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Synthesis, crystal structure and magnetism of $[Cu(\mathit{cyclam})Ni(NCS)_4(H_2O)_2]_n$

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Abstract

$[Cu(\mathit{cyclam})Ni(NCS)_4(H_2O)_2]_n$ (1) (*cyclam* = 1,4,8,11-tetraazacyclodecane) exhibits bent 1D crystal structure in which paramagnetic Cu(II) and Ni(II) atoms are linked by bridging μ_2-NCS$^-$ ligands. The Cu(II) atom exhibit tetragonally elongated hexacoordination in the 4+2 form with one tetradentate macrocyclic *cyclam* ligands placed in the equatorial plane while the axial positions are occupied by S atoms from bridging NCS$^-$ ligands. The Ni(II) atom in NiN_4O_2 donor set is deformed octahedrally coordinated by four isothiocyanato ligands among which two in *trans* positions are bridging in nature; additional aqua ligands occupy the remaining two positions in *trans* arrangement. Weak hydrogen bonding interactions of the O-H···S type links the formed chains into 3D supramolecular structure. The magnetism of 1 is dominated by a sizable single-ion anisotropy D_{Ni}/hc = +7.49 cm^{-1} along with a weak exchange interaction of the ferromagnetic nature.

Introduction

Heterobimetallic compounds represent enhanced interest in magnetic studies as in some case their magnetic properties cannot be viewed as a simple addition of the magnetic properties of the two magnetically active centers. In the case of Cu-Ni heterobimetallic compounds (Černák *et al.* 2012a) the ones exhibiting chain-like structures and containing both Cu and Ni central atoms paramagnetic (p-p type) can be viewed as model compounds for observation of the phenomenon predicted by Furusaki *et al.* (1994), namely, that in some cases such systems may behave as ferromagnets despite the presence of antiferomagnetic interactions between the present metallic centers with half (S = 1/2, Cu(II)) and integer (S = 1, Ni(II)) spins. The literature data shows that p-p type Cu-Ni compounds are numerous (Černák *et al.* 2012a). On the other hand, the number of Cu-Ni compounds with one-dimensional (1D) crystal structures is limited. As examples we can mention $[Ni(\mathit{cyclam})Cu(H_2O)_2(2,4\text{-}\mathit{pydc})_2]_n\cdot 8H_2O$ (*cyclam* = 1,4,8,11-tetraazacyclodecane, 2,4-*pydc* = pyridine-2,4-dicarboxylato) (Huang *et al.* 2013), $[Cu(\mathit{en})_2(\mu_2\text{-}H_2O)_2Ni(\mathit{ac})_4]\cdot 4H_2O$ (*en* = ethane-1,2-diamine, *ac* = acetato) (Nesterova *et al.* 2010) or $\{[Cu(\mathit{en})_2]\ [Ni(C_5O_5)_2(H_2O)_2]\}_n$ (C_5O_5 = 4,5-dihydroxy-cyclopentanetrionate(2-)) (Wang *et al.* 2009). Previously, we have synthesized and structurally characterized several 1D Cu-Ni

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compounds with diamagnetic $[Ni(CN)_4]^{2-}$ bridging anion (p-d type), e.g. Cu(*cyclam*)$Ni(CN)_4$ (Černák *et al*. 2010) or Cu(*bapen*)$Ni(CN)_4$ (*bapen* = N,N'-bis(3-aminopropyl)-1,2-diaminoethane) (Černák *et al*. 2012b). With the aim to prepare Cu-Ni compounds of the p-p type with 1D structure we have replaced in our synthetic procedure the diamagnetic $[Ni(CN)_4]^{2-}$ building block by paramagnetic $[Ni(NCS)_4(H_2O)_2]^{2-}$ one; this complex anion was already used, e.g. in $\{CuL\alpha[Ni(NCS)_4(H_2O)_2]\}$ (Lα = 5,12-dimetyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene). (Bieńko *et al*. 2007). As the results of our experiments we have isolated novel title complex $[Cu(cyclam)Ni(NCS)_4(H_2O)_2]_n$ (1) and here we report its crystal structure, spectroscopic characterization along with its magnetic properties.

