

Structural, magnetic, high-frequency and high-field EPR investigation of double-stranded heterometallic $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ polymer self-assembled from cadmium oxide, nickel thiocyanate and ethylenediamine†

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A novel heterometallic 1D coordination polymer $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ (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*- $\text{Cd}(\text{SCN})_4(\text{NCS})_2^{4-}$ fragment and a rare combination of *cis*- $\text{Ni}(\text{en})_2^{2+}$ and *trans*- $\text{Ni}(\text{en})_2^{2+}$ building blocks linked by $\mu_{1,3}$ -NCS bridges into a double-stranded zigzag chain structure. Each chain is comprised of $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ 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 ($J = 1.55 \text{ cm}^{-1}$) 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 $g = 2.165$, $D = 0.45 \text{ cm}^{-1}$ and $E = 0.03 \text{ cm}^{-1}$. 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*.

Introduction

Synthesis of multidimensional homo- and heterometallic transition metal polymers supported by pseudohalide NCO ,¹ NCS ,² NCS_2 and N_3 ⁴ bridges has attracted a special attention in view of the architectural diversity and interesting magnetic properties of the complexes obtained. In this context, the thiocyanate ligand, which displays ambidentate character of end-to-end or end-on coordination modes, affords a number of discrete, one-, two- and three-dimensional structural assemblies that exhibit weak or strong magnetic interactions of various types.⁵ However, despite of the various modes of the NCS-group coordination to the metal ions and its ability to act as an exchange pathway, it is not widely used in the design and synthesis of inorganic compounds.

While many homometallic complexes exist with single⁶ or double⁷ end-to-end NCS bridges, the heterometallic thiocyanato bridged species are comparatively less numerous.⁸ Simultaneous presence of two different metal centers can potentially give rise to interesting physico-chemical properties and lead to attractive novel topologies and intriguing frameworks.

To construct the novel heterometallic polymer we used a synthetic strategy named “direct synthesis of coordination compounds”, that is based on the one-pot self-assembly of building blocks, formed *in situ*, into supramolecular assemblies. This approach, in which a metal-containing ligand is formed from zerovalent metal or its oxide and subsequently self-assembles with a second metal center in the same reaction vessel⁹ allowed the elimination of the separate step of building block construction. In previous work, it has been shown that heterometallic compounds may be obtained from the following systems ($\text{M}^{(1)} = \text{Cu}, \text{Ni}$, $\text{M}^{(2)} = \text{Zn}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CH}_3\text{COO}, \text{N}(\text{CN})_2$ (dca); $\text{L} =$ ethylenediamine (en), $\text{Solv} = \text{dmf}, \text{dmsO}, \text{CH}_3\text{OH}, \text{CH}_3\text{CN}$):¹⁰



Such investigations resulted in a series of thiocyanato-bridged heterometallic Cu/M ($\text{M} = \text{Zn}, \text{Cd}$) complexes showing zigzag and helical types of chain crystal structures based on $\text{Zn}(\text{NCS})_4^{2-}$ building blocks^{10a} and 2D structures built with $\text{Cd}(\text{NCS})_6^{4-}$,^{10b}

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$\text{Cd}(\text{dca})_2(\text{SCN})_2^{2-}$,^{10c} or $\text{Cd}_2(\text{NCS})_6(\text{CH}_3\text{COO})_2^{2-}$,^{10d} fragments. In this study, while continuing our synthetic approach, we have synthesized a novel heterometallic $\text{Ni}_2^{II}\text{Cd}^{II}$ polymer comprising simultaneously both *cis*- and *trans*- $\text{Ni}(\text{en})_2^{2+}$ building blocks, this being rather rare even for $\text{Ni}(\text{II})$ complexes and, according to the Cambridge Structural Database, was previously found only in cyanide-bridged polymers $\text{Ni}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ (where $n = 5$,^{11a} 2.16^{11b}). In addition, *in situ* preparation of metal-containing ligand allowed us to obtain an uncommon *cis*- $\text{Cd}(\text{SCN})_4(\text{NCS})_2^{4-}$ anionic fragment. Structures similar to that one have been reported only in two homometallic $\text{Cd}(\text{II})$ compounds.¹² In the present paper, we report the synthesis and crystal structure of a one-dimensional double-stranded zigzag polymer $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ as well as its spectroscopic and magnetic properties and high-frequency, high-field EPR.

