

Kom-Bei Shiu,^{a*} Zheng-Wei
Chen,^a Fen-Ling Liao^b and
Sue-Lein Wang^b^aDepartment of Chemistry, National Cheng
Kung University, 701 Tainan City, Taiwan, and^bInstrument Center, National Tsing Hua
University, 300 Hsinchu, TaiwanCorrespondence e-mail:
kbshiu@mail.ncku.edu.tw

Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.028

wR factor = 0.054

Data-to-parameter ratio = 16.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*cis*-Tetraaqua(η^2 -pyridine-2,5-dicarboxylato- $\kappa^2\text{O},\text{N}$)nickel(II) dihydrate

The title compound, $[\text{Ni}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$, was obtained by the reaction of nickel nitrate with 2,5-pyridinedicarboxylic acid (molar ratio 1:1) in water. The compound contains a six-coordinate Ni^{II} ion, which is bonded to the N atom and an O—C group of the carboxylate group in the 2-position of the 2,5-pyridinedicarboxylate ligand, and four water O atoms. Intermolecular hydrogen-bonding interactions are present, linking the nickel complex and water molecules in the crystal structure.

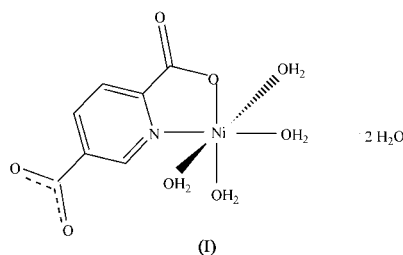
Received 22 October 2003

Accepted 23 October 2003

Online 31 October 2003

Comment

The complexation of metal ions using the deprotonated conjugate base of 2,5-pyridinedicarboxylic acid as a ligand has been reported in the literature (Liang, Hong, Su *et al.*, 2001; Liang, Hong & Cao, 2001; Plater *et al.*, 1998). Presumably as a result of the presence of one pyridine N atom and two carboxylate groups in this ligand and/or of the hydrothermal synthetic conditions, it was found that the ligand coordinates to two or more metal ions in a bridging and chelating mode. In order to compare the results and to understand the possible experimental conditions under which a discrete molecule or a coordination polymer can be obtained, we carried out experiments under ambient conditions. We report here the synthesis and crystal structure of a discrete nickel complex, (I). It appears that the experimental conditions, *viz.* ambient or hydrothermal, are more critical than the multiple functionality of the organic ligands used to obtain discrete or polymeric products.



In the title compound, (I), atom Ni1 is octahedrally coordinated by N1 and O5 of the carboxylate group in the 2-position of the 2,5-pyridinedicarboxylate ligand, and four water O atoms, O1—O4 (Fig. 1). For the four Ni—O bond lengths involving the coordinated water O atoms, we might expect to observe two longer bond lengths for the water O atoms *trans* to N1 and O5 of the 2,5-pyridinedicarboxylate ligand, based on the *trans* influence; the opposite is, in fact, observed [Ni1—O4 = 2.080 (2) Å and Ni1—O2 = 2.022 (2) Å *versus* Ni1—O1 = 2.097 (2) Å and Ni1—O3 = 2.071 (2) Å; Table 1]. The contradiction is apparently caused by many

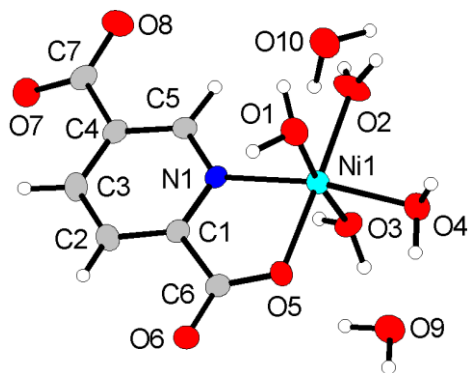


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

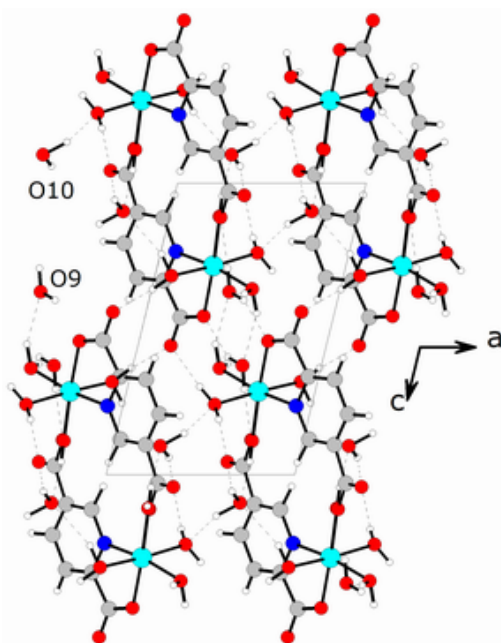


Figure 2
The crystal packing diagram of (I), with hydrogen bonds shown as dashed lines, viewed along the *b* axis.

