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Modulated one-dimensional structure of $[\text{Cd}(\text{NH}_3)_3\text{Ni}(\text{CN})_4]$

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The crystal structure of $[\text{Cd}(\text{NH}_3)_3\text{Ni}(\text{CN})_4]$ has been solved and refined as an incommensurate structure in four-dimensional superspace. The Xcalibur point-detector diffractometer was used for data collection up to the third-order satellites. The structure was refined from 3496 observed reflections to a final R value of 0.0371. The modulation strongly affects all the atoms of the structure. The dominating feature of the modulation is the incommensurate alternation between octahedrally and tetrahedrally coordinated Cd atoms in the electroneutral chains $[-\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_\infty$ (n alternates between 2 and 4). The chain is propagated along the **a** axis, in which the $[\text{Cd}(\text{NH}_3)_n]^{2+}$ cations are linked by square $[\text{Ni}(\text{CN})_4]^{2-}$ anions. The atomic positional modulations, having mainly a transversal character in the *c*-direction, exhibit a switching character that can be described by the crenel and sawtooth functions. The effectively pentagonal coordinated cadmium positions were detected in the intermediate regions.

1. Introduction

The cyano ligand exhibits large flexibility in creating various bonding modes. Among them are the μ_2 - and μ_3 -bridging modes which are of special importance as they enable central atoms to link to formations of homo- and heterobimetallic oligomeric or polymeric coordination compounds of various dimensionalities (Cromer *et al.*, 1965; Dunbar & Heintz, 1997; Mondal *et al.*, 2000). Oligomeric and polymeric coordination compounds based on cyano-complexes and containing paramagnetic central atoms have been intensively studied because of their interesting magnetic properties (Sato *et al.*, 1996; Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Larionova *et al.*, 2000; Černák *et al.*, 2002). Diamagnetic cyano-complexes exhibiting oligomeric and polymeric structures have received attention because of their ability to form various host–guest and mineralomimetic systems (Iwamoto *et al.*, 1993; Kitazawa *et al.*, 1994; Iwamoto, 1996; Iwamoto *et al.*, 1997). They can also be helpful in the study of the thermodynamic properties of paramagnetic analogues as models suitable for the regular separation of lattice contributions from low-temperature specific heat data; this approach was used in the study of isostructural compounds $[\text{M}(\text{en})_2\text{Ni}(\text{CN})_4]$ ($M = \text{Ni}$ and Zn ; en = ethylenediamine; Orendáč *et al.*, 1996).

The compound $[\text{Cd}(\text{NH}_3)_3\text{Ni}(\text{CN})_4]$ was described for the first time by Baur & Schwarzenbach (1960) as an intermediate formed during the thermal degradation of $[\text{Cd}(\text{NH}_3)_6]-[\text{Ni}(\text{CN})_4]$. Later on the title compound was prepared by crystallization from dilute ammonia solution and its thermal

Table 1
Experimental and refinement details.

Crystal data	
Chemical formula	[Cd(NH ₃) ₃ Ni(CN) ₄]
M_r	326.3
Cell setting, space group	Monoclinic, $C2/c(\alpha, 0, \gamma)0s$
a, b, c (Å)	8.4867 (14), 15.951 (3), 7.604 (3)
β (°)	90.48 (2)
V (Å ³)	1029.3 (4)
Z	4
D_x (Mg m ⁻³)	2.105
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	30
θ range (°)	9.08–16.29
μ (mm ⁻¹)	3.86
Temperature (K)	260 (1)
Crystal form, colour	Irregular, gold–yellow
Crystal size (mm)	0.35 × 0.09 × 0.07
Modulation wavevector	$\mathbf{q} = 0.4365$ (11) $\mathbf{a}^* + 0.1307$ (9) \mathbf{c}^* refined from first-order satellites
Data collection	
Diffractometer	Oxford Diffraction point detector
Data collection method	$\theta/2\theta$
Absorption correction	Gaussian
T_{\min}	0.660
T_{\max}	0.807
No. of measured, independent and observed reflections	15 484, 7894, 3496
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.086
θ_{\max} (°)	27.1
Range of h, k, l	$0 \Rightarrow h \Rightarrow 12$ $-20 \Rightarrow k \Rightarrow 20$ $-10 \Rightarrow l \Rightarrow 10$
No. and frequency of standard reflections	Every 100 reflections
Intensity decay (%)	1.4
Refinement	
Refinement on	F
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.043, 1.78
No. of reflections	3496
No. of parameters	275
H-atom treatment	Restrained
Weighting scheme	Based on measured s.u.'s $w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max}$	<0.0001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.95, -0.99

Computer programs used: *SIR97* (Altomare *et al.*, 1997), *JANA2000* (Petříček *et al.*, 2000).

properties were described by Černák & Chomič (1987). Some similar Cd–Ni heterobimetallic compounds containing ammonia and cyano ligands should also be mentioned, for instance [Cd(AMpy)(NH₃)Ni(CN)₄] (AMpy = 2-amino-3-methylpyridine; Hökelek & Ülkü, 1988) or inclusion compounds [Cd(NH₃)₂Ni(CN)₄·2C₆H₆] (Nishikiori *et al.*, 1989) and [Cd(NH₃)₂Ni(CN)₄]·0.5H₂O (Kappenstein & Černák, 1987).

