[Ni(terpy)(H$_2$O)]-*trans*-[Ni-(μ-CN)$_2$-(CN)$_2$]$_n$, a one-dimensional linear tetracyanonickelate chain

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The one-dimensional chain *catena*-poly[[aqua(2,2′:6′,2″-terpyridyl-κ^3N)nickel(II)]-μ-cyano-κ^2N:C-[bis(cyano-κC)nickelate(II)]-μ-cyano-κ^2C:N], [Ni(terpy)(H$_2$O)]-*trans*-[Ni-μ-(CN)$_2$-(CN)$_2$]$_n$ or [Ni$_2$(CN)$_4$(C$_{15}$H$_{11}$N$_3$)(H$_2$O)], consists of infinite linear chains along the crystallographic [10$\overline{1}$] direction. The chains are composed of two distinct types of nickel ions, paramagnetic octahedral [Ni(terpy)(H$_2$O)]$^{2+}$ cations (with twofold crystallographic symmetry) and diamagnetic planar [Ni(CN)$_4$]$^{2-}$ anions (with the Ni atom on an inversion center). The [Ni(CN)$_4$]$^{2-}$ units act as bidentate ligands bridging through two *trans* cyano groups thus giving rise to a new example of a *trans–trans* chain among planar tetracyanonickelate complexes. The coordination geometry of the planar nickel unit is typical of slightly distorted octahedral nickel(II) complexes, but for the [Ni(CN)$_4$]$^{2-}$ units, the geometry deviates from a planar configuration due to steric interactions with the terpyridine ligands.

Comment

Low-dimensional materials, including one-dimensional chains, are of interest to chemists and physicists alike due to characteristic structural and physical properties that are often different from their two and three-dimensional analogs. Alternating linear chains composed of two distinct structural units are a special case of one-dimensional compounds. These materials can be engineered using a 'brick and mortar' synthetic strategy (Willett *et al.*, 1993, and references therein). The bricks, complexes of metal ions and blocking ligands, are linked to one another by the mortar, or bridging units. In the title compound, the bricks are the paramagnetic [Ni(terpy)(H$_2$O)]$^{2+}$ groups where the 2,2′:6′,2″-terpyridine (terpy) ligand not only influences the coordination geometry of the nickel ion within the chain, but 'blocks' the extension of the structure along the second and third dimensions. The mortar, the [Ni(CN)$_4$]$^{2-}$ groups, is the cement that holds the bricks

together within the chain due to the ability of such ligands to coordinate to other metal complexes through cyano groups. There are now several examples of linear chains containing bridging [Ni(CN)$_4$]$^{2-}$ units (Yuge & Iwamoto, 1994; Yuge *et al.*, 1995; Iwamoto, 1996). A *trans–trans* (TT) linear chain structure was observed in Ni(en)$_2$Ni(CN)$_4$ (en is ethylenediamine; Černák, Chromič *et al.*, 1988) and [M(en)$_2$-Ni(CN)$_4$]·2PhNH$_2$ (M = Cd, Zn, Cu and Ni; Yuge & Iwamoto, 1994), where the bridging cyano groups occupy *trans* positions in both the cation and the anion. Conversely, a *cis–cis* (CC) zigzag chain structure was found in Cd(en)$_2$Ni(CN)$_4$ (two polymorphs; Yuge *et al.*, 1995). Furthermore, a *cis–trans* or *trans–cis* (CT or TC) zigzag chain was reported for [Ni(bipy)$_2$Ni(CN)$_4$], where the bridging cyano groups are *trans* within the anion, but occupy alternating *cis* and *trans* positions on the cation along the chain (Černák & Abboud, 2000). A more complicated CCTC chain-like structure was observed in [Ni(en)$_2$Ni(CN)$_4$]·2.16H$_2$O (periodicity doubled; Černák *et al.*, 1990). The coordination geometry of the blocking ligand can influence the stereochemistry of the [Ni(CN)$_4$]$^{2-}$ ligands along the chains by directing the bridging ligands to specific coordination sites on the metal center. This paper describes the crystal structure analysis of a new compound, [Ni(terpy)(H$_2$O)]-*trans*-[Ni(CN)$_4$], (I), a TT linear chain containing tetracyanonickelate bridging units.

