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# $\mathrm{Ni}(\text { bipy })_{2} \mathrm{Ni}(\mathrm{CN})_{4}$, a new type of one-dimensional square tetracyano complex 

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The one-dimensional structure of catena-poly[[bis(2,2'-bipyri-dyl- $1 \kappa^{2} N, N^{\prime}$ )- $\mu$-cyano-1:2 $\kappa^{2} N$ : $C$-dicyano- $2 \kappa^{2} C$-dinickel(II) $]-\mu$ -cyano-C: $N]$, $\left[\mathrm{Ni}_{2}(\mathrm{CN})_{4}\left(\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{2}\right)_{2}\right]_{n}$, consists of infinite zigzag chains running parallel to the $c$ axis. The chains are composed of paramagnetic $\left[\mathrm{Ni}(\text { bipy })_{2}\right]^{2+}$ cations (bricks; nickel on a twofold axis) linked by diamagnetic $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ anions (mortar; nickel on an inversion center) via bridging cyano groups. The bridging cyano groups occupy cis positions in the cation and trans positions in the anion, giving rise to a new previously unknown CT-type chain (i.e. cis-trans-type) among square tetracyano complexes. The coordination polyhedron of the paramagnetic Ni atom (twofold symmetry) is a slightly deformed octahedron with the two $\mathrm{Ni}-\mathrm{N}$ (bipy) bonds in cis positions being somewhat longer $[2.112(3) \AA]$ than the remaining four $\mathrm{Ni}-\mathrm{N}$ bonds with a mean value of 2.065 (6) $\AA$. The bond distances and angles in the anion have typical values.

## Comment

One-dimensional magnetic materials are of current interest due to their interesting magnetic properties (Dagotto, 1996; Chen \& Suslick, 1993; Orendáč et al., 1995; Delhaes \& Drillon, 1987). The synthetic strategy of such materials can be based on the use of the so-called 'brick and mortar' method (Willett et al., 1993), where paramagnetic entities (bricks) are linked by suitable bridging units (mortar). Square-planar tetracyano complexes are suitable bridging units due to the possibility of using cyano groups to link metal atoms. Stereochemical considerations and literature data (Iwamoto, 1996) indicate that various types of one-dimensional structures may be formed. As examples of different types of one-dimensional structures, we can mention $\mathrm{Ni}(\mathrm{en})_{2} \mathrm{Ni}(\mathrm{CN})_{4}$ exhibiting a TTtype chain structure [two bridging cyano groups occupy trans (T) positions in both the cation and anion; Černák, Chomič et al., 1988], diamagnetic $\mathrm{Cd}(\mathrm{en})_{2} \mathrm{Ni}(\mathrm{CN})_{4}$ (two polymorphs, en is ethylenediamine) forming CC-type chains (Yuge et al., 1995),
$\mathrm{Ni}(\mathrm{en})_{2} \mathrm{Ni}(\mathrm{CN})_{4} \cdot n \mathrm{H}_{2} \mathrm{O}$ with more complicated CCTC-type chains (periodicity doubled; Černák et al., 1990) and $\left[\mathrm{Eu}(\mathrm{dmf})_{4} \mathrm{Ni}(\mathrm{CN})_{4}\right](\mathrm{dmf}$ is dimethylformamide) exhibiting a ladder-like one-dimensional structure with three bridging cyano groups (Knoeppel \& Shore, 1996). To date, no crystal structures with CT- or TC-type chains containing squareplanar tetracyano complexes as bridging units have been reported.

