Structural, magnetic, high-frequency and high-field EPR investigation of double-stranded heterometallic $[\{Ni(en)_2\}_2(\mu\text{-}NCS)_4Cd(NCS)_2]_n \cdot nCH_3CN$ polymer self-assembled from cadmium oxide, nickel thiocyanate and ethylenediamine.

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A novel heterometallic 1D coordination polymer $[\{Ni(en)_2\}_2(\mu\text{-}NCS)_4Cd(NCS)_2]_n \cdot nCH_3CN$ (en = ethylenediamine) has been prepared using the self-assembly process in a one-pot reaction of cadmium oxide, nickel and ammonium thiocyanates with an acetonitrile solution of ethylenediamine. The complex consists of an uncommon *cis*-$Cd(SCN)_4(NCS)_2^{4-}$ fragment and a rare combination of *cis*-$Ni(en)_2^{2+}$ and *trans*-$Ni(en)_2^{2+}$ building blocks linked by $\mu_{1,3}$-NCS bridges into a double-stranded zigzag chain structure. Each chain is comprised of $[Ni_2Cd_2(\mu\text{-}NCS\text{–}N,S)_4)]$ macrocycles with chair-like and rectangular-like shapes arrayed alternately. The shortest intrachain Cd···Cd separations are 9.535(1) and 10.868(2) Å, while the nearest Ni···Ni distances are 5.418(1) and 6.612(2) Å. A network of weak N–H···S hydrogen bonds, involving the terminal NCS ligands and NH_2-groups of en, links the infinite chains and results in the formation of an extended supramolecular three-dimensional framework. Variable-temperature (1.8–300 K) magnetic susceptibilities show a slight change of the μ_B value at low temperature, indicative of weak antiferromagnetic interactions (J = 1.55 cm^{-1}) between magnetic canters. High-field, high-frequency (100–400 GHz) EPR spectra were simulated using S = 1 ground state for separate Ni^{2+} ions with the spin Hamiltonian parameters g = 2.165, D = 0.45 cm^{-1} and E = 0.03 cm^{-1}. According to DFT calculations, the D and E parameters are −0.35 cm^{-1} and 0.049 cm^{-1} for the *cis* arrangement of Ni^{2+} and 0.58 cm^{-1} and 0.012 cm^{-1} for *trans*.

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