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New trends in the investigations of macrocyclic magnets[*]

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A study of a series of new type of copper(II), nickel(III) and rhenium(IV) macrocyclic complexes, having an important meaning as macrocyclic magnets is reported. Their magnetic measurements have been carried out over the temperature range 1.8 – 300 K using a Quantum Design SQUID magnetometer (MPMSxL - 5 type). The results indicate that all of them behave as weakly interacting magnets.

Key words: *heterobimetallic magnets; copper(II); nickel(III) and rhenium(IV) complexes; magnetic behaviour*

1. Introduction

In recent years, a great interest has been paid to heterometallic systems obtained on the basis of polyamine complexes and of salts derived from Prussian blue [1]. The literature covering an analogous system in which the thiocyanate group plays the role of a bridging ligand is much more scarce [2]. Due to its ambident character, the thiocyanate group, like the cyanide one, may serve as a bridging ligand. Among a large group of polyamine complexes used for the synthesis of such systems, there are planar tetra-azo copper(II) and nickel(II) complexes. They are all by the square symmetry of the metal ion, owing to which there are additional two free coordinating sites at the axial positions. The access to the metal ion is very easy when there are no substituents in the macrocyclic ring. This situation changes with the size and character of substituents, which may form a steric hindrance, preventing any coordination to the metal ion. Cyclam and its substituted derivatives [2a, 3] are the most widespread tetra-azo macrocyclic ligands. Considering the fact that in unsaturated complexes of the [14]

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dieneN$_4$ type, the N-configuration of the macrocyclic ring influences its conformation, and hence the arrangement of substitutents [4], an attempt was undertaken to study the relation between the N-configuration and the crystal structure and magnetic properties of the compounds obtained [2b].

Bivalent [Ni^{II}LCl$_2$] and trivalent nickel complexes [Ni^{III}LCl$_2$]X, (X = Cl$^-$, ClO_4^-), are especially interesting because of their importance in biological systems [5, 6] and catalytic oxidation reactions [7, 8]. Both nickel ions form exceptionally stable crystals with an octahedral geometry of Ni(II) and Ni(III) surround and a square-planar array of four nitrogen atoms and two Cl$^-$ anions occupying the axial positions [9]. The nickel(II) high-spin complexes with a d^8 electron configuration present the same stereochemistry as that of the corresponding Ni(III) analogues whilst the last one is of the low-spin d^7 configuration, and contains one unpaired electron (S = ½). The properties of macrocyclic nickel complexes were investigated using magnetic and spectroscopic methods [10].

The growing need for macrocyclic ligands and their complexes has stimulated research efforts for methods of their preparation and for studying their interesting chemical and physical properties. In particular, polynuclear systems are interesting because of their magnetic interaction between metallic centres. For this reason, we synthesized a new series of highly unsaturated copper(II) macrocyclic complexes [CuL]X$_2$ (where L = 6,13-bis(dodecylaminomethylidene)-1,4,8,11-tetrazacyclotetradeca-4,7,11,14-tetraene, X = Cl$^-$, Br$^-$, PF_6^-) [11]. Magnetic properties of these compounds were compared indicating that all copper compounds studied behave as weakly interacting magnets. On the other hand, the synthesis of heteropolymetallic systems with extended structures frequently consists in self-assembly processes involving anionic building blocks, which contain a paramagnetic ion, and in assembling complexed cations able of interacting with them [12]. We present also the magnetic properties of a system built of a highly unsaturated cyclidene copper(II) complex cation and hexachlororhenium(IV) or hexabromorhenium(IV) anions.

2. Experimental

2.1. Syntheses of the complexes

All chemicals were reagent grade and were used as commercially obtained. Ni(III) complexes, [Ni^{III}LCl$_2$]$^+$, containing tetraaza macrocyclic ligands with different number of methyl groups (L = [14]aneN$_4$ (L^1), 2-Me[14]aneN$_4$ (L^2), 5,12-Me$_2$[14]aneN$_4$ (L^3), 5,7,7,12,14,14-Me$_6$[14]aneN$_4$ (L^4)) were obtained from the corresponding nickel(II) complexes by oxidation with hydrogen peroxide [13].

