

Polymeric aqua(μ_4 -maleato- κ^4 O)pyridylnickel(II)Yun Chen,^a Ping Liu,^{a*} Jian Wang^a and Wen-Dan Cheng^b

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$

R factor = 0.056

wR factor = 0.138

Data-to-parameter ratio = 10.7

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

The title nickel coordination polymer, $[\text{Ni}(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})]_n$, has been obtained from the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with disodium maleate and pyridine in an alcohol–water solution. Single-crystal X-ray analysis revealed that each Ni atom contains an approximately octahedral coordination environment in the compound with the maleate ligand in a novel coordination mode. The molecule has mirror symmetry. O–H...O hydrogen bonds exist in the corrugated two-dimensional structure; this is further extended into a three-dimensional framework *via* strong non-classical C–H...O interactions between adjacent layers.

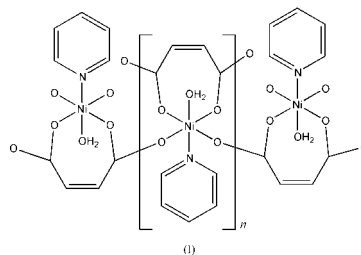
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Comment

In the past decade, polycarboxylate ligands have been widely used in the preparation of coordination polymers with open framework structures because they are capable of forming one-, two-, or three-dimensional networks by bridging between metal centers in a number of different ways (Shi *et al.*, 2000; Kepert *et al.*, 2000; Burrows *et al.*, 2000). Maleate is a versatile ligand, which exhibits the ability to coordinate to metal atoms in several ways (Zhang *et al.*, 1999). Nevertheless, Ni^{II} or Co^{II} maleate complexes are rare. In order to further investigate the coordination behavior of maleate, more data on this type of compound need to be obtained. We have recently prepared some new maleate-bridged Ni^{II} and Co^{II} complexes with pyridine (py) and 2,2'-bipyridine (bipy) as a second ligand. This paper reports the structure of one of them, in which the maleic dianion is coordinated to the metal center in a quite unusual coordination mode (Prout *et al.*, 1971; Lis, 1983; Li *et al.*, 1996), namely, $[\text{Ni}(\mu\text{-maleato})(\text{py})(\text{H}_2\text{O})]_n$, (I).



As shown in Fig. 1, each six-coordinate central Ni^{2+} ion is in an approximately octahedral coordination environment, with the two axial coordination positions occupied by the O atom of the water molecule and the N atom of the pyridine molecule. The molecule has mirror symmetry. The Ni–O distances are in the range 2.060 (4)–2.100 (6) Å and the Ni–N distance is 2.083 (7) Å, with the O–Ni–O(N) angles between 86.8 (2) and 90.8 (2)°. The Ni^{2+} ion is displaced from the equatorial plane about only 0.074 (2) Å toward the axially

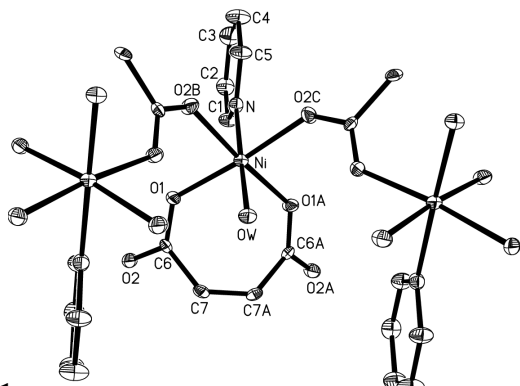


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

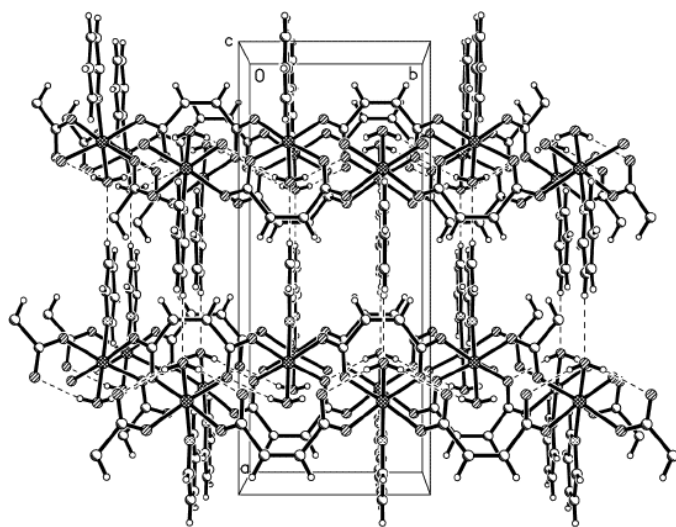


Figure 2
The packing of (I), viewed down the *c* axis, showing the hydrogen bonds.