Experimental

Materials

Nickel(II) dichloride hexahydrate $NiCl_2\cdot6H_2O$, potassium thiocyanate KSCN, copper(II) perchlorate hexahydrate $Cu(ClO_4)_2\cdot6H_2O$ and *cyclam* (1,4,8,11-tetraazacyclodecane) were purchased from commercial sources and used as received.

Syntheses of $[Cu(cyclam)Ni(NCS)_4(H_2O)_2]_n$ *(1)*

In syntheses 15 cm^3 of aqueous-ethanolic solution (2:1, vv) of $NiCl_2\cdot6H_2O$ (0.07 g, 0.3 mmol) were slowly successively under stirring added 0.12 g of KSCN (1.2 mmol) dissolved in 10 cm^3 of water, and 20 cm^3 of aqueous solution formed of $Cu(ClO_4)_2\cdot6H_2O$ (0.11 g, 0.3 mmol) and *cyclam* (0.06 g, 0.3 mmol). The formed violet solution was filtered and left aside for crystallization. Within two weeks light pink needles separated which were collected by filtration and dried on air. Yield: 20 %. Anal. Calc. for C14 H28 Cu N8 Ni O2 S4 (M_r = 590.93) (%): C, 28.46; H, 4.78; N, 18.96; Cu, 10.75; Ni, 9.93. Found: C, 28.50; H, 4.69; N, 18.89; Cu, 10.53; Ni, 9.80. IR (cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad): 3544 msh; 3477 ssh; 3397 vs; 3243 m; 3215 w; 3167 s; 3151 w; 2954 m; 2918 wsh; 2875 w; 2113 vs; 2098 vs; 1652 w; 1614 m; 1455 m; 1422 m; 1386 w; 1317 w; 1295 m; 1235 w; 1120 m; 1093 s; 1064 m; 1024 s; 987 s; 882 m; 806 w; 779 m; 654 m; 517 w; 474 m; 434 m.

Physical measurements

Elemental analyses (C, H, N) were performed on a CHNOS Elemental Analyzer (vario MICRO). The metal contents were determined by complexometry (Cu) and gravimetry (Ni). Infrared spectra were recorded on a FT-IR Avatar 330 Thermo-Nicolet instrument using KBr pellets technique (1:200) in the range of 4000 – 400 cm^{-1}. The magnetic susceptibility of sample 1 (56 mg) was measured using the SQUID magnetometer (MPMS, Quantum Design) at B = 0.1 T and the background contribution arising from the gelcap and straw was subtracted from the experimental data. Raw data was corrected for underlying diamagnetism and transformed to the effective magnetic moment. The magnetization data was taken at T = 2.0 K until B = 5.0 T.

X–ray Crystallography

X–ray experiments were carried out on a four–circle κ–axis Xcalibur2 diffractometer equipped with a CCD detector Sapphire2 (Oxford Diffraction). The CrysAlis software package (Oxford Diffraction 2003) was used for data collection and reduction. Analytical absorption corrections using crystal faces were applied (Clark and Reid 1995). The crystal structure of 1 was solved by direct methods and further refined using the SHELXS–97 and SHELXL–97 program (Sheldrick 2015), respectively, incorporated in the WinGX program package (Farrugia 1999). Hydrogen atoms in the *cyclam* ligand were placed in the calculated positions and allowed to ride on the parent atoms with isotropic thermal parameters tied with the parent atoms (U(H) = 1.2U(CH2), U(H) = 1.2U(N)).
Water hydrogen atoms in 1 were located with the program CALC–OH (Nardelli 1999) and their isotropic thermal parameters were tied with the parent oxygen atoms (U(H) = 1.5U(O)).

Table 1. Crystal data and structure refinement for 1.