Complexes of [CuL]X$_2$ were prepared according to [11]. Nearly unsoluble complexes : [CuL]ReCl$_6$·H$_2$O and [CuL]ReBr$_6$ were precipitated from acetonitrile solution of [CuL](PF$_6$)$_2$ with an excess of [Bu$_4$N]$_2$ReCl$_6$ or [Bu$_4$N]$_2$ReBr$_6$, respectively.

2.2. Magnetic measurements

Magnetic studies of powdered samples were carried out by the Faraday and SQUID methods. The Faraday-method measurements were carried out over the 4.5 –300 K range of temperatures using a $Hg[Co(NCS)_4]$ standard for which the value of the gram susceptibility equals 16.44×10^{-6} $cm^3 \cdot g^{-1}$ at T = 293.1 K. The magnetic susceptibility of the powdered samples was measured over the temperature range of 1.9 –300 K using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The superconducting magnet was generally operated at field strengths ranging from 0.1 to 5 T. The SQUID magnetometer was calibrated with a palladium rod sample for which the gram magnetic susceptibility was taken as 5.30×10^{-6} $cm^3 \cdot g^{-1}$ at T = 293.1 K. The corrections for diamagnetism were estimated from the Pascal constants [14].

2.3 Spectroscopic measurements

FIR spectra (500–100 cm^{-1}) were measured in Nujol mull and the MIR spectra (4000–500 cm^{-1}) in KBr pellets with a Bruker IFS 113 V Spectrophotometer.

Solid state EPR spectra were recorded in the 300–77 K temperature range with a Bruker E600 spectrometer. Reflectance spectra have been recorded with a Beckmann UV 5240 spectrophotometer in the range of 350–2500 nm.

3. Results and discussion

Magnetic susceptibility measurements of investigated complexes $[Ni\ [14]aneN_4Cl_2]Cl$, $[Ni\ 2\text{-}Me[14]aneN_4Cl_2]ClO_4$ and $[Ni\ meso\text{-}5,12\text{-}Me_2[14]aneN_4Cl_2]Cl \cdot CH_3OH$ reveal analogies in their magnetic properties. The values of magnetic moment are shown in Table 1. All complexes investigated obey the Curie–Weiss law in the 100–300 K temperature range. The values of C and Θ are shown in Table 1. The magnetic moment is constant in the temperature range of 30–300 K. There is a slight decrease of magnetic moment below 30 K. The paramagnetic dependencies of magnetic moment as a function of temperature are presented in Figs. 1, 2. Relatively lower value of μ_{eff} in $[Ni\ meso\text{-}5,7,7,12,14,14\text{-}Me_6[14]aneN_4Cl_2]Cl$ can be related to the presence of impurity of Ni(II) form of the complex.

The EPR spectra show considerably greater values of $g_\perp$ than $g_\|$ for $[Ni\ meso\text{-}5,12\text{-}Me_2[14]aneN_4Cl_2]Cl \cdot CH_3OH$ and $[Ni\ meso\text{-}5,7,7,12,14,14\text{-}Me_6[14]aneN_4Cl_2]Cl$ complexes, as expected of a low-spin, d^7 metal centre in an elongated octahedral environment. Compounds $[Ni\ [14]aneN_4Cl_2]Cl$ and $[Ni\ 2\text{-}Me[14]aneN_4Cl_2]ClO_4$ give a rhombic EPR spectrum with g_1, g_2 and g_3 values presented in Table 1. If the first value is taken as $g_\|$ and the average of g_2 and g_3 are taken as pseudo-$g_\perp$, these two complexes belong (as well as the previous ones) to the class having $g_\perp > g_\|$. The form of the EPR spectra for the low-spin Ni(III) complexes with $g_\perp > g_\|$ suggests that the

d_z^2 orbital is favoured for the single unpaired electron. All the compounds investigated have very similar values of $g_\perp$ (as well as of $g_\parallel$) components. There is a slight increase of the $g_\perp$ values observed when the number of methyl groups in the molecule is increased.

