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## Key indicators

Single-crystal X-ray study

T = 273 K

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

R factor = 0.038

wR factor = 0.098

Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*catena*-Poly[[diaquabis[(4-tolylsulfanyl)acetato- $\kappa\text{O}$ ]nickel(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2\text{N:N}'$ ]

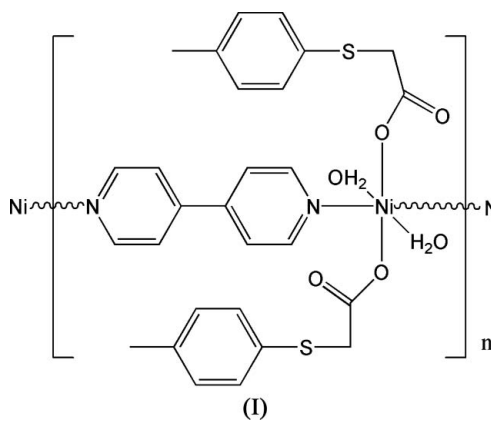
The title complex,  $[\text{Ni}(\text{C}_9\text{H}_9\text{O}_2\text{S})_2(\text{C}_8\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]_n$ , contains 4,4'-bipyridine ligands linking six-coordinate  $\text{Ni}^{\text{II}}$  ions. Each  $\text{Ni}^{\text{II}}$  ion is in an octahedral environment, coordinated by two aqua ligands, two (4-tolylsulfanyl)acetate ligands and two bridging 4,4'-bipyridine ligands, generating linear chains;  $\pi$ – $\pi$  interactions between adjacent chains result in a layered structure. A twofold rotation axis runs through the Ni atom and along the bridging ligand.

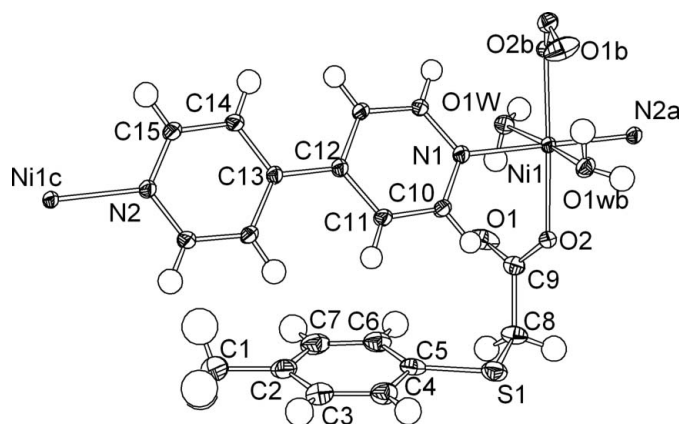
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## Comment

Considerable progress has been made recently on the crystal engineering of supramolecular architectures organized and sustained by means of coordinate covalent bonds, supramolecular contacts (such as hydrogen bonds and  $\pi$ – $\pi$  interactions), aurophilic interactions, and so on (Colacio *et al.*, 2002; Roesky & Andruh, 2003; Guilera & Steed, 1999). As an excellent building block in the design and construction of supramolecular polymers, 4,4'-bipyridine (4,4'-bipy) is relatively well known. Owing to a 4-tolylsulfanyl entity in the acetate residue, the (4-tolylsulfanyl)acetate (tta) ligand can not only coordinate to metal centers through the carboxylate group, but also form  $\pi$ – $\pi$  interactions through the 4-tolylsulfanyl group. Only one copper compound, *viz.*  $[\text{Cu}_2(\text{C}_9\text{H}_9\text{O}_2\text{S})_4(\text{C}_5\text{H}_5\text{N})_2]$  (Gao *et al.*, 2005), based on the tta ligand has been reported as noted from a cursory inspection of the Cambridge Structural Database (Version 5.26; Allen, 2002). Metal–organic complexes from mixed ligands of 4,4'-bipy and tta have not been reported. The combination of 4,4'-bipy and Htta is expected to lead to various polymeric compounds. Here, we report a one-dimensional nickel complex,  $[\text{Ni}(\text{tta})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2]_n$  (I).




