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Bimetallic complexes with macrocyclic ligands. Variation of magnetic exchange interactions in some heteronuclear thiocyanato-bridged compounds

ALINA TOMKIEWICZ, JULIA KŁAK, JERZY MROZIŃSKI[*]

Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

A series of heterobinuclear, thiocyanato-bridged complexes of macrocyclic ligands of copper(II) and nickel(II) have been characterized by variable-temperature magnetic susceptibility (1.72–300 K). The complexes have the following composition: $(CuL_1)_3[Fe(NCS)_6]_2\cdot 3H_2O$ (**1**), $(CuL_1)[Ni(NCS)_6]\cdot 2H_2O$ (**2**), $(CuL_1)[Co(NCS)_4]\cdot 3H_2O$ (**3**), where L_1 is 5,12-dimethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene and $(NiL_2)_3[Fe(NCS)_6]_2\cdot 2H_2O$ (**4**), $(NiL_2)[Co(NCS)_4]\cdot 3H_2O$ (**5**), $(NiL_2)_2[Cr(NCS)_6]\ ClO_4$ (**6**), where L_2 is 5,7,12,14-tetramethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The results indicate that all of them behave as weakly interacting magnets.

Key words: *bimetallic complexes; copper (II); nickel (II); macrocyclic complex*

1. Introduction

The search for new materials exhibiting useful magnetic and magneto-optical properties is one of the main goals of molecular magnetism studies [1]. To design molecular systems with a desired magnetic behaviour, it is necessary to use a novel compound which contains several kinds of metallic ions, organic ligands and novel bridging networks.

The strategies derived from understanding the underlying phenomena play an important role in the syntheses of such compounds. For example, the spin transition phenomena which occur in some transition metal complexes is a spectacular example of molecular bistability [2].

In molecular magnetism, two kinds of molecular magnetisms of isolated molecules and assemblies of molecules can be specified. These molecules may contain one or more

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[*] Corresponding author, e-mail: jmroz@wchuwr.chem.uni.wroc.pl.

magnetic centres. They can also be built from molecular precursors, specially chosen to achieve a 3D covalent bonding network between spin bearing species [3].

One of the simplest and most convenient molecular building blocks is found in the hexacyanometallate family $[B(CN)6]^{n-}$. When $[B(CN)6]^{n-}$ reads with labile $[A(H_2O)_6]$ assembling ions (A and B are metallic ions), tridimensional systems result, which are analogues of the Prussian blue family.

The literature covering an analogous system, in which the thiocyanate group plays the role of a bridging ligand, is much more scarce [4]. Due to its ambient character, the thiocyanate group can serve as a bridging ligand, similarly to the cyanide group. There are a few heterometallic compounds of the type $[CuL]_3[Cr(NCS)_6]_2 \cdot nH_2O$ (L = 2.2-bipyridine, $n = 0$; L = *o*-phenanthroline, $n = 1$; L = diethylenotriamine, $n = 1$) [5]; $[CuL_4]_3[Cr(NCS)_6]_2 \cdot nH_2O$; (L = imidazole, $n = 2$ [6]; $[Cu(en)_2Mn(NCS)_4(H_2O)_2]_n$ (en = ethylendiamine) [7].

The number of such investigations has increased recently, due to the introduction of appropriate ligands of the macrocyclic type [8].

Francese et al. [4] were the first who used a simple macrocyclic copper(II) complex $Cu(cyclam)^{2+}$ to obtain a heterometallic system bridged by a thiocyanate group. Square-planar tetraazomacrocyclic complexes of Cu^{II} and Ni^{II} with two free coordination places at the metal atom can play the role of "building blocks" in this case [9]. There is a good access to the metal ion when there are no substituents in the macrocyclic ring. The situation changes with the size and character of the substituents which may form a steric hindrance and prevent any coordination to the metal ion.

In this paper, we present results concerning systems containing unsaturated substituted complexes of copper(II) (Fig. 1) and nickel(II) (Fig. 2) and simple ions such as $[Ni\ (NCS)_6]^{4-}$, $[Co\ (NCS)_4]^{2-}$, $[Fe\ (NCS)_6]^{3-}$, and $[Cr\ (NCS)_6]^{3-}$.