Table 1. The magnetic parameters of the compounds investigated

Compound	μ_{eff}^{*}	Θ^{**} (K)	C^{**} ($\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$)	Spectroscopic splitting parameter*		
				g_1	g_2	g_3
[Ni [14]aneN_4Cl_2]Cl	1.82	1.9	0.409	2.024	2.105	2.179
[Ni 2-Me[14]aneN_4Cl_2]ClO_4	1.80	1.5	0.406	2.076	2.133	2.180
[Ni meso-5, 12-Me_2[14] -aneN_4Cl_2]Cl · CH_3OH	1.83	2.7	0.412	$g_{\text{II}} = 2.026$	$g_\perp = 2.182$	
[Ni meso-5,7,7,12,14,14 -Me_6[14]aneN_4Cl_2]Cl	1.54	5.9	0.293	$g_{\text{II}} = 2.027$	$g_\perp = 2.209$	

*At a room temperature.
**In the temperature range of 50–300 K.

The solid-state reflectance spectra of these complexes consist of two bands at about 28600 and 12300 cm^{-1}. The position of the second band shifts to a lower frequency while the number of the methyl groups in the complex is increased. The EPR data are presented in Table 1.

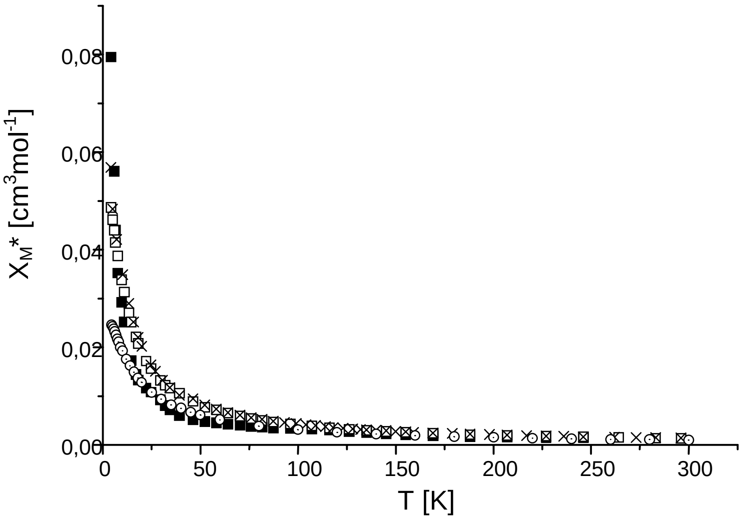

Fig. 1. Experimental magnetic data plotted as a molar magnetic susceptibility χ_M^* vs. temperature for the compound [Ni [14]aneN_4Cl_2]Cl (■), [Ni 2-Me[14]aneN_4Cl_2]ClO_4 (□), [Ni meso-5,12-Me_2[14]aneN_4Cl_2]Cl·CH_3OH (×) and [Ni meso-5,7,7,12,14,14-Me_6[14]aneN_4Cl_2]Cl (○)

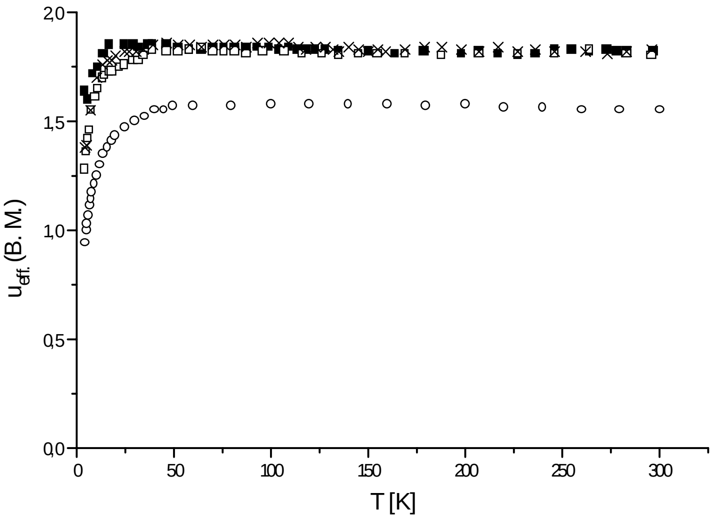

Fig. 2. Experimental magnetic data plotted as a magnetic moment $\mu_{eff.}$ vs. temperature for the compound [Ni [14]aneN_4Cl_2]Cl (■), [Ni 2-Me[14]aneN_4Cl_2]ClO_4 (□), [Ni meso-5,12-Me_2[14]aneN_4Cl_2]Cl·CH_3OH (×) and [Ni meso-5,7,7,12,14,14-Me_6[14]aneN_4Cl_2]Cl (○)