Experimental

General

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy and by standard titrimetric methods for anions at the Department of Chemistry, National Taras Shevchenko University of Kyiv and with a Carlo Erba Strumentazione Analyzer (for C, H and N) at the Institute of Applied Synthetic Chemistry, Vienna University of Technology.

Synthesis of $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2] \cdot \text{CH}_3\text{CN}$. Cadmium oxide (0.32 g, 0.0025 mol), $\text{Ni}(\text{NCS})_2$ (0.87 g, 0.005 mol), NH_4NCS (0.38 g, 0.005 mol), CH_3CN (25 cm³) and ethylenediamine (0.67 cm³, 0.01 mol) were heated to 50–60 °C and stirred magnetically for about 40 min. A light-violet precipitate was obtained after addition of 15 cm³ of $\text{Pr}'\text{OH}$ to the reaction mixture. Violet crystals suitable for X-ray crystallography were isolated from the filtrate within one day. Yield: 0.97 g, 45%. Anal. calc. for $\text{C}_{16}\text{H}_{35}\text{CdN}_{15}\text{Ni}_2\text{S}_6$: Ni, 13.66; Cd, 13.07; NCS, 40.54; C, 22.35; H, 4.10; N, 24.44%. Found: Ni, 13.5; Cd, 13.1; NCS, 40.9; C, 22.4; H, 4.1; N, 24.5%. IR (KBr, cm⁻¹): 3300 s, 3280 s, 3180 w, 2950 m, 2890 m, 2260 w, 2130 vs, 2090 vs, 2045 vs, 1585 m, 1450 w, 1370 w, 1320 w, 1280 w, 1130 w, 1095 w, 1020 s, 975 m, 875 sh, 830 w, 765 w, 680 m, 650 sh, 620 sh, 520 m, 465 w. The compound is sparingly soluble in DMSO and DMF, insoluble in water and it is indefinitely stable in air.

Physical measurements

Infrared spectrum was recorded as KBr disc on a UR-10 spectrophotometer in the 4000–400 cm⁻¹ region using conventional techniques.

UV/VIS spectrum was recorded on a Perkin Elmer 330 (diffuse-reflectance technique) spectrometer.

The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with the Bruker NMR gaussmeter ER 035 M and the Hewlett-Packard microwave frequency counter HP 5350B. High-frequency EPR spectra were recorded on a home-built spectrometer at the EMR facility of NHMFL.¹³ The instrument was a transmission-type device in which waves are propagated in cylindrical lightpipes. The

microwaves were generated by a Gunn oscillator, operating at 95 ± 3 GHz. Frequencies higher by a factor 2, 3, or 4 were obtained using a Schottky diode-based multiplier and appropriate high-pass filters. A phase-locked oscillator (Virginia Diodes) generating a frequency of 13 ± 1 GHz and its 2nd, 4th, 8th, 16th, 24th and 32nd harmonics was also used. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at a magnetic induction of 0.5 T. The corrections for diamagnetism of the constituent atoms were calculated from the Pascal constants.¹⁴

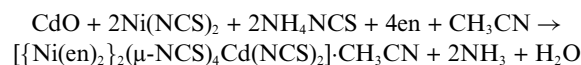
X-Ray structure determination

$\text{C}_{16}\text{H}_{35}\text{CdN}_{15}\text{Ni}_2\text{S}_6$ ($f_w = 859.81$), 150(2) K, monoclinic, $P2_1/n$, $a = 13.458(2)$, $b = 16.955(3)$, $c = 14.681(3)$ Å, $\beta = 91.873(3)^\circ$, $V = 3348.1(10)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 2.15$ mm⁻¹, $\rho_{\text{cal}} = 1.706$ g cm⁻³, 30952 reflections measured ($\theta_{\text{max}} = 28.5^\circ$), 8289 unique ($R_{\text{int}} = 0.041$) and of these 6694 had $I > 2\sigma(I)$ and were considered to be observed. The final R_1 , wR_2 values were 0.051 and 0.122, respectively, for 378 parameters. Data collection was by means of a Bruker SMART CCD diffractometer with full-matrix refinement on F^2 using XTAL 3.7.¹⁵ The carbon atoms of the en groups on Ni(2) were found to be disordered over two sites with site occupancy factors refined to 0.688(2) and $1 - 0.688(2)$.

