

C(45)	0,3023 (3)	0,5248 (7)	0,9225 (4)	0,054 (2)
C(46)	0,2697 (3)	0,4260 (7)	0,8924 (4)	0,046 (2)

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Tabelle 4. Geometrische Parameter (Å, °) für Verbindung (II)

W—Cl(1)	2,348 (2)	P(1)—Cl(4)	1,985 (4)
W—Cl(2)	2,334 (2)	P(1)—O(2)	1,465 (6)
W—Cl(3)	2,367 (3)	P(2)—C(11)	1,793 (8)
W—O(1)	1,683 (5)	P(2)—C(21)	1,791 (7)
W—O(2)	2,229 (5)	P(2)—C(31)	1,804 (7)
W—N	1,883 (1)	P(2)—C(41)	1,810 (7)
Cl(1)—W—Cl(2)	166,9 (1)	O(2)—W—N	81,4 (2)
Cl(1)—W—Cl(3)	88,4 (1)	Cl(4)—P(1)—O(2)	108,0 (2)
Cl(1)—W—O(1)	97,2 (2)	Cl(4)—P(1)—Cl(4')	102,5 (2)
Cl(1)—W—O(2)	83,3 (2)	Cl(4)—P(1)—O(2')	107,6 (2)
Cl(1)—W—N	89,8 (1)	O(2)—P(1)—O(2')	121,5 (4)
Cl(2)—W—Cl(3)	88,2 (1)	W(1)—O(2)—P(1')	134,4 (4)
Cl(2)—W—O(1)	95,8 (2)	W—N—W <sup>i</sup>	166,2 (3)
Cl(2)—W—O(2)	83,7 (2)	C(11)—P(2)—C(21)	108,4 (3)
Cl(2)—W—N	89,9 (1)	C(11)—P(2)—C(31)	110,9 (3)
Cl(3)—W—O(1)	96,0 (2)	C(11)—P(2)—C(41)	110,5 (3)
Cl(3)—W—O(2)	82,1 (2)	C(21)—P(2)—C(31)	107,5 (3)
Cl(3)—W—N	163,5 (2)	C(21)—P(2)—C(41)	109,3 (3)
O(1)—W—O(2)	178,1 (3)	C(31)—P(2)—C(41)	110,3 (3)
O(1)—W—N	100,4 (3)		

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

Geometrisch berechnete Positionen angenommen, je ein gemeinsamer isotroper Temperaturfaktor für die Methyl- bzw. Phenyl-H-Atome. Datensammlung: CAD-4 Meßsoftware. Gitterverfeinerung: CAD-4 Meßsoftware. Datenreduktion: XCAD-4 (Harms, 1987). Lösung der Struktur mit Programm: SHELXTL-Plus (Sheldrick, 1989). Verfeinerung der Struktur mit Programm: SHELXTL-Plus.

Dem Fonds der Chemischen Industrie danken wir für gewährte Unterstützung.

Die Liste der Strukturkoordinaten, anisotropen Verschiebungsfaktoren, H-Atomkoordinaten und vollständigen geometrischen Daten sind bei dem British Library Document Supply Centre (Supplementary Publication No. SUP 71708: 22 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF Aktenzeichen: SE1037]

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## Cd(2,2'-bipyridine-*N,N'*)Ni(CN)<sub>4</sub>, a Highly Bent Close Two-Dimensional Network of [Cd-{(NC)Ni<sub>1/4</sub>}<sub>4</sub>]<sub>n</sub>

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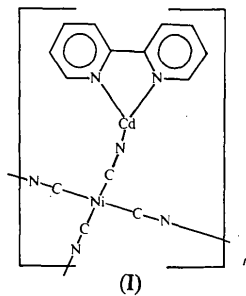
(Received 1 July 1993; accepted 11 October 1993)

