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Poly[[diaquatris(μ_2-4,4′-bipyridine-κ^2N,N')tetrakis(phenylacetato-κO)dinickel(II)] dihydrate]

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The polymeric title molecule, $\{[Ni_2(C_8H_7O_2)_4(C_{10}H_8N_2)_3(H_2O)_2]\cdot 2H_2O\}_n$, lies on a center of symmetry at the mid-point of the $C_{pyridine}-C_{pyridine}$ bond of one of the two 4,4′-bipyridine molecules that link the adjacent aquanickel(II)–dicarboxylate units into a linear chain. The other 4,4′-bipyridine molecule connects adjacent chains into a square $(C_{10}H_8N_2)_3Ni_2$ grid. The ladder-like layer structure is disordered in all the organic groups bonded to the metal atom; the uncoordinated water molecules interact within the layers through hydrogen bonds.

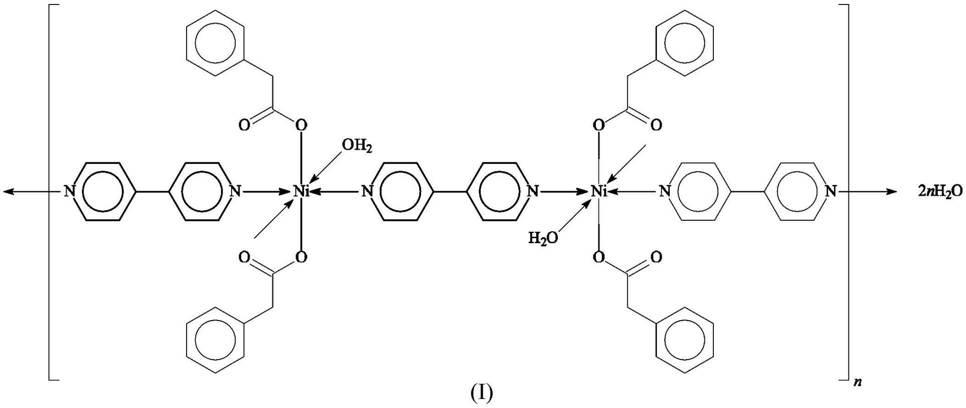
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(O–C) = 0.006 Å
Disorder in main residue
R factor = 0.069
wR factor = 0.196
Data-to-parameter ratio = 14.3

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

Comment

The 4,4′-bipyridine heterocycle has been used as a spacer ligand to connect an enormous range of metal salts to afford coordination polymers that adopt a variety of motifs (Allen, 2002). Among such coordination polymers are the manganese dicarboxylates, those structurally verified being the diaquaphthalate (Ma *et al.*, 2003), the maleate monohydrate, the aquafumarate (Shi *et al.*, 2000) and the aquasuccinate (Ma *et al.*, 2004) complexes. The last two structures contain clathrated 4,4′-bipyridine.



(I)

The present coordination polymer, (I), is the first example of such a compound of phenylacetic acid. The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The synthesis under hydrothermal conditions yields the compound as a water-coordinated complex that also features uncoordinated water molecules. The Ni^{II} atom is six-coordinate in an octahedral environment in which the carboxylate groups occupy *trans* positions. One of the spacers, which lies on a center of symmetry, links the aquanickel(II)di(carboxylate) units into a linear chain; the other, which lies on a general position, connects adjacent chains into a square grid (Fig. 2). The

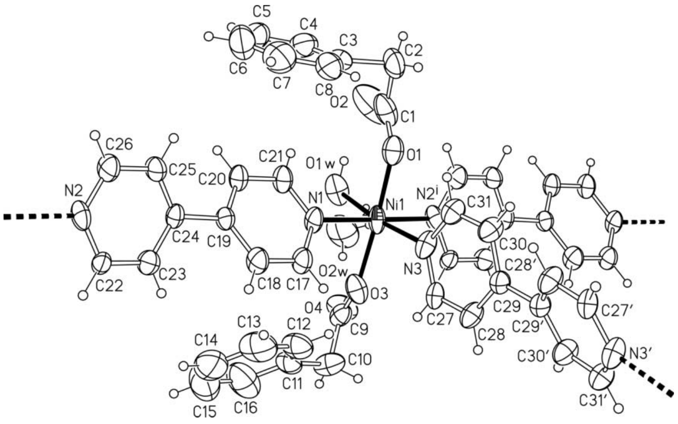


Figure 1

ORTEPII (Johnson, 1976) plot showing the atomic numbering scheme of a portion of the polymeric structure of (I). [Symmetry code: (i) $2 - x, 1 - y, 2 - z$.]