In our previous studies we have determined the crystal structure of the copper compound [Cu(NH₃)₃Ni(CN)₄]₄, which is composed of octanuclear planar molecules (Černák *et al.*, 1990). The title compound was originally only studied for comparison, but it revealed exceptional structural and crystallochemical features.

2. Crystal structure analysis

Preliminary X-ray investigations with an Xcalibur four-circle diffractometer revealed that the main diffraction spots in the diffraction pattern are accompanied by relatively strong satellites typical for modulated crystals. These spots were indexed by the four integers $hklm$ with respect to the four-dimensional base (de Wolff, 1974) $\mathbf{h} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$, where \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are the reciprocal axes of the basic structure and \mathbf{q} is the modulation vector. Refined components of the modulation vector (see Table 1)¹ were significantly different [−0.0079 (11), 0, ±0.012 (9)] from the closest commensurate values (3/7, 0, 1/7).

During the testing procedure we observed slow decomposition of the somewhat hygroscopic crystals under X-ray irradiation. To minimize the effect we protected the crystal by a stream (*ca* 260 K) of nitrogen. The satellite reflections were measured up to third order. The data were corrected for linear decay, Lorentz and polarization effects, and absorption based on the analytical shape. The apparent Laue class $2/m$ and reflection conditions ($hklm$, $h + k = 2n$) and ($h0lm$, $l + m = 2n$) allowed two possible superspace groups: $C2/c(\alpha, 0, \gamma)0s$ and $Cc(\alpha, 0, \gamma)s$, the former being proved by the refinement.

As the solution of the crystal structure was not trivial we shall now describe the basic steps. The average starting positions of the heavy atoms obtained from the main reflections by direct methods (*SIR97*; Altomare *et al.*, 1997) could not account for the strong Patterson maximum at (0, 0.063, 0). This maximum, corresponding to an interatomic distance of *ca* 1 Å, indicated the splitting of some heavy-atom positions. The Fourier maps revealed that the Cd atom occupied two separated positions, Cd1 and Cd2, related by a short Patterson vector, while the Ni atom did not exhibit any splitting. The split heavy-atom model was used to localize the remaining light atoms by subsequent Fourier syntheses. The refinement of the average structure converged to $R \simeq 0.061$.

The two positions of cadmium in the average structure had different coordination modes: tetrahedral (Cd1) and octahedral (Cd2); see Fig. 1. The occupancy of the octahedral position was slightly above $\frac{1}{2}$, as was the occupancy of the N4 atom which was coordinated only to the Cd2 atom.

The average structure offered us a good starting point for the refinement of the modulated structure. The first phasing model was refined using only the occupational modulation. As a first step we refined two harmonic waves for the occupational modulation of Cd1 and Cd2 under the restriction that constant and full occupancy of the Cd positions was assured for every t section. The refined modulation function (see Fig. 2) exhibited a crenel-like behavior (Petříček *et al.*, 1995), which corresponded to the fact that high-order satellites were detected. We then introduced one simple positional wave for all the remaining atoms.

In the next step all the occupational waves were removed, except that of N4, and a model with one harmonic positional

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN5017). Services for accessing these data are described at the back of the journal.

wave for N4 and two harmonic positional waves was refined for all the remaining atoms. The refinement converged to $R \simeq 0.086$ for the observed [$I > 3\sigma(I)$] main and satellite reflections.

At this stage, the introduction of the crenel functions for Cd1, Cd2 and N4 was possible in order to describe the discontinuous character of their modulation. In Fig. 3 we show the behavior of the Cd1 and Cd2 atoms, and their neighborhood before, during and after the 'Cd jump' using two-dimensional sections through the four-dimensional electron density map (the map was calculated for the model with crenel functions). The first section was plotted for the internal coordinate $t = -0.05$, which was close to the refined end point of the crenel function definition interval, *i.e.* it shows the situation just before the 'jump'. The Cd1 atom (green) still keeps the tetrahedral coordination but a new octahedral position (Cd2) arises. The distances between the new (arising) Cd2 position and two neighboring N1 atoms are 1.6 and 2.1 Å, respectively. The first distance (1.6 Å), which is too short, forces an abrupt change in the coordination that is visible in the second section for $t = 0$. Here the Cd atom is already localized in the new octahedral position (Cd2) and the cyano group C1–N1 on the right is shifted to achieve a more realistic distance to Cd2. This shift also influences the cyano group and the Cd atoms related by the superspace translation $(x_1 - 1, x_2, x_3, x_4)$. The central Ni atom is also affected because of its strong coordination change. In the third section for $t = 0.05$ we see the new arrangement stabilized. The figure also shows another symmetry-related position of Cd1/Cd2, where the reverse change from an octahedral position to a tetrahedral one is realised. However, this change does not force abrupt changes in the adjacent N1 positions.

