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Synthesis and Crystal Structure of a Cyanide-Bridged One-Dimensional Nickel Complex with *trans*-Cn–Ni(En)$_2$–CN Structure[1]

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Abstract—The synthesis and crystal structure of the cyano-bridged complex $\{Ni(En)_2[Ni(CN)_4]\}_n$ are reported. The complex was synthesized by the reaction of $[Ni(En)_2](ClO_4)_2$ and $K_2[Ni(CN)_4]$ in an H-shaped tube. The crystals are monoclinic, space group $P2_1/c$ with a = 7.0917(4), b = 10.6629(5), c = 9.4975(5) Å, β = 108.193°, M = 170.85, Z = 4, V = 682.27(6) Å^3. The title complex reveals the *trans*-CN–Ni(En)$_2$–NC structure.

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INTRODUCTION

In recent years, the design and synthesis of cyano-bridged complexes become an interesting area because of their rich and interesting structure, magnetic properties, and strong tendency to construct rigid coordination bonding networks [1–4]. The most popular approach to the synthesis of cyano-bridged magnetic materials was to use an anionic building block $[M(CN)_x]^{n-}$ in conjunction with cationic assembler units of the type $[M'(ligand)_x]^{m+}$ [5]. Cyanometallate anions can be diamagnetic, viz., $[Ag(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Au(CN)_4]^-$, $[Fe(CN)_6]^{4-}$, or paramagnetic, viz., $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Mo(CN)_8]^{4-}$ etc. [6]. The tetracyano-niclate anion $[Ni(CN)_4]^{2-}$ is an ideal building block, because it possesses the ability to link various central atoms and thus form molecules with 1D, 2D, and 3D structures [7–13]. In this paper, we reported the synthesis and structures of the 1D cyano-bridged complex $\{Ni(En)_2[Ni(CN)_4]\}_n$ (**I**), which reveals the wave-shaped structure using the *trans*-CN–Ni(En)$_2$–NC chain.

EXPERIMENTAL

Physical measurement. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using an EA3000 CHNS/O elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet Avatar 370 FT-IR spectrometer. The crystal determination was recorded on a Bruker Smart Apex CCD diffractometer.

Materials and synthesis. $[Ni(En)_2](ClO_4)_2$ and $K_2[Ni(CN)_4]$ were prepared according to the literature procedure [14]. All chemicals and solvents were of reagent grade and used as received.

Single crystals of **I** were grown in a methanol–water solution by a slow diffusion method using an H-shape tube. Crystals of $[Ni(En)_2](ClO_4)_2$ (0.38 g, 1 mmol) were dissolved in methanol–water (10 ml) and added in one arm, $K_2[Ni(CN)_4]$ (0.24 g, 1 mmol) was dissolved in water (10 ml) and added in another arm. Methanol–water solution filled the middle. Shiny deep purple single crystals suitable for X-ray analysis were obtained after a few days.

For $C_4H_8N_4Ni$			
anal. calcd, %:	C, 28.12;	H, 4.72;	N, 32.80.
Found, %:	C, 28.14;	H, 4.64;	N, 31.41.

IR spectrum (KBr; ν, cm^{-1}): 2115.06 s, 2145.46 s ν(C≡N).

Structure of X-ray determination. Crystal data and details of data collections and refinements for the structures reported are summarized in Table 1. Diffraction data were carried out on a Bruker Smart Apex CCD diffractometer with a graphite monochromate MoK_α radiation (λ = 0.71073 Å) at 299(2) K. The structure was solved by a direct method and refined by the full-matrix least-squares procedure on F^2 by the SHELXL-97 program [15]. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (no. 711445; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

[1] The article is published in the original.

Table 1. Crystal data and structure refinements of complex $\{Ni(En)_2[Ni(CN)_4]\}_n$

Parameter	Value
Formula weight	170.85
Temperature, K	299(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	7.0917(4)
b, Å	10.6629(5)
c, Å	9.4975(5)
β, deg	108.196(3)
V, Å^3	682.27(6)
Z	4
ρ_c, mg m^{-3}	1.663
μ_{Mo}, mm^{-1}	2.755
F(000)	352
θ range for data collection, deg	2.96–26.00
Index ranges	$-8 \le h \le 7$, $-13 \le k \le 12$, $-11 \le l \le 11$
Reflections collected/unique	4197/1332 (R_{int} = 0.0208)
Completeness to θ, %	99.6
Max and min transmission	0.6088 and 0.4920
Parameters	105
Goodness-of-fit on F^2	1.070
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0237, wR_2 = 0.0563
R indices (all data)	R_1 = 0.0305, wR_2 = 0.0601
Largest diff. peak and hole, e Å^{-3}	0.324 and –0.274

