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Key indicators

Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{N}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.023
wR factor = 0.062
Data-to-parameter ratio = 11.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**catena-Poly[[bis(*N,N*-dimethylformamide- κO)-nickel(II)]-di- μ -1,5-dicyanamido- $\kappa\text{N}^1:\kappa\text{N}^5$]**

In the crystal structure of the title complex, $[\text{Ni}(\text{C}_2\text{N}_3)_2(\text{C}_3\text{H}_7\text{NO})_2]_n$ or $[\text{Ni}(\text{dca})_2(\text{DMF})_2]_n$, where dca is dicyanamide and DMF is *N,N*-dimethylformamide, each Ni^{II} atom is six-coordinated in a distorted octahedral coordination environment. Four N atoms from four dca ligands fill the equatorial positions, and two O atoms from two DMF ligands fill the axial positions. The structure is isostructural with $[\text{Co}(\text{dca})_2(\text{DMF})_2]_n$ but is not isostructural with $[\text{Mn}(\text{dca})_2(\text{DMF})_2]_n$. The Ni^{II} atom and the dicyanamide bridging ligand occupy special positions of symmetry $2/m$ and m , respectively. The structure consists of uniform neutral chains where neighbouring Ni^{II} atoms are connected through two asymmetric end-to-end dca bridges.

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Comment

Dicyanamide (dca), $[\text{N}(\text{CN})_2]^-$, complexes have been studied extensively recently because of their fascinating topologies and interesting magnetic properties (Batten *et al.*, 1998; Miller & Manson 2001; Jensen *et al.*, 2000; Riggio *et al.*, 2001). A number of nickel(II)-dca complexes have been reported (Sun, *et al.*, 2000; Wang *et al.*, 2004; Konor *et al.*, 2005). Our research interest is the construction of novel topologies of cyano complexes and studying their magnetic properties (Shen *et al.*, 2004, 2003). In the present work, we report the crystal structure of a one-dimensional chain polymer, *viz.* $[\text{Ni}(\text{dca})_2(\text{DMF})_2]_n$, (I).

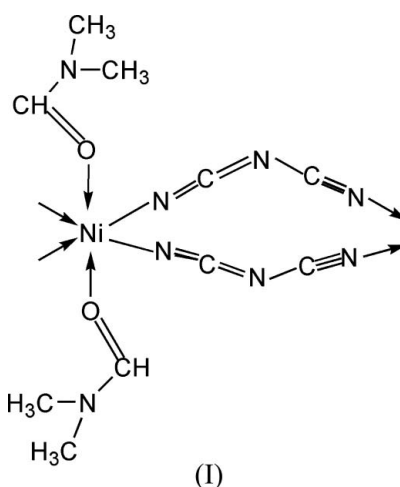


Fig. 1 shows the local coordination about the nickel(II) centre in (I). The structure of (I) is isostructural with $[\text{Co}(\text{dca})_2(\text{DMF})_2]_n$ (Tong *et al.*, 2003) but is not isostructural with $[\text{Mn}(\text{dca})_2(\text{DMF})_2]_n$ (Batten *et al.*, 1999). The space group of $[\text{Co}(\text{dca})_2(\text{DMF})_2]_n$ reported by Dong *et al.* (2003)

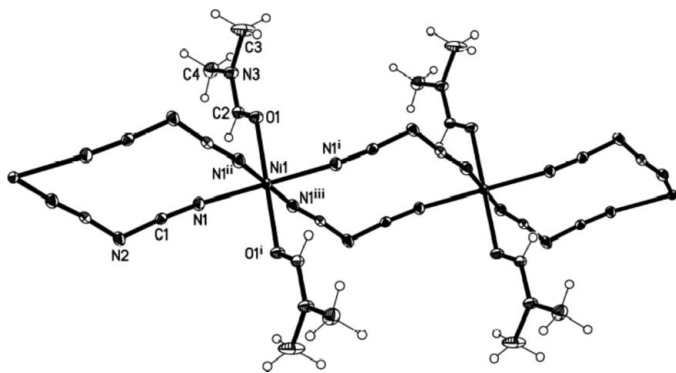


Figure 1
Part of the polymeric structure of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, y, 1 - z$; (iii) $x, 1 - y, z$.]

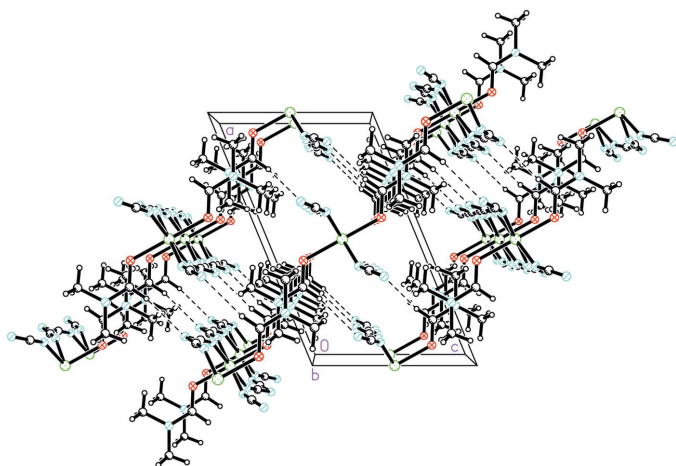


Figure 2
The packing in (I), showing the C—H...N hydrogen-bond interactions as dashed lines.