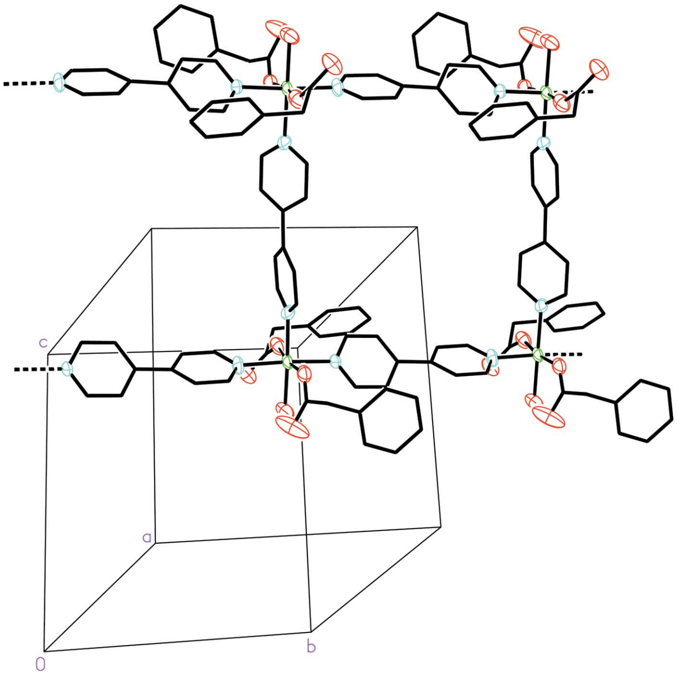


Figure 2

Schematic representation of the layer structure illustrating the rectangular grid; the uncoordinated water molecules are not shown. H atoms have been omitted.

uncoordinated water molecules interact only within a layer (Table 2).

Experimental

Nickel dichloride hexahydrate (0.24 g, 1 mmol), 4,4′-bipyridine (0.08 g 0.5 mmol), phenylacetic acid (0.14 g, 1 mmol), sodium hydroxide (0.06 g, 1.5 mmol) and water (10 ml) were sealed in a 23 ml Teflon-lined Parr bomb. The bomb was heated at 443 K for 48 h and then cooled at 10 K h^{-1} to yield pale-green crystals.

Crystal data

$[Ni_2(C_8H_7O_2)_4(C_{10}H_8N_2)_3(H_2O)_2]\cdot 2H_2O$
$M_r = 1198.58$
Triclinic, $P\overline{1}$
$a = 10.1103$ (6) Å
$b = 11.2803$ (6) Å
$c = 13.2962$ (8) Å
$\alpha = 83.458$ (1)°
$\beta = 83.829$ (1)°
$\gamma = 74.640$ (1)°
$V = 1448.0$ (1) Å^3
$Z = 1$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4355 reflections
$\theta = 2.6$–25.7°
$\mu = 0.72$ mm^{-1}
$T = 295$ (2) K
Plate, pale green
0.15 × 0.14 × 0.05 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.747$, $T_{max} = 0.965$
12473 measured reflections
6386 independent reflections
5230 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.196$
$S = 1.05$
6386 reflections
446 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1075P)^2 + 1.8386P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ni1—O1	2.063 (3)	Ni1—N1	2.100 (3)
Ni1—O3	2.054 (3)	Ni1—N2^i	2.117 (4)
Ni1—O1*w*	2.087 (3)	Ni1—N3	2.130 (4)
O1—Ni1—O3	170.8 (1)	O3—Ni1—N3	90.3 (2)
O1—Ni1—O1*w*	89.1 (2)	O1*w*—Ni1—N1	89.2 (2)
O1—Ni1—N1	88.7 (2)	O1*w*—Ni1—N2^i	87.4 (2)
O1—Ni1—N2^i	92.0 (2)	O1*w*—Ni1—N3	173.2 (2)
O1—Ni1—N3	85.5 (2)	N1—Ni1—N2^i	176.5 (2)
O3—Ni1—O1*w*	95.6 (2)	N1—Ni1—N3	94.8 (3)
O3—Ni1—N1	83.5 (2)	N2^i—Ni1—N3	88.7 (3)
O3—Ni1—N2^i	96.1 (2)		