Results and discussion

Synthesis and spectroscopic characterization

The polymer was synthesized in a one-step self-assembly reaction from cadmium oxide, nickel and ammonium thiocyanates in acetonitrile solution of ethylenediamine, using molar ratios $\text{CdO} : \text{Ni}(\text{NCS})_2 : \text{NH}_4\text{NCS} : \text{en} = 1 : 2 : 2 : 4$. The light-violet solution obtained at the completion of the reaction afforded upon addition of $\text{Pr}'\text{OH}$ a light-violet precipitate of the heterometallic complex. The interaction proceeds in the following way:



The IR spectrum of the compound exhibits three strong absorptions in the 2130–2045 cm⁻¹ region characteristic of the NCS ligand.¹⁶ The very strong bands (2045 cm⁻¹ and 2090 cm⁻¹) are due to the $\nu(\text{C-N})$ vibrations, and the weak band at a lower frequency (830 cm⁻¹) is attributable to the $\nu(\text{C-S})$ absorption peak. These data could be a proof of the presence of a terminal N-bonded thiocyanate in the titled complex. Furthermore, the very strong $\nu(\text{C-N})$ stretching at 2130 cm⁻¹ shows the presence of $\mu_{1,3}$ -NCS ligands which is in agreement with the generally employed criterion that $\nu(\text{C-N}) \geq 2100$ cm⁻¹ indicates a thiocyanate bridge with a $\mu_{1,3}$ -NCS or $\mu_{1,1,3}$ -NCS bridging mode. Three strong $\nu(\text{N-H})$, $\delta(\text{NH}_2)$ and $\nu(\text{C-N})$ absorptions (3330, 1585 and 1020 cm⁻¹, respectively) and middle $\nu(\text{C-H})$ and $\nu(\text{C-C})$ vibrations (2950 and 975 cm⁻¹) can be easily attributed to the ethylenediamine ligand. The presence of the solvate molecules of CH_3CN can be identified by the weak $\nu(\text{C}\equiv\text{N})$ absorption peak at 2260 cm⁻¹.

The diffuse reflectance spectrum of the compound exhibits two middle-intensity broad peaks at 11500 and 18200 cm^{-1} , that correspond to spin-allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ in six-coordinated Ni(II).¹⁷ Two low-intensity absorptions at 27750 and 31100 cm^{-1} can be attributed to spin-allowed transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ for nickel(II) atoms in *trans*-Ni(en)₂²⁺ and *cis*-Ni(en)₂²⁺. The spectrum displays also a ligand-to-metal charge transfer transition at 40000 cm^{-1} .

Description of the structure

The crystal structure of the $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ consists of three types of building blocks: *cis*-Ni(en)₂²⁺, *trans*-Ni(en)₂²⁺ and *cis*-Cd(SCN)₄(NCS)₂⁴⁻. The CH₃CN molecules occupy cavities in the crystal lattice. The alternate pairs of *cis*-Ni(en)₂²⁺ or *trans*-Ni(en)₂²⁺ link the adjacent cadmium blocks by bridging $\mu_{1,3}$ -NCS groups forming a double-stranded zigzag chain structure (Fig. 1). The polymer contains two crystallographically independent nickel(II) atoms, Ni(1) and Ni(2), both of which are six-coordinated and have an NiN₆ donor set formed by N atoms from two bidentate en ligands and two thiocyanate groups. In the *trans*-Ni(en)₂²⁺ the Ni(1)–N distances range from 2.089(5) to 2.110(5) Å, while in the *cis*-Ni(en)₂²⁺ the Ni(2)–N bond lengths vary from 2.077(5) to 2.119(5) Å (Table 1). The coordination spheres of both Ni(1) and Ni(2) centers are distorted, which can be seen from the N–Ni–N_{trans} angles varying from 175.94(17) to 178.87(18)° and 174.4(2) to 175.68(19)°, respectively. The bond distances and angles in the en ligands are in accordance with those found for similar nickel(II) complexes.^{10e,11,18} Each cadmium(II) atom is coordinated by four bridging and two terminal NCS groups and exhibits a distorted octahedral geometry with a *cis*-CdS₄N₂ chromophore. The Cd–S bond lengths vary between 2.7120(15) and 2.7505(14) Å. The Cd–N distances are 2.289(5) and 2.293(5) Å. As a result of the *cis* orientation of two terminal N-bonded thiocyanate groups around the Cd(II) atom, the bond angle N(5)–Cd(1)–N(6) is 92.49(18)°. The distances of S–C and C–N bonds of the thiocyanates are in the range 1.635(6)–1.658(5) Å and 1.137(7) Å–1.158(7) Å, respectively, which is in accordance with the values observed in other thiocyanato-containing metal complexes.¹⁹