The IR spectra of all complexes show absorption of NH groups (ν_{NH}) between 3198 and 3046 cm^{-1}. One compound of the formula [Ni meso-5,12-Me_2[14]ane-N_4Cl_2]Cl exhibits a ν_{OH} band at 3541 cm^{-1} originating from coordinated methanol molecule.

The study of the magnetic susceptibility data for the complexes [CuL]X_2 (where L= 6,13-Bis(dodecylaminomethylidene)-1,4,8,11-tetrazacyclotetradeca-4,7,11,14-tetraene), Fig. 3) has been performed within the temperature range of 1.90–300 K. The experimental data, plotted as the thermal variations of the $\chi_M T$ product, are shown in Fig. 4 for [CuL](Cl_2)·$2H_2O$, [CuL](Br_2), [CuL]$(PF_6)_2$ and [Cu(L-2H$^+$)] complexes.

In all the cases the χ_M value increases slowly with the decrease of temperature, but in the low-temperature region a rapid increase of molar susceptibility values occurs without showing a maximum. The values of $\chi_M T$ for [CuL](Br_2) and [Cu(L-2H$^+$)] complexes decrease very slowly with T in a wide range of temperature. At low temperatures (below 20 K), they decrease to 0.19 cm^3·mol^{-1}·K and to 0.24 cm^3·mol^{-1}·K at 1.90 K, respectively. In the case of [CuL](Cl_2)·$2H_2O$ a rapid decrease of $\chi_M T$ values is observed, from 0.75 cm^3·mol^{-1}·K at a room temperature to 0.29 cm^3·mol^{-1}·K at 1.90 K.

For the [CuL]$(PF_6)_2$ complex the $\chi_M T$ values remain nearly constant in a wide range of temperatures and

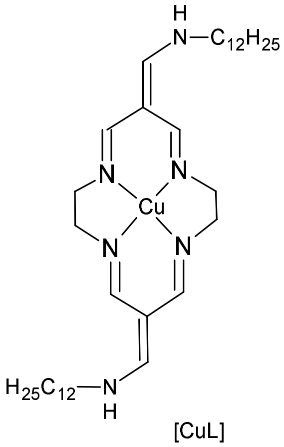

Fig. 3. Schematic view of [CuL]$^{2+}$ cation

below 10 K $\chi_M T$ increases upon cooling. This indicates that some exchange interaction between copper atoms in the crystal lattices of compounds examined can exist. In such situations the exchange parameter zJ' can be determined only by a susceptibility equation with a molecular field correction [15].

$$\chi_M = \frac{g^2 N\beta^2}{3kT} S(S+1) \qquad \chi'_M = \frac{\chi_M}{1 - \left(\dfrac{2zJ'}{Ng^2\beta^2}\right)\chi_M} \tag{1}$$

where N is the Avogadro number, g – the spectroscopic splitting factor, β – the Bohr magneton, k – the Boltzmann constant and zJ'– intermolecular exchange parameter.