### Abstract

The crystal structure of poly[(2,2'-bipyridine-*N,N'*)cadmium(II) tetra-μ-cyanonickelate(II)], [Cd(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]-[Ni(CN)<sub>4</sub>], has been determined. The tetracyanonickelate(II) ion, Ni(CN)<sub>4</sub><sup>2-</sup>, bridges four Cd<sup>2+</sup> ions to form an infinite two-dimensional folded network stacking along the *b* axis. The 2,2'-bipyridine ligands chelate to the Cd atoms alternately above and below the folded network. The distortion about the octahedrally coordinated Cd atom is so large, as a result of the unusual coordination behaviour of the Ni(CN)<sub>4</sub> in the network formation, that one of the Cd—N—C angles is markedly bent [143.1(3)°].

### Comment

The authors have investigated the multi-dimensional cyano-complex formation and inclusion phenomena of the title complex (I). In one series of these studies, the Cd<sup>2+</sup>-Ni(CN)<sub>4</sub><sup>2-</sup> or Cd<sup>2+</sup>-Ni(CN)<sub>4</sub><sup>2-</sup>-amine (or diamine) systems have shown a wide range of complexation patterns involving two- or three-dimensional networks, and a wide variety in the shape or environment of the cavity where mainly aromatic organic compounds are accommodated.



Structural patterns typical of square-planar tetracyanonickelate(II) have been studied with respect to their ability to form multi-dimensional networks, or frameworks,

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with other metal cations (Černák, Dunaj-Jurčo, Melník, Chomič & Skorsepa, 1988; Iwamoto, 1991). A close two-dimensional network is the most popular mode adopted by complexes of the  $\text{Ni}(\text{CN})_4$  moiety with another metal ( $M$ ), forming a square-meshed array of  $[\text{NiC}_4]$  and  $[\text{MN}_4]$  moieties whose C and N atoms are from the cyanide groups. This has been shown by a number of crystal structures analysed for the Hofmann-type and analogous clathrates, and related metal complexes. In these multi-dimensional structures,  $M$  is always ligated with other complementarily donating atoms at *trans* positions, *i.e.* from both sides of the network, in order to hold an octahedral coordination. The network is coplanar in Hofmann-type hosts, but usually folded in the Hofmann-diam-type hosts (Iwamoto, 1991). An ORTEPII (Johnson, 1976) diagram of the independent moiety of the compound, along with atomic numbering scheme, is shown in Fig. 1, and the packing diagram of the crystal is presented in Fig. 2.

The whole structure is a folded two-dimensional infinite complex, with 2,2'-bipyridine ligands sticking out from both sides of the  $\text{Cd}-\text{Ni}(\text{CN})_4$  complex sheet, and is stacked along the  $b$  axis. The catenation pattern of the  $\text{Cd}-\text{Ni}(\text{CN})_4$  complex can be classified in the close two-dimensional group. But the present close two-dimensional structure is unusual in comparison to known structures of octahedral Cd with 2,3,4,5(equatorial) coor-

dination by four N atoms from four CN groups and 1,6(axial) coordination by complimentary donors. The chelating 2,2'-bipyridine occupies the 1,2(*cis*) positions and the bridging cyanides hold the 3,4,5,6 positions.

Although  $\text{Ni}(\text{CN})_4$  maintains the square-planar configuration with little distortion, deformation occurs at every joint between the  $\text{Ni}(\text{CN})_4$  and the octahedral Cd. The  $\text{Cd}-\text{N1}-\text{C1}$  angle of  $143.1(3)^\circ$  indicates that the joint between the corners of the octahedron and the square plane deviates greatly from colinearity. The close two-dimensional network extending along the  $ac$  plane is twisted at every Ni atom and gives an up-and-down bending along the  $c$  axis, although all Ni atoms are on (010) or (020). The network has an alternate  $a/2 + b/2$  shift between (010) and (020) which is a result of the  $\text{C2}/c$  space group. The bipyridine ligands coordinate to the Cd atoms at the top and bottom of the bending network. The coordination sphere about the Cd atom is considerably distorted from a regular octahedron with bonding angles from  $84.6(1)$  to  $103.6(2)^\circ$ .