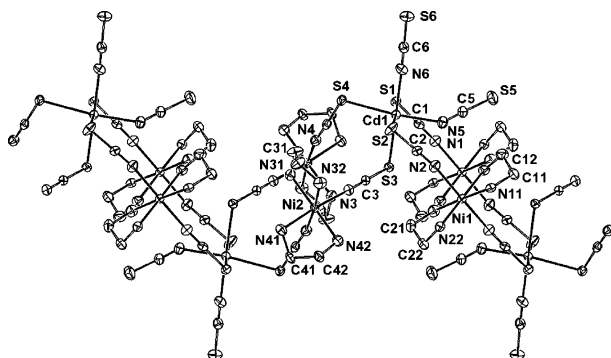


Fig. 1 Fragment of the double-stranded chain structure of $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ with the atom numbering scheme. H atoms are omitted for clarity. Atom displacement ellipsoids are shown at the 50% probability level.

The overall double-stranded polymeric chain includes macrocycles $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ (Fig. 2) which fold in a zigzag

Table 1 Selected bond distances (Å) and angles (°) for $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2] \cdot \text{CH}_3\text{CN}$

Ni(1)–N(2)	2.110(5)	Ni(2)–N(41)	2.119(5)
Ni(1)–N(11)	2.098(4)	Ni(2)–N(42)	2.095(5)
Ni(1)–N(12)	2.104(5)	Ni(2)–N(4) ^b	2.114(5)
Ni(1)–N(21)	2.091(5)	Cd(1)–S(1)	2.7505(14)
Ni(1)–N(22)	2.092(4)	Cd(1)–S(2)	2.7120(15)
Ni(1)–N(1) ^a	2.089(5)	Cd(1)–S(3)	2.7304(14)
Ni(2)–N(3)	2.077(5)	Cd(1)–S(4)	2.7322(14)
Ni(2)–N(31)	2.093(5)	Cd(1)–N(5)	2.289(5)
Ni(2)–N(32)	2.114(5)	Cd(1)–N(6)	2.293(5)
N(2)–Ni(1)–N(11)	94.50(18)	N(31)–Ni(2)–N(4) ^b	92.19(18)
N(2)–Ni(1)–N(12)	86.64(18)	N(32)–Ni(2)–N(41)	93.5(2)
N(2)–Ni(1)–N(21)	87.3(2)	N(32)–Ni(2)–N(42)	94.2(2)
N(2)–Ni(1)–N(22)	92.42(18)	N(32)–Ni(2)–N(4) ^b	174.4(2)
N(2)–Ni(1)–N(1) ^a	175.94(17)	N(41)–Ni(2)–N(42)	83.36(19)
N(11)–Ni(1)–N(12)	83.07(17)	N(41)–Ni(2)–N(4) ^b	85.65(18)
N(11)–Ni(1)–N(21)	178.03(18)	N(42)–Ni(2)–N(4) ^b	91.2(2)
N(11)–Ni(1)–N(22)	96.39(17)	S(1)–Cd(1)–S(2)	174.82(4)
N(11)–Ni(1)–N(1) ^a	87.91(17)	S(1)–Cd(1)–S(3)	83.72(4)
N(12)–Ni(1)–N(21)	97.94(18)	S(1)–Cd(1)–S(4)	87.89(4)
N(12)–Ni(1)–N(22)	178.87(18)	S(1)–Cd(1)–N(5)	91.16(12)
N(12)–Ni(1)–N(1) ^a	90.42(18)	S(1)–Cd(1)–N(6)	90.11(13)
N(21)–Ni(1)–N(22)	82.63(18)	S(2)–Cd(1)–S(3)	94.43(5)
N(21)–Ni(1)–N(1) ^a	90.39(19)	S(2)–Cd(1)–S(4)	87.55(5)
N(22)–Ni(1)–N(1) ^a	90.55(17)	S(2)–Cd(1)–N(5)	93.62(12)
N(3)–Ni(2)–N(31)	89.81(18)	S(2)–Cd(1)–N(6)	91.69(13)
N(3)–Ni(2)–N(32)	90.4(2)	S(3)–Cd(1)–S(4)	97.34(4)
N(3)–Ni(2)–N(41)	174.8(2)	S(3)–Cd(1)–N(5)	88.03(13)
N(3)–Ni(2)–N(42)	92.84(19)	S(3)–Cd(1)–N(6)	173.82(13)
N(3)–Ni(2)–N(4) ^b	90.87(18)	S(4)–Cd(1)–N(5)	174.41(13)
N(31)–Ni(2)–N(32)	82.4(2)	S(4)–Cd(1)–N(6)	82.00(13)
N(31)–Ni(2)–N(41)	94.20(18)	N(5)–Cd(1)–N(6)	92.49(18)
N(31)–Ni(2)–N(42)	175.68(19)		