Empirical formula	$C_{14} H_{28} Cu N_8 Ni O_2 S_4$
Formula weight	590.93
Temperature	[K]291(2)
Wavelength [Å]	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions [Å, °]	a= 7.4927(5)
	b=8.0603(6)
	c=11.1747(8)
	α=106.318(7)
	β=100.658(6)
	γ=105.429(8)
Volume [Å^3]	599.25(8)
Z	1
Density (calculated) [g.cm^{-3}]	1.638
Absorption coefficient [mm^{-1}]	2.049
Crystal dimensions [mm^3]	0.1x0.2x0.5
θ range for data collection [°]	2.80 to 25.00
Index ranges	$-8 \leq h \leq 8, -9 \leq k \leq 9, -13 \leq l \leq 13$
Reflections coll./ obs.	2116/1638
Absorption correction	analytical
T_{min}/T_{max}	0.565/0.882
Goodness-of-fit on F^2 (all/obs.)	0.997/0.998
Final R indices [I>2σ(I)]	$R1$ = 0.0505, $wR2$ = 0.1299
R indices (all data)	$R1$ = 0.0639, $wR2$ = 0.1355
Largest diff. peak and hole [e Å^{-3}]	1.07 and –0.74

The structural figures were drawn using the Diamond software (Brandenburg 2008). Crystal data and final parameters of the structure refinement are summarized in Table 1, while selected geometric parameters are given in Table 2. Possible hydrogen bonds are gathered in Table 3.

Results and Discussion

Synthesis and spectroscopic characterization

From the aqueous-ethanol systems Cu^{2+} – *cyclam* – Ni^{2+} – $NCS^{–}$ the complex [Cu(*cyclam*)$Ni(NCS)_4(H_2O)_2]_n$ (1) was isolated and chemically characterized. The choice of the *cyclam* as blocking ligand coordinated to the Cu(II) atom, in the lack of another chelating ligand, was motivated by significantly higher stability of the [Cu(*cyclam*]$^{2+}$ complex (log$K$= 27.2) with respect to the analogous Ni(II) one (log$K$= 22.2) (King 2005). Similar mild conditions were used for preparation of analogous compound {CuLα$[Ni(NCS)_4(H_2O)_2]$} with (Lα = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene) (Bieńko *et al.* 2007).

The most characteristic absorption band in the IR spectrum of 1 (Fig. 1) is the very strong split one with close peak positions at 2113 and 2098 cm$^{–1}$ due to the presence of the N-bonded NCS^- ligand (Nakamoto 1997; Chandra *et al.* 2008). In analogous {CuLα$[Ni(NCS)_4(H_2O)_2]$} with two different structural functions of $NCS^–$ ligands (terminal and bridging) the values of 2121 and 2088 cm^{-1} were reported (Bieńko *et al.* 2007). The presence of *cyclam* ligand is indicated by several observed absorption bands. As characteristic absorption bands we can mention those arising from N─H stretching vibrations, which were observed in the regions of 3244─3228 cm$^{–1}$, in line with the literature data 3265─3180 cm$^{–1}$ (Nakamoto 1997) as well as those arising from stretching vibrations of the methylene groups observed in the region 2954─2875 cm$^{–1}$. The presence of aqua ligands manifest itself by broad and strong absorption band at 3397 cm$^{–1}$ with two shoulders at 3544 and 3477 cm$^{–1}$ which were ascribed to asymmetric and symmetric ν(OH) stretching vibrations; the corresponding absorption band due to δ(H_2O) vibrations was located at 1652 cm$^{–1}$. Further absorption bands are gathered in the experimental part.

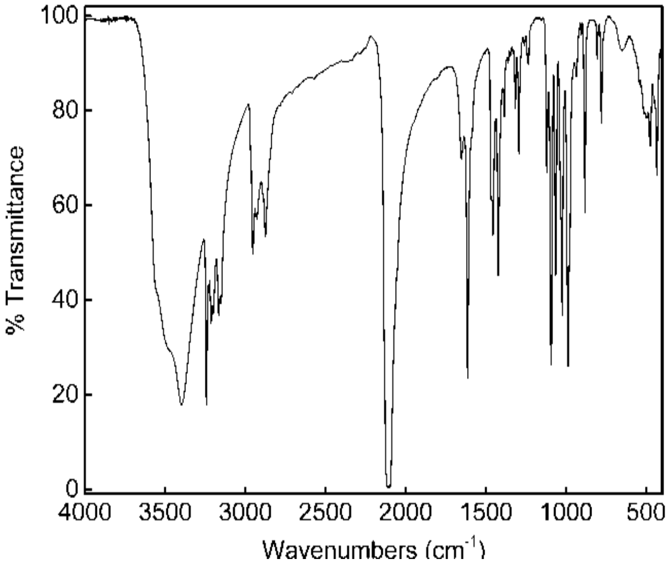

Fig. 1. IR spectrum of 1.

