Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A one-dimensional nickel(II) coordination polymer containing 2,6-dipicolinate and dipyrido[3,2-*a*:2′,3′-*c*]phenazine

Yi Ma,[a] Li-Tian Zhang,[a] Xiao-Fang Wang,[b] Yong-Ke He[a] and Zheng-Bo Han[a]*

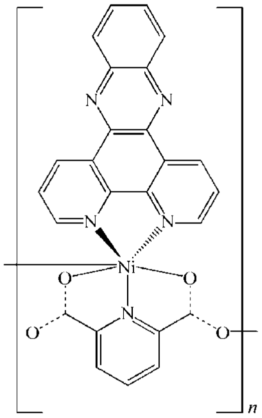
[a]College of Chemistry, Liaoning University, 110036 Shenyang, People's Republic of China, and [b]Department of Pharmaceutic Engineering, Liaoning University, 110036 Shenyang, People's Republic of China
Correspondence e-mail: ceshzb@lnu.edu.cn

Received 5 October 2007
Accepted 28 October 2007
Online 24 November 2007

A new coordination polymer, *catena*-poly[[(dipyrido[3,2-*a*:2′,3′-*c*]phenazine-κ^2N,N')nickel(II)]-μ-2,6-dipicolinato-$\kappa^4O^2,N,O^6:O^{2'}$], $[\mathrm{Ni(C_7H_3NO_4)(C_{18}H_{10}N_4)}]_n$, exhibits a one-dimensional structure in which 2,6-dipicolinate acts as a bridging ligand interconnecting adjacent nickel(II) centers to form a chain structure. The asymmetric unit contains one Ni$^{\rm II}$ center, one dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand and one 2,6-dipicolinate ligand. Each Ni$^{\rm II}$ center is six-coordinated and surrounded by three N atoms and three O atoms from one dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand and two different 2,6-dipicolinate ligands, leading to a distorted octahedral geometry. Adjacent chains are linked by π–π stacking interactions and weak interactions to form a three-dimensional supramolecular network.

Comment

In the past decade, the technology of the design and synthesis of inorganic–organic coordination polymers has developed very quickly because there has been much interest in their intriguing topologies and fascinating applications as functional materials (Moulton & Zaworotko, 2001; Eddaoudi *et al.*, 2001; Tong *et al.*, 2003; Zhang *et al.*, 2004; Seo *et al.*, 2000; Tao *et al.*, 2000). Many networks with various structural motifs, including honeycomb, brick-wall, rectangular grid, bilayer, ladder, herring-bone, diamondoid and octahedral geometries, have been documented (Hayashi *et al.*, 1991; Gable *et al.*, 1990; Fujita *et al.*, 1994; Kondo *et al.*, 1997; Losier & Zaworotko,



(I)

