reported the crystal structures of polymeric complexes incorporating 4-CPOA and 1,10-phenanthroline (phen), $[\text{Co}(4\text{-CPOA})(\text{phen})(\text{H}_2\text{O})]_n$ (Gao, Gu *et al.*, 2005) and its Cd^{II} analogue (Gao, Huo *et al.*, 2005), in which the terminal carboxyl groups of the 4-CPOA ligand display both monodentate and bidentate modes, respectively. We recently synthesized the related Ni^{II} complex, (I), and report its structure here.



In the structure of (I), both terminal carboxylate groups coordinate in monodentate fashion to the Ni^{II} ion, as shown in

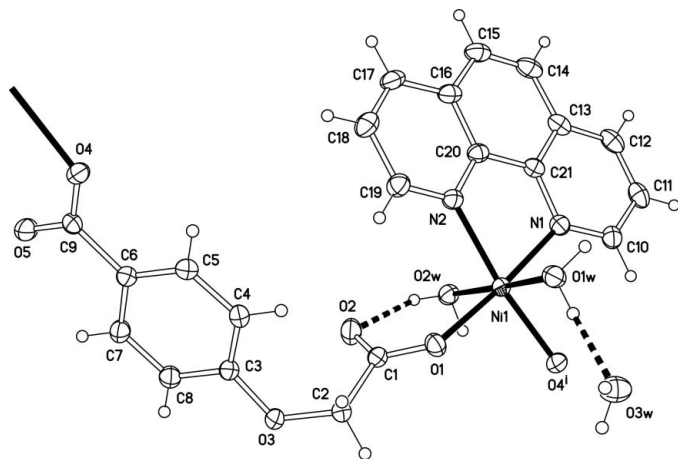


Figure 1

A plot of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate the hydrogen bonding [symmetry code: (i) $x, y + 1, z$].

Fig. 1. The Ni^{II} ion assumes a distorted octahedral coordination geometry, formed by two carboxylate O atoms from different 4-CPOA ligands, two N atoms of a phen ligand and two coordinated water molecules. The C9 carboxylate group is nearly coplanar with the benzene plane [dihedral angle 8.60 (5)°], while the oxyacetate group is approximately perpendicular to the benzene plane [dihedral angle 79.4 (3)°]. Adjacent Ni^{II} ions are bridged by the 4-CPOA ligands through both terminal carboxylate groups to form a one-dimensional chain structure. Within the chain, the shortest Ni···Ni separation is 10.725 (3) Å, which is somewhat longer than the Cd···Cd separation of 10.455 (2) Å found in the Cd^{II} polymer (Gao, Huo *et al.*, 2005).

The centroid–centroid distance of 3.690 (3) Å between parallel benzene rings, related by an inversion centre at (0, 0, 1/2), suggests the existence of π – π stacking. π – π stacking is also observed between the nearly parallel N1-pyridine and N2^v-pyridine rings [symmetry code: (v) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$], as verified by the centroid–centroid distance of 3.646 (3) Å and dihedral angle of 3.6 (3)°. An extensive hydrogen-bonding network occurs in the crystal structure of (I) (Table 2), leading to a double-chain structural motif, as shown in Fig. 2.

Experimental

1,10-Phenanthroline (1.99 g, 10 mmol) and nickel diacetate (1.44 g, 10 mmol) were dissolved in a hot aqueous solution of 4-carboxyphenoxyacetic acid (1.96 g, 10 mmol) and the pH of the solution was adjusted to 6 with 0.1 M sodium hydroxide solution. The solution was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 423 K for 4 d. The bomb was then cooled naturally to room temperature. Green prismatic crystals of (I) were obtained after several days. CHN analysis, calculated for C₂₁H₂₀N₂O₈Ni: C 51.85, H 4.15, N 5.76%; found: C 51.81, H 4.18, N 5.79%.