^a Symmetry operation: $1 - x, -y, 1 - z$. ^b Symmetry operation: $1 - x, -y, -z$.

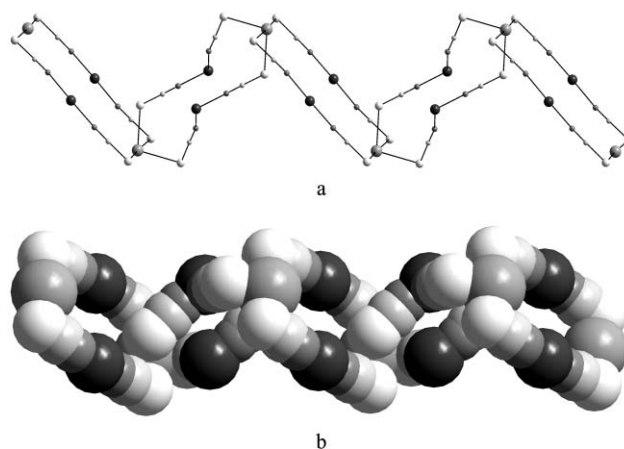


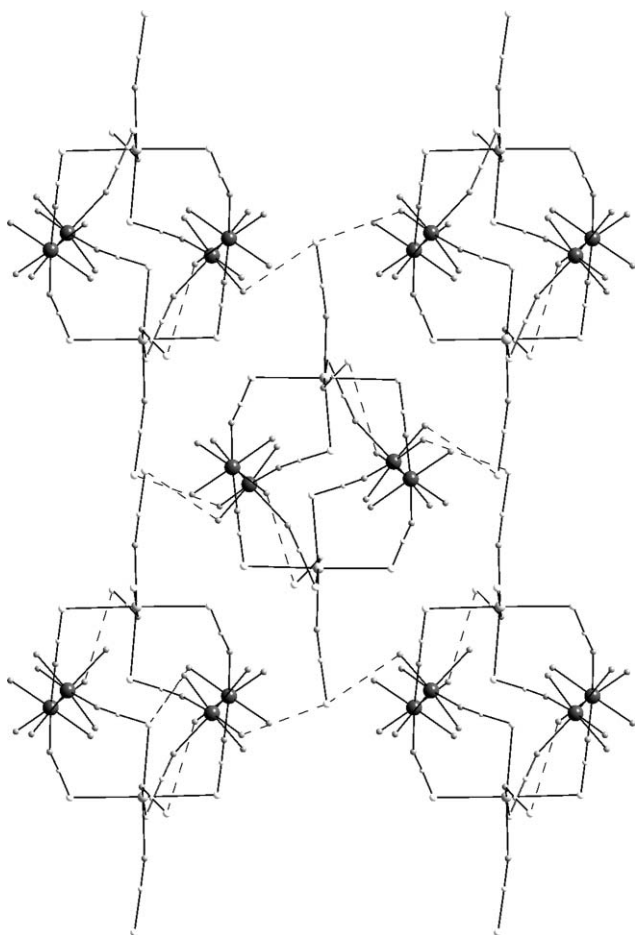
Fig. 2 Fragment of the polymer (a) and space-filling projection (b), showing the chair-like and rectangular-like shapes of $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ rings arrayed alternatively in a zigzag manner.