## Experimental

A 10 ml diethyl ether solution of 2,2'-bipyridine was settled onto 10 ml of an aqueous solution of 0.1 M  $\text{CdCl}_2$  and 0.1 M  $\text{K}_2[\text{Ni}(\text{CN})_4]$  buffered at about pH 9.6 with citric acid and 2-aminoethanol in a screw-capped 50 ml glass vial. On standing the bi-phase mother solution at room temperature, orange coloured prismatic crystals appeared at the interface within a week.

### Crystal data

$[\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)][\text{Ni}(\text{CN})_4]$

$M_r = 431.36$

Monoclinic

$\text{C2}/c$

$a = 6.790(1) \text{ \AA}$

$b = 17.238(1) \text{ \AA}$

$c = 12.464(1) \text{ \AA}$

$\beta = 91.14(1)^\circ$

$V = 1458.6(3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.96 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 17.15-17.47^\circ$

$\mu = 2.755 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Prism

$0.70 \times 0.20 \times 0.20 \text{ mm}$

Orange

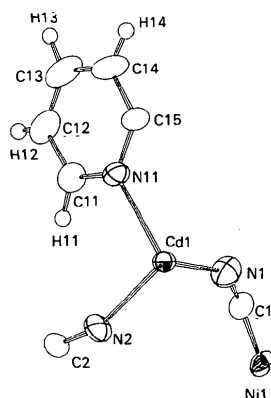


Fig. 1. The asymmetric unit of  $\text{Cd}(2,2'\text{-bipyridine-}N,N')\text{Ni}(\text{CN})_4$ , with the atomic numbering scheme.

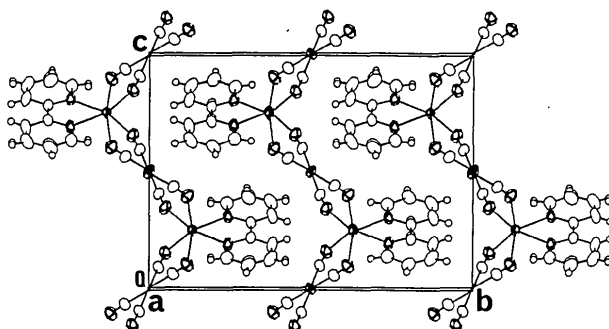


Fig. 2. Packing diagram of  $\text{Cd}(2,2'\text{-bipyridine-}N,N')\text{Ni}(\text{CN})_4$ .

### Data collection

Rigaku AFC-5R diffractometer

$\theta/2\theta$  scans

Absorption correction:

empirical  $\psi$  scan

$T_{\min} = 0.60$ ,  $T_{\max} = 1.00$

7070 measured reflections

6633 independent reflections

2328 observed reflections

$[I \geq 3.0\sigma(I)]$

$\theta_{\max} = 35.1^\circ$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 27$

$l = -20 \rightarrow 20$

3 standard reflections

monitored every 200

reflections

intensity variation: 0.9%

### Refinement

Refinement on  $F$

$R = 0.036$

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.002$

wR = 0.041  
S = 1.42  
2328 reflections  
118 parameters  
All H atoms were refined isotropically

$\Delta\rho_{\max} = 2.00 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{Å}^{-3}$   
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Occupancy	x	y	z	<i>U</i> <sub>eq</sub>
Cd1	1/2	1/2	0.13139 (2)	1/4	0.0281 (1)
Ni1	1/2	0	0	0	0.0309 (3)
N1	1	0.2739 (5)	0.1167 (2)	0.1018 (3)	0.046 (1)
N2	1	0.3055 (4)	0.0499 (2)	0.3444 (3)	0.043 (1)
C1	1	0.1704 (4)	0.0738 (2)	0.0606 (3)	0.035 (1)
C2	1	0.1904 (4)	0.0292 (2)	0.4031 (3)	0.034 (1)
N11	1	0.3341 (4)	0.2421 (2)	0.3075 (2)	0.035 (1)
C11	1	0.4069 (5)	0.3114 (2)	0.2807 (3)	0.035 (1)
C12	1	0.3125 (7)	0.3790 (2)	0.3096 (4)	0.052 (3)
C13	1	0.1407 (7)	0.3750 (3)	0.3673 (4)	0.060 (3)
C14	1	0.0679 (6)	0.3043 (3)	0.3939 (4)	0.052 (3)
C15	1	0.1663 (5)	0.2389 (2)	0.3626 (3)	0.046 (1)