Crystal structure

The crystal structure of compound [Cu(*cyclam*)$Ni(NCS)_4(H_2O)_2]_n$ consists of quasi-linear chains exhibiting composition [-Cu(*cyclam*)-

μ-SCN-Ni(NCS)$_2$(H$_2$O)$_2$-μ-NCS-]$_n$ with *trans*-positions of the bridging ligand in the respective coordination polyhedra (Fig. 2). Analogous chain-like structure was reported for [Cu(*en*)$_2$][Mn(NCS)$_4$(H$_2$O)$_2$] (Kou *et al*. 1998). The Cu(II) atom in the title complex exhibitstetragonally elongated hexacoordination with elongated axial bonds as the consequence of the Jahn-Teller effect. In the equatorial plane there are nitrogen atoms from the *cyclam* ligand situated, while bond lengths of Cu-N are 2.014(4) (4×) Å (Table 2) and are comparable with the average value of (2.0205(3)) Å found in {CuLα[Ni(NCS)$_4$(H$_2$O)$_2$]} (Lα = 5,12-dimethyl-1,4,8,11-tetraazacyclo tetradecane-4,11-diene) (Bieńko *et al*. 2007). The axial positions are occupied by sulfur atoms from bridging thiocyanato ligands, bond length of Cu-S is 3.027(2) Å. The observed value is slightly shorter as the reported values of 3.071(1) and 3.065(3) Å for {Cu(*en*)$_2$[Ni(*en*)(SCN)$_3$]$_2$}$_n$ (Shen *et al*. 2001) and [Cu(*en*)$_2$][Mn(NCS)$_4$(H$_2$O)$_2$] (Kou *et al*. 1998), respectively.

The Ni(II) central atom (-1 site) in [Ni(NCS)$_4$(H$_2$O)$_2$]$^{2-}$ anionis deformed octahedrally coordinated. The equatorial plane is occupied by four atoms of nitrogen from NCS$^-$ ligands, while in the axial ones are placed two aqua ligands (donor set is O$_2$N$_4$) (Fig. 2). Two trans-positioned NCS$^-$ ligands link Ni(II) and Cu(II) central atoms generating those chain-like structure (Fig. 2). Ni-N bond lengths are from the range from 2.050(4) to 2.069(4) Å, while the Ni-O bond (2.123(3) Å, 2x) is somewhat longer; the experimental values well correspond to those observed in the similar compound {CuLα[Ni(NCS)$_4$(H$_2$O)$_2$]} (Bieńko *et al*. 2007). As to the other geometric parameters it should be noted that the formed chains are substantially bent on the sulfur atom with the value of the angle (N2)-C2-S2-Cu1 97.10(2) (Table 2) which support the assumption about weak coordination of the bridging SCN$^-$ ligand to the Cu(II) central atom. Nevertheless, such bent coordination is not uncommon as almost the same value 97.109(2)° was reported for {Cu(*en*)$_2$[Ni(*en*)(SCN)$_3$]$_2$}$_n$ (Shen *et al*. 2001).