It should be noted here that the crenel-like behavior of the cadmium coordinates could generally induce two symmetrically related discontinuities in $t \in (0, 1)$ for both N1 and N3 coordinated atoms. In terms of Fig. 3 we would see an abrupt shift of N1 atoms not only on the right but also on the left. In reality, only one discontinuity occurs for N1 and no discontinuity was detected for N3, which is sufficiently described using positional modulation waves. The N4 atom was modulated by

a crenel function with $x_{40} \simeq 0.75$ as the center and a width of *ca* 0.5. According to the site symmetry both parameters can be refined; nevertheless, the second parameter was fixed at 0.5 to avoid short N4...N4 distances.

As both Cd atoms are located at special positions we can restrict the x_{40} centers of the relevant crenel functions to 1/4 and 3/4. The complementarity condition requires the widths of the crenel functions to be restricted by the equation $\Delta(\text{Cd2}) = 1 - \Delta(\text{Cd1})$. From the symmetry considerations (the jump in the cadmium position must occur for all symmetry equivalents) we can find the relationship between the width of the crenel function and the first component of the modulation q vector

$$\begin{aligned}\Delta(\text{Cd1}) &= q_1 = 0.4365 \\ \Delta(\text{Cd2}) &= 1 - q_1 = 0.5635.\end{aligned}$$

The modulation of N1, C1 and Ni atoms can be best described using the sawtooth function (Petříček *et al.*, 1990) in combination with two harmonic position modulation functions. The central point of the sawtooth function for the Ni atom is fixed by the site symmetry (twofold axis). The central points for the remaining atoms were related with the Ni atom to ensure that the discontinuity takes place for the same t value and that it corresponds with the Cd jump. The width of the sawtooth function used was fixed to 1 because Ni exists in the full x_4 interval. Thus, the crenel and sawtooth parameters are fully determined from the symmetry and geometrical considerations and need not be refined. In Fig. 4 we see that the

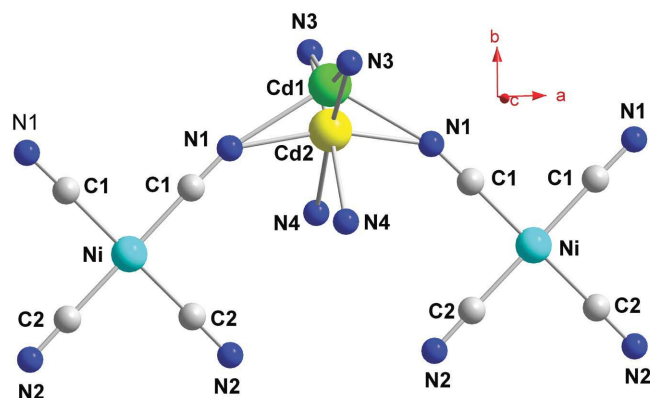


Figure 1

The average structure as found and refined from main reflections. Two positions for CD are possible. Cd1 (green) has tetrahedral coordination, Cd2 (yellow) is coordinated octahedrally.

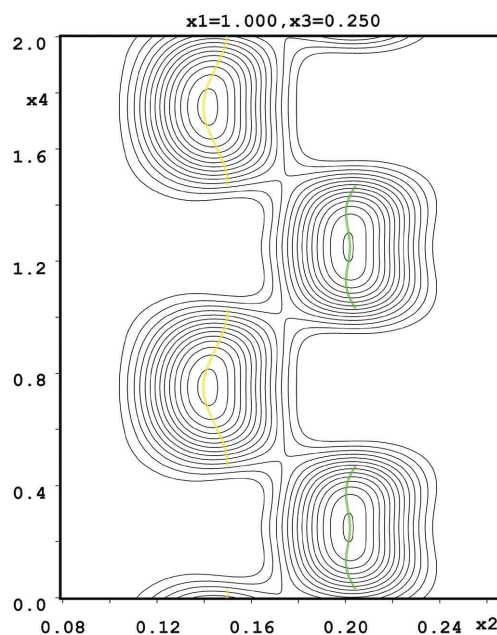


Figure 2

The x_2 – x_4 section through the four-dimensional Fourier map showing the positional modulation of the Cd atom. The coordinates x_1, x_3 are equal to those of Cd1 or Cd2 in the basic structure. The two basic positions are clearly separated into two crenel-like intervals (yellow for Cd2, green for Cd1).

modulation function of N1 corresponds to the previously described discontinuity.

