

catena-Poly[[[diaquabis[*cis*-2-methyl-but-2-enedioate(1-)-O]nickel(II)]- μ -4,4'-bipyridine-*N:N'*] dihydrate]

Ju-Hsiou Liao,* Ching-Ting Su
and Che-Chih Hsu

Department of Chemistry, National Chung
Cheng University, 160 San-Hsing, Min-Hsiung,
Chia-Yi 621, Taiwan

Correspondence e-mail:
chejhl@ccunix.ccu.edu.tw

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.029
 wR factor = 0.058
Data-to-parameter ratio = 12.4

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

In the title compound, $[\{\text{Ni}(\text{H}_2\text{O})_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_5\text{H}_5\text{O}_4)_2\} \cdot 2\text{H}_2\text{O}]_n$, (I), the Ni^{II} atom is located at a center of inversion, and the bridging 4,4'-bipyridine has a center of symmetry. Each Ni^{II} is in an octahedral environment, coordinated by two H_2O , two *cis*-2-methyl-but-2-enedioate (citraconate) and two bridging 4,4'-bipyridine ligands to generate linear chains which interact with the water molecules of crystallization to form a hydrogen-bonding network.

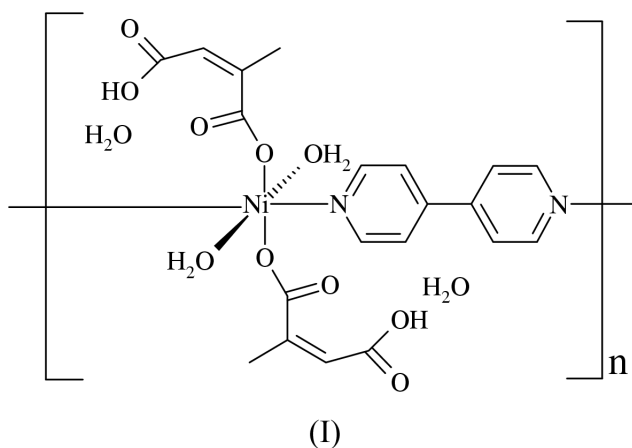
Received 11 September 2001

Accepted 26 September 2001

Online 6 October 2001

Comment

The design of extended frameworks by linking metal centers with multidentate ligands has drawn great attention. Polycarboxylates have been widely used as building blocks to construct many coordination polymers with interesting crystal structures (Eddaoudi *et al.*, 2001). The reaction of a dicarboxylic acid (citraconic acid), a dipyrindyl spacer (4,4'-bipyridine) and Ni^{2+} resulted in the formation of the title compound, $[\text{Ni}(\text{H}_2\text{O})_2(4,4'\text{-bipyridine})(\text{citraconate})_2 \cdot 2\text{H}_2\text{O}]_n$, (I) (Fig. 1).



The structure of (I) is composed of parallel straight chains running in the [001] direction and water molecules of crystallization (Fig. 2). Each Ni^{2+} ion is located at a crystallographic center of inversion, coordinated by two H_2O molecules, two bridging 4,4'-bipyridine ligands and two dangling citraconates, each of which binds to Ni^{2+} with one O atom of a carboxylate at C6, while the other carboxylic acid at C9 remains protonated. The conformation of the citraconate ligand is similar to that of free citraconic acid (Batchelor & Jones, 1998), with C6, C7, C8, C9, C10, O3 and O4 nearly in the same plane (r.m.s. deviation = 0.027 \AA). The plane formed by the coordinated carboxylate (C6, C7, O1 and O2) is nearly

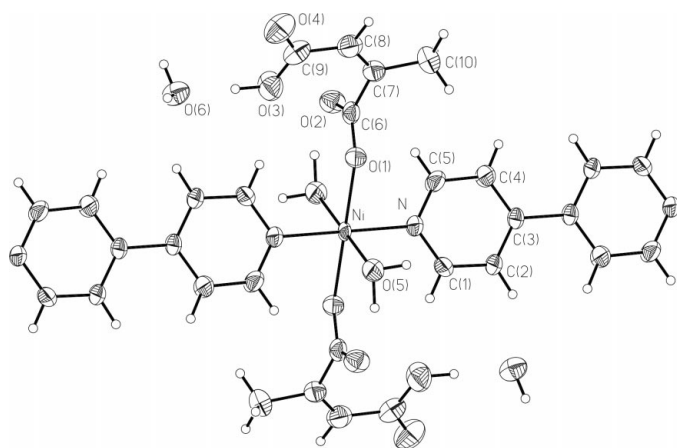


Figure 1
The structure and labeling scheme of (I) showing 50% probability displacement ellipsoids.

perpendicular to the former plane at $88.06 (8)^\circ$ owing to steric hindrance. The linkage of the Ni^{2+} ions and 4,4'-bipyridines is similar to that of the straight $[\text{Ni}(4,4'\text{-bipyridine})]^{2+}$ chains observed in $\text{Ni}(\text{oxalate})(4,4'\text{-bipyridine})$ (Lu *et al.*, 1999), where the pyridine rings are coplanar in one chain. The Ni—O1(carboxylate) distance, 2.2933 (16) Å, is significantly longer than that of Ni—O5(water), 2.0767 (17) Å. Hydrogen bondings is observed among the water molecules and the nearby carboxylic groups, forming a three-dimensional hydrogen-bonding network (Table 2).