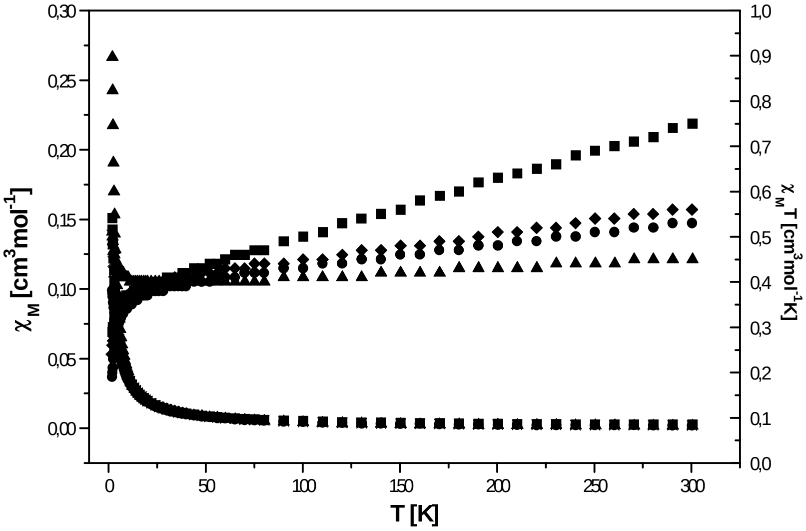

Fig. 4. Thermal dependence of χ_M and $\chi_M T$ for: ■ – [CuL](Cl$_2$)·2H$_2$O, • – [CuL](Br$_2$), ▲ – [CuL](PF$_6$)$_2$, ◆ – [Cu(L-2H$^+$)].

The best fit parameters are g = 2.06 and zJ' = –0.52 cm^{-1} for [CuL](Cl$_2$)·2H$_2$O, g = 2.16 and zJ' = –1.53 cm^{-1} for [CuL](Br$_2$), g = 2,12 and zJ' = –0.84 cm^{-1} [Cu(L-2H$^+$)] and g = 2.05 and zJ' = 0.29 cm^{-1} for [CuL](PF$_6$)$_2$, obtained with good agreement factors $R = 2.30\cdot10^{-5}$ for [CuL](Cl$_2$)·2H$_2$O, $R = 4.57\cdot10^{-5}$ for [CuL](Br$_2$) and $R = 8.40\cdot10^{-5}$ for [Cu(L-2H$^+$)] and $R = 1.86\cdot10^{-5}$ for [CuL](PF$_6$)$_2$.

The EPR spectra of the compound examined at a room temperature and 77 K present only single lines of $H = 3500g$ for ν = 9.771 Ghz. The spectroscopic splitting factor was typical of copper(II) centres, g amounting to 2.08 for all compounds. In principle, the observed weak antiferromagnetic interactions in [CuL](Cl$_2$)·2H$_2$O, [CuL](Br$_2$) and [Cu(L-2H$^+$)] complexes and weak ferromagnetic interactions in [CuL](PF$_6$)$_2$ could be attributed to intermolecular interactions between copper centres, which may be transmitted through Cl^-, Br^-, PF_6^- anions or H^+ cations in a crystal lacttice.

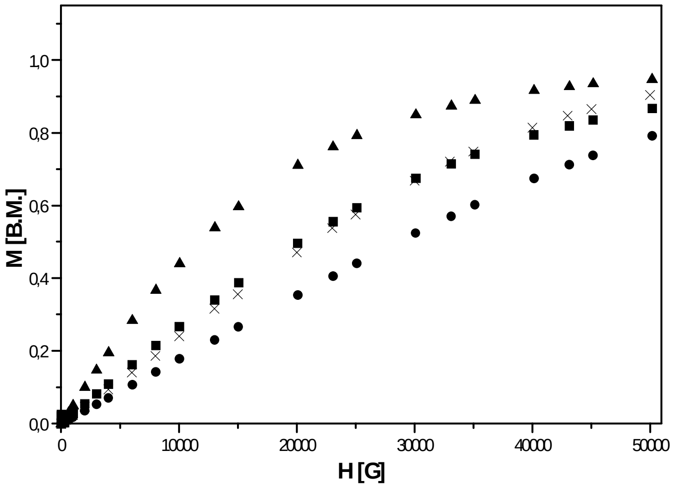

Fig. 5. Field dependence of the magnetization at 1.9 K for the complexes:
■ – $[CuL](Cl_2)\cdot 2H_2O$, • – $[CuL](Br_2)$, ▲– $[CuL](PF_6)_2$, × – $[Cu(L\text{-}2H^+)]$

The field dependence of magnetization for all complexes at 1.9 K (Fig. 5) clearly supports the occurrence of very weak interactions in all complexes. In consequence, one can say that the communication between copper(II) centres in crystal lacttice is higher in the case of $[CuL](Br_2)$ than in $[CuL](Cl_2)\cdot 2H_2O$ and $[Cu(L\text{-}2H^+)]$ complexes and have an opposite character than that in the $[CuL](PF_6)_2$ compound.