In the final refinement we used three harmonic positional waves for all the fully occupied atoms: two waves for Cd1 and Cd2, and one wave for N4. The occupational modulation of Cd1, Cd2 and N4 was described by the crenel function. The combination of discontinuous (crenel or sawtooth) modulation functions with harmonic positional modulation functions causes a strong correlation between positional parameters. Therefore, we used the orthogonalization method as described by Petříček *et al.* (1995) that replaces the regular harmonic functions used in ordinary modulated structures by orthogonalized sets of functions. Besides the occupational and positional modulation we also used two harmonic waves for the modulation of harmonic ADP (atomic displacement parameters) for Cd1 and Cd2, and one wave for Ni. The H atoms bonded to N3 were located from the difference Fourier map

and refined under restraints, keeping the ideal tetrahedral coordination to the central atom. The remaining H atoms were bonded to N4 (described by the crenel function) and they were on average only half occupied. This is probably the reason why they could not be localized from Fourier maps. The final refinement converged smoothly to $R = 0.037$. The refined atomic positional parameters, their modulations and the orthogonalized sets of functions have been deposited. The distances and angles important for understanding the structure together with bond-valence sums for Cd1 and Cd2 are summarized in Table 2.

3. Results and discussion

The structure is built up of electroneutral chains $[-\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_\infty$ (n alternates between 2 and 4) oriented along the **a** axis, in which the $[\text{Cd}(\text{NH}_3)_n]^{2+}$ cations are linked by square $[\text{Ni}(\text{CN})_4]^{2-}$ anions. Both building species exhibit connectivity 2. The two bridging cyano groups are in *cis* positions in the anion. A similar *cis* bridging mode of the tetracyanonickelate anion was found in only a few cases, e.g. in two polymorphs of the one-dimensional coordination polymer $[\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4]$ (Yuge *et al.*, 1995). The alternation of N4 atoms between two distinct positions, related by the superspace symmetry operation, leads to a change in the octahedral and tetrahedral coordination of Cd atoms in adjacent $[\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}]$ building units, as shown in Fig. 5. In the most common situation the octahedral and tetrahedral coordination modes regularly alternate (see Fig. 5a). There are, however, regions (*ca* 13% of cases) where the tetrahedral and octahedral coordination modes are not clearly distinguished (see Fig. 5b) and cadmium exhibits the effective coordination number five, despite its position being close to that for octahedral coordination. At the same time the modulation of anisotropic displacement parameters leads to a smearing of the Cd-atom position, indicating that the penta-coordination results in fact from averaging of the two basic coordination modes. This also means that the transition area