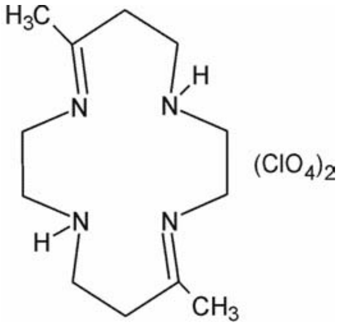

Fig. 1. Schematic view of 5,12-dimethyl -1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (L_1)

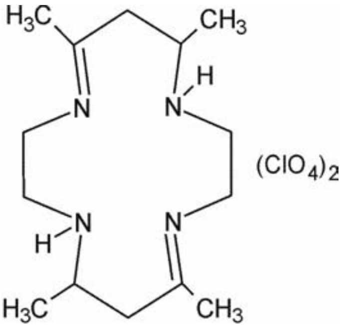

Fig. 2. Schematic view of 5,7,12,14-tetramethyl -1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (L_2)

It was interesting to verify whether the configuration of the nitrogen donor atoms and the kind of metal ions influences the crystalline structure or magnetic properties of the complexes.

2. Experimental

2.1. Materials. All chemicals were of reagent grade and were used as commercially obtained. $[CuL_1](ClO_4)_2$ [10], $[NiL_2](ClO_4)_2$ [11], $[(C_4H_9)_4N]_2[Co(NCS)_4]$ [12], $[(C_4H_9)_4N]_3[Ni(NCS)_6]$, $[(C_4H_9)_4N]_3[Cr(NCS)_6]$ and $[(C_4H_9)_4N]_3[Fe(NCS)_6]$ [12–14] were prepared following the methods described in literature.

Synthesis of complexes: The complexes, $(CuL_1)_3[Fe(NCS)_6]_2\cdot 3H_2O$ (**1**), $(CuL_1)[Ni(NCS)_6]\cdot 2H_2O$ **(2)**, $(CuL_1)[Co(NCS)_4]\cdot 3H_2O$ **(3)**, $(NiL_2)_3[Fe(NCS)_6]_2\cdot 2H_2O$ **(4)**, $(NiL_2)[Co(NCS)_4]\cdot 3H_2O$ (**5**), and $(NiL_2)_2[Cr(NCS)_6]ClO_4$ (**6**), were prepared by the methods described below.

The complexes **2**, **3,** and **5** were obtained by adding 10 ml of CH_3CN solution containing 0.3 mmol of $[(C_4H_9)_4N]_2[M(NCS)_6]$ to 20 ml of CH_3CN solution containing 0.3 mmol of the appropriate ligand ($[CuL_1](ClO_4)_2$ or $[NiL_2](ClO_4)_2$) at room temperature. The solutions were stirred continuously. The resulting precipitate was filtered off, washed with CH_3CN and C_2H_5OH solutions, and dried over P_2O_5.

Elemental analysis calculated for $C_{18}H_{34}N_8S_4NiCo$ (656.43) **(5):** C, 32.93; H, 5.23; N, 17.07; S, 19.54%. Found: C, 31.25; H, 4.84; N, 16.41; S, 18.97%.

Elemental analysis calculated for $C_{16}H_{30}N_8S_4CuCo$ (633.21) **(3):** C, 30.35; H, 4.78; N, 17.70; S, 19.45%. Found: C, 31.73; H, 4.13; N, 17.72; S, 19.02%.

Elemental analysis calculated for $C_{18}H_{28}N_{10}S_6CuNi$ (731.13) **(2):** C, 29.57; H, 3.87; N, 19.16; S, 19,11%. Found: C, 29.39; H, 4.31; N, 18.12; S, 19,01%.

The compounds **1**, **4**, and **6** were obtained by adding 15 ml of CH_3CN solution containing 0.5 mmol of $[(C_4H_9)_4N]_3[M(NCS)_6]$ to 25 ml of CH_3CN solution containing 0.3 mmol of the appropriate ligand ($[CuL_1](ClO_4)_2$ or $[NiL_2](ClO_4)_2$) at room temperature. The solutions were stirred continuously. The resulting precipitate was filtered off, washed with CH_3CN and C_2H_5OH solutions, and dried over P_2O_5.

Elemental analysis calculated for $C_{48}H_{78}N_{24}S_{12}Cu_3Fe_2$ (1726.44) **(1):** C, 33.39; H, 4.55; N, 19.47; S, 21.50%. Found: C, 32.44; H, 3.95; N, 18.77; S, 20.21%.