manner with the angle $\text{Cd}^1\text{-Cd-Cd}^2$ [$1 - x, -y, 1 - z$; $2 1 - x, -y, -z$] of 91.80(2)° as a result of the *cis* orientation of $\text{Cd}(\text{SCN})_4(\text{NCS})_2^{4-}$ block. In the first type of the $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ macrocycle, in which the $\text{Ni}(\text{en})_2^{2+}$ have *cis* conformation, this macrocycle has a chair-like shape with angles: $\text{S}(3)\text{-Cd}(1)\text{-S}(4) = 97.34(4)^\circ$, $\text{N}(3)\text{-Ni}(2)\text{-N}(4)^2 = 90.88(17)^\circ$ [$1 - x, -y, -z$], $\text{Cd}(1)\text{-S}(3)\text{-C}(3) = 103.91(18)^\circ$ and $\text{Cd}(1)\text{-S}(4)\text{-C}(4) = 103.23(18)^\circ$. The shape of the other type of $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ section,

Table 2 Hydrogen-bonding interactions (distances in Å and angles in °) in $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]\cdot\text{CH}_3\text{CN}$

D–H...A	Symmetry of A	D–H	H...A	D...A	D–H...A
N(21)–H(21aN)...S(5)	$1-x, -y, 1-z$	0.927	2.814	3.555(5)	137.7
N(41)–H(41bN)...S(6)	$-0.5+x, 0.5-y, -0.5+z$	0.916	2.680	3.515(5)	151.9
N(42)–H(42aN)...S(6)	$0.5-x, -0.5+z, 0.5-z$	0.920	2.860	3.632(6)	142.4

which involves *trans*-Ni(en)₂²⁺ moieties, is almost rectangular with angles: S(1)–Cd(1)–S(2) = 174.82(4)°, N(2)–Ni(1)–N(1)¹ = 175.95(19)° [$1-x, -y, 1-z$], Cd(1)–S(2)–C(2) = 100.71(20)° and Cd(1)–S(1)–C(1) = 96.39(19)°. The shortest intrachain Cd...Cd separations are equal to 9.535(1) and 10.868(2) Å, while the nearest Ni...Ni distances are 5.418(1) and 6.612(2) Å between *cis*-Ni(en)₂²⁺ and *trans*-Ni(en)₂²⁺, respectively. The infinite chains are linked in a supramolecular three-dimensional framework by weak N–H...S hydrogen bonds between hydrogen atoms from NH₂ group of en and sulfur atoms from terminal N-bonded thiocyanate ligands of four neighboring chains (Fig. 3, Table 2).

**Fig. 3** Projection onto the *ab* plane showing packing of 1D polymeric chains into 3D H-bonded network. H and C atoms of chelating rings are omitted for clarity.

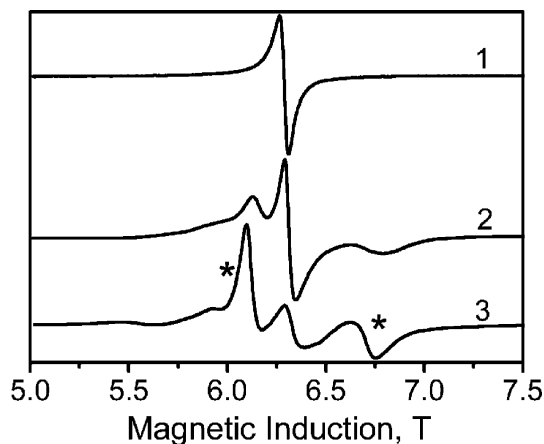
EPR spectra

The compound exhibits a broad, featureless X-band EPR spectrum at room temperature and at 77 K. The high-field EPR spectra indicate a dynamic process that causes averaging-out of the fine