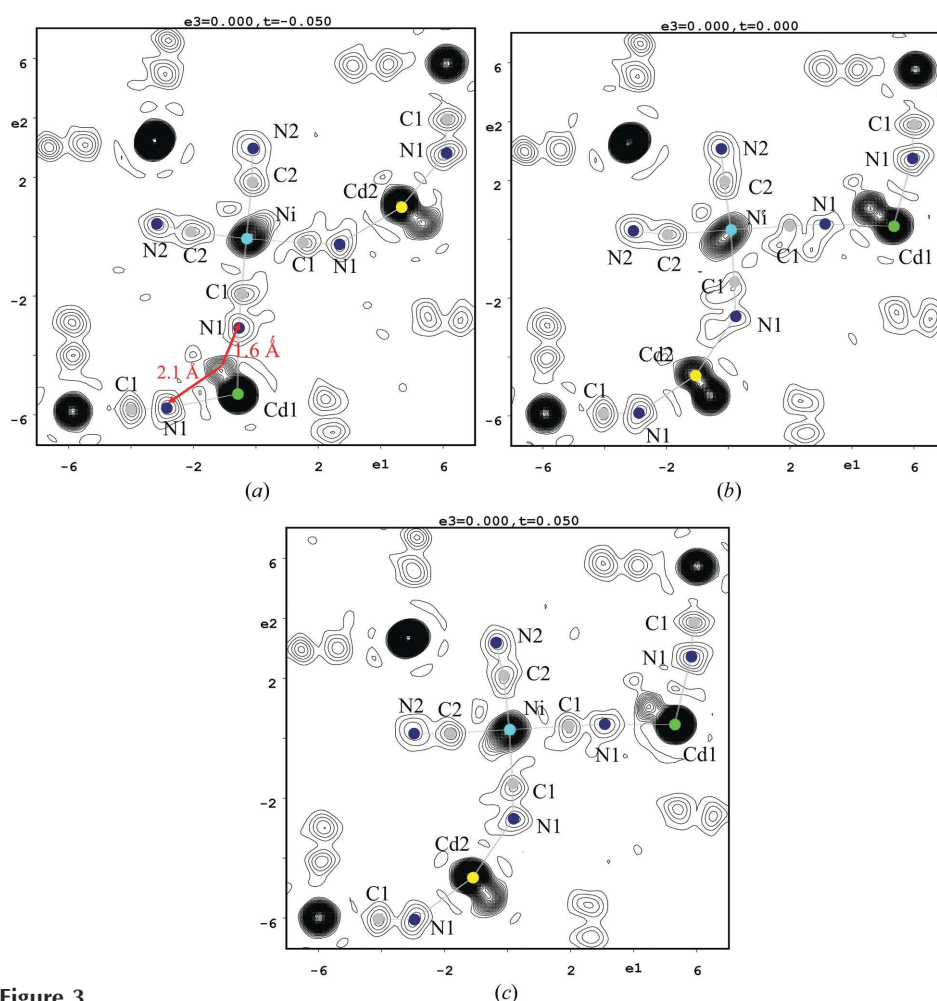


Figure 3

Sections through the four-dimensional Fourier map showing the coordination of cadmium by two symmetry-related cyano C1–N1 groups. The section runs through the plane of $\text{Ni}(\text{CN})_2$ in the basic structure; e_1, e_2, e_3 are the Cartesian axis. The t coordinate of the sections is chosen to show the behaviour of the structure during an abrupt change in configuration. (a) The section for $t = -0.05$ shows the situation just before the jump. The Cd1 atom occupies the tetrahedral position, but the octahedral position Cd2 is already arising. (b) The section for $t = 0$ shows the situation during the jump. Both possible positions for Cd, C1 and N1 prolonged to the new Ni position. (c) The section for $t = 0.05$ shows the situation just after the jump. The tetrahedral position of cadmium is vanishing.

between the two discontinuous coordination modes is not as sharp as expected and that some mixing probably exists between them. However, all attempts to describe the behavior of the structure in this transition area in more detail were unsuccessful. It is important to note that the tetrahedral coordination of the cationic central atom is rather rare among tetracyanonickelates. $[\text{Zn}_2(\text{en})_3\{\text{Ni}(\text{CN})_4\}_2]\cdot 3\text{H}_2\text{O}$ (Černák *et al.*, 1992) was considered as an example. The existence of both coordination modes of Cd atoms within the same compound may be explained by the small energy difference between the two coordination modes due to the spherically symmetric electronic configuration d^{10} of the central Cd atom.

Fig. 6 gives a detailed view of the neighborhood of cadmium with tetrahedral and octahedral coordination. The $[-\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_\infty$ chain to which the central Cd atom belongs is surrounded by six other chains, of

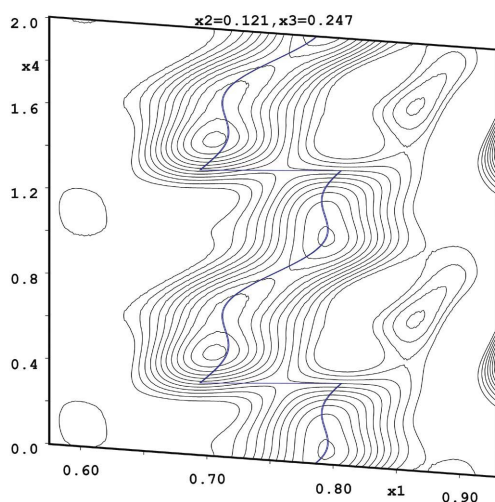


Figure 4

The x_3 - x_4 section through the four-dimensional Fourier map showing the positional modulation of the N1 atom. The x_2, x_3 coordinates are equal to those of N1 in the basic structure. The refined modulation curve is the combination of a sawtooth function with two harmonic waves.

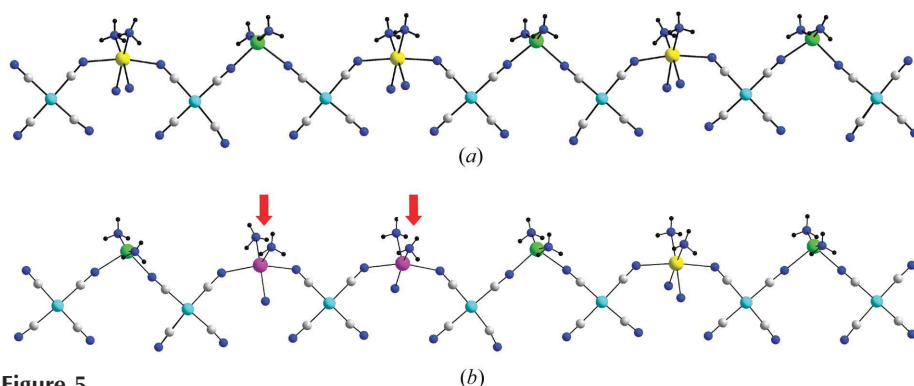


Figure 5

The modulation along the $[-\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_\infty$ chain. The non-localized H atoms are not indicated in the figures. (a) The most common situation: cadmium has alternating octahedral and tetrahedral coordination. (b) Intermediate states in which cadmium exhibits penta coordination are indicated by red arrows.

Table 2

Selected interatomic distances (Å) and angles (°) in the modulated structure of $[\text{Cd}(\text{NH}_3)_3\text{Ni}(\text{CN})_4]$.