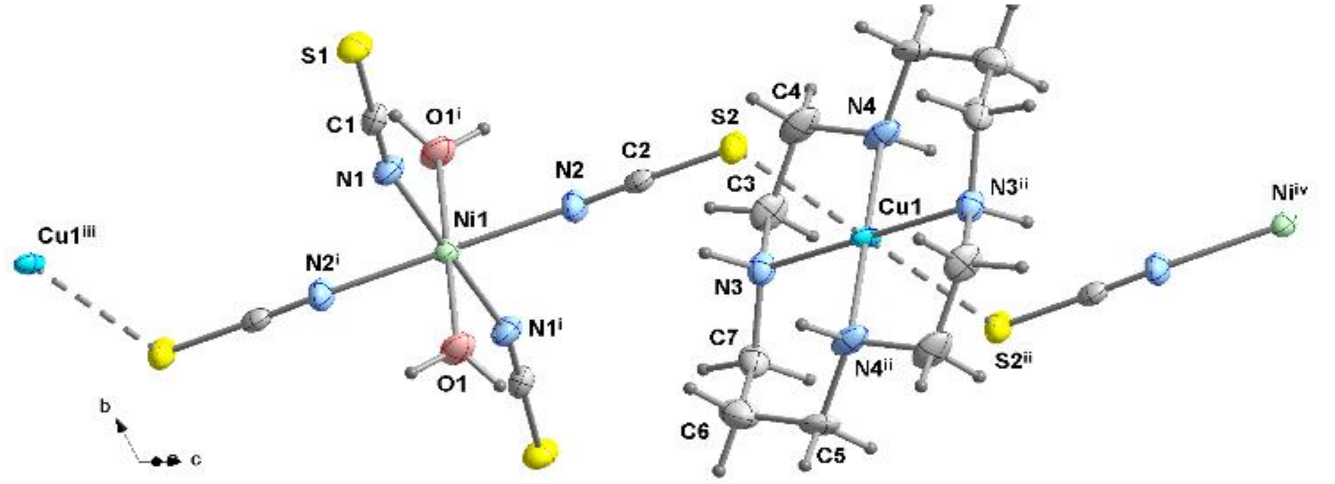

Fig. 2. View of the chain-like structure of [Cu(*cyclam*)Ni(NCS)$_4$(H$_2$O)$_2$]$_n$. The thermal ellipsoids are drawn on 30 % probability level. Dashed line represents the weaker Cu-S coordination bond. Symmetry codes: i: 1-x, -y, -z; ii: 2-x, -y, 1-z ; iii: -1+x, y, -1+z; iv: 1+x, y, 1+z.

The formed chains [-Cu(*cyclam*)-μ-SCN-Ni(NCS)$_2$(H$_2$O)$_2$-μ-NCS-]$_n$ are interconnected by hydrogen bonding interactions of the O-H···S type formed by aqua ligands and sulfur atoms from thiocyanato ligands (Fig. 3, Table 3). The 2Dhydrogen bonding network can be described as formed of two topologically different fused rings *R*1 and *R*2 with descriptors $R_4^2(8)$ and $R_2^2(12)$, respectively (Fig. 3); for the nomenclature of the descriptors see (Bernstein *et al*. 1995).

The geometric parameters associated with O-H···S hydrogen bonding interactions (Table 3) are comparable with those observed in {$CuL_\alpha[Ni(NCS)_4(H_2O)_2]$} (L = L = *N*-dl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) (Bieńko *et al.* 2007).

Table 2. Selected geometric parameters [Å, °] for 1.

Cu1-N4	2.011(4)
Cu1-N3	2.012(4)
Ni1-N1	2.047(4)
Ni1-N2	2.066(4)
Ni1-O1	2.120(3)
S2-C2	1.643(5)
S1-C1	1.638(5)
C1-N1	1.158(5)
C2-N2	1.146(6)
N4-Cu1-N3	85.39(18)
N1-Ni1-N2	88.91(15)
N1-Ni1-O1	89.66(15)
N2-Ni1-O1	88.61(17)
C1-N1-Ni1	165.4(4)
C2-N2-Ni1	169.9(4)
N1-C1-S1	179.5(4)
N2-C2-S2	178.4(4)
C2-S2-Cu1	97.08(18)