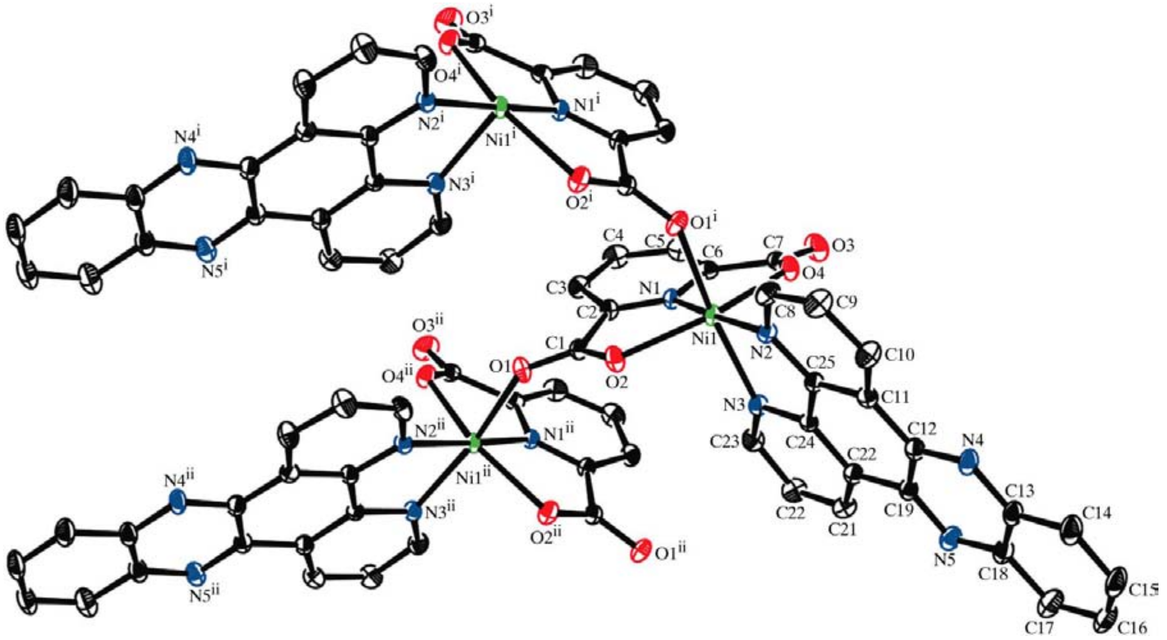


Figure 1
The coordination environment of the Ni$^{\rm II}$ center, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.]

DOI: 10.1107/S0108270107053851

1996; Withersby *et al.*, 1999; Yaghi & Li, 1995; Soma *et al.*, 1994). Recently, building blocks with heterocyclic carboxylic acids, such as pyridine-, pyrazole- and imidazolecarboxylic acids, have been used in the construction of coordination polymers (Tong *et al.*, 2005; Zhao *et al.*, 2005; Pan *et al.*, 2001; Lu *et al.*, 2006; Han *et al.*, 2006). Among them, 2,6-dipicolinate (pydc) is an important ligand for transition metal complexes owing to its having versatile bidentate, tridentate or bridging coordination modes, applications to diverse areas of technology, and the capacity to stabilize unusual oxidation states (Ma *et al.*, 2003; Scapin *et al.*, 1997; Pocker & Fong, 1980).

With the intention of studying the influences of the size of the aromatic chelate ligands on the framework structure of the *M*/pydc/*L* system (*M* is a transition metal and *L* is a chelating ligand), we choose the planar aromatic chelate dipyrido[3,2-*a*:2′,3′-*c*]phenazine (DPPZ) as a second ligand (Han, Cheng & Chen, 2005), and a new coordination polymer, $[Ni(pydc)(DPPZ)]_n$, (I), was successfully synthesized. The coordination environment of the nickel center in complex (I) is shown in Fig. 1. The six atoms around the nickel center form a distorted octahedron. The *O*,*N*,*O*′-tridentate chelation of the pydc ligand and the bidentate chelation of the DPPZ ligand have an important effect on the distorted octahedron. Each Ni^{II} ion is six-coordinated by three N atoms and three O atoms from a chelating DPPZ ligand and two different pydc ligands (Table 1), so the Ni center is octahedral with a *mer* arrangement (three N and three O atoms in two perpendicular planes).

The pydc ligand adopts *O*,*N*,*O*′-tridentate chelating and monodentate bridging coordination modes linking two adjacent Ni^{II} centers to form a one-dimensional chain, in which the 2-carboxyl group of the pydc ligand bridges two adjacent Ni^{II} centers in an *anti–anti* coordination mode; the DPPZ ligands point away from the chain like wings, as shown in Fig. 2, forming a roof-like arrangement. The conformation of the chain is severely puckered, with an Ni$\cdots$Ni$\cdots$Ni angle between adjacent metal centres of 80.72 (7)°. The pydc ligands within the chain form a dihedral angle of 32.8 (3)° and the minimum distance observed between two adjacent pyridine ring centroids is 4.131 (2) Å (Streb *et al.*, 2007).

The lateral DPPZ ligands from adjacent chains are paired to furnish π–π stacking interactions (Han, Cheng, Li & Chen, 2005; Han *et al.*, 2007) and the data are listed in Table 3. π–π stacking is observed between two phenazine rings of the DPPZ ligands with a perpendicular separation of 3.338 Å, a centroid-to-centroid distance of 3.510 Å and a slip angle (the angle between the centroid vector normal to the plane) of 18.38 (5)°. These values are typical for aromatic π–π stacking interactions (Hunter, 1994). Atom O3 of the pydc ligand also has weak interactions with a DPPZ aromatic ring [C11/C12/C19/C20/C24/C25 at $(x - 1, y, z)$] of an adjacent chain [the O3 atom–ring centroid distance is *ca* 2.662 (2) Å]. Adjacent chains are further linked *via* hydrogen bonds and π–π stacking interactions to construct a three-dimensional supramolecular network (Table 2). These weak interactions enhance the stability of the complex.