	Average	Minimal	Maximal
Cd1—N1	2.28 (3)	2.23 (3)	2.38 (2)
N1—Cd1—N1 ⁱ	101.6 (12)	99.7 (15)	102.8 (12)
N1—Cd1—N3	98.6 (9)	95.0 (8)	102.3 (10)
N1—Cd1—N3 ⁱ	99.4 (9)	92.1 (7)	106.0 (11)
N1—Cd1—N2 ⁱⁱ	170.6 (11)	162.9 (8)	174.6 (10)
N1—Cd1—N2 ⁱⁱⁱ	87.5 (7)	80.4 (6)	93.4 (9)
Cd1—N3	2.187 (19)	2.046 (19)	2.25 (2)
N3—Cd1—N3 ⁱ	150.3 (14)	148.8 (13)	152.6 (19)
N3—Cd1—N2 ⁱⁱ	79.0 (8)	75.4 (7)	82.3 (8)
N3—Cd1—N2 ⁱⁱⁱ	79.4 (8)	76.7 (7)	81.6 (8)
Cd1—N2 ⁱⁱ	3.03 (3)	2.70 (3)	3.33 (3)
N2 ⁱⁱ —Cd1—N2 ⁱⁱⁱ	83.4 (8)	83.1 (7)	83.7 (10)
Bond-valence sum	2.08 (15)	2.03 (15)	2.33 (15)
Cd2—N1	2.39 (2)	2.249 (15)	2.470 (17)
N1—Cd2—N1 ⁱ	165.1 (10)	155.0 (10)	172.7 (12)
N1—Cd2—N3	93.7 (7)	91.4 (7)	96.1 (9)
N1—Cd2—N3 ⁱ	95.2 (7)	85.7 (6)	109.0 (9)
N1—Cd2—N4	85.5 (9)	78.4 (7)	88.3 (9)
N1—Cd2—N4 ⁱ	85.3 (8)	82.7 (8)	86.8 (8)
Cd2—N3	2.305 (18)	2.222 (17)	2.516 (17)
N3—Cd2—N3 ⁱ	100.6 (8)	95.4 (10)	109.5 (7)
N3—Cd2—N4	169.3 (8)	152.7 (7)	175.6 (11)
N3—Cd2—N4 ⁱ	90.2 (7)	82.5 (5)	96.0 (6)
Cd2—N4	2.40 (2)	2.320 (18)	2.596 (18)
N4—Cd2—N4 ⁱ	83.0 (10)	77.8 (8)	86.4 (12)
Bond-valence sum	1.97 (5)	1.69 (4)	2.16 (5)
Ni—C1	1.85 (2)	1.78 (3)	1.89 (3)
C1—Ni—C1 ^{iv}	90.5 (9)	89.8 (6)	90.9 (10)
C1—Ni—C2	89.6 (9)	87.5 (8)	93.1 (11)
C1—Ni—C2 ^{iv}	178.4 (10)	175.9 (13)	179.9 (9)
Ni—C2	1.865 (19)	1.687 (19)	2.065 (19)
C2—Ni—C2 ^{iv}	90.2 (8)	87.1 (8)	94.1 (8)
N1—C1	1.15 (3)	1.12 (2)	1.18 (4)
Cd1—1—C1	175 (2)	167.9 (14)	178 (2)
Cd2—N1—C1	140.8 (18)	135.9 (14)	145.4 (14)
Ni—C1—N1	178 (2)	177 (2)	179.4 (17)
N2—C2	1.15 (3)	1.11 (3)	1.20 (3)
Ni—C2—N2	176.1 (18)	168.5 (17)	179.9 (18)
Cd1—N2—C2	98.9 (14)	90.3 (13)	108.9 (14)

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

which only three independent ones are plotted. Several interactions contribute to the packing forces between the chains; among them the important role of hydrogen bonds of the $\text{N}-\text{H}\cdots\text{N}(\equiv\text{C})$ type is obvious (for $\text{N}\cdots\text{N}$ distances shorter than 3.35 Å, see Table 3). Such hydrogen bonds are often present in the structures of cyanocomplexes. The non-localized H atoms bonded to the N4 atom cannot make any contribution to the interchain interactions as the relevant $\text{N}\cdots\text{N}$ distances are too long (>3.5 Å).

Fig. 6(a) shows the weak interactions around the Cd atom in the

Table 3
Possible hydrogen bonds in the structure.

