Structural, Magnetic, High-Frequency and High-Field EPR Studies on a Double-Stranded Heterometallic $[\{Ni(en)_2\}_2(\mu\text{–}NCS)_4Cd(NCS)_2]_n\cdot nCH_3CN$ Polymer

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Introduction

Synthesis of multidimensional homo- and heterometallic transition metal polymers supported by pseudohalide NCO, NCS, NCSe and N_3 bridges has received attention in view of architectonical 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. In the present paper, we report the synthesis and crystal structure of a one-dimensional double-stranded zigzag polymer $[\{Ni(en)_2\}_2(\mu\text{–}NCS)_4Cd(NCS)_2]_n\cdot nCH_3CN$, where en is ethylene diamine, as well as its spectroscopic and magnetic properties and high-frequency, high-field EPR.

Experimental

High-frequency EPR spectra up to 413 GHz were recorded on the transmission spectrometer at the EMR facility of the NHMFL. 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 the magnetic induction of 0.5 T.

Results and Discussion

The 'one-pot' direct synthesis yielded the polymer $[\{Ni(en)_2\}_2(\mu\text{–}NCS)_4Cd(NCS)_2]_n\cdot nCH_3CN$ with uncommon presence of both *cis*–$Ni(en)_2^{2+}$ and *trans*–$Ni(en)_2^{2+}$ moieties as well as quite rare *cis*–$Cd(SCN)_4(NCS)_2^{4-}$ anionic fragment. The thiocyanate ligands bridge the nickel and cadmium centers to give a 1D double-stranded zigzag polymer with chair-like and rectangular-like shapes of $[Ni_2Cd_2(\mu\text{–}NCS\text{–}N,S)_4)]$ rings. Variable-temperature magnetic susceptibility measurements show very weak antiferromagnetic interactions between the paramagnetic centers arranged in an infinite chain, with the exchange integral $J = 1.55$ cm^{-1}. For this reason, the high-field, high-frequency EPR spectra are likely due to separate Ni^{2+} ions. The EPR parameters of one of the two overlapping spectra could be determined; $|D|=0.45$ cm^{-1} and $|E|=0.03$ cm^{-1}. We have estimated the expected zero-field splitting parameters by means of DFT calculations, by using the software package 'ORCA'[1] and have calculated $D = -0.35$ cm^{-1}, $E = 0.049$ cm^{-1} for the *cis* arrangement, and $D = 0.58$ cm^{-1}, $E = 0.012$ cm^{-1} for *trans*.

Conclusions

Magnetic susceptibility measurements and high-frequency EPR studies revealed very weak exchange interactions between the nickel ions. The single-ion zero-field splitting parameter D was satisfactorily reproduced by a DFT calculation.

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References

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