INTRODUCTION

During the past years interest in the cyanocomplexes was revived due to the fact that they are building blocks of magnetic clusters and networks [1-7]. One of the great advantages of these materials is that novel functions like control of the magnetic properties via external stimuli, can be incorporated through a proper design of their electronic structure. It has been reported the examples of magnetic ordering temperature ($T_C$) control, via electrochemical stimuli [8] on chromium cyanide thin film and optical stimuli [9], where first example of a photo-induced reversible change between a paramagnet and a ferrimagnet was described in a Prussian blue analog, $K_{0.2}Co_{1.4}[Fe(CN)_{6}]·6.9H_2O$. Similar photo-induced change of magnetization can be observed on other types of cyanometallates; photo-magnetic effect was investigated on $Cu_2[Mo(CN)_{8}]·8H_2O$ [10]. Since no complete study of OCMs has been reported we prepared and studied physical properties of $TM^{2+}_{2}[Mo^{IV}(CN)_{8}]·nH_2O$, where $TM$ is Mn, Fe, Co, Ni, Cu.

EXPERIMENTAL

Sample preparation

Potassium octacyanomolybdate (IV) was prepared by the method of Brauer [11]. The divalent cation salts (TMCl$_2$) were of p.a. grade. All the OCMs were prepared by the same technique; by slow mixing of saturated aqueous solutions of $K_4[Mo(CN)_{8}]·2H_2O$ (22-25 ml) with the aqueous solution ($c = 0.5 M$) of TMCl$_2$ (except Fe$^{2+}$, where FeSO$_4$ was used) at room temperature following the formal equation:

$$2TMCl_2 (aq) + K_4[Mo(CN)_{8}] (aq) \rightarrow TM_{2}[Mo(CN)_{8}]·nH_2O (s) + 4KCl (aq)$$

In all cases, except Mn$^{2+}$, process of precipitation started immediately. In the case of Mn$_{2}[Mo(CN)_{8}]·8H_2O$ the process started in about 10 min. The solids were collected by filtration, washed two times with 10 ml of water and dried above KOH. The typical distribution of well crystalline particles for the Mn$_{2}[Mo(CN)_{8}]·8H_2O$ sample can be seen from scanning electron micrograph (figure 1). The remaining OCMs crystallize worse, for example $Cu_{2}[Mo(CN)_{8}]·7H_2O$ (also shown in figure 1).

Instruments

Infrared spectra were observed by using FT-IR spectrometer Avatar 330 in the range from 400 to 4000 cm$^{-1}$ using KBr tablets. UV-VIS spectra were also measured in pressed KBr pellets by an Ocean Optics SD 1000 fiber optic spectrometer (low resolution), and a JASCO V-550 dual-channel spectrophotometer (high resolution).
RESULTS AND DISCUSSION

Infrared spectroscopy

The analysis of IR spectra showed that the spectrum of K$_4$[Mo(CN)$_8$]·2H$_2$O agrees well with that reported by Kettle and Parish [13] for dodecahedral D$_{2d}$ structure of [Mo(CN)$_8$] unit [14]. Four strong bands are seen at 2102, 2123, 2127, and 2135 cm$^{-1}$ (figure 3). In the case of OCMs the geometry of [Mo(CN)$_8$] unit is changed from D$_{2d}$ one in the starting K$_4$[Mo(CN)$_8$]·2H$_2$O to square antiprismatic D$_{4d}$ (figure 2) [18, 20, 21].

The IR spectra of OCMs (summarized in table 1) shows a single strong $\nu$(CN) peak about 60 cm$^{-1}$ wide at half height. (See the case of Ni$_2$[Mo(CN)$_8$]·8H$_2$O in figure 3, for example.)

Table 1. Summarization of infrared measurements of TM$_2$[Mo(CN)$_8$]$_n$H$_2$O in the cyanide stretching region.

<table>
<thead>
<tr>
<th>TM</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(CN) (cm$^{-1}$)</td>
<td>2133</td>
<td>2137</td>
<td>2144</td>
<td>2152</td>
<td>2164</td>
</tr>
</tbody>
</table>

Figure 1. Scanning electron micrographs of Cu$_2$[Mo(CN)$_8$]·7H$_2$O (left) and Mn$_2$[Mo(CN)$_8$]·8H$_2$O (right) powder particles.

Figure 2. Dodecahedral D$_{2d}$ and square antiprismatic D$_{4d}$ geometries of the OCMs [15].
Our results correspond with recently published results in [16]. The values of ν(CN) for all OCMs are shifted to higher frequencies than those of K₄[Mo(CN)₈]·2H₂O that indicate the bridging nature of the cyano groups –TM–NC–Mo–CN–TM–.