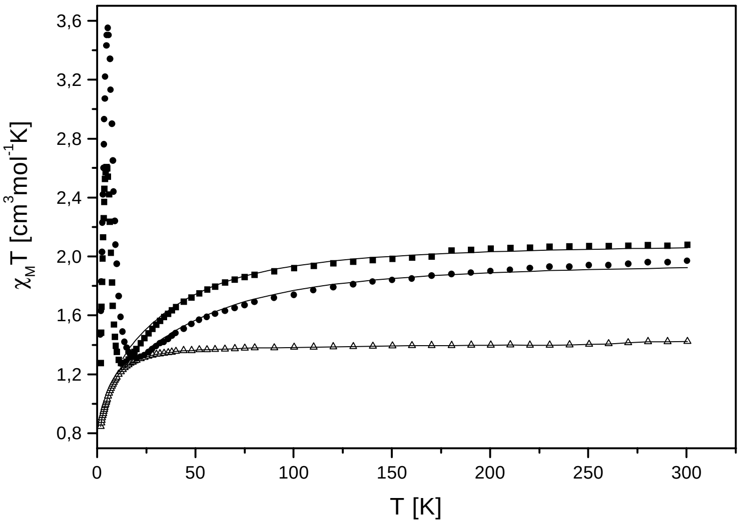

Fig. 6. Temperature dependencies of $\chi_M T$ for: ■ – $[CuL]ReCl_6\cdot H_2O$, • – $[CuL]ReBr_6$, Δ – $[Bu_4N]_2ReCl_6$; the solid lines are the calculated curves

The magnetic properties of complexes [CuL]ReCl$_6$·H$_2$O and [CuL]ReBr$_6$ as the plot of $\chi_M T$ vs. T (χ_M being the molar magnetic susceptibility per Re^{IV}Cu^{II} heterobinuclear unit) are shown in Fig. 6 and the $\chi_M T$ data of (Bu$_4$N)$_2$ReCl$_6$ are also included for comparison.

At a room temperature $\chi_M T$ for heterometallic compounds are equal to 2.08 cm^3·K·mol^{-1} and 1.97 cm^3·K·mol^{-1} for [CuL]ReCl$_6$·H$_2$O and [CuL]ReBr$_6$, respectively. These values are close to the expected one for uncoupled Re^{IV}–Cu^{II} ions. As the temperature is lowered, the $\chi_M T$ smoothly decrease and reach rounded minima at 13.0 K with $\chi_M T$ =1.27 cm^3·K·mol^{-1} and at 20 K with 1.31 cm^3·K·mol^{-1} for [CuL]ReCl$_6$·H$_2$O and [CuL]ReBr$_6$, respectively. The presence of a minimum in the $\chi_M T$ curve is indicative of antiferromagnetic coupling between Re^{IV} and Cu^{II} and is characteristic of one-dimensional ferrimagnetic chain compounds [16]. Below the temperatures: 13.0 K for [CuL]ReCl$_6$·H$_2$O and 20 K for [CuL]ReBr$_6$, the values of $\chi_M T$ for both compounds increase, then reach maxima at 4.73 K with $\chi_M T$ = 2.61 cm^3·K·mol^{-1} for [CuL]ReCl$_6$·H$_2$O and 5.49 K with $\chi_M T$ = 3.55 cm^3·K·mol^{-1} for [CuL]ReBr$_6$ compound and finally decrease rapidly below 4.73 for [CuL]ReCl$_6$·H$_2$O and 5.49 K for [CuL]ReBr$_6$, respectively (Fig. 6).

