Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# A one-dimensional ladder-like coordination polymer derived from chains formed *via* hydrogen bonds: *catena*-poly[[aquadipyridinenickel(**II**)]-$\mu$-2,2′-dithiodibenzoato-$\kappa^3$*O*,*O*′:*O*″]

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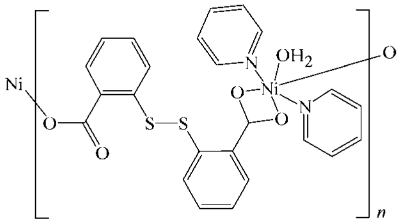
Received 14 May 2004
Accepted 16 July 2004
Online 11 August 2004

The title one-dimensional chain nickel(II)–disulfide complex, $[Ni(C_{14}H_8O_4S_2)(C_5H_5N)_2(H_2O)]_n$, has each $Ni^{II}$ cation coordinated by two N atoms from two pyridine ligands, three carboxylate O atoms from two different dithiodibenzoate ligands and one O atom from a coordinated water molecule, in a distorted octahedral coordination geometry. Each dithiodibenzoate ion links two $Ni^{II}$ cations through its carboxylate O atoms, making the structure polymeric. Hydrogen-bond interactions between two shoulder-to-shoulder chains lead to the formation of a ladder-like structure.

## Comment

The rational design of coordination polymers has attracted much attention, due to the potential applications of these materials, which range from gas storage and ion exchange to heterogeneous catalysis (Moulton & Zaworotko, 2001; Janiak, 2003). The construction of metal–organic frameworks can be achieved *via* two kinds of interaction, *i.e.* coordinate covalent bonds and weaker intermolecular forces. Weaker non-covalent interactions, such as hydrogen bonds or $\pi$–$\pi$ interactions, are important for the packing of one-dimensional chains, two-dimensional nets and three-dimensional open frameworks. Furthermore, the selection or design of suitable ligands containing certain features, such as flexibility and versatile binding modes, is crucial for the construction of specific supramolecular architectures. This concept has been demonstrated by the great variety of structural topologies of discrete supramolecular complexes or infinite supramolecular arrays (Leininger *et al.*, 2000; Janiak, 2003).

Against this background, we chose 2,2′-dithiodibenzoic acid (2,2′-$H_2$dtdb) as an organic ligand for study, based on the following considerations. Firstly, the twisted binding site passing through the centre of the S—S bond makes the ligand flexible. Secondly, the carboxylate binding groups, coupled with the different coordination modes of 2,2′-dtdb, should allow the fabrication of different coordination polymer topologies. Finally, the ligand has a strong capability of forming hydrogen bonds, which play an important role in the assembly of supramolecular compounds. Thus, we prepared the title compound, (I), by the hydrothermal reaction of an $Ni^{II}$ salt with the ligand and pyridine in a 1:1:4 molar ratio at 383 K for 2 d.



(I)

The present crystallographic analysis reveals that (I) is a one-dimensional ladder-like coordination polymer. As shown in Fig. 1, each $Ni^{II}$ cation is coordinated by two N atoms from two pyridine ligands, three carboxylate O atoms from two different dithiodibenzoate ligands and one O atom from a coordinated water molecule. One N atom (N2) and three O atoms (O1, O2 and O3*A*) form the equatorial plane, while the axial positions are occupied by one N atom (N1) and one O atom (O5), with an N1—Ni1—O5 bond angle of 177.25 (5)°. Thus, the coordination environment around the $Ni^{II}$ centre can be best described as having a distorted octahedral geometry. The $Ni^{II}$ cation is approximately coplanar with the coordination atoms in the equatorial plane, with a slight deviation of 0.001 Å. The Ni—N and Ni—O distances are in the ranges 2.0594 (14)–2.1279 (14) and 2.0216 (13)–2.1588 (11) Å, respectively (Table 1), which are typical values for Ni—N and Ni—O coordination distances (Kongshaug & Fgellvag, 2003).