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*1···O2	0.85 (1)	1.87 (2)	2.682 (7)	160 (6)
O1*w*—H1*w*2···O2*w*	0.85 (1)	1.97 (2)	2.801 (7)	168 (6)
O2*w*—H2*w*1···O2^{ii}	0.85 (1)	2.10 (3)	2.896 (8)	155 (7)
O2*w*—H2*w*2···O4	0.85 (1)	1.87 (2)	2.716 (6)	173 (8)

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

The structure is disordered in the two phenylacetate groups as well as in the 4,4′-bipyridine spacers, one of which lies on a center of inversion. The phenylacetate groups were refined as two groups sharing a common carboxyl C atom; their phenyl rings were refined as rigid hexagons. The $C_{carboxyl}—C_{methylene}$ bond distances were restrained to within 0.01 (1) Å of each other, as were the $C_{methylene}$—

C_{phenyl} bond distances and the $C_{carboxyl}—C_{phenyl}$ distances. In the 4,4′-bipyridine molecules, owing to the extensive disorder, the pyridyl rings were refined as rigid hexagons of 1.39 Å sides. The 4,4′-bipyridine molecule (N1/C17–C21/N2/C22–C26) lying on a general position was refined as two pairs of pyridine rings. The atomic positions of the primed N1′ and N2′ atoms of the second component were restrained to within 0.01 (1) Å of the unprimed N1 and N2 atoms. This restraint along with two other restraints (the Ni1—N1 bond distance being restrained to within 0.01 Å of the Ni1—N1′ bond distance, and the Ni1—N2 bond distance being similarly paired with the Ni1—N2′ bond distance) effectively made atom N1′ coincident with atom N1 (and atom N2′ coincident with atom N2). The displacement parameters of the primed and unprimed atoms were set to be equal to each other. The pairing of the four pyridyl units leads to twists of 32.8 (3)° in the unprimed molecule, and 30.7 (2)° in the primed molecule. The alternative pairing (N1/C17–C21/N2′/C22′–C26′ and N1′/C17′–C21′/N2/C22–C26) leads to twist angles twice as large, and is less plausible. The other 4,4′-bipyridine lies on an inversion site; however, as the inversion symmetry excludes the possibility of any twist, the molecule was instead refined as disordered over this element. The molecule was refined as a ten-atom unit, N3/C27–C31/N3′/C27′–C31′. The displacement parameters of the primed atoms were set to those of the unprimed ones. The twist angle is 30.9 (3)°. Atoms N3 and N3′ are not, however, coincident, and the Ni1—N3 bond [2.130 (4) Å] is statistically different from the symmetry-related Ni1—N3′ bond [2.153 (5) Å; symmetry code: $2 - x$, $1 - y$, $1 - z$]. The $C_{pyridine}—C_{pyridine}$ bonds in the five independent 4,4′-bipyridine molecules were restrained to within 0.01 Å of each other. As the disorder for each component refined to almost 0.5:0.5, the disorder was fixed as exactly 0.5:0.5. The vibration of all C atoms was restrained to be approximately isotropic. In Fig. 1, only one of the disordered components is shown.

C-bound H atoms were placed at calculated positions (C—H = 0.93 Å) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were located in difference Fourier maps, and were refined with distance restraints of O—H = 0.85 (1) Å and H···H = 1.39 (1) Å; the atomic displacement parameters were refined. All distances between H atoms exceed 2.0 Å.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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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