Elemental analysis calculated for $C_{54}H_{88}N_{24}S_{12}Ni_3Fe_2$ (1778.02) **(4):** C, 36.48; H, 4.87; N, 18.91; S, 21.64%. Found: C, 36.28; H, 4.80; N, 18.32; S, 20.21%.

Elemental analysis calculated for $C_{34}H_{28}N_{14}S_6Ni_2Cr$ (1122.11) **(6):** C, 40.89; H, 5.03; N, 17.47; S, 17.14%. Found: C, 41.63; H, 5.34; N, 16.71; S, 17.25%.

Physical techniques. Magnetic measurements in the temperature range of 1.7–300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with a palladium rod sample (Materials Research Corporation, of the purity 99.9985%). Measurement samples of the compounds under study were made at the magnetic field of 0.5 T. Corrections are based on subtracting the sample holder signal and contribution from χ_D estimated from the Pascal constants [15].

The FIR spectra were recorded in Nujol mulls (500–100 cm^{-1}), and the MIR spectra in KBr pellets (4000–500 cm^{-1}), with a Brucker IFS 113V Spectrophotometer.

3. Results and discussion

A major task in understanding magnetic exchange interactions is to sort out various effects of molecular and electronic structure on coupling parameters. Our approach has been to control the molecular structures to an extent as great as possible and to simultaneously vary electronic properties of the paramagnetic centres.

Initially, we reported the magnetic exchange interactions for complexes **1**, **2,** and **3** which contain the same symmetric macrocyclic ligands with different metal ions.

The magnetic properties of complex **1** as temperature dependencies of χ_M and $\chi_M T$ (χ_M being the molar magnetic susceptibility) are shown in Figure 3.

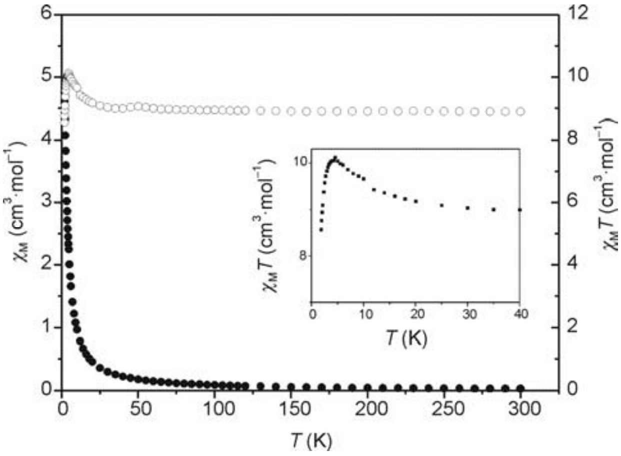

Fig. 3. Temperature dependence of the magnetic susceptibility χ_M (full symbols) and $\chi_M T$ (empty symbols) for the compound $(CuL_1)_3[Fe(NCS)_6]_2 \cdot 3H_2O$ (1).
The inset shows the low temperature region of $\chi_M T$ vs. T

At room temperature, $\chi_M T$ for this complex is 8.95 cm^3·mol^{-1}·K (μ_{eff} = 8.47 B.M.). Such a value corresponds to that calculated for two high-spin Fe$^{\text{III}}$ ions and three Cu$^{\text{II}}$ ions which are antiferromagnetically coupled. The values of the constants C and Θ, determined from the relation $1/\chi_M$ vs. T over the 300–100 K temperature range, are equal to 8.93 cm^3·mol^{-1}·K and 0.40 K, respectively. The $\chi_M T$ value remains nearly constant at a wide range of temperatures, and increases upon cooling below 50 K. It reaches a maximum at 4.5 K, with $\chi_M T$ = 10.1 cm^3·mol^{-1}·K (μ_{eff} = 9.00 B.M.), and finally decreases rapidly for temperatures below 4.5 K.