The two carboxylate groups of each 2,2′-dtdb ligand adopt different coordination modes, namely monodentate and chelating–bidentate. As a result, the O1—C1—O2 angle [120.07 (13)°] is about 5° smaller than that of O3—C14—O4 [125.22 (14)°]. The dihedral angle between the two phenyl

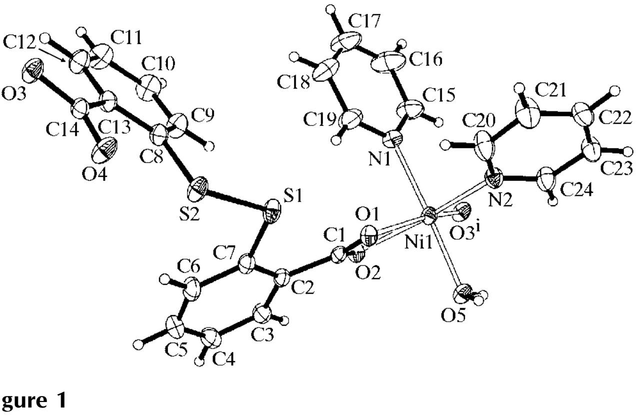


**Figure 1**
A perspective view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $x, y, z - 1$.]

DOI: 10.1107/S0108270104017469

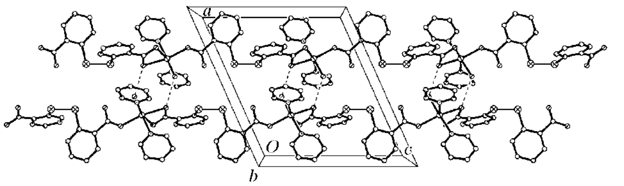


**Figure 2**

A view of the one-dimensional ladder-like structure in (I), which propagates along the *c* axis. Hydrogen-bond interactions are indicated by dashed lines.

rings is 96.7 (5)°, which is close to the angle in the analogous Co–2,2′-dtdb complex (Ganesh *et al.*, 1990).

Each dithiodibenzoate anion links two $Ni^{II}$ cations through its carboxylate O atoms, making the structure polymeric. The Ni···Ni distance bridged by 2,2′-dtdb is 12.581 (8) Å. Furthermore, hydrogen-bond interactions between two shoulder-to-shoulder chains lead to the formation of a ladder-like structure (Fig. 2). The hydrogen-bond distances of O5—H5*A*···O4(*x*, *y*, *z* − 1) and O5—H5*C*···O1(1 − *x*, 1 − *y*, 1 − *z*) are 2.6642 (19) and 2.837 (2) Å, respectively (Table 2). A bimetallic six-membered hydrogen-bonded ring is thus formed, with an Ni···Ni distance of 5.374 (8) Å.

The bimetallic unit can be viewed as the basic building block of the structure, and these are joined together through sharing of the $Ni^{II}$ apices with 2,2′-dtdb ligands to give the final one-dimensional polymer, which consists of rectangular grids with dimensions of 12.6 × 5.4 Å, based on the metal-to-metal distances. Therefore, the presence of hydrogen bonds in (I) plays an important role in the formation of the final ladder-like coordination polymer, which is notably different from other ladder-like structures based on coordinate covalent bonds (Liu *et al.*, 2004).

## Experimental

For the preparation of (I), a mixture of $Ni(NO_3)_2\cdot6H_2O$ (0.2 mmol) with 2,2′-$H_2$dtdb (0.2 mmol) and pyridine (0.4 mmol) in a 1:1:4 molar ratio dissolved in water (10 ml) was sealed in a stainless-steel reactor with a Teflon liner and heated at 383 K for 2 d. A number of green prism-shaped crystals of (I) were obtained after cooling the solution to room temperature. The yield of (I) was *ca* 65%, based on 2,2′-dtdb.