Experimental

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.145 g, 0.5 mmol), 4,4'-bipyridine (0.078 g, 0.5 mmol) and citraconic acid (0.065 g, 0.5 mmol) were dissolved in 5 ml and 15 ml distilled water respectively at 353 K. The two solutions were mixed slowly and sealed in a 30 ml test tube, forming a green solution with pH = 3.6. Then the solution was kept at 298 K for 5 days until many crystals of (I) were observed (yield 95.0%).

Crystal data

$[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_5\text{H}_5\text{O}_4)_2 \cdot (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 545.12$
 Monoclinic, $P2_1/n$
 $a = 7.065 (1) \text{ \AA}$
 $b = 15.148 (3) \text{ \AA}$
 $c = 11.113 (2) \text{ \AA}$
 $\beta = 98.09 (1)^\circ$
 $V = 1177.5 (4) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.538 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.2\text{--}12.5^\circ$
 $\mu = 0.89 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Parallelepiped, green
 $0.25 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.808$, $T_{\max} = 0.842$
 2831 measured reflections
 2077 independent reflections
 1627 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -1 \rightarrow 8$
 $k = -1 \rightarrow 18$
 $l = -13 \rightarrow 13$
 3 standard reflections
 every 97 reflections
 intensity decay: none

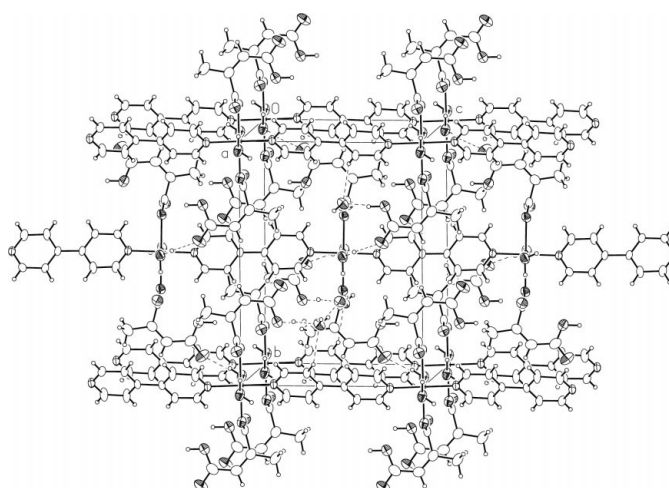


Figure 2
The packing diagram and H-bonding network of (I).

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.058$
 $S = 1.04$
 2077 reflections
 167 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.42P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0067 (3)

Table 1

Selected geometric parameters (Å, °).

Ni—N	2.0128 (16)	Ni—O1	2.2933 (16)
Ni—O5	2.0767 (17)	C3—C3 ⁱ	1.491 (3)
N ⁱⁱ —Ni—O5	89.43 (7)	N—Ni—O1	90.88 (7)
N—Ni—O5	90.57 (7)	O5—Ni—O1	88.26 (6)
N ⁱⁱ —Ni—O1	89.12 (7)	O5 ⁱⁱ —Ni—O1	91.74 (6)

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O3—H3···O6	0.89	1.71	2.590 (2)	169
O5—H5A···O4 ⁱ	0.87	1.95	2.814 (3)	175
O5—H5B···O2 ⁱⁱ	0.96	1.85	2.741 (3)	153
O6—H6A···O2 ⁱⁱⁱ	0.83	1.94	2.752 (2)	164
O6—H6B···O1 ^{iv}	0.86	1.91	2.753 (2)	165

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

All the H atoms were observed in difference electron density maps. During refinement, the coordinates of all H atoms were fixed, except for H3, H5A, H5B, where O—H bonds were allowed to vary and rotate about the C—O or Ni—O bonds, and for H6A, H6B, where the O—H bonds were allowed to vary.

Data collection: *XSCANS* (Siemens, 1992); cell refinement: *XSCANS*; data reduction: *SHELXTL XPREP* (Siemens, 1994); program(s) used to solve structure: *SHELXS-97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL XP*; software used to prepare material for publication: *SHELXTL XCIF*.

JHL thanks the National Science Council of Taiwan for financial support.

References

- Batchelor, E. & Jones, W. (1998). *Acta Cryst.* **C54**, 238–240.
- Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O’Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
- Lu, J. Y., Lawandy, M. A., Li, J., Yuen, T. & Lin, C. L. (1999). *Inorg. Chem.* **38**, 2695–2704.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1992). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.