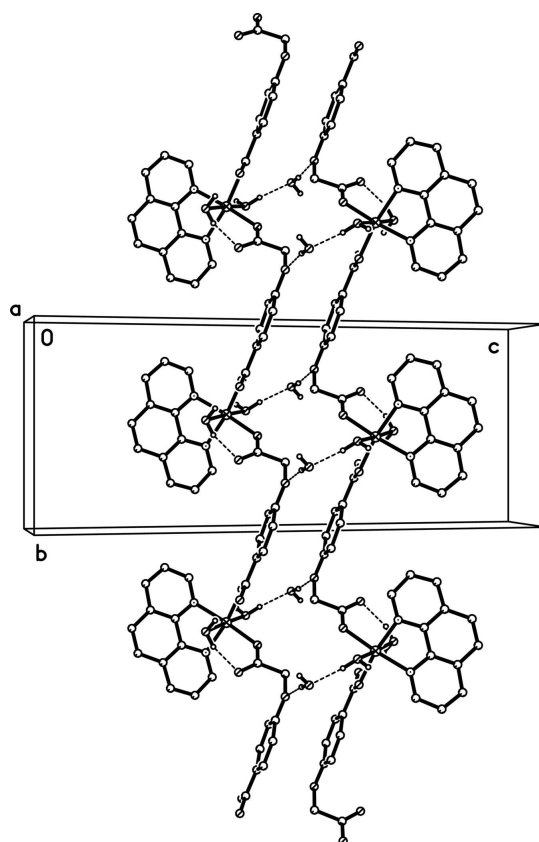


Figure 2

The double-chain structure of (I), constructed by hydrogen bonds and π – π interactions. Hydrogen bonds are shown as dashed lines. C-bound H atoms have been omitted for clarity.

Crystal data

[Ni(C₉H₆O₅)(C₁₂H₈N₂)(H₂O)₂] \cdot -
H₂O
 $M_r = 487.08$
Monoclinic, $P2_1/c$
 $a = 6.8077$ (14) Å
 $b = 10.725$ (2) Å
 $c = 27.313$ (6) Å
 $\beta = 96.76$ (3)°
 $V = 1980.3$ (7) Å³
 $Z = 4$

$D_x = 1.634$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 8221
reflections
 $\theta = 3.0$ – 27.5°
 $\mu = 1.03$ mm⁻¹
 $T = 295$ (2) K
Prism, green
 $0.36 \times 0.25 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer
 ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.707$, $T_{\max} = 0.835$
8696 measured reflections

4528 independent reflections
3552 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 27.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -35 \rightarrow 35$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.082$
 $S = 1.03$
4528 reflections
307 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—O1	2.0421 (14)	Ni1—N2	2.0983 (16)
Ni1—O4 ⁱ	2.0454 (13)	O1—C1	1.277 (2)
Ni1—O1W	2.0605 (16)	O2—C1	1.225 (2)
Ni1—O2W	2.1384 (16)	O4—C9	1.259 (2)
Ni1—N1	2.0740 (16)	O5—C9	1.259 (2)
O1—Ni1—N1	175.35 (6)	O4 ⁱ —Ni1—O2W	91.28 (6)
O1—Ni1—N2	95.82 (6)	O1W—Ni1—N1	92.52 (6)
O1—Ni1—O1W	87.55 (6)	O1W—Ni1—N2	90.21 (6)
O1—Ni1—O2W	91.48 (6)	O1W—Ni1—O2W	177.65 (6)
O1—Ni1—O4 ⁱ	93.00 (6)	O2W—Ni1—N1	88.28 (6)
O4 ⁱ —Ni1—N1	91.64 (6)	O2W—Ni1—N2	87.75 (6)
O4 ⁱ —Ni1—N2	171.14 (6)	N1—Ni1—N2	79.53 (6)
O4 ⁱ —Ni1—O1W	90.92 (6)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2W—H2W1 ^{..} ·O2	0.86 (2)	1.82 (2)	2.646 (2)	162 (2)
O2W—H2W2 ^{..} ·O5 ⁱ	0.86 (2)	1.77 (2)	2.626 (2)	169 (2)
O1W—H1W1 ^{..} ·O3W	0.86 (2)	1.84 (2)	2.706 (2)	170 (2)
O1W—H1W2 ^{..} ·O5 ⁱⁱ	0.85 (2)	1.93 (2)	2.783 (2)	175 (2)
O3W—H3W2 ^{..} ·O1 ⁱⁱⁱ	0.84 (2)	2.01 (2)	2.829 (2)	163 (2)
O3W—H3W1 ^{..} ·O3 ^{iv}	0.84 (2)	1.95 (2)	2.791 (2)	172 (3)

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

Water H atoms were located in a difference Fourier map and refined with O—H and H^{..}·H distances restrained to 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. C-bound H

atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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References

- Adams, H., Fenton, D. E. & McHugh P. E. (2004). *Inorg. Chem. Commun.* **7**, 140–145.
- Gao, S., Gu, C.-S., Huo, L.-H. & Zhao, J.-G. (2005). *Acta Cryst.* **E61**, m198–m200.
- Gao, S., Huo, L.-H., Gu, C.-S., Liu, J.-W. & Zhao, J.-G. (2005). *Acta Cryst.* **E61**, m496–m498.
- Groeneman, R. H., MacGillivray, L. R. & Atwood, J. L. (1998). *Chem. Commun.* pp. 2735–2736.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MS (2002). *CrystalStructure*. Version 3.00. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.