

A novel nickel(II) coordination polymer incorporating 1,4-phenylenediacetic acid and 1,10-phenanthroline

Zi-Lu Chen,* Yu-Zhen Zhang and Fu-Pei Liang

College of Chemistry and Chemical Engineering, Guangxi Normal University, Yucui Road 15, Guilin 541004, People's Republic of China
Correspondence e-mail: chenziluczl@yahoo.co.uk

Received 8 November 2005

Accepted 20 December 2005

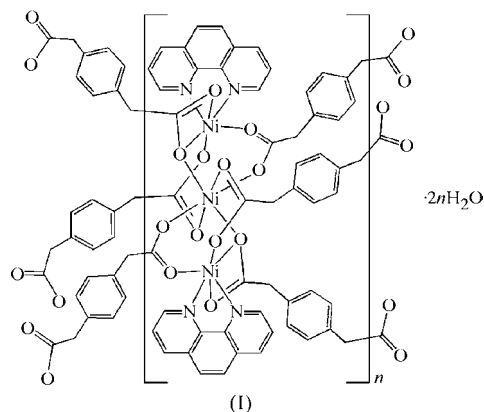
Online 14 January 2006

The title nickel(II) coordination polymer, *viz.* poly[[bis(1,10-phenanthroline)tris(μ_3 -1,4-phenylenediacetato)trinickel(II)] dihydrate], $\{[\text{Ni}_3(\text{C}_{10}\text{H}_8\text{O}_4)_3(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O}\}_n$, consists of linear trinuclear building blocks with two crystallographically unique Ni atoms. One Ni^{II} atom and the geometric centre of one 1,4-phenylenediacetate ligand in the trinuclear unit both lie on inversion centres, while the other unique Ni^{II} atom lies near the inversion centre, together with another 1,4-phenylenediacetate ligand. Each pair of adjacent trinuclear units is bridged by 1,4-phenylenediacetate ligands, forming two kinds of infinite chains along the *a* and *b* axes, respectively. These two kinds of chains crosslink to yield a two-dimensional network in the *ab* plane. The two-dimensional sheets further stack along the *c* axis *via* π - π stacking interactions and hydrogen bonds, forming a three-dimensional supramolecular structure.

Comment

The rational design of high-dimensional metal-organic frameworks has attracted much attention, owing to their fascinating framework structures and their potential applications as functional solid materials, such as gas storage, heterogeneous catalysis and magnetic materials (Kitaura *et al.*, 2002; Seo *et al.*, 2000; Pavlishchuk *et al.*, 2001; Swiegers *et al.*, 2000; Hagrman *et al.*, 1999). Among the linker molecules, carboxylic acids with aromatic rings have been extensively studied because of their versatile properties. Such work has usually concentrated on rigid aromatic carboxylic acids, such as benzene-1,4-dicarboxylic acid and benzene-1,2,4-tricarboxylic acid (Stepanow *et al.*, 2004; Rosi *et al.*, 2003). The use of much more flexible aromatic carboxylic acids, such as 1,4-phenylenediacetic acids (H_2PDA) (Lin *et al.*, 2005; Babb *et al.*, 2003), is rare. Metal-organic frameworks assembled with 1,4-phenylenediacetic acids may show much more interesting properties. It is also interesting to investigate the structural changes while such compounds are functioning as solid materials. In this work, we introduce an ancillary ligand 1,10-

phenanthroline (phen) to tune the structure and report here the synthesis and X-ray structure of $\{[\text{Ni}_3(\text{PDA})_3(\text{phen})_2] \cdot 2\text{H}_2\text{O}\}_n$ (I), which exhibits a two-dimensional network structure assembled from Ni^{II} cations and 1,4-phenylenediacetate anions *via* two kinds of crosslinked one-dimensional chains.



