# Synthesis and Characterization of New Thiocyanato Bridged Complexes with the General Formula [MLn]3[Cr(NCS)6]2·mH2O, where M = Cu(II), Ni(II), Co(II); L = Various Substituted Imidazoles

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New thiocyanato bridged complexes of the type $[CuL_4]_3[Cr(NCS)_6]_2 \cdot mH_2O$ [L = 1-methylimidazole (1-Meim), 2-methylimidazole (2-Meim), 1,2-dimethylimidazole (1,2-Me$_2$im)] and $[M(1\text{-Meim})_6]_n[\{M(1\text{-Meim})_4Cr(NCS)_6\}_{2n}] \cdot mH_2O$ (M = Ni(II), Co(II) were prepared by the reaction of $[Cr(NCS)_6]^{3-}$ with the appropriate $[ML_n]^{2+}$ complex in an aqueous solution and characterized by elemental and thermal analysis, IR, UV-VIS, EPR and temperature variable magnetic susceptibility. The presence of NCS bridges between M(II)–Cr(III) centres is evident from IR spectra. The electronic spectra correlate with proposal of different composition of $Cu_3Cr_2$ and $M_3Cr_2$ (M = Ni, Co) systems. The parameters determined from temperature dependence on magnetic susceptibility (80–300 K) indicate weak or negligible antiferromagnetic interaction for obtained Cu(II)–Cr(III), Ni(II)–Cr(III) and Co(II)–Cr(III) systems. Thermal decomposition after dehydration is multistage and yields $CuO + CuCrO_2$ and $M^{II}O + M^{II}Cr_2O_4$ as final products, respectively.

**Key words**: heteropolynuclear complexes, thiocyanato bridges, chromium(III), copper(II), nickel(II), cobalt(II), imidazole, magnetic properties, EPR, IR, electronic spectra, thermal analysis

The recent growing studies of bimetallic polynuclear systems containing paramagnetic central atoms linked by bridging ligands leads to advance in our understanding of various phenomena connected with magnetism and photochemical behaviour [1–3]. So far most attention has been devoted to cyano complexes generated by hexacyanometalate anions. This results from possibility of prediction magnetic interactions between metal centres linked by linear CN bridges in face-centred cubic structure of Prussian Blue analogues. Interesting magnetic properties of this type of compounds such as high $T_c$ some of them [4] gave an impulse to extended studies of cyano complexes of various dimensionality obtained by using coordinatively unsaturated metal complexes instead of simple metal ions [5,6]. Other researches on magnetism have been concerned with oxalato [7], oxamato [8], oxamido [9] complexes. We focus our attention on hexaisothiocyanatochromate(III) anions and bridging properties of NCS⁻ ions. The literature on thiocyanato bridged bimetallic systems is very limited. There exist only few papers presenting the correlation the magnetic coupling with the structure [10–15] and several others describing magnetic behaviour without

structural data [16–20]. Thiocyanato ions are more flexible than cyano ions and although $NCS^-$ seems less efficient as a transmitter they can cause unexpected magnetic behaviour. For $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ system where thiocyanato bridged ions occupy *cis* positions at both metallic centres in the anionic chains, moderate antiferromagnetic coupling between Ni(II)–Cr(III) ($J \approx 20$ cm$^{-1}$) has been observed [21]. Continuing study of heteronuclear thiocyanato bridged complexes, we present the synthesis, spectroscopic and magnetic properties of the new bimetallic systems using $[Cr(NCS)_6]^{3-}$ as a building block: $[Cu(1\text{-}Meim)_4]_3[Cr(NCS)_6]_2$ (**1**), $[Cu(2\text{-}Meim)_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ (**2**), $[Cu(1,2\text{-}Me_2im)_4]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**3**), $[Ni(1\text{-}Meim)_6]_n[\{Ni(1\text{-}Meim)_4Cr(NCS)_6\}_{2n}] \cdot 5nH_2O$ (**4**), $[Co(1\text{-}Meim)_6]_n[\{Co(1\text{-}Meim)_4Cr(NCS)_6\}_{2n}] \cdot 2nH_2O$ (**5**).

## EXPERIMENTAL

**Materials**: $K_3[Cr(NCS)_6] \cdot 4H_2O$ was synthesized as described in [22]. Other reagents used, *i.e.* 1-methylimidazole (99%), 2-methylimidazole (99%), 1,2-dimethylimidazole (98%) purchased from Aldrich Chemical Company; $HNO_3$ (65%), $H_2O_2$ (30%), NaOH, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, purchased from POCh Gliwice were reagent grade and used without further purification.

**Instrumentation**: Analyses for C, H, N contents were carried out with a Perkin Elmer Analyzer Model 240. Cobalt, nickel, and copper contents were determined using the AAS method. Chromium content was determined spectrophotometrically as $CrO_4^{2-}$ at $\lambda = 372$ nm and with the AAS method for **5**. IR spectra were recorded on a Perkin Elmer FT-IR 2000 spectrophotometer within the range 450 to 4000 cm$^{-1}$ and 30 to 700 cm$^{-1}$ applying KBr and polyethylene discs, respectively. Electronic spectra of the solid complexes diluted in MgO were measured with the spectrophotometer SPECORD M-40 (Carl Zeiss, Jena) using a block for reflectance spectra R 8°/d within the range from 11000 to 50000 cm$^{-1}$. Thermogravimetric analyses were performed on a MOM derivatograph type OD-102. Room temperature EPR spectra were recorded on an ESR Bruker Physik 418S reflection type spectrometer in X-band (*ca.* 9.5 GHz) with a 100 kHz modulation of the steady magnetic field. Magnetic susceptibility was measured between 80–300 K by Faraday method on the balance constructed in our laboratory with $Hg[Co(NCS)_4]$ as a calibrant [23].

