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Crystallographic report

Chain-like crystal structure of $[Ni(en)_2Ag(CN)_2][Ag(CN)_2]$

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[*catena*-Bis(1,2-diaminoethane)nickel(II)-μ-dicyanoargentate]-dicyanoargentate, $[Ni(en)_2Ag_2(CN)_4]$, was synthesized and its chain-like crystal structure was determined by X-ray crystal analysis.

KEYWORDS: nickel; diaminoethane; dicyanoargentate; coordination polymer

COMMENT

Dicyanoargenate anion $[Ag(CN)2]^-$ can act as a bridging spacer between central atoms leading to polymeric structures such as the chain-like coordination polymer of $[Cu(en)_2Ag_2CN_4]$.[1] It can be used to construct host–guest complexes,[2,3] supramolecules,[4,5] and low-dimensional magnetic materials, which are of current interest.[6] Other similar coordination polymers have been synthesized and characterized with X-ray crystal structure analysis.[7,8] Here, we report the synthesis and structure determination of the chain-like crystal $[Ni(en)_2Ag_2(CN)_4]$. The ORTEP view of the structure is shown in Fig. 1. It is formed of linear $[Ag(CN)_2]^-$ and infinite cationic chains of $[Ni(en)_2NCAgCN]^+$, containing nickel atoms bridged by a second kind of linear $[Ag(CN)_2]^-$, whose central silver has a small interaction with the central silver of the second linear $[Ag(CN)_2]^-$ (the distance is 3.289(3) Å). The cationic chain is not linear, but bent at the C2 atom with an angle of 164.4° and at the N2 atom with an angle of 170.6°. The layer configuration is woven by connecting the infinite cationic chains of $[Ni(en)_2NCAgCN]^+$ with $[Ag(CN)_2]^-$ by the weak interaction between Ag···Ag in the linear chain. Figure 2 shows how the three layers pack together, in which the two CN in $[Ag(CN)_2]^-$, just like two arms, point at the gap of two five-membered rings.

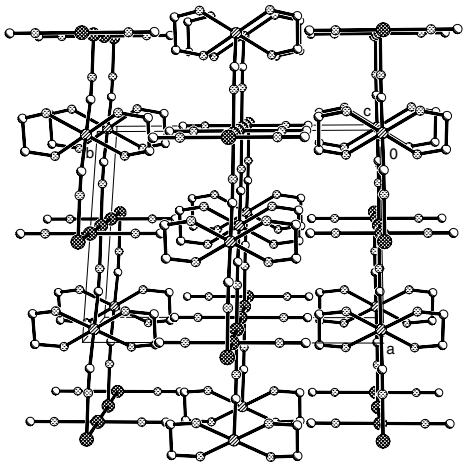

Figure 1. ORTEP plot showing the coordination environment of nickel and silver atoms at the 50% probability level. Key geometry parameters: Ni(1)–N(1) 2.093(3), Ni(1)–C(2) 2.113(4), Ag(1)–N(2) 2.051(5), Ag(1)–Ag(2) 3.289(3), Ag(2)–N(3) 2.045(7), C(2)–N(2) 1.135(7), N(1)–C(1) 1.450(5), N(3)–C(3) 1.126(9) Å; N(1)–Ni(1)–N(1)#1 180.00(11), N(1)–Ni(1)–N(1)#2 82.22(19), N(1)#1–Ni(1)–N(1)#2 97.78(18), N(1)–Ni(1)–C(2)#1 91.42(12), N(1)#1–Ni(1)–C(2)#1 88.58(12), N(2)–Ag(1)–N(2)#4 180.00(7), N(2)–Ag(1)–Ag(2) 71.12(14), N(2)#4–Ag(1)–Ag(2) 108.88(14), Ag(2)–Ag(1)–Ag(2)#5 180.0, N(3)#6–Ag(2)–N(3) 180.0, N(3)–Ag(2)–Ag(1) 90.0, N(2)–C(2)–Ni(1) 164.4(4), C(1)–N(1)–Ni(1) 107.7(2), C(2)–N(2)–Ag(1)170.6(4), C(3)–N(3)–Ag(2) 180.0, N(1)–C(1)–C(1)#2 107.6(3)°. Symmetry transformations used to generate equivalent atoms: #1, $-x, -y, -z+1$; #2, $-x, y, -z+1$; #3, $x, -y, z$; #4, $-x+1, -y, -z+1$; #5, $x, y, z-1$; #6, $-x+1, -y, -z+2$.

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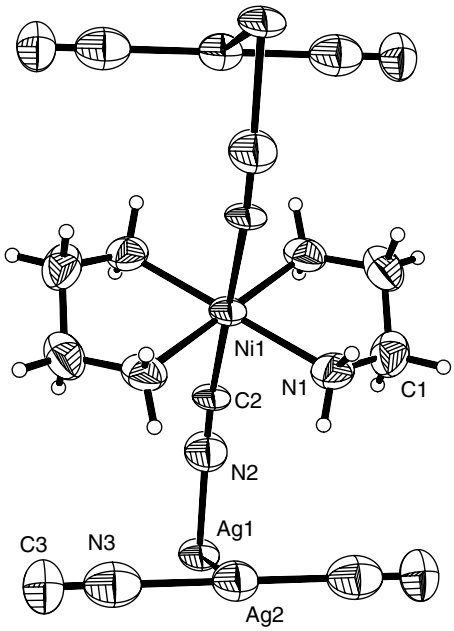

Figure 2. Packing diagram of the three layers.

EXPERIMENTAL

Synthesis

A mixture solution of 0.17 g (1 mmol) $AgNO_2$ and 0.19 g (3 mmol) of KCN was added to another mixture solution of 0.15 g (0.5 mmol) $Ni(NO_3)_2{\cdot}6H_2O$ and ethyldiamine. After stirring, a light-purple solution was obtained. Blue–purple block crystals were obtained 1 week later.

Crystallography

Intensity data were collected at 298 K on Smart Apex 2000 diffractometer for a crystal, $0.36 \times 0.35 \times 0.30\ mm^3$. $C_{16}H_{32}Ag_4N_{16}Ni_2$, $M = 2001.60$, monoclinic, $C2/m$, $a = 10.398(9)$ Å, $b = 13.054(11)$ Å, $c = 6.579(5)$ Å, $\alpha = 90.00°$, $\beta = 120.86(2)°$, $\gamma = 90.00°$, $V = 766.5(11)$ Å^3, $Z = 2$, 864 unique data ($\theta_{max} = 28.3°$), 855 data with $I > 2\sigma(I)$. $R_1 = 0.0336$, $wR_2 = 0.1040$, $\rho_{max} = 0.14\ e^-$ Å^{-3}. Programs used: SHELXL and ORTEP. CCDC deposition number: 226 896.

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