Single-crystal X-ray diffraction analysis reveals that compound (I) consists of trinuclear nickel building blocks, $[\text{Ni}_3(\text{PDA})_3(\text{phen})_2]$ (Fig. 1), in which atom Ni1 and the geometric centre of one PDA^{2-} ligand both lie on inversion centres. Another crystallographically unique Ni^{II} atom (Ni2)

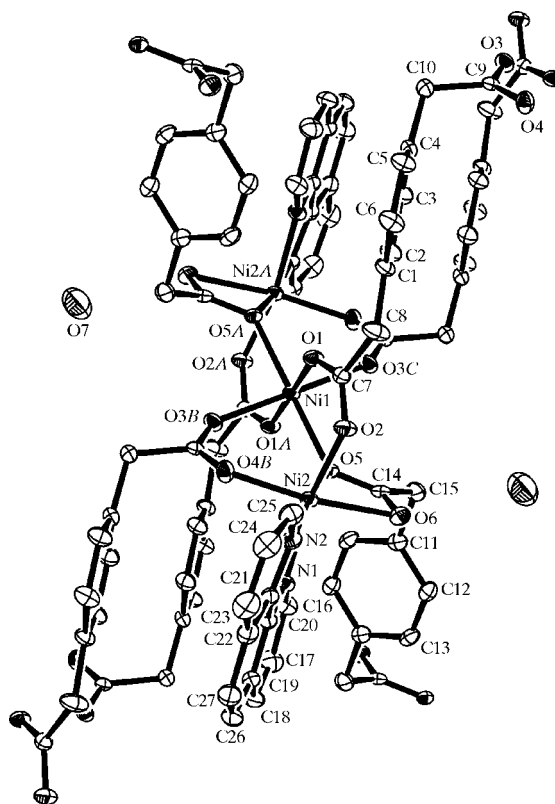


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. For clarity, H atoms have been omitted. Atoms labelled with the suffixes A–C are at the symmetry positions $(-x + 1, -y + 1, -z + 2)$, $(x - 1, y, z)$ and $(-x + 2, -y + 1, -z + 2)$, respectively.

and another PDA^{2-} ligand are located near the inversion centre. Both crystallographically unique Ni^{II} atoms (Ni1 and Ni2) have distorted octahedral coordination environments. Atom Ni1 is coordinated to six carboxylate O atoms from six PDA^{2-} ligands, with Ni—O bond lengths in the range 2.031 (2)–2.104 (2) Å and O—Ni1—O bond angles varying from 85.27 (9) to 180.0° (Table 1). Atom Ni2 is coordinated to two N atoms from one phen molecule and four carboxylate O atoms from three carboxylate groups of PDA^{2-} ligands, with Ni—N and Ni—O bond lengths in the ranges 2.071 (3)–2.089 (3) and 1.990 (2)–2.268 (2) Å, respectively. The O—Ni2—O bond angles range from 60.31 (8) to 159.39 (9)°. These carboxylate groups of the 1,4-phenylenediacetate ligands show two types of coordination mode. One type of carboxylate group chelates to one Ni^{II} atom and, at the same time, affords one of the carboxylate O atoms to bridge another Ni^{II} atom. The other type of carboxylate group acts simply as a bidentate bridge connecting two Ni^{II} atoms. Therefore, two Ni2 atoms are bridged to one Ni1 atom *via* six bridging carboxylate groups, resulting in the formation of a linear trinuclear nickel unit with an Ni1···Ni2 separation of 3.4714 (7) Å.

Each pair of neighbouring trinuclear $[\text{Ni}_3(\text{PDA})_3(\text{phen})_2]$ units is connected by two PDA^{2-} ligands to form an infinite

coordination chain along the *a* axis. The shortest Ni1···Ni1 or Ni2···Ni2 separation in this chain is 10.708 (3) Å. Alternatively, another kind of one-dimensional coordination chain is constructed *via* the bridging of each pair of adjacent trinuclear $[\text{Ni}_3(\text{PDA})_3(\text{phen})_2]$ units by one PDA^{2-} ligand along the *b* axis. The shortest Ni1···Ni1 or Ni2···Ni2 separation in this chain is 11.172 (3) Å. The two types of infinite chains crosslink in the *ab* plane to yield a two-dimensional network, as shown in Fig. 2. This differs from the reported structures of 1,4-phenylenediacetate complexes, which exhibit only one-dimensional infinite chains (Lin *et al.*, 2005; Babb *et al.*, 2003).