The presence of a maximum in the $\chi_M T$ curve is indicative of ferromagnetic coupling between unpaired electrons at Fe$^{\text{III}}$ magnetic centres. From the magnetic point of view, this compound will thus be considered as a linear pentamer. The variation of susceptibility with temperature for [Cu$^{\text{II}}$Fe$^{\text{III}}$Cu$^{\text{II}}$Fe$^{\text{III}}$Cu$^{\text{II}}$] should be calculated using the formula for χ_M with five linearly coupled spins. Two of these spins – J_1, J_2 – represent the exchange interactions between adjacent iron and copper ions, and the spin J_3

describes the interaction between the iron nuclei within the pentamer complex, shown pictorially as follows:

$$\begin{array}{ccccccccc} & J_2 & & J_1 & & J_1 & & J_2 & \\ \mathrm{Cu^{II}} & \text{———} & \mathrm{Fe^{III}} & \text{———} & \mathrm{Cu^{II}} & \text{———} & \mathrm{Fe^{III}} & \text{———} & \mathrm{Cu^{II}} \\ & & & \longleftarrow & J_3 & \longrightarrow & & & \end{array}$$

Based on our previous paper [16] and the well known crystal structure of $(NiL)_3[Fe(NCS)_6]_2$, where L = 5,6,12,13-Me_4-[14]-4,11-dieneN_4, we suggest that the exchange interaction between Cu^{II} and Fe^{III} ions is transmitted by the thiocyanate groups. The environment of the Fe^{III} ion is octahedral, while the thiocyanate groups are nearly linear. Each Fe^{III} ion is bound to two copper(II) ions. The thiocyanate groups coordinate to the copper(II) ions by their sulphur atom. A proposed schematic view of complex **1** is presented in Figure 4.

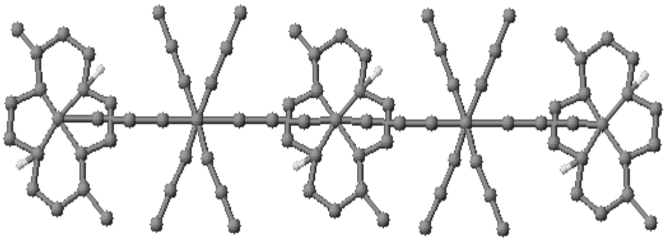

Fig. 4. A schematic view of $(CuL_1)_3[Fe(NCS)_6]_2 \cdot 3H_2O$ (**1**)

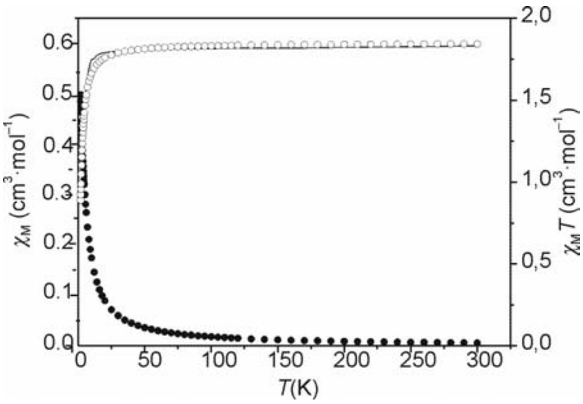

Fig. 5. Temperature dependence of magnetic susceptibility χ_M (full symbols) and $\chi_M T$ (empty symbols) for the compound $(CuL_1)[Ni(NCS)_6] \cdot 2H_2O$ (2). The solid line represents the least squares fit or the theoretical Eq. (1) to the experimental data

The magnetic susceptibility data for complex **2** are shown in Fig. 5. An antiferromagnetic exchange interaction is present as indicated by the fact that the value of $\chi_M T$

decreases very slowly in a wide range of temperatures and rapidly decreases below 30 K. When there is no magnetic exchange interaction in Cu^{II}-Ni^{II} binuclear compounds, the paramagnetic susceptibilities of the two different metal centres add up to the paramagnetic susceptibility of the binuclear complex. Consequently, the expected spin only value of μ_{eff} for the Cu^{II}-Ni^{II} compound, in absence of an exchange interaction, would be 3.83 B.M.

An antiferromagnetic exchange interaction in the Cu^{II}-Ni^{II} binuclear complex leads to an $S = ½$ ground state with an $S = {}^3/_2$ excited state. The observed value of μ_{eff} per binuclear complex is 3.83 B.M. at 300 K which indicates that most of the molecules are in the $S = {}^3/_2$ state. Below ca. 30 K there is a more pronounced decrease of μ_{eff} with decreasing temperature, which most likely reflects antiferromagnetic interactions and zero field effects for the Ni^{II} ion.