UV-VIS spectroscopy

UV-VIS spectra of OCMs, which include Mn, Fe, Co, Ni are a simple superposition of the bands of their components. Such is the case of Mn₄[Mo(CN)₈]·8H₂O in the inset in figure 4). In the case of Cu₂[Mo(CN)₈]·7H₂O we can see a supplementary band in the visible region at around 510 nm (figure 4). This absorption band corresponds to the optical absorption spectra of ion pair Cu²⁺[Mo⁶⁺(CN)₈]⁺ in the solution. By excitation of this band the intramolecular electron transfer process produces the metastable valence isomer Cu⁺[Mo⁴⁺(CN)₈]⁺ [17]. This same photo-induced electron transfer occurs in the corresponding solid phase and Cu²⁺[Mo⁶⁺(CN)₈] will be changed by irradiation to Cu²⁺Cu⁺[Mo⁵⁺(CN)₈] [5].

X-ray diffraction

A set of powder samples TM₂[Mo(CN)₈]·nH₂O (TM is Mn, Fe, Co, Ni, and Cu) was investigated by X-ray diffraction. The crystal structure of Fe₂[Mo(CN)₈]·8H₂O was refined in accordance with the structural model described by Sra et al. [18]. The obtained results are summarized in figure 5 and table 2. The structural model suggested by Willemijn et al. [20] was used for the crystal structure refinement of Mn₂[Mo(CN)₈]·8H₂O phase. The structure is tetragonal (space group I₄/mcm), refined values of lattice parameters are a = b = 11.679 (4) Å, c = 13.205 (6) Å. The crystal structure of Ni₂[Mo(CN)₈]·8H₂O phase has not been determined. Indexing procedure confirmed for the phase tetragonal symmetry, too. The structureless profile matching fit gave refined values of lattice parameters a = b = 11.555 (4) Å and c = 14.044 (6) Å. Co₂[Mo(CN)₈]·8H₂O phase was reported to crystallize in the tetragonal system (I₄/m) [20, 21]. Unfortunately in our case the indexing procedure failed for TM is Co and Cu. However, for Cu₂[Mo(CN)₈]·8H₂O it was probably caused by the low

Table 2. Refined values of selected structural parameters of Fe₂[Mo(CN)₈]·8H₂O.

<table>
<thead>
<tr>
<th>Space group</th>
<th>I 4 2 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>11.8032 (15)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.8032 (15)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.1008 (2)</td>
</tr>
<tr>
<td>α</td>
<td>90.0</td>
</tr>
<tr>
<td>β</td>
<td>90.0</td>
</tr>
<tr>
<td>γ</td>
<td>90.0</td>
</tr>
<tr>
<td>Cell volume (Å³)</td>
<td>1825.15 (5)</td>
</tr>
</tbody>
</table>

Table 3. Infrared spectra of K₄[Mo(CN)₈]·2H₂O and Ni₂[Mo(CN)₈]·8H₂O.

Figure 3. Infrared spectra of K₄[Mo(CN)₈]·2H₂O and Ni₂[Mo(CN)₈]·8H₂O.
quality of powder diffraction pattern due to significant contribution of poor crystallized component. Similarly Cu-OCM was reported as poorly crystallized sample [19, 23] unlike Cu$_2$[W(CN)$_8$]·8H$_2$O which crystallizes well in the orthorhombic system (space group $Pbcn$).

The $^1$H nuclei in the water molecules served as local probes in the NMR experiments. The FID signals showed a behaviour peculiar to paramagnetic samples. They decayed more rapidly in a higher applied static field $B_0 = \omega_0/\gamma_1$ (figure 6b). Their decay rates described by an effective spin-spin relaxation time ($T_{2\text{eff}}$) increase as the magnetic moment of the transition-metal ions (table 3).

The amplitude of the FID signal at $t = 0$ is proportional to the number of $^1$H nuclei in the sample. This makes possible to determine the amount of water i.e. the molar ratio $n$. Unfortunately the resonance frequency of the protons near to the first-row transition metal ions is shifted by the local magnetic moments so far from the applied frequency that the signal of these protons is not detected. This means that a part of the water content is unseen and the water concentration cannot be determined. Only a lower limit for $n$ could be calculated in an ideal case. The FID signal at $0 > t > (10-20) \mu$s is concealed by the dead time of the spectrometer. There is no theoretical model for the exact shape of the FID measured in this kind of samples. The extrapolation to $t = 0$ has not been made because of a big error of the extrapolated value resulting from a fit with a trial function.