As shown in Fig. 3, 1,10-phenanthroline molecules from adjacent two-dimensional sheets are parallel to each other and partly overlap in a head-to-tail mode with a separation of 3.4296 Å, indicating significant π – π stacking effects. These π – π stacking interactions between 1,10-phenanthroline molecules lead to the formation of a three-dimensional supramolecular network by the stacking of two-dimensional sheets along the *c* axis. Free water molecules in the structure interact with adjacent two-dimensional sheets by formation of hydrogen bonds (Table 2), further stabilizing the three-dimensional supramolecular structure.

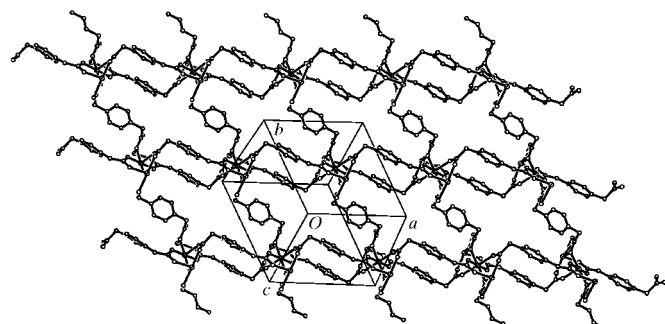


Figure 2
The two-dimensional network in the structure of (I). For clarity, H atoms and 1,10-phenanthroline molecules have been omitted.

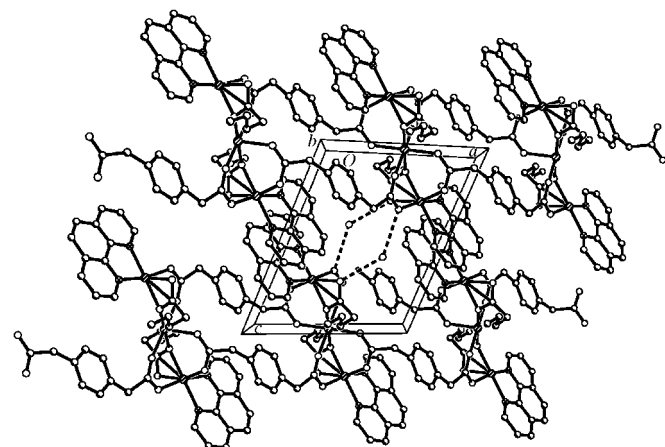


Figure 3
A packing diagram of the two-dimensional sheets along the *c* axis. Dashed lines indicate O—H···O hydrogen bonds.

Experimental

To a mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0951 g, 0.4 mmol), 1,4-phenylenediacetic acid (0.1572 g, 0.8 mmol), NaOH (0.064 g, 1.6 mmol) and phen (0.0793 g, 0.4 mmol), placed in a 23 ml Teflon-lined autoclave, were added distilled water (8 ml) and ethanol (2 ml). The mixture was then heated at 433 K for 200 h. The autoclave was cooled over a period of 48 h and the resulting green crystals of (I) were separated from the solution and dried. Elemental analysis for $\text{C}_{54}\text{H}_{44}\text{N}_4\text{Ni}_3\text{O}_{14}$ calculated: C 56.45, H 3.86, N 4.88%; found: C 56.47, H 3.65, N 4.24%.