Magnetic study

The effective magnetic moment at the room temperature for 1 adopts a value of μ_{eff} = 3.62 μ_B (Fig. 4). Such a value can be reconstructed by applying the high-temperature formula $\mu_{eff} = [g^2_{Ni}S_{Ni}(S_{Ni}+1) + g^2_{Cu}S_{Cu}(S_{Cu}+1)]^{1/2}$. Using the constituent spins S_{Ni} = 1 and S_{Cu} = 1/2, an estimate for the uniform g-factor is g_{av} = 2.18. Cooling down to about 15 K does not cause visible changes of the effective magnetic moment, however, below 15 K its sharp decrease is detected; at 1.8 K μ_{eff} = 2.55 μ_B. The observed behavior indicates a strong magnetic anisotropy characterized by the axial zero-field splitting parameter D_{Ni}. There is no indication for a pronounced exchange coupling and if this is the case, it has to be of the ferromagnetic nature. For heteroleptic complexes with *trans*-{NiO_2N_4} chromophore the formula for estimation of the structural distortion parameter D_{str} based on bond distances around the Ni(II) central atom was elaborated elsewhere (Ivaniková *et al.* 2006). The calculated value of D_{str} = 15.4 pm for 1 suggests a presence of sizable and positive value of D>> 0. Analogous strongly elongated bipyramid was found in heteroleptic complexes [$Ni(im)_4(ac)_2$] (D_{str} = 15.5 pm; *im* = imidazole) (Titiš *et al.* 2007) and [$Ni(dmeiz)_4(H_2O)_2]Cl_2$ (D_{cal} = 10.67 using CASSCF calculations; *dmeiz* = 1,2-dimethyl-imidazole) (Singh *et al.* 2014).

The magnetization per formula unit at T = 2.0 and B = 5 T adopts a value of $M_1 = M_{mol}/N_A\mu_B$ = 2.62; this value is far from the spin-only estimate $M_1 = g_{Ni}S_{Ni} + g_{Cu}S_{Cu}$ ~ 3.27 so that also this data confirms a presence of the considerable D_{Ni}.

The magnetic functions have been fitted simultaneously by minimizing the error functional $F = R(\chi)\times R(M)$ consisting of the relative errors for the susceptibility and magnetization, respectively. The exchange Hamiltonian of the form:

$$\hat{H}_{kl} = -J(\vec{S}_{Ni}\cdot\vec{S}_{Cu})\hbar^{-2} + D_{Ni}(\hat{S}^2_{Ni,z} - \vec{S}^2_{Ni}/3)\hbar^{-2}$$
$$+\mu_B B g_{Ni}(S_{Ni,z}\cos\vartheta_k + S_{Ni,x}\sin\vartheta_k\cos\varphi_l + S_{Ni,y}\sin\vartheta_k\sin\varphi_l)\hbar^{-1}$$
$$+\mu_B B g_{Cu}(S_{Cu,z}\cos\vartheta_k + S_{Cu,x}\sin\vartheta_k\cos\varphi_l + S_{Cu,y}\sin\vartheta_k\sin\varphi_l)\hbar^{-1}$$

has been used where the first term refers to the isotropic exchange, the second is the single-ion anisotropy of the Ni-center, and the remaining terms represent the Zeeman interaction for a set of orientations of the field along grids {k, l} distributed uniformly over one hemisphere (Hudák *et al.* 2013). This form secures a correct powder average: the eigenvalues are inserted into the partition function Z_{kl} from which the magnetization M_{kl} and susceptibility χ_{kl} are calculated, and then averaged.

The fitting procedure converged to the following set of magnetic parameters: J/hc = +0.15 cm^{-1}, g_{Ni} = 2.284 (g_{Cu} = 2.1, fixed), D_{Ni}/hc = +7.49 cm^{-1}, and the temperature-independent magnetism χ_{TIM} = –1.9 × 10^{-9} m^3 mol^{-1}.

The quality of the fit is excellent, as the discrepancy factors are $R(\chi)$ = 0.038 and $R(M)$ = 0.012. To this end, a sizable and positive (easy plane) magnetic anisotropy has been confirmed along with a weak exchange coupling of the ferromagnetic nature.

Table 3. Possible hydrogen bonding interactions [Å, °] in **1**.

D-H...A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O1-H2O1···S1^{vi}	0.85	2.52	3.336(4)	160
O1-H1O1···S1^{v}	0.85	2.64	3.447(4)	159

Symmetry codes: v: x, -1+y, z; vi: -x, -y, -z.