The data for compound **2** were initially fit to the susceptibility expression (Eq. (1)) derived from the simple spin Hamiltonian

$$\hat{H} = -2J\hat{S}_1\hat{S}_2$$

$$\chi_M = \frac{N\beta^2}{4kT}\left[\frac{g_{1/2}^2 + 10g_{3/2}^2 \exp(3J/kT)}{1 + 2\exp(3J/kT)}\right] \tag{1}$$

$$g_{1/2} = \frac{4g_{\mathrm{Ni}} - g_{\mathrm{Cu}}}{3}; \qquad g_{3/2} = \frac{2g_{\mathrm{Ni}} + g_{\mathrm{Cu}}}{3}$$

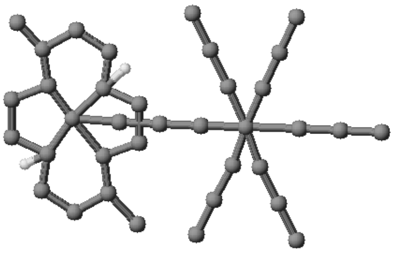

Fig. 6. A schematic view of $(CuL_1)[Ni(NCS)_6]\cdot 2H_2O$ (**2**)

A least squares fit of Eq. (1) to the data gave $J = -1.87$ cm^{-1}, $g_{Cu} = 2.20$, and $g_{Ni} = 2.36$ ($R = 3.07\times10^{-4}$). A small and negative value of the exchange parameter confirms weak antiferromagnetic interaction in complex **2** transmitted by the thiocyanato group (Fig. 6).

The $\chi_M T$ plots for complex **3** are shown in Figure 7. At room temperature, $\chi_M T$ is 2.96 cm^3·mol^{-1}·K (4.87 B.M.), which is slightly larger than expected for copper(II) ($S = ½$) and cobalt(II) ($S = {}^3/_2$) ions. The value of $\chi_M T$ is independent of temperature in the range of 50–300 K, but gradually decreases at lower temperatures. The $1/\chi_M$ vs. T plots in the range of 15–300 K obey the Curie–Weiss law with small and negative Weiss constant: $\Theta = -0.34$ K and $C = 2.95$ cm^3·mol^{-1}.

The interaction of cobalt(II) with copper(II) gives rise to low-lying spin triplet and spin quintet states, separated by $2J$. The decrease of $\chi_M T$ upon cooling would be expected for high-spin $\mathrm{Co^{II}}$, which interacts antiferromagnetically with $\mathrm{Cu^{II}}$ ions through the thiocyanato bridge.

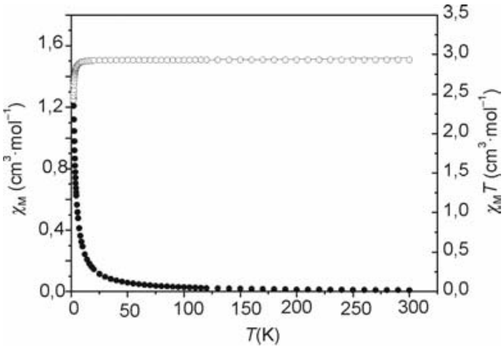

Fig. 7. Temperature dependence of magnetic susceptibility χ_M (full symbols) and $\chi_M T$ (empty symbols) for the compound $(\mathrm{CuL_1})[\mathrm{Co(NCS)_4}]\cdot 3\mathrm{H_2O}$ (3). The solid line represents the least squares fit of the theoretical equations (2)–(4) to the experimental data

The attenuation of μ_{eff} as the temperature of the sample approaches 1.80 K is most pronounced for the complex **3** which agrees with the expectation that the $\mathrm{Co^{II}}$ ion would exhibit the greatest zero-field splitting. The data for compound **3** were fit to Equations (2)–(4) using the least squares method:

$$\chi_{II} = \frac{2N\beta^2}{kT}\left[\frac{g_1^2\exp(-D/kT) + 5g_2^2\exp(2J/kT)}{1 + 2\exp(-D/kT) + 5(2J/kT)}\right] \tag{2}$$

$$\chi = 2N\beta^2\,\frac{\dfrac{g_1^2}{D}\left[1 - \exp(-D/kT)\right] + \dfrac{5g_2^2}{kT}\exp(2J/kT)}{1 + 2\exp(-D/kT) + 5\exp(2J/kT)} \tag{3}$$

$$g_1 = \frac{5g_{\mathrm{Co}} - g_{\mathrm{Cu}}}{4}, \qquad g_2 = \frac{3g_{\mathrm{Co}} + g_{\mathrm{Cu}}}{4}$$