structure so that only one line with $g = 2.166$ is observed at the room temperature. Upon temperature lowering, a more complex spectrum emerges whose detailed analysis is impossible due to the complicated nature of the system that contains two different nickel entities, one with nickel in a *cis* environment and the other in *trans*. The metal–metal interactions are very weak (see discussion of the magnetic susceptibility below) and it is possible that the observed spectra are a superposition of two single-ion triplet signals, but it cannot be excluded that signals are due to the exchange-coupled system. Moreover, the resonances are quite broad and poor in features. Ni²⁺ in *cis* and *trans* environments must have substantially different zero-field splitting parameters D and E . In addition, the dynamic process mentioned above causes partial averaging out of the fine structure even at temperatures as low as 10 K.²⁰ Two prominent lines indicated by asterisks in the 4 K spectrum (Fig. 4) could be followed over the frequency range *ca.* 100–400 GHz. The g values for these two signals could be determined from the slope of the resonance field *versus* frequency plots (Fig. 5), giving $g = 2.165$ for each. This is essentially the same as g observed at room temperature, which represents the average g value, thus indicating no significant g anisotropy in the system under study. In fact, the g values should not exceed 2.22 with the transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ observed at 11500 cm⁻¹ (see above). g values for Ni²⁺ may be estimated from formulas:

$$g_{x,y} = 2.0023 - 8\lambda \frac{\kappa_{x,y}^2}{\Delta({}^3\text{A}_{2g} - {}^3\text{T}_{2g})} \quad (1)$$
$$g_z = 2.0023 - 8\lambda \frac{\kappa_z^2}{\Delta({}^3\text{A}_{2g} - {}^3\text{T}_{2g})}$$

where $\lambda = -315$ cm⁻¹ is the spin–orbit coupling constant for nickel and $\kappa \leq 1$ are the orbital reduction factors depending on bond covalency.²²

**Fig. 4** 190.1 GHz EPR spectra recorded at 279 K (1), 10 K (2) and 4 K (3). The central resonance in the 4 K spectrum appears to be the double-quantum transition,²¹ often encountered in nickel(II) spectra.

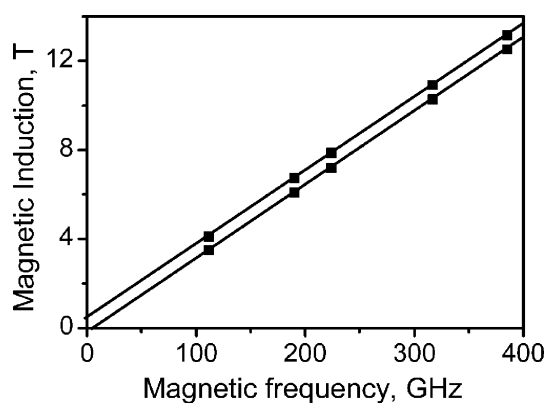


Fig. 5 Frequency dependencies of two resonances marked with asterisks in Fig. 4. The g value can be calculated from the slope of the straight lines. The extrapolated intersection point between the high-field resonance plot and the frequency axis allows estimation of the zero-field splitting between the levels involved in an EPR transition.

The low-field and the high-field resonances in Fig. 5 are not positioned symmetrically about $g = 2.165$, and therefore they must correspond to the ‘perpendicular’ and the ‘parallel’ orientations, respectively, of molecules *versus* the magnetic field. The zero-field splitting between levels involved in these transitions must be about 0.45 cm^{-1} as judged from the extrapolated intersection point of the assumed ‘parallel’ line with the frequency axis. If the spectra were due to separate Ni^{2+} ions with $S = 1$, the D and E values determined from Fig. 5 would be 0.45 cm^{-1} and 0.03 cm^{-1} , respectively. We have tried to estimate the expected zero-field splitting parameters by means of DFT calculations using the software package ‘ORCA’ by Frank Neese.²³

The program calculated $D = -0.35 \text{ cm}^{-1}$, $E = 0.049 \text{ cm}^{-1}$ for the *cis* arrangement, and $D = 0.58 \text{ cm}^{-1}$, $E = 0.012 \text{ cm}^{-1}$ for *trans*. These numbers should not be taken too literally, as the same software produced poor estimation of the g values, but they emphasise differences between the zero-field splitting in *cis* and *trans* arrangements.