**Figure 1**

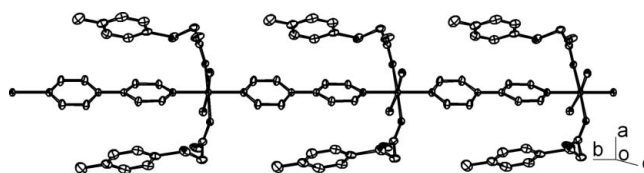
A view of part of the title structure, showing 30% probability displacement ellipsoids [symmetry codes: (a)  $x, -1 + y, z$ ; (b)  $-x, y, \frac{1}{2} - z$ ; (c)  $x, 1 + y, z$ ].

Fig. 1, the Ni<sup>II</sup> ion has distorted octahedral geometry. A twofold rotation axis runs through Ni and along the 4,4'-bipy ligand. Two *trans*-related N donors of two 4,4'-bipy ligands and two coordinated water molecules lie in the equatorial plane, while two O-atom donors of two tta ligands are in the axial positions. The 4,4'-bipy ligand functions as a spacer between two Ni<sup>II</sup> ions with an Ni...Ni separation of 11.271 (2) Å. The dihedral angle between the two pyridine rings is 11.82 (3)°. The tta ligand acts as a monodentate ligand through one carboxylate O atom (O2), the uncoordinated carboxylate atom O1 and an adjacent uncoordinated water molecule, forming an O—H...O hydrogen bond [O1...O1W = 2.622 (2) Å].

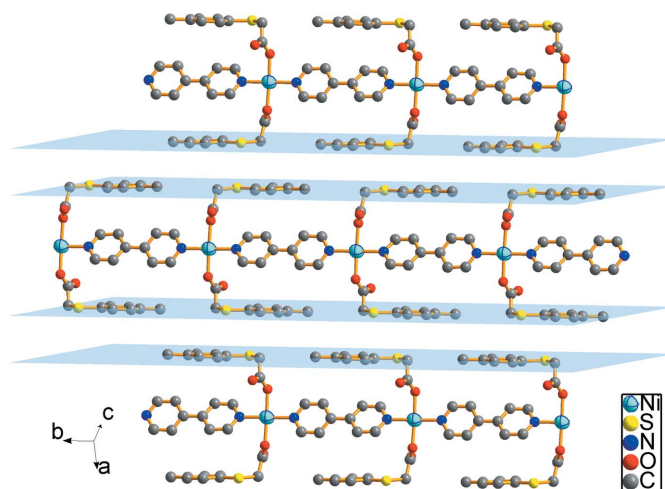
The twist in the tta ligand occurs at atom C8; the C5—S1—C8—C9 torsion angle is 79.16 (2)°. The dihedral angle between the carboxylate plane and the 4-tolylsulfanyl group is 75.10 (3)°. As shown in Fig. 2, the Ni<sup>II</sup> ions are linked by the 4,4'-bipy ligands, generating a linear chain along the *b* axis. A noteworthy feature of the chain is that the 4-tolylsulfanyl groups, which extend in the same direction along the chain, are situated on both sides of the backbone. On each side, the 4-tolylsulfanyl groups are almost coplanar. The polymer chains are arranged in an alternating manner in a two-dimensional arrangement and interact with each other through  $\pi$ - $\pi$  interactions. The arrangement of the polymer chains, in a truncated form, is shown in Fig. 3. It is evident that  $\pi$ - $\pi$  interactions occur between the 4-tolylsulfanyl groups of adjacent chains. The average distance between the planes of adjacent chains is 3.452 (3) Å. Such layers are further stacked through O—H...O hydrogen bonds (O1W...O2<sup>i</sup>; symmetry code as in Table 1) to complete the final three-dimensional structure.

## Experimental

A mixture of NiSO<sub>4</sub> (0.154 g, 1 mmol), (4-tolylsulfanyl)acetic acid (0.127 g, 0.5 mmol), 4,4'-bipyridine (0.078 g, 0.5 mmol) and H<sub>2</sub>O (18 ml) was sealed in a Teflon-lined 25 ml stainless steel reactor and


**Figure 2**

The chain structure of the title compound. H atoms have been omitted.