Table 2. Selected geometric parameters (Å, °)

Cd1—N1	2.392 (3)	Ni1—C2 <sup>i</sup>	1.856 (3)
Cd1—N2	2.273 (3)	N1—C1	1.135 (4)
Cd1—N11	2.336 (3)	N2—C2	1.139 (4)
Ni1—C1	1.869 (3)		
N1—Cd1—N1 <sup>ii</sup>	167.8 (2)	C1—Ni1—C1 <sup>iii</sup>	180
N1—Cd1—N2	87.9 (1)	C1—Ni1—C2 <sup>i</sup>	89.2 (1)
N1—Cd1—N2 <sup>ii</sup>	84.6 (1)	C1—Ni1—C2 <sup>iv</sup>	90.8 (1)
N1—Cd1—N11	91.0 (1)	C2 <sup>i</sup> —Ni1—C2 <sup>iv</sup>	180
N1—Cd1—N11 <sup>ii</sup>	99.0 (1)	Cd1—N1—C1	143.1 (3)
N2—Cd1—N2 <sup>ii</sup>	103.6 (2)	Cd1—N2—C2	160.0 (3)
N2—Cd1—N11	93.3 (1)	Ni1—C1—N1	176.8 (3)
N2—Cd1—N11 <sup>ii</sup>	162.3 (1)	Ni1—C2 <sup>i</sup> —N2 <sup>i</sup>	177.5 (3)
N11—Cd1—N11 <sup>ii</sup>	70.4 (1)		

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

All non-H atoms were refined anisotropically. All H atoms were located from the difference Fourier map and refined isotropically without a special damping factor for each parameter. In the weighting scheme,  $\sigma^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$ , where  $S$  = scan rate,  $C$  = total integrated peak count,  $R$  = ratio of scan time to background counting time,  $B$  = total background count,  $Lp$  = Lorentz-polarization factor,  $p$  =  $p$  factor. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71738 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1078]

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## (Hexasulfanediy)di(pyridine-*N*)zinc

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## Abstract

The title compound {[hexasulfido(2-)-S<sup>1</sup>, S<sup>6</sup>]di(pyridine-*N*)zinc, [Zn(S<sub>6</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]} contains a distorted tetrahedrally coordinated core of ZnS<sub>2</sub>N<sub>2</sub>, in which the bond lengths Zn—S and Zn—N are 2.286 (1) and 2.064 (3) Å, respectively.

## Comment

In recent years, zinc compounds containing sulfur and nitrogen ligands have attracted much attention because of their bioinorganic relevance. For example, it has been suggested recently (Corwin & Koch, 1988) that [Zn(cysteine-S)<sub>2</sub>(histidine)<sub>2</sub>] is the active centre of the transcription factor IIIA. Several polysulfido metal complexes containing S<sub>2</sub><sup>2-</sup>, S<sub>4</sub><sup>2-</sup>, S<sub>5</sub><sup>2-</sup> and S<sub>7</sub><sup>2-</sup> ligands have been synthesized (Wu, Lu, Zhu, Wu & Lu, 1987; Du, Zhu, Wu & Lu, 1992) but compounds with an S<sub>6</sub><sup>2-</sup> ligand are rare. The title compound (I) is similar to [ZnS<sub>6</sub>(*N*-methylimidazole)<sub>2</sub>] reported by Dev, Ramli, Rauchfuss & Stern (1990).