Magnetic properties

Magnetic data shown in Fig. 6 in the form of μ_{eff} *versus* T indicate very weak antiferromagnetic exchange interactions in the system. The effective magnetic moment of 4.54 BM per two nickel ions

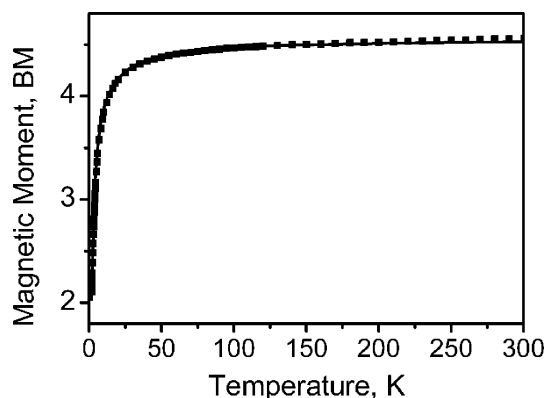


Fig. 6 Experimental effective magnetic moments (■) and calculated using eqn 2 with $J = 1.55 \text{ cm}^{-1}$, $g = 2.28$, (solid line, see text).

observed at 300 K implies the g_{average} value of 2.27, while a smaller value of 2.17 is observed in EPR. Discrepancies between the g values obtained from EPR and from the magnetic susceptibility measurements are common.

The system studied in this work is an infinite, double-stranded chain of nickel ions. We fitted the magnetic moments using eqn (2),²⁴ although it is not perfectly suited to our system, in which not all exchange interactions can be equal. Eqn (2) corresponds to a Hamiltonian $H = J \sum_i S_i S_{i+1}$

$$\chi = \frac{2N\mu_B^2 g^2 (A + Bx^2)}{kT(C + Dx + Ex^3)} \quad (2)$$

with $A = 0.6667$, $B = 0.64558$, $C = 1.000$, $D = 1.8018$, $E = 4.9448$ and $x = J/kT$.

The fit shown in Fig. 6 gave $J = 1.55 \text{ cm}^{-1}$, $g = 2.28$. Exchange interactions in the system are indeed expected to be weak because they involve (for each interacting pair of nickel atoms) two long bridges $\text{Ni}(\textit{cis} \text{ or } \textit{trans})\text{-NCS-Cd-SCN-Ni}(\textit{cis} \text{ or } \textit{trans})$.

Conclusions

In this work, we have reported the synthesis of a heterometallic Ni/Cd complex using a one-step self-assembly process from cadmium oxide, nickel and ammonium thiocyanates, ethylenediamine and CH_3CN . The research presented shows that *in situ* formation of building blocks yielded the polymer $[\{\text{Ni}(\text{en})_2\}_2(\mu\text{-NCS})_4\text{Cd}(\text{NCS})_2]_n \cdot n\text{CH}_3\text{CN}$ with uncommon simultaneous presence of *cis*- $\text{Ni}(\text{en})_2^{2+}$ and *trans*- $\text{Ni}(\text{en})_2^{2+}$ moieties as well as a quite rare *cis*- $\text{Cd}(\text{SCN})_4(\text{NCS})_2^{4-}$ anionic fragment. The thiocyanate ligands bridge the nickel and cadmium centres to give a 1D double-stranded zigzag polymer with chair-like and rectangular-like shapes of $[\text{Ni}_2\text{Cd}_2(\mu\text{-NCS-}N,S)_4]$ rings. Variable-temperature magnetic susceptibility measurements show very weak antiferromagnetic interactions between the paramagnetic centres in an infinite chain. High-field, high-frequency EPR spectra are likely due to separate Ni^{2+} ions and the D and E parameters for *cis* and *trans* arrangements were predicted using DFT calculations.

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