The recovery of the magnetization in the spin-lattice relaxation experiments was single-exponential at $\nu_0 = 27.694$ MHz and it could be described by a sum of two exponentials at $\nu_0 = 82.556$ MHz (table 3). Mn$_2$[Mo(CN)$_8$]·8H$_2$O showed two-exponential relaxation at the lower frequency also ($93.4\% \times \exp[t/(0.0187 \text{ ms})] + 6.6\% \times \exp[t/(3 \text{ ms})]$). The not single-exponential behaviour can be accounted for the local magnetic moments of the first-row transition metal ions. The effect is more expressed with the increased effective magnetic moment. That is why only the manganese sample with the largest magnetic moment had two-exponential relaxation at the lower measuring frequency while at the higher frequency even the copper sample had non-exponential behaviour.

### Table 3. Effective spin-spin relaxation times and $^1$H spin-lattice relaxation times of TM$_2$[Mo(CN)$_8$]·nH$_2$O

<table>
<thead>
<tr>
<th>TM</th>
<th>$\nu_0 = 27.694$ MHz</th>
<th></th>
<th>$\nu_0 = 82.556$ MHz</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{2\text{eff}}$ (µs)</td>
<td>$T_1$ (ms)</td>
<td>$T_{2\text{eff}}$ (µs)</td>
<td>$T_1$ (ms)</td>
</tr>
<tr>
<td>Cu</td>
<td>155.9 0.45</td>
<td>80.5 0.680</td>
<td>97% 7.00</td>
<td>3%</td>
</tr>
<tr>
<td>Ni</td>
<td>54.6 0.33</td>
<td>23.6 0.102</td>
<td>94% 1.50</td>
<td>6%</td>
</tr>
<tr>
<td>Co</td>
<td>39.2 1.1</td>
<td>12.3 0.020</td>
<td>13% 1.26</td>
<td>87%</td>
</tr>
<tr>
<td>Fe</td>
<td>30.3 0.156</td>
<td>10.1 0.018</td>
<td>50% 0.21</td>
<td>50%</td>
</tr>
<tr>
<td>Mn</td>
<td>12.8 0.0187</td>
<td>5.5 0.016</td>
<td>93% 0.50</td>
<td>7%</td>
</tr>
</tbody>
</table>

Figure 4. Absorbance UV-VIS spectra of Cu$_2$[Mo(CN)$_8$]·7H$_2$O (left) and Mn$_2$[Mo(CN)$_8$]·8H$_2$O (right), where MLCT is metal ligand charge transfer.
Magnetic measurements

The $\chi(T)$ plots shown in figure 7(a) were measured in magnetic field $\mu_0 H = 1$ T. The sharp decrease of $\chi(T)$ below $T = 30$ K can indicate onset of antiferromagnetic exchange interaction. In the case of Co$^{2+}$ phase, $\chi(T)$ decreases in the entire temperature range. Such a decrease of $\chi(T)$ with $T$ can be attributed to the intrinsic behaviour of Co$^{2+}$ ion rather than to antiferromagnetic exchange interactions among these ions in the 3D network. The samples obey the Curie-Weiss law $\chi = C/(T - \theta)$ nearly in the whole measured temperature range except of Co$^{2+}$ sample, where $1/\chi(T)$ decreases remarkably below $T = 50$ K [22]. The paramagnetic Curie temperature is negative for Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$ samples ($\theta = -1.3$ K, -3.1 K, -25.6 K) and close to zero for Ni$^{2+}$, Cu$^{2+}$ samples ($\theta = 0.0$ K, 0.3 K). We tried to determine the Curie temperature by several different methods. The classical method for obtaining the Curie temperature $T_c$ by plotting $M^2$ vs. $T$ and extrapolating the linear part to the temperature axis (Weiss method) gave the values, which varies in the range $3 \text{ K} < T_c < 4$ K for TM is Mn, Fe, and Co. On the other hand, the method of determining $T_c$ by plotting $H/M(H,T)$ vs. $M(H,T)$ (Belov-Arrott's plots) gave the value of $T_c = 4$ K only in the case of Mn$^{2+}$ and Co$^{2+}$ containing samples. A ferromagnetic-like behaviour is seen also in the $M(H,T)$ vs. $H$ curves of Fe$^{2+}[\text{Mo(CN)}_8] \cdot 8\text{H}_2\text{O}$. However, the fact that the Curie temperature could not be defined by using the Belov-Arrott method leads to the conclusion that there is only a short-range ordering in this sample in the vicinity of $T = 2$ K. Remaining complexes with Ni$^{2+}$ and Cu$^{2+}$ are paramagnetic in the whole temperature range. The results of the magnetic isotherms show that the magnetization is proportional to the magnetic field at higher temperatures and tends to saturate at very low temperatures and at higher magnetic fields (TM is Mn and Co). Magnetization curves of Mn$^{2+}[\text{Mo(CN)}_8] \cdot 8\text{H}_2\text{O}$ shown in figure 7b confirm the gradual development of magnetically ordered state in Mn$^{2+}$ sample with magne-
magnetization reaching the value of $\mu_S = 8.2 \mu_B/f.u.$ at $T = 1.9$ K. Similar behaviour we have observed for Co$_2^[Mo(CN)8]·6H_2O$ with magnetization $\mu_S = 3.95 \mu_B/f.u.$