### *Crystal data*

$[Ni(C_{14}H_8O_4S_2)(C_5H_5N)_2(H_2O)]$
$M_r = 539.25$
Monoclinic, $P2_1/c$
$a = 13.925$ (3) Å
$b = 15.099$ (3) Å
$c = 12.581$ (3) Å
$\beta = 114.00$ (3)°
$V = 2416.5$ (11) Å$^3$
$Z = 4$

$D_x = 1.482$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5535 reflections
$\theta = 1.6$–27.5°
$\mu = 1.01$ mm$^{-1}$
$T = 293$ (2) K
Prism, green
0.26 × 0.20 × 0.18 mm

### *Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.784$, $T_{\max} = 0.833$
5535 measured reflections

5535 independent reflections
4673 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.5°$
$h = -18 \rightarrow 16$
$k = -19 \rightarrow 0$
$l = 0 \rightarrow 16$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.082$
$S = 1.07$
5535 reflections
315 parameters

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.43$ e Å$^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—O3$^i$ | 2.0216 (13) | Ni1—O1 | 2.1588 (11) |
| Ni1—N2 | 2.0594 (14) | S1—C7 | 1.7976 (18) |
| Ni1—O5 | 2.0877 (13) | S1—S2 | 2.0502 (7) |
| Ni1—O2 | 2.1079 (12) | S2—C8 | 1.7970 (17) |
| Ni1—N1 | 2.1279 (14) | | |
| O3$^i$—Ni1—N2 | 97.68 (6) | O2—Ni1—N1 | 89.31 (5) |
| O3$^i$—Ni1—O5 | 91.87 (6) | O3$^i$—Ni1—O1 | 159.57 (5) |
| N2—Ni1—O5 | 91.92 (6) | N2—Ni1—O1 | 102.73 (5) |
| O3$^i$—Ni1—O2 | 97.87 (5) | O5—Ni1—O1 | 86.58 (5) |
| N2—Ni1—O2 | 164.42 (5) | O2—Ni1—O1 | 61.75 (4) |
| O5—Ni1—O2 | 88.65 (5) | N1—Ni1—O1 | 90.84 (5) |
| O3$^i$—Ni1—N1 | 90.23 (6) | C7—S1—S2 | 106.17 (6) |
| N2—Ni1—N1 | 89.56 (6) | C8—S2—S1 | 104.46 (6) |
| O5—Ni1—N1 | 177.25 (5) | | |

Symmetry code: (i) *x*, *y*, *z* − 1.

**Table 2**

Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H5*A*···O4$^i$ | 0.74 (2) | 1.96 (2) | 2.6642 (19) | 159 (2) |
| O5—H5*C*···O1$^{ii}$ | 0.78 (3) | 2.06 (3) | 2.837 (2) | 173 (3) |

Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) 1 − *x*, 1 − *y*, 1 − *z*.

H atoms on C atoms were generated geometrically and allowed to ride on their respective parent atoms, with C—H = 0.95 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C). Water H atoms were located in difference maps and refined freely.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*.

This work was supported by the Natural Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1161). Services for accessing these data are described at the back of the journal.

## References

Ganesh, V., Radha, A., Seshasayee, M., Subrahmaniyan, T. & Aravamudan, G. (1990). *Acta Cryst.* C**46**, 2302–2305.
Janiak, C. (2003). *J. Chem. Soc. Dalton Trans.* pp. 2781–2804.
Kongshaug, K. O. & Fgellvag, H. (2003). *Solid State Sci.* **5**, 303–310.
Leininger, S., Olenvuk, B. & Stang, P. J. (2000). *Chem. Rev.* **100**, 853–908.
Liu, Z., Zhang, D., Liu, C. & Zhu, D. (2004). *Chem. Lett.* **33**, 180–181.
Moulton, B. & Zaworotko, M. Z. (2001). *Chem. Rev.* **101**, 1629–1658.
Sheldrick G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*b*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.