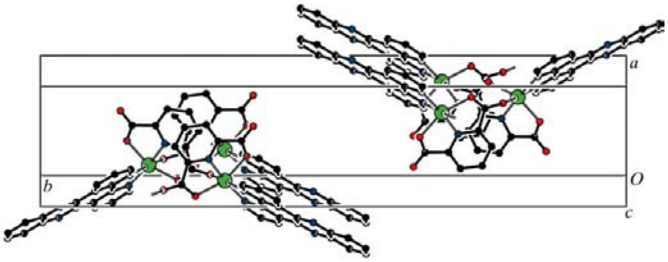


Figure 2
A partial packing view, showing the roof-like arrangement of the chains.

In the *M*/pydc/*L* system, the similar complexes [Cu(pydc)(2,2′-bipyridine)] (Bresciain-Pahor *et al.*, 1985), [Mn(pydc)(1,10-phenanthroline)] (Ma *et al.*, 2002) and [Co(pydc)(1,10-phenanthroline)] (Yin & Jiang, 2001) have been reported before. These complexes have simple discrete structures. In this paper, the notable feature of (I) is that the title complex has a roof-like chain. To the best of our knowledge, this type of roof-like chain has not been reported previously.

Experimental

DPPZ was prepared according to the method of Dickeson & Summers (1970). A mixture of $Ni(NO_3)_2{\cdot}6H_2O$ (0.145 g, 0.5 mmol), H_2pydc (0.084 g, 0.5 mmol), DPPZ (0.141 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and water (10 ml) was mixed in a 23 ml Teflon reactor and stirred for 20 min in air. It was then heated at 433 K for 5 d followed by cooling to room temperature at a rate of 5 K h^{-1}. Green block-shaped crystals of (I) were isolated.

Crystal data

$[Ni(C_7H_3NO_4)(C_{18}H_{10}N_4)]$
$M_r = 506.11$
Monoclinic, $P2_1/c$
$a = 7.3482$ (11) Å
$b = 35.825$ (4) Å
$c = 7.8986$ (12) Å
$\beta = 106.906$ (12)°
$V = 1989.4$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.02$ mm^{-1}
$T = 293$ (2) K
0.37 × 0.32 × 0.26 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.704$, $T_{max} = 0.780$
4459 measured reflections
3504 independent reflections
2860 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.111$
$S = 1.08$
3504 reflections
316 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.921 (3)	Ni1—O2	2.155 (2)
Ni1—N2	2.015 (3)	Ni1—N3	2.175 (3)
Ni1—O4	2.021 (2)	Ni1—O1^{i}	2.233 (2)
N1—Ni1—N2	173.60 (11)	N2—Ni1—O2	113.65 (10)
N1—Ni1—O4	83.48 (10)	O4—Ni1—O2	155.40 (9)
N2—Ni1—O4	90.72 (10)	O2—Ni1—O1^{i}	92.29 (9)
N1—Ni1—O2	72.01 (9)		

Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···O2^{iii}	0.93	2.48	3.190 (4)	134
C22—H22A···O4^{iv}	0.93	2.56	3.456 (4)	162

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

Table 3
π–π stacking parameters (Å) for the title compound.

$Cg\cdots Cg$ is the distance between ring centroids; CgI–Perp is the perpendicular distance of CgI from ring J; CgJ–Perp is the perpendicular distance of CgJ on ring I; slippage is the distance between CgI and the perpendicular projection of CgJ on ring I. $Cg7$ is the centroid of the N4/C12/C19/N5/C18/C13 plane, $Cg8$ is the centroid of the C11/C12/C19/C20/C24/C25 plane and $Cg9$ is the centroid of the C13–C18 plane.

CgI, CgJ	$CgI\cdots CgJ$	CgI–Perp	CgJ–Perp	Slippage
$Cg7$, $Cg7^{v}$	3.5102 (18)	3.294	3.294	1.14
$Cg7$, $Cg9^{v}$	3.574 (2)	3.290	3.304	1.29
$Cg8$, $Cg9^{v}$	3.509 (2)	3.294	3.298	1.14
$Cg9$, $Cg9^{vi}$	3.410 (2)	3.256	3.256	0.97

Symmetry codes: (v) $-x+2, -y, -z+1$; (vi) $-x+3, -y, -z+1$.

The H atoms were placed at calculated positions in the riding-model approximation (C—H = 0.93 Å), with $U_{\rm iso}$(H) displacement parameters set at $1.2U_{\rm eq}$ of the parent atoms. Standard DFIX restraints (*SHELXL97*; Sheldrick, 1997) were used for atoms C11 and C25 [C11—C25 = 1.395 (5) Å].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

This work was granted financial support from the Program for Liaoning Excellent Talents in Universities (grant No. RC-05-11).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3067). Services for accessing these data are described at the back of the journal.