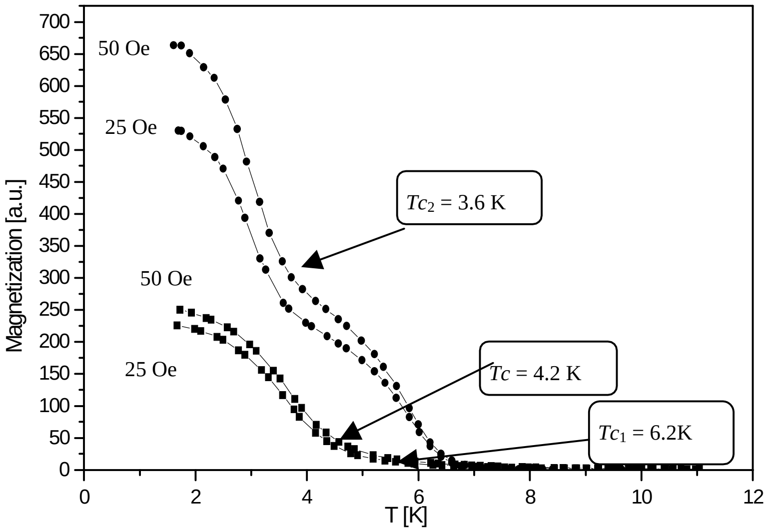

Fig. 7. *M*. versus *T* plots in the low-temperature range for two different values of the applied magnetic field for: ■ – [CuL]ReCl$_6$·H$_2$O, • – [CuL]ReBr$_6$

The variation of susceptibility with temperature for these compounds could be satisfactorily fitted using the spin Hamiltonian defined by Eq. (2) [17–19]:

$$H = \sum_i \left\{ \begin{array}{l} -JS^z_{2i-1}S^z_{2i} + g_{\mathrm{II}Cu}\beta S^z_{2i-1}H_z + g_{\mathrm{II\,Re}}\beta S^z_{2i}H_z + \\ g_{\perp Cu}\beta\left(S^x_{2i-1}H_x + S^y_{2i-1}H_y\right) + g_{\perp \mathrm{Re}}\beta\left(S^x_{2i}H_x + S^y_{2i}H_y\right) + D\left[\left(S^z_{2i}\right)^2 - \frac{5}{4}\right] \end{array} \right\} \quad (2)$$

The least-squares fitting of the experimental data with this expression was limited to the range of 13–300 K for $[\mathrm{CuL}]\mathrm{ReCl_6{\cdot}H_2O}$ and 20–300 K for $[\mathrm{CuL}]\mathrm{ReBr_6}$ yielding $D = 53.4$ cm^{-1}, $g_{\mathrm{IIRe}} = 1.94$ and $g_{\perp\mathrm{Re}} = 1.90$, $g_{\mathrm{IICu}} = 2.29$, $g_{\perp\mathrm{Cu}} = 1.93$ and $J = -9.1$ cm^{-1} for $[\mathrm{CuL}]\mathrm{ReCl_6{\cdot}H_2O}$ and $D = 63.6$ cm^{-1}, $g_{\mathrm{IIRe}} = 1.84$ and $g_{\perp\mathrm{Re}} = 1.82$, $g_{\mathrm{IICu}} = 2.29$ $g_{\perp\mathrm{Cu}} = 1.99$ and $J = -12.2$ cm^{-1} for $[\mathrm{CuL}]\mathrm{ReBr_6}$. We conclude that $\mathrm{Re^{IV}}$ in $[\mathrm{CuL}]\mathrm{ReCl_6{\cdot}H_2O}$ and $[\mathrm{CuL}]\mathrm{ReBr_6}$ exhibits a large zero-field splitting parameter together with weak antiferromagnetic interactions with $\mathrm{Cu^{II}}$.

The magnetization vs. temperature curves (Fig. 7) reveal magnetic transitions at $Tc = 4.2$ K for $[\mathrm{CuL}]\mathrm{ReCl_6{\cdot}H_2O}$ as well as at $Tc_1 = 6.2$ K and $Tc_2 = 3.6$ K for $[\mathrm{CuL}]\mathrm{ReBr_6}$. $[\mathrm{CuL}]\mathrm{ReCl_6{\cdot}H_2O}$ and $[\mathrm{CuL}]\mathrm{ReBr_6}$ are ferrimagnetic chains as a result of ordering [19]. The occurrence of the second Curie temperature ($Tc_2 = 3.6$ K) in the $[\mathrm{CuL}]\mathrm{ReBr_6}$ complex does not follow the phenomenon of the compensation temperature in ferrimagnets. Probably, there are two different kinds of sublattices in $[\mathrm{CuL}]\mathrm{ReBr_6}$, both of ferromagnetic character.

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