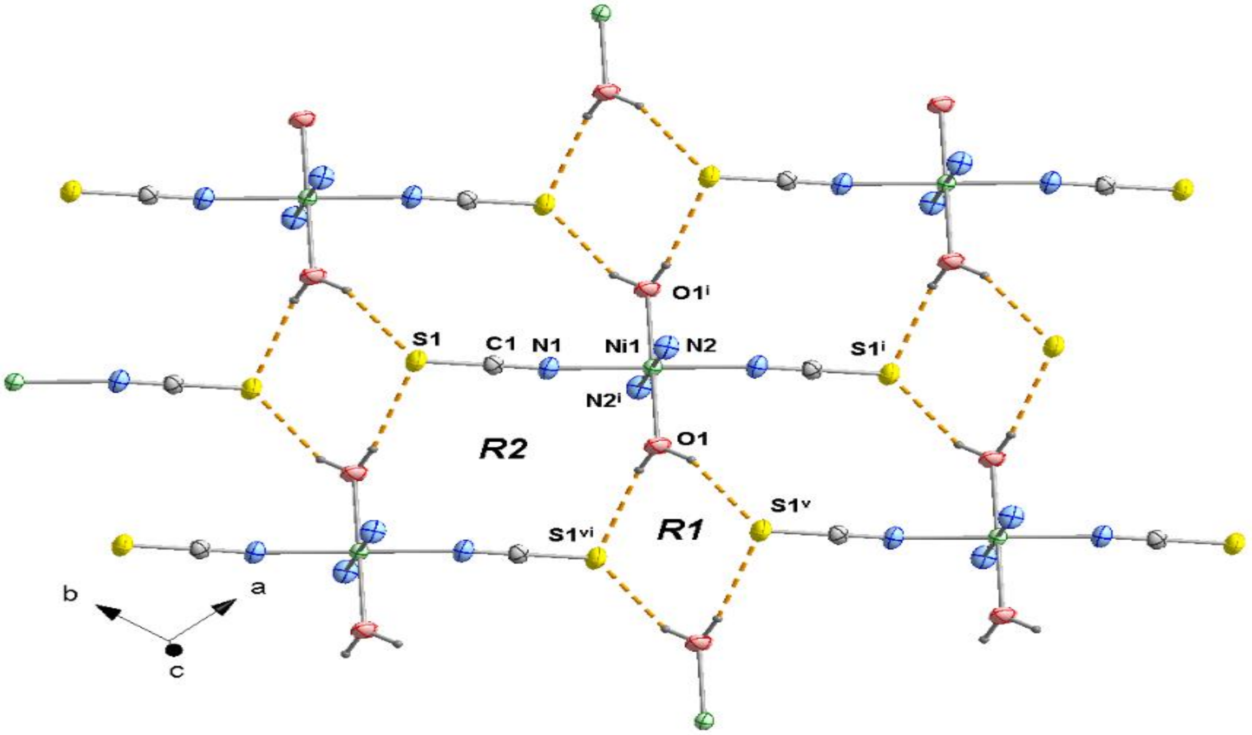

Fig. 3. View on the supramolecular structure formed by hydrogen bonding interactions in [Cu(*cyclam*)Ni(NCS)$_4$(H$_2$O)$_2$]$_n$. *R*1 and *R*2 are hydrogen bonded rings with descriptors $R_4^2(8)$ and $R_2^2(12)$, respectively. Only selected atoms are shown for clarity. Symmetry codes: i: 1-x, -y, -z; v: x, -1+y, z; vi: -x, -y, -z.

The model could be extended by considering more centers in exchange interaction within the chain and/or plane. However, the magnetic centers are rather far each other and thus such kind of interaction would be visible only at very low temperature.

Although the crystal structure itself suggests that 1 might be considered as a new representative of alternating chain with alternation of half (S =1/2) and an integer (S = 1) spins, yet more detailed study in the milikelvin temperature range is necessary to elucidate this conjecture. The study involving specific heat and magnetization measurements would clarify the role of hydrogen bonds as potential exchange bridges as well as the effect of single–ion anisotropy of Ni(II) ions.