References

Bresciain-Pahor, N., Nardin, G., Bonomo, R. P. & Purrello, R. (1985). *Transition Met. Chem.* **10**, 316–318.

Bruker (2001). *SAINT*, *SMART* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Dickeson, J. E. & Summers, L. A. (1970). *Aust. J. Chem.* **23**, 1023–1027.

Eddaoudi, M., Moler, D. B., Li, H. L., Chen, B. L., Reineke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.

Gable, R. W., Hoskins, B. F. & Robson, R. (1990). *Chem. Commun.* p. 1677.

Han, Z. B., Cheng, X. N. & Chen, X. M. (2005). *Cryst. Growth Des.* **5**, 695–700.

Han, Z. B., Cheng, X. N., Li, X. F. & Chen, X. M. (2005). *Z. Anorg. Allg. Chem.* **631**, 937–942.

Han, Z. B., He, Y. K., Ge, C. H., Ribas, J. & Xu, L. (2007). *Dalton Trans.* pp. 3020–3024.

Han, Z. B., Ma, Y., Sun, Z. G. & You, W. S. (2006). *Inorg. Chem. Commun.* **9**, 844–847.

Hayashi, M., Miyamoto, Y., Inoue, T. & Oguni, N. (1991). *Chem. Commun.* p. 1752.

Hunter, C. A. (1994). *Chem. Soc. Rev.* **23**, 101–102.

Kondo, M., Yoshitomi, T., Matsuzaka, H., Kitagawa, S. & Seki, K. (1997). *Angew. Chem. Int. Ed.* **36**, 1725–1727.

Losier, P. & Zaworotko, M. J. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2779–2782.

Lu, W. G., Jiang, L., Feng, X. L. & Lu, T. B. (2006). *Cryst. Growth Des.* **6**, 564–571.

Ma, C. B., Chen, C. N., Liu, Q. T., Liao, D. Z. & Li, L. C. (2003). *Eur. J. Inorg. Chem.* **6**, 1227–1231.

Ma, C.-B., Fan, C., Chen, C.-N. & Liu, Q.-T. (2002). *Acta Cryst.* C**58**, m553–m555.

Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.

Pan, L., Frydel, T., Sander, M., Huang, X. Y. & Li, J. (2001). *Inorg. Chem.* **40**, 1271–1283.

Pocker, Y. & Fong, C. T. O. (1980). *Biochemistry*, **19**, 2045–2050.

Scapin, G., Reddy, S. G., Zheng, R. & Blanchard, J. S. (1997). *Biochemistry*, **36**, 15081–15088.

Seo, J. S., Whang, D., Lee, H., Jun, S. I., Oh, J., Jeon, Y. J. & Kim, K. (2000). *Nature* (*London*), **404**, 982–985.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Soma, T., Yuge, H. & Lwamoto, T. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1665–1666.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Streb, C., Long, D. L. & Cronin, L. (2007). *Chem. Commun.* pp. 471–473.

Tao, J., Tong, M. L., Shi, J. X., Chen, X. M. & Ng, S. W. (2000). *Chem. Commun.* pp. 2043–2044.

Tong, M. L., Chen, X. M. & Batten, S. R. (2003). *J. Am. Chem. Soc.* **125**, 16170–16171.

Tong, M. L., Hu, S., Wang, J., Kitagawa, S. & Ng, S. W. (2005). *Cryst. Growth Des.* **5**, 837–839.

Withersby, M. A., Blake, A. J., Champness, N. R., Cooke, P. A., Hubberstey, P. & Schroder, M. (1999). *New J. Chem.* **23**, 573–576.

Yaghi, O. M. & Li, H. (1995). *J. Am. Chem. Soc.* **117**, 10401–10402.

Yin, X. J. & Jiang, Y. M. (2001). *Chin. J. Struct. Chem.* **20**, 299–300.

Zhang, J. P., Zheng, S. L., Huang, X. C. & Chen, X. M. (2004). *Angew. Chem. Int. Ed.* **43**, 206–209.

Zhao, B., Yi, L., Dai, Y., Chen, X. Y., Cheng, P., Liao, D. Z., Yan, S. P. & Jiang, Z. H. (2005). *Inorg. Chem.* **44**, 911–920.