Crystal data

$[\text{Ni}_3(\text{C}_{10}\text{H}_8\text{O}_4)_3(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$	$Z = 1$
$M_r = 1149.06$	$D_x = 1.604 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.708$ (3) Å	Cell parameters from 2429 reflections
$b = 11.172$ (3) Å	$\theta = 2.2$ – 27.8°
$c = 12.448$ (3) Å	$\mu = 1.25 \text{ mm}^{-1}$
$\alpha = 107.126$ (4)°	$T = 298$ (2) K
$\beta = 101.059$ (4)°	Block, green
$\gamma = 115.803$ (3)°	$0.29 \times 0.17 \times 0.14 \text{ mm}$
$V = 1189.3$ (5) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	4148 independent reflections
φ and ω scans	3102 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.713$, $T_{\text{max}} = 0.844$	$\theta_{\text{max}} = 25.0^\circ$
6299 measured reflections	$h = -12 \rightarrow 12$
	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 8$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.6844P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.084$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
4148 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$
346 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ni1—O3 ⁱ	2.031 (2)	Ni2—O5	2.067 (2)
Ni1—O5	2.099 (2)	Ni2—N2	2.071 (3)
Ni1—O1	2.104 (2)	Ni2—N1	2.089 (3)
Ni2—O2	1.990 (2)	Ni2—O6	2.268 (2)
Ni2—O4 ⁱ	1.999 (2)		
O3 ⁱ —Ni1—O5	90.90 (8)	O2—Ni2—N1	166.22 (9)
O3 ⁱ —Ni1—O1 ⁱⁱ	85.27 (9)	O4 ⁱ —Ni2—N1	93.07 (10)
O5—Ni1—O1 ⁱⁱ	90.55 (8)	O5—Ni2—N1	94.51 (9)
O2—Ni2—O4 ⁱ	96.62 (10)	N2—Ni2—N1	79.57 (10)
O2—Ni2—O5	93.60 (9)	O2—Ni2—O6	85.80 (9)
O4 ⁱ —Ni2—O5	99.08 (9)	O4 ⁱ —Ni2—O6	159.39 (9)
O2—Ni2—N2	91.37 (10)	O5—Ni2—O6	60.31 (8)
O4 ⁱ —Ni2—N2	85.83 (10)	N2—Ni2—O6	114.64 (10)
O5—Ni2—N2	172.56 (9)	N1—Ni2—O6	88.57 (10)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H28 ⁱⁱⁱ ···O6 ⁱⁱⁱ	0.84 (5)	2.51 (6)	2.990 (5)	117 (5)
O7—H29 ⁱⁱⁱ ···O2	0.85 (6)	2.54 (5)	3.193 (5)	135 (6)

 Symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$.

H atoms of water molecules were located in a difference Fourier map. During refinement, O—H and H···H distances were restrained to ensure a reasonable geometry for the water molecules. H atoms on C atoms were placed in calculated positions, with aromatic C—H distances of 0.93 Å and other C—H distances of 0.97 Å, and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors thank the Scientific Research Foundation of Guangxi Normal University and the Science Foundation of Guangxi (Guikeqing 0542021), China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1273). Services for accessing these data are described at the back of the journal.

References

- Babb, J. E. V., Burrows, A. D., Harrington, R. W. & Mahon, M. F. (2003). *Polyhedron*, **22**, 673–686.
- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1998). *SMART* (Version 5.051), *SAINTE* (Version 5.01) and *SADABS* (Version 2.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Hagman, P. J., Hagman, D. & Zubietta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
- Kitaura, R., Kitagawa, S., Kubota, Y., Kobayashi, T. C., Kindo, K., Mita, Y., Matsuo, A., Kobayashi, M., Chang, H.-C., Ozawa, T. C., Suzuki, M., Sakata, M. & Takata, M. (2002). *Science*, **298**, 2358–2361.
- Lin, X., Wang, Y.-Q., Cao, R., Li, F. & Bi, W.-H. (2005). *Acta Cryst.* **C61**, m292–m294.
- Pavlishchuk, V. V., Koval, I. A., Goreschnik, E., Addison, A. W., Albada, G. A. & Reedijk, J. (2001). *Eur. J. Inorg. Chem.* **1**, 297–301.
- Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O'Keeffe, M. & Yaghi, O. M. (2003). *Science*, **300**, 1127–1129.
- Seo, J. S., Whang, D., Lee, H., Jun, S. I., Oh, J., Jeon, Y. J. & Kim, K. (2000). *Nature (London)*, **404**, 982–986.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stepanow, S., Lingensfelder, M., Dmitriev, A., Spillmann, H., Delvigne, E., Deng, X., Cai, C., Barth, J. V. & Kern, K. (2004). *Nature Mater.* **3**, 229–233.
- Swiegers, G. F. & Malefetse, T. J. (2000). *Chem. Rev.* **100**, 3483–3538.