The results of crystal structure analyses of the one-dimensional compounds $\left[\mathrm{Ni}(\text { bipy })_{2} \mathrm{~N}_{3}\right] \mathrm{ClO}_{4}$ and $\left[\mathrm{Ni}(\text { bipy })_{2} \mathrm{~N}_{3}\right] \mathrm{PF}_{6}$ (Urtiaga et al., 1994) have shown that the presence of two bulky 2,2'-bipyridine (bipy) ligands in the nickel octahedral coordination sphere leads to zigzag-type chains. CT-type chains were found in $\left[\mathrm{Cu}(\text { bipy })_{2} \mathrm{Ag}_{2}(\mathrm{CN})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, a compound with linear dicyanoargentate anions (Černák et al., 1993). These results indicate that the $\mathrm{Ni}(\text { bipy })_{2} \mathrm{Ni}(\mathrm{CN})_{4}$ compound, (I), initially described a long time ago (Feigl et al., 1945), may be a good candidate for a CT (or CC) type chain. The results of its crystal structure analysis are reported here and are discussed with respect to similar one-dimensional structures containing square-planar tetracyano complex anions.

(I)

The centrosymmetric structure of the title compound consists of zigzag-type chains. The chains are composed of paramagnetic $\left[\mathrm{Ni}(\text { bipy })_{2}\right]^{2+}$ cations (bricks), which are linked by diamagnetic $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ anions (mortar). The bridging cyano groups occupy cis positions in the cation, thereby completing the chromophore to $\mathrm{NiN}_{4} \mathrm{~N}_{2}$. On the other hand, they occupy trans positions in the anion, giving rise to a CTtype chain not yet found among square tetracyano complexes. Only van der Waals forces operate between the chains, so the packing of the chains is directed mainly by geometric requirements. The shortest distance between two atoms of neighboring chains is 2.42 (1) $\AA\left[\mathrm{H} 11 A \cdots \mathrm{H} 4 A\left(x-\frac{1}{2}, y-\frac{1}{2}\right.\right.$, $\left.\frac{1}{2}-z\right)$ ], which is in line with the sum of the van der Waals radii of H atoms (2.40 $\AA$; Taylor \& Kennard, 1982). The shortest distance between two paramagnetic Ni atoms is 8.681 (1) $\AA$ [e.g. $\mathrm{Ni} 2 \cdots \mathrm{Ni} 2\left(x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}-z\right)$ ], but there is no effective bridging between these atoms. Two paramagnetic Ni atoms (Ni2) within the chain are separated by 10.116 (2) $\AA$ and the $-\mathrm{N}-\mathrm{C}-\mathrm{Ni}-\mathrm{C}-\mathrm{N}-$ five-atom bridge may serve as an exchange path for the observed superexchange-type interaction (Orendáč et al., 2000). The bridge is quite linear; the greatest deviation from linearity is represented by the Ni2$\mathrm{N} 2-\mathrm{C} 2-(\mathrm{Ni} 1)$ angle $\left[171.1(3)^{\circ}\right]$. Similar but positively charged chains were found in the $\left[\mathrm{Cu}(\text { bipy })_{2} \mathrm{Ag}_{2}(\mathrm{CN})_{4}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ compound with linear dicyanoargentate anions, where the positive charge of the chains is counterbalanced by the
negative charge of free dicyanoargentate anions (Černák et al., 1993). The same type of five-atom bridges were found in many other tetracyanonickellates or dicyanoargentates (Iwamoto, 1996).

The Ni atom in the anion (Ni1) lies on a symmetry center, so the $\mathrm{NiC}_{4}$ chromophore is exactly planar. The geometrical parameters (bond distances and angles) have typical values and are similar to those found in other tetracyanonickellates (Černák, Dunaj-Jurčo et al., 1988).

The central Ni atom in the cation exhibits a hexacoordination in the cis- $\mathrm{NiN}_{4} \mathrm{~N}_{2}$ form and exhibits twofold symmetry. If we assign the coordination sites letters $A$ to $F$, with $A$ and $D$ being axial sites, the bridging cyano groups occupy neighboring positions $E$ and $F$. Geometrical considerations indicate two possible arrangements of the chelate bipy ligands; they can be bound in positions $A-B$ and $C-D$, or in positions $A-C$ and $B-D$, respectively. Both orientations in the form of disorder were found to a different extent in various crystals.


Figure 1
Displacement-ellipsoid ( $30 \%$ probability) drawing of the title compound displaying its one-dimensional character along with the atom-numbering scheme. [Symmetry codes: (i) $-x, 2-y,-z$; (ii) $-x, y, \frac{1}{2}-z$; (iii) $-x, y$, $-\frac{1}{2}-z$; (iv) $-x, 2-y, 1-z$.]