has been described incorrectly in C_2 ; it should be C_2/m , as reported by Tong *et al.* (2003). The structure of (I) consists of uniform neutral chains in which neighbouring nickel(II) atoms are connected through two asymmetric end-to-end dca bridges. The coordination geometry of the nickel(II) atom is distorted octahedral, being coordinated by four N atoms of four symmetry-related dca ligands in the equatorial plane and two O atoms of two symmetry-related DMF ligands at the axial positions. The N—Ni—N bond angles are in the range $87.84(6)$ – $92.16(6)^\circ$, close to 90° . The four Ni—N(dca) bond lengths in (I) are all $2.0733(11)$ Å, corresponding to the values reported in the dca-bridged nickel(II) complexes [Ni(apo)-(dca)₂] [$2.043(4)$ – $2.096(4)$ Å; apo = 2-aminopyridine N-oxide; Sun *et al.*, 2000] and [Ni(tn)₂(dca)](ClO₄) [$2.095(4)$ and $2.116(4)$ Å; tn = trimethylenediamine; Li *et al.*, 2002], and shorter than the Mn—N bond lengths [$2.218(2)$ and $2.203(2)$ Å] in [Mn(dca)₂(DMF)₂]_n (Batten *et al.*, 1999) and the Co—N bond lengths [$2.123(2)$ Å] in [Co(dca)₂(DMF)₂]_n (Tong *et al.*, 2003); this is what one would expect from the ionic radii ($\text{Ni}^{2+} < \text{Co}^{2+} < \text{Mn}^{2+}$). The two Ni—O (DMF) bond

lengths are both $2.0670(13)$ Å, corresponding to the values [$2.0776(19)$ Å] in [Ni(pmbp)₂(DMF)₂] [Hpmbp = 1-phenyl-3-methyl-4-benzoyl-1*H*-pyrazol-5(4*H*)-one; Shen & Yuan 2004] and shorter than the M—O bond lengths in [Mn(dca)₂(DMF)₂]_n [Mn—O = $2.199(2)$ Å] and [Co(dca)₂(DMF)₂]_n [Co—O = $2.096(2)$ Å].

The dicyanamide (dca) ligand adopts an end-to-end coordination mode. Two dca ions link two nickel(II) atoms to form a 12-membered Ni(dca)₂Ni ring and neighbouring rings share the nickel(II) atoms to form a chain of [Ni(dca)₂]_n. The chains are linear, the Ni(dca)₂Ni rings being in a slight chair conformation.

The free dicyanamide (dca) ligand possesses C_{2v} symmetry. The dca ligand in (I) also adopts essentially C_{2v} symmetry, with a nitrile C≡N bond length of $1.1545(18)$ Å for N1≡C1, showing the triple-bond character. The bond angle related to the amide N atom, C1—N2—C1($x, 1 - y, z$), is $118.61(16)^\circ$, corresponding to an amide N atom with an sp^2 hybrid orbital; that related to the nitrile group, N1≡C1—N2, is $174.95(13)^\circ$, corresponding to N1 and C1 with an sp hybrid orbital.

The chains propagate parallel to the crystallographic b axis, the Ni...Ni distance along the chain being equal to the b axis length, $7.3166(7)$ Å. The chains interdigitate such that each DMF ligand lies between two DMF ligands of an adjacent chain, with a shortest Ni...Ni interchain distance of $7.628(2)$ Å. Adjacent chains are held together by a weak C—H...N hydrogen bond, forming layers parallel to the ab plane (Fig. 2 and Table 2).

Experimental

An aqueous solution (10 ml) of Ni(NO₃)₂·6H₂O (0.146 g, 0.5 mmol) was added to a DMF solution (10 ml) of Na[N(CN)₂] (0.090 g, 1.0 mmol). Slow evaporation of the resulting mixture led to green crystals suitable for X-ray diffraction analysis. Analysis found: C 35.53, H 4.12, N 33.31%; calculated for C₁₀H₁₄N₈NiO₂: C 35.64, H 4.19, N 33.26%.

Crystal data

[Ni(C₂N₃)₂(C₃H₇NO)₂]
 $M_r = 336.98$
 Monoclinic, C_2/m
 $a = 13.3866(17)$ Å
 $b = 7.3166(7)$ Å
 $c = 8.0595(10)$ Å
 $\beta = 112.503(3)^\circ$
 $V = 729.28(15)$ Å³
 $Z = 2$

$D_x = 1.535$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1804 reflections
 $\theta = 3.2$ – 27.5°
 $\mu = 1.35$ mm⁻¹
 $T = 193(2)$ K
 Block, green
 $0.40 \times 0.21 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.646$, $T_{\max} = 0.774$
 4029 measured reflections

900 independent reflections
 887 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 27.5^\circ$
 $h = -17 \rightarrow 15$
 $k = -8 \rightarrow 9$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.062$
 $S = 1.03$
 900 reflections
 76 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.3824P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni1—O1	2.0670 (13)	N2—C1	1.3074 (15)
Ni1—N1	2.0733 (11)	N3—C2	1.319 (2)
O1—C2	1.243 (2)	N3—C3	1.448 (3)
N1—C1	1.1545 (18)	N3—C4	1.458 (3)
O1—Ni1—N1	91.61 (4)	N1—Ni1—N1 ⁱⁱⁱ	87.84 (6)
O1 ⁱ —Ni1—N1	88.39 (4)	C1 ^{iv} —N2—C1	118.61 (16)
N1—Ni1—N1 ⁱⁱ	92.16 (6)	N1—C1—N2	174.95 (13)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + 1, z$; (iii) $-x + 1, y, -z + 1$; (iv) $x, -y + 2, z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots N2 ^v	0.95 (1)	2.51 (1)	3.453 (2)	169 (2)

Symmetry code: (v) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.

H atoms were found in a difference Fourier map and refined with bond-length restraints of C—H = 0.95 (1) \AA for the methyl groups and the H \cdots H distance restrained to 1.50 (1) \AA . One of two independent H atoms lies on the mirror plane.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; method used to solve

structure: the coordinates of the Co structure of Tong *et al.* (2003) were used; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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