$$D_1 = \frac{3D_{\mathrm{Co}}}{2} - \frac{D_{\mathrm{CuCo}}}{4}$$

$$\chi_{av} = 13\chi_{\parallel} + 23\chi_{\perp} \tag{4}$$

The best fit gave $g_{\mathrm{Cu}} = 2.20$, $g_{\mathrm{Co}} = 2.30$, $J = -0.9\ \mathrm{cm^{-1}}$, and $D = 2.5\ \mathrm{cm^{-1}}$ ($R = 8.88 \times 10^{-5}$), as indicated by the solid curve in Fig 7. A small and negative value of the exchange parameter suggests a very weak antiferromagnetic interaction between Cu^{II} and Co^{II} ions. A relatively large value of *g* for this Cu^{II}-Co^{II} complex is somewhat in line with the average value of g quoted for square-pyramidal complexes.

Our previous crystallographic results concerned similar compounds, namely (CuL)[Co(NCS)$_4$], with L = N-rac-(5,12-Me$_2$-7,14-Et$_2$-[14]-4,11-dieneN$_4$) [17]. Those results allow us to suggest that the asymmetric unit of the complex **3** consists of an $[Co(NCS)_4]^{2-}$ anion and a N-rac$[CuL_1]^{2+}$ cation, bridged by a thiocyanate ligand. One of the Cu^{II} ion coordination sites is blocked by the axial methyl group. Therefore, it forms the distorted square-pyramidal structure of the complex 3, with four equatorial nitrogen atoms of macrocyclic ligand and one sulfur atom from the thiocyanato bridging group in an axial position. The coordination geometry around the Co ion is distorted tetrahedrally. The cobalt(II) centre posses one bridging and three non-bridging thiocyanate ligands. The proposed schematic structure of the complex **3** is presented in Fig. 8.

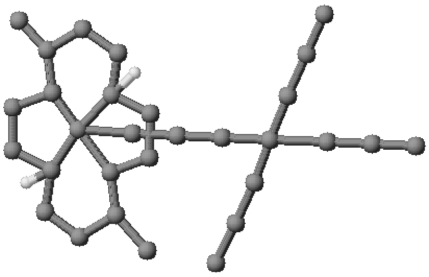

Fig. 8. A schematic view of (CuL$_1$)[Co (NCS)$_4$]·3H$_2$O (**3**)

The series of heterobinuclear complexes, containing the same symmetric macrocyclic ligand with different metal ions, were characterized by variable-temperature magnetic susceptibility. The trend observed in this series of complexes is a change of magnetic interactions due to the number of unpaired metal ion electrons. This suggests the occurrence of both ferro (F) and antiferromagnetic (AF) interactions in the examined compounds with heterometallic cores. We assumed that the F interaction is stronger than the AF interaction in complex **1**, in contrast to compounds **2** and **3**.

The second series of the compounds contained the metal within the ligand with more substituents. We attempted to verify whether the configuration at the nitrogen atoms influence the magnetic properties.

The magnetic properties of complexes **4**, **5**, and **6** are illustrated in Figure 9.

The values of $\chi_M T$ at room temperature are 8.54 cm^3·mol^{-1}·K (8.27 B.M.) for complex **4,** 1.65 cm^3·mol^{-1}·K (3.64 B.M.) for complex **5**, and 1.64 cm^3·mol^{-1}·K (3.62 B.M.) for complex **6,** all of which are expected for paramagnetic ions. The $\chi_M T$ versus *T* values remain nearly constant for all compounds in a wide range of temperatures and rapidly decrease at the lowest temperatures. A slight decrease in $\chi_M T$ may be due to either the effect of zero-field splitting parameters for the metal ions or/and intermolecular exchange interactions between paramagnetic centres. The constants *C* and *Θ* were determined from the relation $1/\chi_M$ vs. *T* over the temperature range of 300–100 K. The results are presented in Table 1.

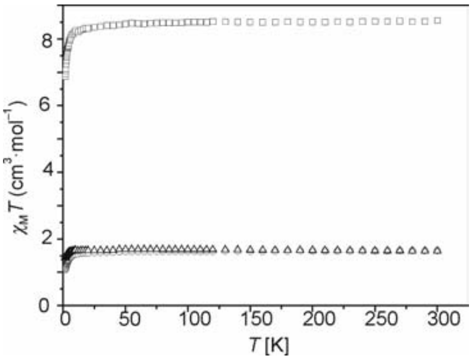

Fig. 9. Temperature dependence of $\chi_M T$ for: (□) $(NiL_2)_3[Fe(NCS)_6]_2\cdot 2H_2O$ (**4**); (○) $(NiL_2)[Co(NCS)_4]\cdot 3H_2O$ (**5**); (Δ) $(NiL_2)_2[Cr(NCS)_6]ClO_4$ (**6**)

A small negative value of *Θ* shows weak antiferromagnetic exchange interactions between each pair of metal ions.