The shape of the nickel coordination sphere is significant in connection with the zero-field splitting of the ${ }^{3} A_{2}$ ground state as an important parameter in the interpretation of the magnetic properties. In the present compound, the nickel coordination sphere exhibits a rather unusual deformation from the ideal octahedral arrangement; four $\mathrm{Ni}-\mathrm{N}$ coordination bonds [two $\mathrm{Ni}-\mathrm{N}(\mathrm{C})$ and two among four $\mathrm{Ni}-$ $\mathrm{N}($ bipy )] exhibit the same value within experimental error ( $3 \sigma$ ) with a mean value of 2.065 (6) $\AA$; the remaining two $\mathrm{Ni}-$ N (bipy) bonds (Ni2-N4) in trans positions with respect to the bridging cyano groups are somewhat longer with a distance of 2.112 (3) A. A similar elongation of the trans-positioned Ni N (bipy) bonds ( 2.114 and $2.091 \AA$ ) versus cis-positioned $\mathrm{Ni}-$ $\mathrm{N}($ bipy ) bonds (2.083 and $2.066 \AA$ ) was observed in the $\left[\mathrm{Ni}(\text { bipy })_{2}\left(\mathrm{~N}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ compound (Urtiaga et al., 1995). On the other hand, in the $\mathrm{Ni}(\mathrm{en})_{2} \mathrm{Ni}(\mathrm{CN})_{4} \cdot n \mathrm{H}_{2} \mathrm{O}$ compound with en as chelating ligands, the $\mathrm{Ni}-\mathrm{N}(\mathrm{en})$ bonds are almost the same within s.u. [2.11 (1) and 2.12 (1) Å], regardless of their positions in the bridging cyano groups (Černák et al., 1990). The normalized bite value ( $b=1.272$; Kepert, 1982), and the bond distances and angles in the bipy ligands have standard values (Wada et al., 1976).

## Experimental

Single crystals of the title compound in the form of violet prisms suitable for X-ray studies were crystallized from a solution formed by the following procedure. $\mathrm{Ni}\left(\mathrm{NO}_{3}\right)_{2}$ solution $(10 \mathrm{ml}$ of 0.1 M solution, 1 mmol ), water $(500 \mathrm{ml})$ and $\mathrm{K}_{2} \mathrm{Ni}(\mathrm{CN})_{4}(10 \mathrm{ml}$ of 0.1 M solution, $1 \mathrm{mmol})$ were mixed and yielded a nickel cyanide precipitate, which was immediately dissolved by addition of a concentrated solution of ammonia ( $25 \%$ ). To the resultant solution, bipy ( $0.3124 \mathrm{~g}, 2 \mathrm{mmol}$ ) in methanol $(20 \mathrm{ml})$ was added. Finally, the solution was filtered and left to crystallize in an Erlenmayer flask at room temperature ( 291 K ). At first, large needles of $\left[\mathrm{Ni}(\text { bipy })_{3}\right]\left[\mathrm{Ni}(\mathrm{CN})_{4}\right] \cdot 6 \mathrm{H}_{2} \mathrm{O} \cdot \frac{1}{2}$ bipy (Černák et al., 1996; Akyüz et al., 1996) appeared and redissolved after a short time. Small single crystals of the title compound suitable for X-ray work formed after one month. The IR spectrum was measured on a Specord M40 spectrometer. $v(\mathrm{CH}): 3112(v w), 3080(b v w) ; v(\mathrm{CN})$ : 2148 (vs), $2120(v s) ; \rho(\mathrm{NH}): 1600(v s) ;(\mathrm{C}=\mathrm{C}): 1576(m), 1568(m)$; $\delta(\mathrm{Ni}-\mathrm{CN}): 428(s), 418(s)$.