(I)
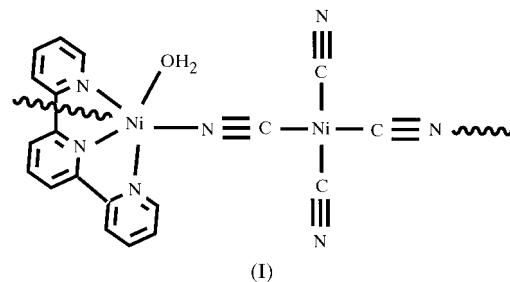
The structure of the title compound consists of linear chains along the [10$\overline{1}$] direction composed of alternating paramagnetic octahedral [Ni(terpy)(H$_2$O)]$^{2+}$ cations and diamagnetic [Ni(CN)$_4$]$^{2-}$ anions. The bridging cyano N atoms from the anion are coordinated *trans* to one another on the cation, completing the NiN$_3$ON$_2$ chromophore. The blocking ligands coordinated to the cation are 2,2′:6′,2″-terpyridine, a tris-*mer*-chelating ligand, and a water molecule. The terpy ligands are staggered along the chain in an alternating fashion, while the terminal cyano groups coordinated to the anion are arranged perpendicular to those of adjacent tetracyanonickelate ligands. Within a chain, the distance between paramagnetic and diamagnetic nickel ions is approximately 5.075 Å, while the distance between two paramagnetic or diamagnetic metal centers is about 10.149 Å. It is known that bridging cyano groups effectively transmit magnetic superexchange interactions and that the five-atom *trans*-N—C—Ni—C—N bridge may permit coupling between the two paramagnetic nickel ions (Orendáč *et al.*, 2000). However, the diamagnetic tetracyanonickelate units turn out to be poor mediators of magnetic exchange since no significant coupling was observed along the chains (Woodward *et al.*, 1999).
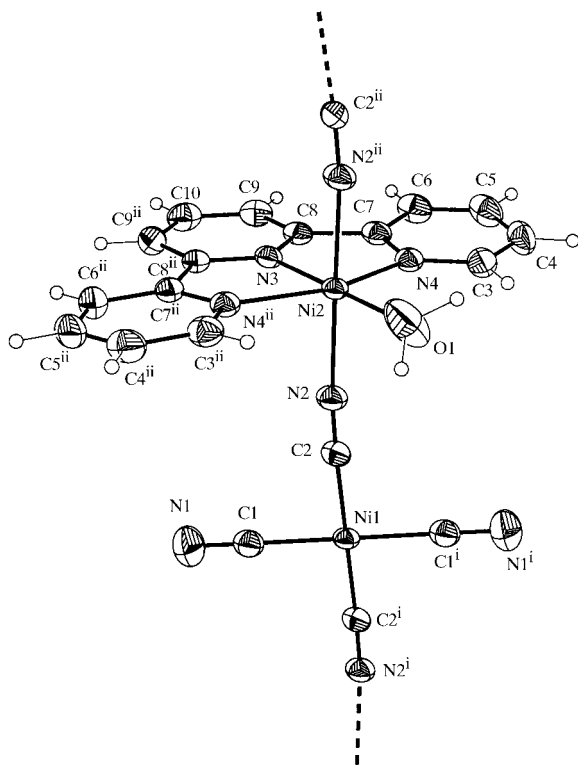
metal-organic compounds

Figure 1
The molecular structure of (I) (50% probability ellipsoids), showing the atom-numbering scheme [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$].

The chains are held together by a combination of inter-digitating terpy ligands between chains (with a terpy–terpy separation distance of alternating 3.416 and 3.509 Å distances) and hydrogen-bonding interactions between the H atoms of the coordinated water molecules and the N atoms of the terminal cyano groups on adjacent chains. No interstitial molecules are present between the chains.

Interactions between the $[Ni(CN)_4]^{2-}$ chromophore and nearby terpyridine ligands force the bridging ligand to twist, thereby relieving the repulsion between the terpy and the terminal cyano ligand. This twist forces the Ni2—N2—C2
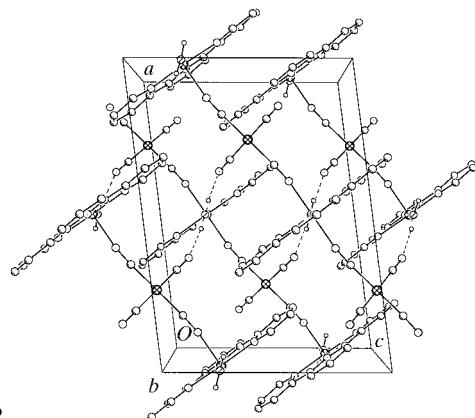

Figure 2
Packing diagram showing the chains and the hydrogen bonds linking them.

[172.2 (2)°] and Ni1—C2—N2 [176.2 (2)°] angles to deviate significantly from ideal geometry (180°). This repulsion can also be seen in the opening of angle C1—Ni1—C2 to 91.1 (1)°. The bond distances for the $[Ni(CN)_4]^{2-}$ complex are typical of those found in similar tetracyanonickelate chains (Černák, Dunaj-Jurčo et al., 1988). In the octahedral NiN_3ON_2 chromophore, the equatorial coordination sites are comprised of three N atoms from the terpyridine ligand, one O atom from the coordinated water, and two axial positions are filled by N atoms from the *trans* bridging cyano groups. A deviation from true octahedral geometry is observed due to the geometric requirements of the sterically bulky terpy ligand. The Ni—O (water) and Ni—N(terpy) bond angles and distances agree well with those of similar monomeric complexes, e.g. [Ni(terpy)(NO$_2$)(ONO)(H$_2$O)] (Cortés et al., 1986), [Ni(terpy)(Cl)(H$_2$O)$_2$]Cl·H$_2$O (Cortés et al., 1985), and [Ni(terpy)$_2$](ClO$_4$)$_2$·H$_2$O (Baker et al., 1995). The Ni—N bond distances on the cation involving the bridging cyano groups are also comparable to those found in [Ni(en)$_2$Ni(CN)$_4$]·2PhNH$_2$ (Yuge & Iwamoto, 1994) and [Ni(bipy)$_2$Ni(CN)$_4$] (Černák & Abboud, 2000).