The magnetic ordering of TM$^{2+}$[Mo$^{V}(CN)_8]·nH_2O$ octacyanometallates (TM is Mn, Fe, Co, Ni and Cu) is driven by the antiferromagnetic interaction between paramagnetic TM$^{2+}$ ions through the NC–Mo$^{IV}$–CN diamagnetic spacer. The value of the exchange interaction is very weak due to contribution of diamagnetic Mo$^{IV}$ resulting in the low value of the Curie temperature. The analysis of our magnetization measurements revealed that only Mn$_2^[Mo(CN)8]·8H_2O$ and Co$_2^[Mo(CN)8]·6H_2O$ show long range magnetic ordering of ferrimagnetic type below $T_C = 4$ K and a short range ordering starts to form in Fe$_2^[Mo(CN)8]·8H_2O$ at about $T = 2$ K. Our results are consistent with results already published on Mn, Fe, and Cu OCMs [18, 19, 23]; to our knowledge, the results on Co and Ni OCMs have not been presented by another authors yet.

CONCLUSIONS

Cyano-bridged complexes TM$^{2+}$[Mo(CN)$_8$]$\cdot nH_2O$, where TM is Mn, Fe, Co, Ni, Cu were synthesised, characterised by IR spectroscopy and UV-VIS spectroscopy. The UV-VIS spectrum taken on the Cu$_2^[Mo(CN)8]·7H_2O$ showed the (IVCT) between Mo$^{IV}$–CN–Cu$^{II}$ and Mo$^{V}$–CN–Cu$^{I}$ at around 510 nm. The amount of water in structural formulae $n$ varies between 6 and 8. The Rietveld refinement showed that Mn$_2^[Mo(CN)8]·8H_2O$ and Fe$_2^[Mo(CN)8]·8H_2O$ adopt tetragonal crystal structure (space group $I4/mcm$ and $I422$) with values of lattice parameters $a = 11.679(4)\ A$, $c = 13.205(6)\ A$, and $a = 11.80321(15)\ A$, $c = 14.044(6)\ A$, respectively. Profile matching procedure confirmed the tetragonal symmetry for Ni$_2^[Mo(CN)8]·7H_2O$ with lattice parameters $a = 11.555(4)\ A$ and $c = 14.044(6)\ A$. The indexing procedure failed for Cu$_2^[Mo(CN)8]·7H_2O$ due to poor crystallinity of the sample. The $^1$H NMR signals reflect the magnetic moment of the TM$^{2+}$ ions ($\mu_P$). The decay rates of FID signals increase as $\mu_P$ and the applied static rf-field increases. The spin-lattice relaxation times at 27.7 MHz vary from 0.0187 ms (Mn) up to 0.45 ms (Cu). Magnetic behaviour of the investigated OCMs is determined by the electronic structure of the TM$^{2+}$ ion and by the antiferromagnetic interaction between TM$^{2+}$ ions through the NC–Mo$^{IV}$–CN diamagnetic spacer. Magnetization measurements indicate long-range magnetic ordering in Mn- and Co-OCMs with the Curie temperature about $T_C = 4$ K. The remaining OCMs (TM is Fe, Ni and Cu) are paramagnetic at least down to $T = 1.9$ K.

Acknowledgement

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References


Synthesis, structural and magnetic properties of TM$^{2+}$:Mo(CN)$_8$·nH$_2$O

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Oktakyonamolybdenitany (OCM) TM$^{2+}$:Mo(CN)$_8$·nH$_2$O, kde TM je Mn, Fe, Co, Ni, Cu, byly syntetizovány a charakterizovány IČ a UV-VIS spektroskopii. V UV-VIS spektru jsou patrné pásy intervaleného přenosu náboje (IVCT) mezi Mo$^{IV}$-CN-Cu$^{II}$ a Mo$^{V}$-CN-Cu$^{I}$ kolem 510 nm. Studované OCM mají tetragonální krystalovou strukturu. 1H NMR signál ukazuje na magnetický moment iontů TM$^{2+}$ ($\mu_P$). Rychlost poklesu volného indukovaného rozkladu (FID) signálu roste s poklesem $\mu_P$ a vloženého statického rf-pole. Spinové-mířkové relaxační časy při 27.7 MHz kolísají mezi 0.0187 ms (Mn) až 0.45 ms (Cu). Měření magnetizace svědčí o magnetickém uspořádání na dlouhou vzdálenost v OCM s Mn a Co s Curieovou teplotou $T_c = 4$ K. Ostatní OCM (TM je Fe, Ni, Cu) jsou paramagnetické až do $T = 1.9$ K.