	Average	Minimal	Maximal
N3...N2 ⁱ	3.22 (2)	3.11 (2)	3.28 (2)
N3—H31	0.85†	0.85†	0.85†
H31...N2 ⁱ	2.45 (11)	2.28 (11)	2.66 (12)
N3—H31—N2 ⁱ	153 (10)	129 (10)	164 (11)
N3...N2 ⁱⁱ	3.22 (2)	3.11 (2)	3.28 (2)
N3—H32	0.85†	0.85†	0.85†
H32...N2 ⁱⁱ	2.43 (10)	2.32 (10)	2.58 (9)
N3—H32—N2 ⁱⁱ	159 (9)	154 (9)	166 (9)

Symmetry codes: (i) $x, -y, -\frac{1}{2} + z$; (ii) $2 - x, -y, -z$. † Restrained to that value during the refinement.

tetrahedral position. The NH₃ ligands bonded to the Cd atom form hydrogen bonds 1, 2, 3 and 4 to the neighboring chains on the right and on the left. The bonds are relatively stable during the modulation. Moreover, the Cd atom is rather close (distances 5,6) to the two symmetrically related N atoms of the

terminal cyano groups of the third chain. These two distances are strongly affected by the modulation and vary between 2.7 and 3.33 Å, see Table 2. Their importance for the structure is apparent from the fact that they never achieve their maximum length simultaneously. It should be noted that the tetrahedral coordination of Cd1 in the direction towards the 5,6 bonds is strongly distorted (flattened), which is perceptible from the N3—Cd1—N3ⁱ angle. A situation comparable to that observed for Cd (tetrahedral with an additional somewhat weaker interaction) was found in K₂[Cd(H₂O)Cu₄(CN)₈].1.5H₂O; in this compound the Cd atom is coordinated by four N atoms from the bridging cyano groups with Cd—N bond lengths in the range 2.178–2.253 Å, and by an O atom of the ligand water at a longer distance of 2.603 (7) Å. The N—Cd—N angles exhibit values in the range 92.4–137.2°, while the O—Cd—N angles are equal to 80.5, 80.8, 84.9 and 173.0° (Nishikiori, 1996). Quite a regular square-pyramidal coordination of the Cd atom was found in [Cd(H₂O)₂Cu(CN)₃].2H₂O, in which