Table. 1. Curie constant, Weiss constant and magnetic moment of the investigated compounds

Compound	Curie constant *C* [cm^3·K·mol^{-1}]	Weiss constant *θ* [K]	Magnetic moment at 300 K [M.B.]
$(NiL_2)_3[Fe(NCS)_6]_2\cdot 2H_2O$ (**4**)	8.547	–0.66	8.27
$(NiL_2)[Co(NCS)_4]\cdot 3H_2O$ (**5**)	1.662	–1.89	3.64
$(NiL_2)_2[Cr(NCS)_6]\ ClO_4$ (**6**)	1.619	–1.90	3.62

For a system consisting of three Ni^{II} ions ($S = 3\times1$) and two Fe^{III} ions ($S = 2\times{}^5/_2$) (**4**), the calculated value of magnetic moment at room temperature suggests that two terminal Ni^{II} ions are diamagnetic [16], which is a configuration in which the low-spin electronic configuration for this ion occurs. From the magnetic point of view, this compound will thus be considered as a linear FeNiFe core.

In the case of the two latter compounds (**5, 6**), the magnetic moment at room temperature confirms the diamagnetic character of the Ni^{II} ions. The magnetism of this compound should originate from the Co^{II} (**5**) and Cr^{III} (**6**) ions only. A decrease in $\chi_M T$ for both compounds will be thus caused by antiferromagnetic interaction between Co^{II} (**5**) and Cr^{III} (**6**) ions in the crystal lattice and by the zero-field splitting factor.

The compounds obtained in series 1 and 2 display an analogous composition, suggesting structural similarity. However, the results obtained from magnetic studies contradict this suggestion.

This fact is undoubtedly linked to a change in the number of methyl substituents in the macrocyclic ligands L_1 and L_2 and to a change in the N-configuration of six-membered chelating ring. An increase in the number of substituents results in a bigger steric hindrance during the coordination of the thiocyanate group to nickel(II) or copper(II) ions and caused by a different packing in the crystal lattice and a different mutual arrangement of the magnetic centres.

Although the crystal structures of the examined compounds have not been fully elucidated, some essential conclusions result from the IR spectra.

For the compound $(NiL_2)[Co(NCS)_4]\cdot 3H_2O$ **(5)**, a single sharp band was observed in the 4000–500 cm^{-1} spectrum, situated at 2056 cm^{-1} and originating from the stretching vibration ν(CN). No band is observed in the spectrum of this compound above 2100 cm^{-1}. This suggests the presence of a non-bridging thiocyanato ligand and appearance of electrostatic interactions between the macrocyclic cation $[NiL_2]^{2+}$ and anion $[Co(NCS)_6]^{2-}$ in the complex **(5).**

The infrared spectra of the complexes $(CuL_1)_3[Fe(NCS)_6]_2\cdot 3H_2O$ **(1)** (2062 cm^{-1} and 2154 cm^{-1}), $(CuL_1)[Ni(NCS)_6]\cdot 2H_2O$ **(2)** (2078 cm^{-1} and 2121cm^{-1}), $(CuL_1)[Co(NCS)_4]\cdot 3H_2O$ **(3)** (2059 cm^{-1} and 2074 cm^{-1}), $(NiL_2)_3[Fe(NCS)_6]_2\cdot 2H_2O$ **(4)** (2046cm^{-1} and 2093 cm^{-1}), and $(NiL_2)_2[Cr(NCS)_6]\ ClO_4$ **(6)** (2076 cm^{-1} and 2121 cm^{-1}) exhibit two bands near 2000 cm^{-1} corresponding to the ν_1(NCS) stretching mode. Additionally, bands above 2100 cm^{-1} are observed in the spectra of all the compounds, indicating the presence of a bridging thiocyanate group. This feature results from a combination of three effects: (a) the presence of a bridging thiocyanate ligand, (b) the presence of a non-bridging thiocyanate ligand, (c) the distorted environments of the metals cobalt (II), iron (III), chromium (III), nickel (II), and copper (II).

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