**Figure 3**

The two-dimensional arrangement of the chains. H atoms have been omitted.

heated at 433 K for 3 d. On completion of the reaction, the reactor was cooled slowly to room temperature and the mixture was filtered, giving green single crystals suitable for X-ray analysis.

## Crystal data

[Ni(C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>S)<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 613.37  
 Monoclinic, *C*2/*c*  
*a* = 21.649 (4) Å  
*b* = 11.271 (2) Å  
*c* = 11.050 (2) Å  
 $\beta$  = 92.59 (3)°  
*V* = 2693.5 (8) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.513 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 2318 reflections  
 $\theta$  = 1.9–27.9°  
 $\mu$  = 0.92 mm<sup>-1</sup>  
*T* = 273 (2) K  
 Prism, green  
 0.28 × 0.16 × 0.12 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\min}$  = 0.838,  $T_{\max}$  = 0.895  
 8799 measured reflections

3198 independent reflections  
 2417 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.029  
 $\theta_{\text{max}}$  = 27.9°  
 $h$  = -28 → 28  
 $k$  = -14 → 13  
 $l$  = -9 → 14

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.038  
 $wR(F^2)$  = 0.098  
 $S$  = 1.01  
 3198 reflections  
 186 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0586P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.13 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

|                                        |             |                          |             |
|----------------------------------------|-------------|--------------------------|-------------|
| Ni1—O1W <sup>i</sup>                   | 2.0766 (17) | Ni1—N2 <sup>ii</sup>     | 2.087 (2)   |
| Ni1—N1                                 | 2.082 (2)   | Ni1—O2 <sup>i</sup>      | 2.0927 (14) |
| O1W <sup>i</sup> —Ni1—O1W              | 173.86 (8)  | O1W <sup>i</sup> —Ni1—O2 | 87.45 (6)   |
| O1W <sup>i</sup> —Ni1—N1               | 86.93 (4)   | N1—Ni1—O2                | 88.90 (4)   |
| O1W <sup>i</sup> —Ni1—N2 <sup>ii</sup> | 93.07 (4)   | N2 <sup>ii</sup> —Ni1—O2 | 91.10 (4)   |
| O1W <sup>i</sup> —Ni1—O2 <sup>i</sup>  | 92.43 (6)   | O2 <sup>i</sup> —Ni1—O2  | 177.80 (7)  |

Symmetry codes: (i)  $-x, y, -z + \frac{1}{2}$ ; (ii)  $x, y - 1, z$ .**Table 2**  
Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                      | $D-H$      | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------------------|------------|--------------|--------------|----------------|
| O1W—H1WA $\cdots$ O2 <sup>iii</sup> | 0.817 (15) | 2.146 (19)   | 2.879 (2)    | 149 (3)        |
| O1W—H1WA $\cdots$ S1 <sup>iii</sup> | 0.817 (15) | 2.96 (2)     | 3.5572 (17)  | 132 (2)        |
| O1W—H1WB $\cdots$ O1                | 0.850 (15) | 1.800 (16)   | 2.622 (2)    | 162 (3)        |

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

The methyl groups were allowed to rotate to fit the electron density [ $C-H = 0.96 \text{ \AA}$  and  $U_{iso}(H) = 1.5U_{eq}(C)$ ]; the other H atoms were positioned geometrically [aromatic  $C-H = 0.93 \text{ \AA}$  and aliphatic  $C-H = 0.97 \text{ \AA}$ , with  $U_{iso}(H) = 1.2U_{eq}(C)$ ]. Water H atoms were

located and refined with distance restraints of  $O-H = 0.85 (2) \text{ \AA}$  and  $H \cdots H = 1.30 (2) \text{ \AA}$ ; their displacement parameters were set at  $1.5U_{eq}(O)$ . The highest peak is located  $1.13 \text{ \AA}$  from atom Ni1.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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