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The crystal structure of poly[bis(*N,N*-dimethylformamide- κ^1O)-tetrakis(μ_2 -cyanido- κ^2C :*N*)dinickel(II)], $C_{10}H_{14}N_6O_2Ni_2$

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.2 × 0.08 × 0.05 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	3.30 mm ⁻¹
Diffractometer, scan mode:	XtaLAB AFC12, ω -scans
$\theta_{\max}$, completeness:	73.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2748, 783, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 713
$N(\text{param})_{\text{refined}}$:	71
Programs:	CrysAlis ^{PRO} [1], OLEX2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	1.0000	0.5000	0.5000	0.0171(3)
Ni2	0.5000	0.0000	0.5000	0.0178(3)
O1	0.8655(3)	0.5000	0.36693(15)	0.0253(5)
N1	0.8040(3)	0.2983(3)	0.53023(13)	0.0218(4)
N2	0.5848(4)	0.5000	0.2681(2)	0.0272(6)
C1	0.6917(3)	0.1821(3)	0.52274(15)	0.0206(5)
C2	0.6801(5)	0.5000	0.3500(2)	0.0233(7)
H2	0.6040	0.5000	0.3987	0.028*
C3	0.3670(6)	0.5000	0.2541(3)	0.0405(10)
H3A	0.315(6)	0.5000	0.320(3)	0.030(11)*
H3B	0.329(5)	0.396(5)	0.217(3)	0.059(10)*
C4	0.6906(7)	0.5000	0.1877(3)	0.0408(10)
H4A	0.654(5)	0.397(5)	0.153(2)	0.055(10)*
H4B	0.828(8)	0.5000	0.202(4)	0.055(15)*

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Abstract

$C_{10}H_{14}N_6O_2Ni_2$, monoclinic, $I2/m$ (no. 12), $a = 6.7377(1)$ Å, $b = 7.3500(1)$ Å, $c = 14.8647(2)$ Å, $\beta = 96.051(1)^\circ$, $V = 732.030(18)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0314$, $wR_{\text{ref}}(F^2) = 0.0996$, $T = 150.01(10)$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Source of materials

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.030 g), 5,15-bis(4-carboxyphenyl)porphyrin (0.05 mmol, 0.023 g), *N,N*-dimethylformamide (4 mL), acetonitrile (2 mL) and water (1 mL) was sonicated for 30 min. Then the reaction mixture was transferred to Teflon-lined stainless steel reactor and placed in the oven. Subsequently, the temperature was kept 393 K for 3 days. After cooling to room temperature at a rate of 6 K·h⁻¹, brown block crystals of the title compound were

obtained as a side product. Yield: 5 mg (27%, based on Ni). Anal. Calcd. for C_{2.5}H_{3.5}N_{1.5}O_{0.5}Ni_{0.5} (%): C, 32.67; H, 3.84; N, 22.86. Found: C, 32.25.; H, 3.26; N, 22.43.

Experimental details

Crystallographic data collection and reduction were performed using the program CrysAlis^{PRO} [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with the ShelXL [4] refinement package. Coordinates of some hydrogen atoms were refined without any constraints or restraints others were included using a riding model (see Suppl. Material). The U_{iso} values were set to be $1.5U_{eq}$ of the carrier atom for methyl hydrogen atoms and $1.2U_{eq}$ for formyl hydrogen atom.

Comment

Hofmann type complexes, as one of the longest-known cyano-bridged coordination compounds, are still extensively investigated in recent years due to their unique structures and properties [5–9]. Up to now, a number of Hofmann complexes, varying from two-dimensional to three-dimensional structures, have been synthesized by mediating metal ions, coordinated small molecules and guest molecules [10–19]. However, the preparation method remains the classic solution chemistry method. To the best of our knowledge, the effective solvothermal method for preparing Hofmann complexes has not been reported so far. Fortunately, a Hofmann-DMF-type compound, [Ni(DMF)₂Ni(CN)₄]_n (where DMF = *N,N*-dimethyl formamide), was unexpectedly synthesized by solvothermal method when the porphyrin-based Ni-MOFs were attempted to synthesize by assembling 5,15-bis(4-carboxyphenyl)porphyrin ligand and Ni(NO₃)₂. Although two isomorphous compounds have been reported [5, 6], their central metal ions and preparation method are different from those of the title compound.

The asymmetric unit of the title compound contains two Ni(II) ions with occupancies of 0.25, one cyanide ion (CN[−]), a half DMF molecule. It is particularly worth mentioning that the coordinated CN[−] ions derive not from the addition of the cyano compounds, but from the thermal decomposition of the solvent acetonitrile. Each Ni1 center is coordinated by four cyanide ligands in the equatorial positions and two oxygen atoms from two coordinated DMF molecules at the axial positions to form an approximately regular octahedron geometry (NiO₂N₄; A = $-x + 2, -y + 1, -z + 1$; B = $-x + 2, y, -z + 1$; C = $x, -y + 1, z$; cf. the figure). Ni1 and four coordinated nitrogen atoms are in the same plane (p1). Each Ni2 center exhibits a four-coordinated square geometry (NiC₄; D = $-x + 1, -y, -z + 1$; E = $x, -y, z$; F = $-x + 1, y, -z + 1$; cf. the figure) by four carbon atoms from four cyanide ligands. Ni2 and four

coordinated carbon atoms are also coplanar (p2). The dihedral angle between the two planes (p1 and p2) is 146.9(9)^o (cf. the figure). The Ni–C, Ni–N and Ni–O bond lengths are 1.866(2), 2.0663(19) and 2.088(2) Å, respectively. The neighbouring Ni1 and Ni2 centers are connected by cyanide ligands to furnish a two-dimensional layered structure. The adjacent layers are further assembled by van-der-Waals forces to extend into a three-dimensional network structure. All bond lengths and bond angles within the title structure are in the typical ranges [20, 21].

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