coordinated water molecule. O atoms of the maleate dianion coordinate to Ni^{2+} in two different modes: each carboxyl group of a maleic ligand offers one O atom to chelate an Ni atom, forming a seven-membered ring in a boat conformation, with a C=C distance of 1.33 (1) Å, while the two remaining O atoms of the same maleate ligand bridge to two other Ni atoms. As a result, the Ni^{2+} ions are bridged by maleate anions in an unusual tetradentate coordination fashion, with a *syn-anti* coplanar conformation of the carboxyl groups, forming a two-dimensional corrugated structure. In addition, there exist two kinds of hydrogen-bond interactions in the crystal: (i) intralayer hydrogen bond $\text{OW}-\text{HWA}\cdots\text{O1}$; (ii) interlayer hydrogen bond $\text{C4}(\text{pyridine})-\text{H4A}\cdots\text{OW}$. These weak interactions further stabilize the crystal structure.

Experimental

An aqueous solution (10 ml) of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.238 g, 1.0 mmol) was added to an alcohol–water (1:1) solution (10 ml) containing maleic acid (0.116 g, 1.0 mmol) and sodium hydroxide (0.080 g, 2.0 mmol) with stirring. After 80 min, pyridine (0.1 ml, 1.2 mmol) was added dropwise to the above reaction mixture, which was stirred for 30 min, then filtered. The filtrate was finally left at room temperature and

single crystals suitable for X-ray diffraction studies were obtained after two weeks.

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})]$
 $M_r = 269.88$
 Orthorhombic, *Pnma*
 $a = 17.9522$ (13) Å
 $b = 7.5712$ (5) Å
 $c = 7.4092$ (6) Å
 $V = 1007.06$ (13) Å³
 $Z = 4$
 $D_x = 1.780$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 29 reflections
 $\theta = 2.3\text{--}25.0^\circ$
 $\mu = 1.93$ mm⁻¹
 $T = 293$ (2) K
 Block, green
 $0.22 \times 0.14 \times 0.10$ mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.695$, $T_{\max} = 0.824$
 3021 measured reflections

950 independent reflections
 701 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\max} = 25.0^\circ$
 $h = -21 \rightarrow 12$
 $k = -6 \rightarrow 9$
 $l = -8 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.138$
 $S = 1.04$
 950 reflections
 89 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 5.62P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.49$ e Å⁻³
 $\Delta\rho_{\min} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni–O2 ⁱ	2.060 (4)	Ni–O1 ⁱⁱⁱ	2.072 (4)
Ni–O2 ⁱⁱ	2.060 (4)	Ni–N	2.083 (7)
Ni–O1	2.072 (4)	Ni–OW	2.100 (6)
O2 ⁱ –Ni–O2 ⁱⁱ	87.3 (2)	O1–Ni–N	88.02 (18)
O2 ⁱ –Ni–O1	174.60 (16)	O2 ⁱ –Ni–OW	89.99 (17)
O2 ⁱⁱ –Ni–O1	90.78 (17)	O1–Ni–OW	95.06 (17)
O1–Ni–O1 ⁱⁱⁱ	90.7 (2)	N–Ni–OW	175.6 (3)
O2 ⁱ –Ni–N	86.83 (19)		

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
OW–HWA \cdots O1 ⁱⁱ	0.82 (7)	2.01 (7)	2.780 (5)	159 (?)
C4–H4A \cdots OW ^{iv}	0.93	2.57	3.435 (12)	155

Symmetry codes: (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, y, \frac{3}{2} - z$.

H atoms were all positioned geometrically and refined as riding, except for atom HWA which was refined isotropically.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: XPREP/SAINT (Siemens, 1994); program(s) used to solve structure: SHELXTL (Siemens, 1994); program(s) used to refine structure: SHELXTL (Siemens, 1994); molecular graphics: SHELXL97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

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