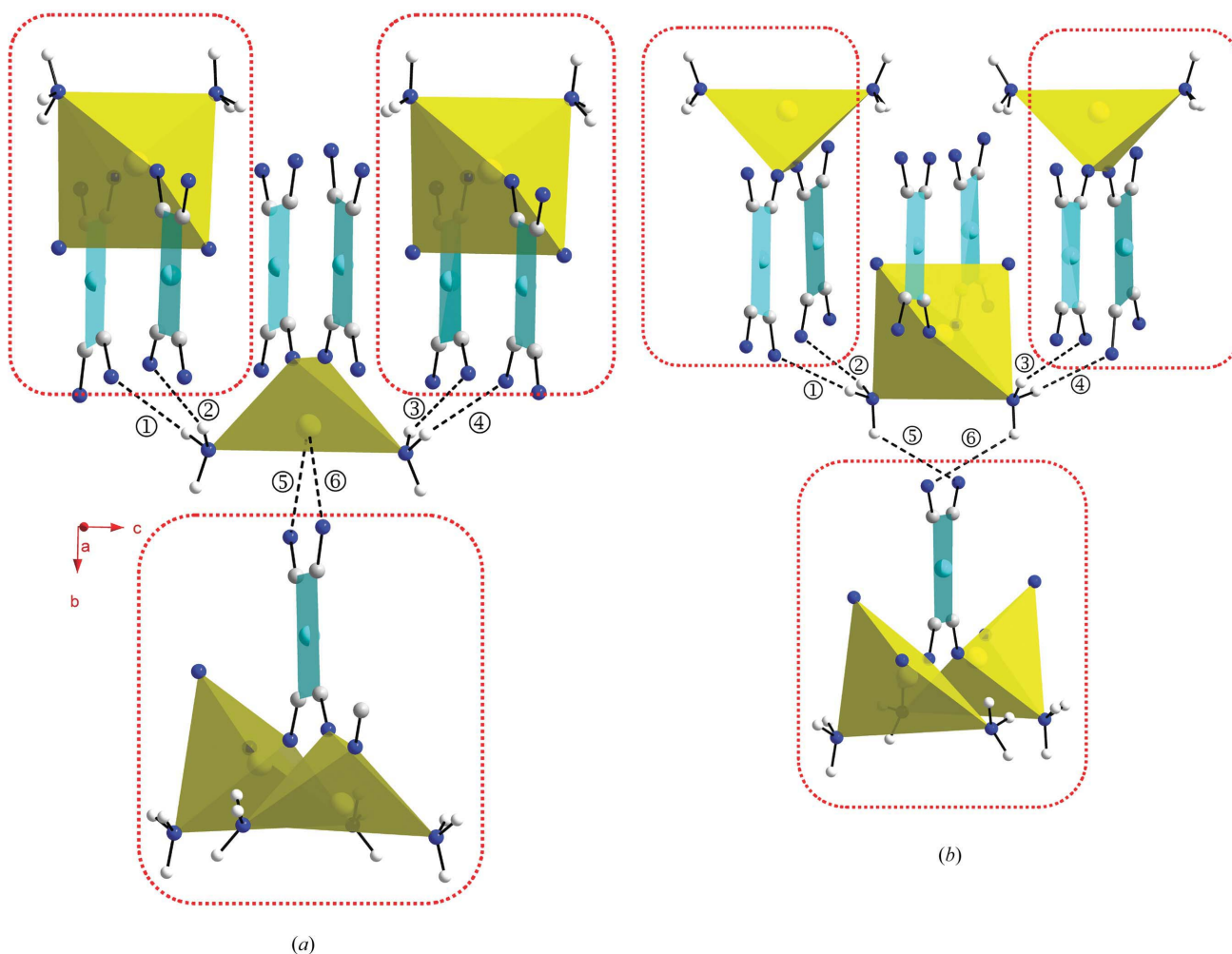


Figure 6
The inter-chain contacts between the $[-\text{Cd}(\text{NH}_3)_n-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_\infty$ chains. The central chain is surrounded by six other symmetry-equivalent chains; only three of them (enclosed in the dotted rectangles) are plotted to provide a simple view. The chains are propagated along the plane of the $[\text{Ni}(\text{CN})_4]^{2-}$ groups, see Fig. 5. (a) Possible hydrogen bonds for the tetrahedral cadmium position. The distances (Å): (1) 2.34, (2) 2.43, (3) 2.41, (4) 2.38, (5) 3.117 and (6) 2.864. (b) Possible hydrogen bonds for the octahedral cadmium position. The distances (Å): (1) 2.41, (2) 2.43, (3) 2.46, (4) 2.45, (5) 3.042, (6) 2.973.

the Cd—N bonds range from 2.219 (3) to 2.265 (6) Å and the Cd—O distances are 2.383 (6) and 2.393 (10) Å (Nishikiori, 1996).

In the octahedral position (Fig. 6*b*) the interactions with the left and the right chains remain of the same nature, being realised through bonds 1, 2, 3 and 4. On the other hand, the essential shift of cadmium upwards does not allow direct contact with the cyano groups of the third chain. We can speculate that the contacts to the third chain are replaced by 5,6 hydrogen bonds, which are, however, too weak to be of any significance. In fact, the basic positions of both the Cd atoms are unsatisfactory; the tetrahedral position allows bonding of the third chain, but it is not suitable for the Cd atom, while in the octahedral coordination bonding to the third chain is difficult. This contradiction may be considered to be the driving force for the modulation in the crystal.

Previous structure analyses of similar compounds [$\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, [$\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ and [$\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$], all containing the octahedral CdN_6 unit; Nishikiori *et al.*, 1989; Kappenstein & Černák, 1987; Yuge *et al.*, 1995] showed bond lengths of 2.32–2.44, 1.85–1.88 and 1.13–1.15 Å for Cd—N, Ni—C and C≡N bonds, respectively. In the title compound the observed average values for the tetracyanonickelate anion are practically the same (see Table 2). Cd2—N bonds of octahedrally coordinated cadmium exhibit values in the range 2.30–2.41 Å, while the minimal (2.22 Å) and maximal (2.60 Å) values deviate somewhat more. These values (taking into account the modulation) are in agreement with those previously reported. Tetrahedrally coordinated cadmium exists in $\text{Cd}(\text{CN})_2$, where the Cd—N distance at 295 K is 2.196 (3) Å (Hoskins & Robson, 1990). This is in line with the average Cd1—N distances we observed between 2.19 and 2.28 Å.

The C—Ni—C and Ni—C≡N angles observed in the anion were close to the ideal values of 90 and 180°. With regard to the N—Cd—N bond angles in Cd1N_4 and Cd2N_6 units, the angles in the Cd1N_4 tetrahedron are more affected by the modulation (see Table 2). The largest deviation [$150.3(14)^\circ$] of the angle, the N3—Cd—N3^i , has already been discussed in detail. The observed values of the Cd—N1≡C1 angles are modulated between 167.9 and 178° and between 135.9 and 145.4° for tetrahedrally and octahedrally coordinated Cd atoms, respectively; such values are often found in polymeric cyano-complexes (Yuge *et al.*, 1995).

The crystal structure of [$\text{Cd}(\text{NH}_3)_3\text{Ni}(\text{CN})_4$] displays some similarity with the structure of [$\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$] due to the one-dimensional character of the structure and the *cis* positions of the bridging cyano ligands. On the other hand, it is, despite a similar general composition, different from that of [$\text{Cu}(\text{NH}_3)_3\text{Ni}(\text{CN})_4$] with regard to the dimensionality as well as the coordination numbers of the cationic central atom (five in the Cu^{II} compound *versus* four and six in the Cd^{II} compound); the only similarity being the *cis* positions of the bridging cyano ligands in the tetracyanonickelate anions. The modulated character and coordination of the central cation

make the title compound a unique representative of cyano-complexes.

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