## Crystal data

$\left[\mathrm{Ni}_{2}(\mathrm{CN})_{4}\left(\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{2}\right)_{2}\right]$
$M_{r}=533.87$
Orthorhombic, Pbcn
$a=14.067$ (1) $\AA$ A
$b=10.1759$ (7) $\AA$
$c=15.755$ (1) $\AA$
$V=2255.2(3) \AA^{3}$
$Z=4$
$D_{x}=1.572 \mathrm{Mg} \mathrm{m}^{-3}$

## Data collection

## SMART platform/CCD diffract-

 ometer$\omega$ scans
Absorption correction: faceindexed (Gaussian)
$T_{\text {min }}=0.684, T_{\text {max }}=0.911$
13421 measured reflections

Mo $K \alpha$ radiation
Cell parameters from 3962 reflections $\theta=2.5-27.5^{\circ}$
$\mu=1.700 \mathrm{~mm}^{-1}$
$T=173$ (2) K
Platelet, light violet
$0.19 \times 0.19 \times 0.06 \mathrm{~mm}$

2591 independent reflections 1498 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.056$
$\theta_{\text {max }}=27.48^{\circ}$
$h=-17 \rightarrow 18$
$k=-13 \rightarrow 6$
$l=-20 \rightarrow 20$

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.046$
$w R\left(F^{2}\right)=0.142$
$S=1.007$
2591 reflections
156 parameters
H -atom parameters constrained

Table 1
Selected geometric parameters ( $\left({ }^{\circ},{ }^{\circ}\right)$.

| $\mathrm{Ni} 1-\mathrm{C} 1$ | $1.860(6)$ | $\mathrm{Ni} 2-\mathrm{N} 3$ | $2.060(4)$ |
| :--- | :---: | :--- | ---: |
| $\mathrm{Ni} 1-\mathrm{C} 2$ | $1.871(4)$ | $\mathrm{Ni} 2-\mathrm{N} 4$ | $2.112(3)$ |
| $\mathrm{Ni} 2-\mathrm{N} 2$ | $2.070(3)$ |  |  |
| $\mathrm{C}^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{C} 1$ | 180.0 | $\mathrm{~N}^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 2^{\mathrm{ii}}$ | $91.3(1)$ |
| $\mathrm{C} 1^{\mathrm{i}}-\mathrm{Ni} 1-\mathrm{C} 2$ | $92.6(2)$ | $\mathrm{N} 2^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 2$ | $92.7(2)$ |
| $\mathrm{C} 1-\mathrm{Ni} 1-\mathrm{C} 2$ | $87.4(2)$ | $\mathrm{N} 3-\mathrm{Ni} 2-\mathrm{N} 4$ | $79.0(1)$ |
| $\mathrm{C} 2-\mathrm{Ni} 1-\mathrm{C} 2^{\mathrm{i}}$ | $180.0(2)$ | $\mathrm{N} 3^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 4$ | $93.3(1)$ |
| $\mathrm{N} 3-\mathrm{Ni} 2-\mathrm{N} 3^{\mathrm{ii}}$ | $169.5(2)$ | $\mathrm{N} 2^{\mathrm{ii}}-\mathrm{Ni} 2-\mathrm{N} 4$ | $174.2(1)$ |
| $\mathrm{N} 3-\mathrm{Ni} 2-\mathrm{N} 2^{\mathrm{ii}}$ | $96.0(1)$ | $\mathrm{N} 2-\mathrm{Ni} 2-\mathrm{N} 4$ | $90.3(1)$ |

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

The H atoms were placed in idealized positions and were refined riding on their parent atoms. A C-H distance of $0.95 \AA$ was used for all $\mathrm{Csp}{ }^{2}$ atoms. The H -atom displacement parameters were set at $1.2 U_{\text {eq }}$ of the parent C atom. Full data collection details are reported elsewhere (Abboud et al., 1997). Four data sets using four different crystals were collected for this structure and each solution revealed the presence of disorder in the position of the two bipyridine ligands. The data reported here have the least disorder (less than $5 \%$ ) and it was not possible to resolve.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998) and SHELXTL (Bruker, 1998); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: $S H E L X T L$; molecular graphics: $S H E L X T L$; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1357). Services for accessing these data are described at the back of the journal.

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