intermolecular hydrogen-bonding interactions between H atoms of the coordinated water molecules and O atoms of either the crystallization water molecules O9 and O10, or atoms O5–O8 of the 2,5-pyridinedicarboxylate ligand (Fig. 2). The hydrogen-bonding interactions are normal (Steed & Atwood, 2000), based on H...*A* distances of 1.79–2.08 Å, *D*...*A* distances of 2.663 (3)–2.933 (3) Å and bond angles of 147–175° (Table 2).

Experimental

2,5-Pyridinedicarboxylic acid (0.085 g, 0.5 mmol) and water (3 ml) were combined and the pH value adjusted to ~7.0 with drops of an aqueous NaOH solution. The resulting solution was layered on top of another aqueous solution (3 ml) of nickel(II) nitrate hexahydrate (0.151 g, 0.5 mmol). After one week, blue single crystals of (I) were collected and dried in air (yield 50%).

Crystal data

[Ni(C₇H₃NO₄)(H₂O)₄]₂·2H₂O
M_r = 331.91
 Triclinic, *P* $\bar{1}$
a = 7.0177 (5) Å
b = 8.3138 (6) Å
c = 11.3906 (8) Å
 α = 107.128 (1)°
 β = 99.039 (1)°
 γ = 102.748 (1)°
V = 601.60 (7) Å³

Z = 2
D_x = 1.832 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1951 reflections
 θ = 2.5–25°
 μ = 1.66 mm⁻¹
T = 296 (2) K
 Tablet, blue
 0.25 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1995)
T_{min} = 0.733, *T_{max}* = 0.847
 6432 measured reflections

2857 independent reflections
 1894 reflections with *I* > 2σ(*I*)
R_{int} = 0.036
 θ_{\max} = 28.3°
h = -9 → 9
k = -10 → 11
l = -15 → 15

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.028
wR(*F*²) = 0.054
S = 0.82
 2857 reflections
 172 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—O1	2.0970 (16)	Ni1—N1	2.0637 (16)
Ni1—O2	2.0217 (15)	O5—C6	1.258 (2)
Ni1—O3	2.0709 (15)	O6—C6	1.235 (2)
Ni1—O5	2.0324 (14)	O7—C7	1.253 (2)
Ni1—O4	2.0801 (14)	O8—C7	1.250 (3)
O1—Ni1—O3	174.32 (6)	O4—Ni1—N1	169.62 (6)
O2—Ni1—O5	175.81 (7)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O10 ⁱ	0.89	2.08	2.933 (2)	160
O1—H1B...O6 ⁱⁱ	0.95	1.83	2.776 (2)	175
O2—H2A...O8 ⁱ	0.88	1.81	2.680 (2)	171
O2—H2B...O10	0.83	1.89	2.712 (2)	168
O3—H3A...O6 ⁱⁱⁱ	0.88	1.84	2.674 (2)	158
O3—H3B...O7 ^{iv}	0.92	1.79	2.663 (2)	157
O4—H4A...O9	0.93	1.99	2.848 (2)	153
O4—H4B...O9 ^v	0.93	1.81	2.727 (2)	168
O9—H9A...O5	0.94	1.92	2.758 (2)	147
O9—H9B...O8 ^{vi}	0.86	1.91	2.722 (2)	157
O10—H10A...O7 ^{iv}	0.95	1.86	2.779 (2)	164
O10—H10B...O3 ^{vii}	1.03	1.88	2.853 (2)	158

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

The H atoms were located in a difference Fourier synthesis but were not refined; their *U*_{iso} values were set to 0.05 Å².

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Financial support for this work *via* a research grant for gifted high-school students from the Ministry of Education of the Republic of China, administered by the Science Educational Center, National Taiwan Normal University, is gratefully acknowledged.

References

- Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Liang, Y., Hong, M. & Cao, R. (2001). *Acta Cryst.* **E57**, m145–m147.
- Liang, Y., Hong, M., Su, W., Cao, R. & Zhang, W. (2001). *Inorg. Chem.* **40**, 4574–4582.
- Plater, M. J., Foreman, M. R. St J., Howie, R. A. & Lachowski, E. E. (1998). *J. Chem. Res. (S)*, pp. 754–755.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467.
- Sheldrick, G. M. (1995). *SADABS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Steed, J. W. & Atwood, J. L. (2000). In *Supramolecular Chemistry*. New York: Wiley.