Table 2. Bond lengths and angles for complex **I**

Bond	d, Å	Bond	d, Å
Ni(1)–N(2)	2.0915(15)	Ni(2)–C(4)	1.869(2)
Ni(1)–N(1)	2.0953(15)	C(1)–N(1)	1.465(4)
Ni(1)–N(3)	2.1168(15)	C(2)–N(2)	1.478(4)
C(1)–C(2)	1.501(5)	C(3)–N(3)	1.150(2)
Ni(2)–C(3)	1.8639(19)	C(4)–N(4)	1.146(2)
Angle	ω, deg	Angle	ω, deg
N(2)Ni(1)N(1)	82.80(6)	C(3)N(3)Ni(1)	154.79(14)
N(2)Ni(1)N(3)	90.06(6)	C(3)Ni(2)C(4)	86.95(8)
N(2)C(2)C(1)	108.1(3)	N(1)C(1)C(2)	107.0(3)
N(3)C(3)Ni(2)	172.89(16)	C(1)N(1)Ni(1)	107.3(2)
N(4)C(4)Ni(2)	176.37(18)	C(2)N(2)Ni(1)	106.2(2)

RESULTS AND DISCUSSION

The IR spectra of complex **I** showed two strong cyanide stretching peaks at 2115.06 and 2145.46 cm^{-1}. Usually, splitting of cyanide stretching bands at about 2000–2100 cm^{-1} may be expected [16], and the formation of the cyano-bridges shifts the bands toward higher frequencies [17]. The strong band at 2145.46 cm^{-1} may, therefore, be attributed to ν(CN) of the bridging cyanides and that at 2115.06 cm^{-1} to the non-bridged ones. The ν(NH) stretching bands were found at 3335.98 and 3285.80 cm^{-1}, perhaps, due to the formation of hydrogen bonds.

The selected bond lengths and angles are presented in Table 2. The molecular structure and crystal packing scheme of the title complex is shown in Figs. 1 and 2, respectively.

The structure of complex **I** consists of alternating $[Ni(En)_2]^{2+}$ and $[Ni(CN)_4]^{2-}$ fragments linked by two cyanide ligands in a wave fashion. In the complex, the Ni(1) center is octahedral coordinated to the four nitro-

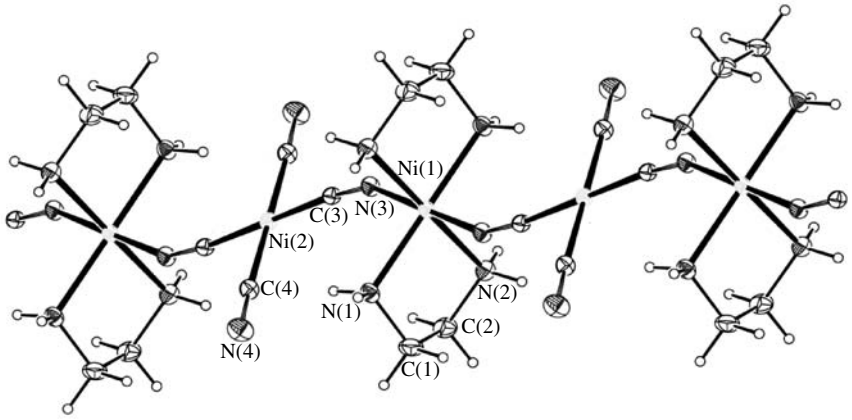

Fig. 1. The drawing showing the molecular structure of complex $\{Ni(En)_2[Ni(CN)_4]\}_n$.

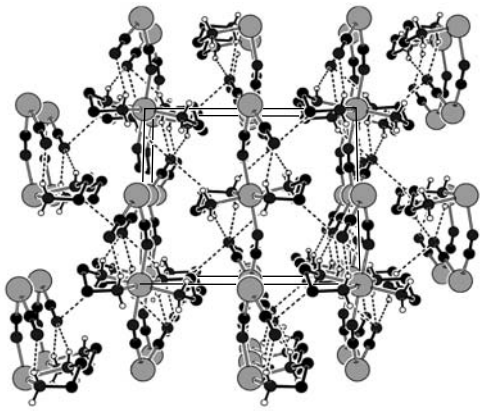

Fig. 2. Crystal packing of complex $\{Ni(En)_2[Ni(CN)_4]\}_n$.

gen atoms of two ethylenediamine molecules and two cyano nitrogen atoms in a *trans* configuration. One $[Ni(En)_2]^{2+}$ unit is linked by two $[Ni(CN)_4]^{2-}$ units via bridging cyano groups to produce a one dimensional wave-shaped structure using Ni(2)–CN–Ni$(En)_2$–NC chain. The title complex has no water molecules.

In summary, the cyanide-bridged one-dimensional nickel complex using the slow diffusion method has been synthesized and structurally characterized. X-ray crystallography of the complex reveals a wave-shaped structure using *trans*-Ni(2)–CN–Ni$(En)_2$–NC chain. The structure differs from the molecular structure of complex $[Ni(En)_2][Ni(CN)_4] \cdot 5H_2O$ [18], which owns the alternant *cis*-form and *trans*-form structures.

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