Conclusions

From the aqueous-ethanol system Cu(II) – *cyclam* – Ni(II) – NCS$^-$ a novel chain-like compound [Cu(*cyclam*)Ni(NCS)$_4$(H$_2$O)$_2$]$_n$ (**1**)was isolated and characterized. Results of X-ray structure analysis have shown that its crystal structure is formed of infinite chains in which the paramagnetic Cu(II) and Ni(II) atoms are linked by bridging μ_2-NCS$^-$ groups; the chains are further interlinked by hydrogen bonding interactions of the O-H···S type yielding a 2D supramolecular system. Investigation of magnetic properties revealed the presence of a weak ferromagnetic interaction and a sizable single–ion anisotropy of the Ni(II) atom as predicted by the calculated value of structural distortion parameter D_{str}.

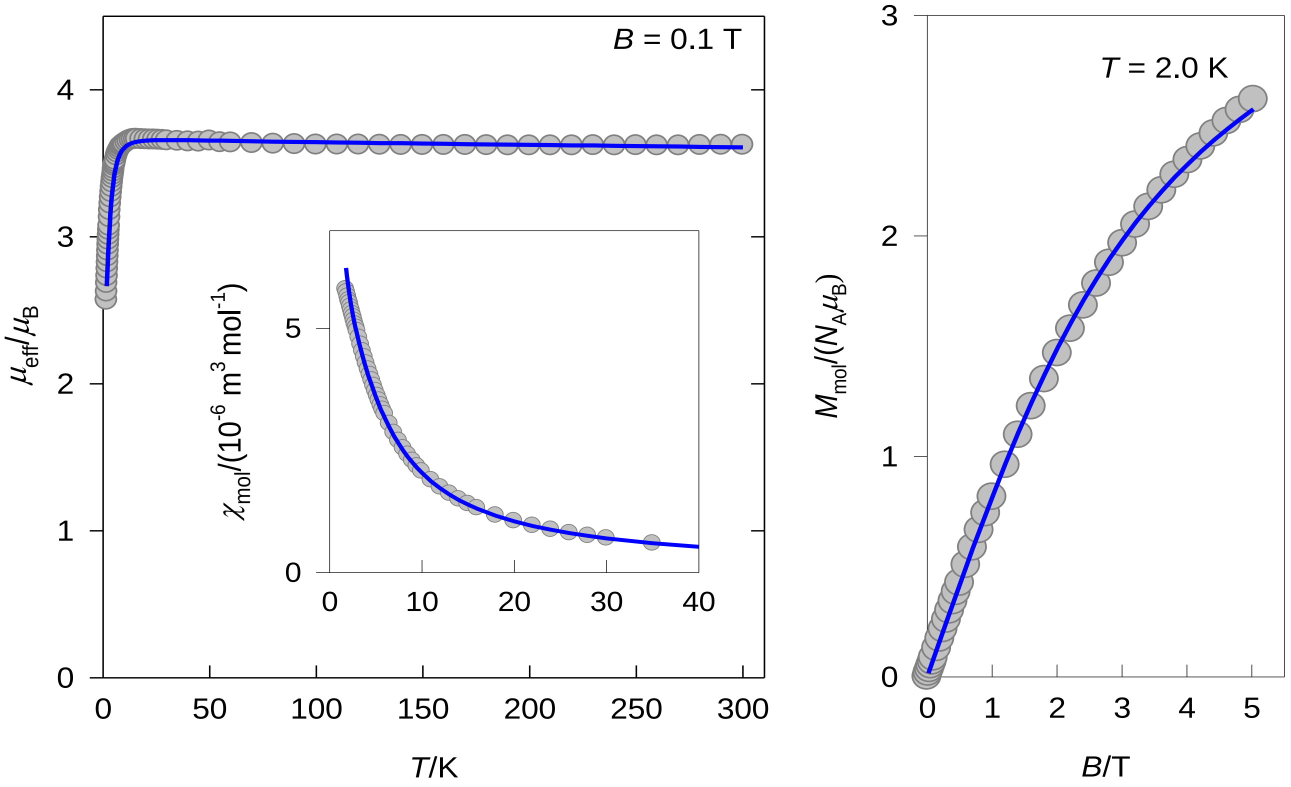

Fig. 4. Magnetic functions for 1. Left – effective magnetic moment (inset: molar magnetic susceptibility); right – magnetization per formula unit. Lines – fitted.

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