Experimental

The nickel(II) perchlorate hexahydrate (98%) and 2,2′:6′,2″-terpyridine (98%) starting materials were purchased from the Aldrich Chemical Co. (Milwaukee, Wisconsin) and potassium cyanide (99.9%) was purchased from Fisher Scientific (Pittsburgh, Pennsylvania). All reagents were used without further purification. The combination of Ni(ClO$_4$)$_2$·6H$_2$O (366 mg, 1 mmol) with terpy (234 mg, 1 mmol) and KCN (97.5 mg, 1.5 mmol) in water (50 ml) produced a tan precipitate. Addition of NH$_3$ (20 ml, 15 M) solution and 50 ml of ethanol with stirring dissolved the precipitate, resulting in a yellow solution. The reaction mixture was filtered into a 500 ml Erlenmeyer flask, capped with paraffin (punctured with small holes), and set aside for crystallization. Within about four months, small brown blocks appeared in solution. These blocks were determined to be [Ni(terpy)$_2$](ClO$_4$)$_2$·H$_2$O, a known material (Baker et al., 1995). After five months, collection of the product revealed the presence of gray needles, which turned out to be the title compound.

Crystal data

[Ni$_2$(CN)$_4$(C$_{15}$H$_{11}$N$_3$)(H$_2$O)]	$D_x = 1.564$ Mg m^{-3}
$M_r = 472.74$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2835
$a = 15.5712$ (8) Å	reflections
$b = 11.5546$ (6) Å	$\theta = 2.5$–27.5°
$c = 11.2428$ (6) Å	$\mu = 1.90$ mm^{-1}
$\beta = 97.076$ (1)°	$T = 173$ (2) K
$V = 2007.4$ (2) Å^3	Needle, gray
$Z = 4$	0.17 × 0.09 × 0.09 mm

Data collection

SMART CCD area-detector diffractometer	6721 measured reflections
	2307 independent reflections
ω scans	1602 reflections with $I > 2\sigma(I)$
Absorption correction: by integration based on measured indexed crystal faces (*SHELXTL*; Bruker, 1998)	$R_{int} = 0.029$
	$\theta_{max} = 27.5°$
	$h = -20 \rightarrow 20$
	$k = -15 \rightarrow 12$
$T_{min} = 0.726$, $T_{max} = 0.871$	$l = -12 \rightarrow 14$

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2$	
$R[F^2 > 2\sigma(F^2)] = 0.031$		$\quad + 2.9223P]$	
$wR(F^2) = 0.072$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.07$		$(\Delta/\sigma)_{max} < 0.001$	
2307 reflections		$\Delta\rho_{max} = 0.29$ e Å^{-3}	
140 parameters		$\Delta\rho_{min} = -0.32$ e Å^{-3}	
H atoms treated by a mixture of independent and constrained refinement			

Table 1
Selected geometric parameters (Å, °).

Ni1—C2	1.863 (2)	N2—Ni2	2.085 (2)
Ni1—C1	1.863 (3)	Ni2—N3	2.008 (3)
C1—N1	1.145 (3)	Ni2—O1	2.041 (3)
C2—N2	1.147 (3)	Ni2—N4	2.125 (2)
C2—Ni1—C1^i	88.9 (1)	O1—Ni2—N2	89.34 (6)
C2—Ni1—C1	91.1 (1)	N3—Ni2—N4	77.97 (6)
N1—C1—Ni1	179.5 (3)	O1—Ni2—N4	102.03 (6)
N2—C2—Ni1	176.2 (2)	N2—Ni2—N4	90.85 (7)
C2—N2—Ni2	172.2 (2)	N2^{ii}—Ni2—N4	89.43 (7)
N3—Ni2—O1	180.0	Ni2—O1—H1	128 (2)
N3—Ni2—N2	90.66 (6)	H1—O1—H1^{ii}	104 (4)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$N1^i	1.00 (3)	1.94 (3)	2.926 (3)	171 (3)

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

A C—H distance of 0.95 Å was used for the Csp^2 atoms with displacement parameters set at $1.2U_{eq}$ of the parent C atoms. A hemisphere of frames, 0.3° in ω, was collected. The lone unique H atom of the water molecule was obtained from a difference Fourier map and was refined freely. All other H atoms were refined riding on their parent atoms.

Cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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