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catena-Poly[[bis(*N*,*N*-dimethylformamide-κO)-nickel(II)]-di-μ-1,5-dicyanamido-κN^1:κN^5]

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(N–C) = 0.003 Å
R factor = 0.023
wR factor = 0.062
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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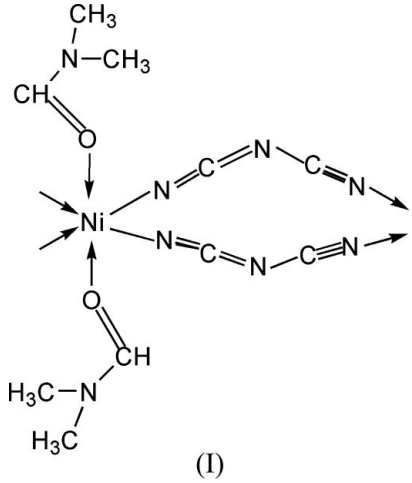
In the crystal structure of the title complex, $[Ni(C_2N_3)_2(C_3H_7NO)_2]_n$ or $[Ni(dca)_2(DMF)_2]_n$, where dca is dicyanamide and DMF is *N*,*N*-dimethylformamide, each Ni^{II} atom is six-coordinated in a distorted octahedral coordination environment. Four N atoms from four dca ligands fill the equatorial positions, and two O atoms from two DMF ligands fill the axial positions. The structure is isostructural with $[Co(dca)_2(DMF)_2]_n$ but is not isostructural with $[Mn(dca)_2(DMF)_2]_n$. 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.

Comment

Dicyanamide (dca), $[N(CN)_2]^-$, 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*. $[Ni(dca)_2(DMF)_2]_n$, (I).



(I)

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

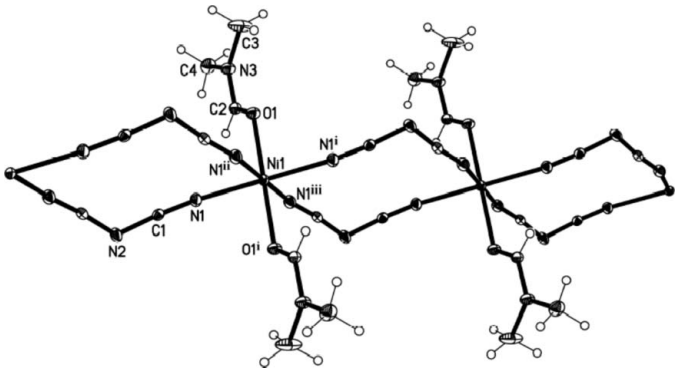


Figure 1
Part of the polymeric structure of (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, 1-z$; (iii) $x, 1-y, z$.]

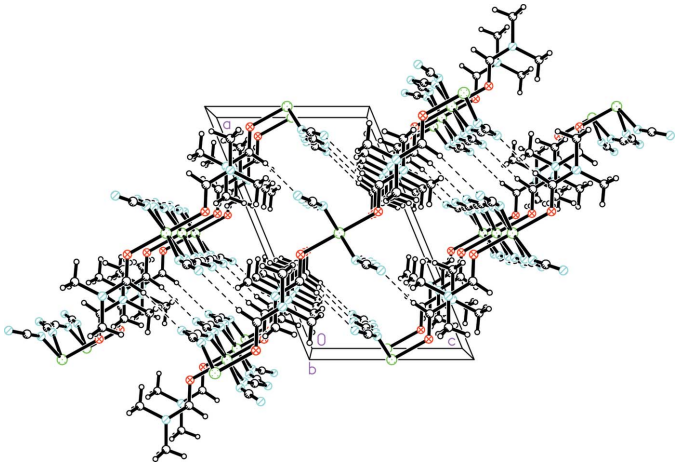


Figure 2
The packing in (I), showing the C—H···N hydrogen-bond interactions as dashed lines.

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)°, 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 $[Ni(apo)_2(dca)_2]$ [2.043 (4)–2.096 (4) Å; apo = 2-aminopyridine N-oxide; Sun *et al.*, 2000] and $[Ni(tn)_2(dca)](ClO_4)$ [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 ($Ni^{2+} < Co^{2+} < Mn^{2+}$). 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)°, 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)°, 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 $Ni(NO_3)_2·6H_2O$ (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 $C_{10}H_{14}N_8NiO_2$: C 35.64, H 4.19, N 33.26%.

Crystal data

$[Ni(C_2N_3)_2(C_3H_7NO)_2]$
M_r = 336.98
Monoclinic, *C*2/*m*
a = 13.3866 (17) Å
b = 7.3166 (7) Å
c = 8.0595 (10) Å
β = 112.503 (3)°
V = 729.28 (15) Å^3
Z = 2
D_x = 1.535 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1804 reflections
θ = 3.2–27.5°
μ = 1.35 mm^{-1}
T = 193 (2) K
Block, green
0.40 × 0.21 × 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_{int} = 0.018
θ_{max} = 27.5°
h = −17 → 15
k = −8 → 9
l = −10 → 10

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.3824P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.062$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.47$ e Å^{-3}
900 reflections	
76 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···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) Å for the methyl groups and the H···H distance restrained to 1.50 (1) Å. 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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