**Synthesis**: The complexes **1**, **4**, **5** were prepared using the following procedure: To a hot aqueous solution of appropriate metals sulphates (1 mmol in 25 cm$^3$), aqueous solution of 1-methylimidazole (4 mmol in 40 cm$^3$) was slowly added dropwise. During mixing a dark blue (**1**), turquoise (**4**), pink (**5**) solution was formed. This mixture was added dropwise to a solution of $K_3[Cr(NCS)_6] \cdot 4H_2O$ (1 mmol in 20 cm$^3$). A grey (**1**), violet (**4**), dark blue (**5**), precipitates were formed immediately. The products were collected by filtration, washed with water and left to air dry. Compound **2** was prepared by adding 25 cm$^3$ of aqueous solution of $K_3[Cr(NCS)_6] \cdot 4H_2O$ (1 mmol) to 75 ml of aqueous solution containing $CuSO_4 \cdot 5H_2O$ (1.5 mmol) and 2-methylimidazole (6 mmol). The resultant deep blue precipitate was collected by filtration, washed with 1% aqueous solution of 2-methylimidazole and left to air dry. Compound **3** was synthesized in similar manner using 1,2-dimethylimidazole (9 mmol) instead of 2-methylimidazole. The blue product was collected by filtration, washed with water and left to air dry. The yields were 55% (**1**), 48% (**2**), 44% (**3**), 72% (**4**) and 32% (**5**). Anal. Calcd. for $C_{60}H_{72}N_{36}S_{12}Cu_3Cr_2$ (**1**): C, 36.45; H, 3.67; N, 25.51; Cu, 9.64; Cr, 5.26. Found: C, 37.18; H, 3.67; N, 25.71; Cu, 9.16; Cr, 5.58%. Calcd. for $C_{60}H_{76}N_{36}S_{12}O_2Cu_3Cr_2$ (**2**): C, 35.80; H, 3.81; N, 25.05; Cu, 9.47; Cr, 5.17. Found: C, 35.77; H, 3.61; N, 24.66; Cu, 8.69; Cr, 5.63%. Calcd. for $C_{72}H_{98}N_{36}S_{12}OCu_3Cr_2$ (**3**): C, 39.98; H, 4.57; N, 23.31; Cu, 8.81; Cr, 4.81. Found: C, 39.70; H, 4.45; N, 23.20; Cu, 9.27; Cr, 5.56%. Calcd. for $C_{68}H_{94}N_{40}S_{12}O_5Ni_3Cr_2$ (**4**): C, 36.85; H, 4.27; N, 25.28; Ni, 7.94; Cr, 4.69. Found: C, 37.48; H, 4.39; N, 25.58; Ni, 8.03; Cr, 4.98%. Calcd. for $C_{68}H_{88}N_{40}S_{12}O_2Co_3Cr_2$ (**5**): C, 37.75; H, 4.10; N, 25.90; Co, 8.17; Cr, 4.81. Found: C, 37.07; H, 3.90; N, 25.93; Co, 9.02; Cr, 5.08%. All analyses confirmed the composition of the complexes investigated. All complexes are air stable and insoluble in water and most organic solvents.

## RESULTS AND DISCUSSION

**Spectroscopic properties**: Selected IR data for complexes are summarized in Table 1. The interest in the IR of the compounds lies mainly in the bands due to the $NCS^-$ groups. The strong broad band at ~2085 cm$^{-1}$ with shoulder at the higher frequency indicates the existence of the terminal and bridging thiocyanato groups. The lower frequency band can be ascribed to non-bridging $NCS^-$ groups and the higher frequency band is attributed to the bridging groups [24]. The expected stretching $\nu(CS)$ vibrations are unfortunately masked by the intensive bands of parent M(II)–imidazole complexes appearing in the region 650–850 cm$^{-1}$. The $NCS^-$ bending vibration is observed in all analysed spectra as a strong band at *ca.* 480 cm$^{-1}$. Hydrated complexes, *i.e.* **2–5** in their IR spectra show also bands of water molecules at 3405–3447 and 1602–1607 cm$^{-1}$. They are attributed to the stretching and bending vibrations, respectively.

FIR spectra show a very broad band at *ca.* 360 cm$^{-1}$ which consists of a few shoulders due to superposition of bands from $\nu(Cr–NCS)$ and $\nu(M(II)–N)$. In this region, spectra of Cu(II)–Cr(III) systems exhibit also bands at 248, 240, 227 cm$^{-1}$ for **1–3** complexes, respectively. They can be assigned to the Cu–S stretching vibrations.

The bands in the electronic spectra are presented in Table 2. The reflectance spectra of **1–3** are very similar. They are dominated by the bands of octahedral Cr(III) chromophore. In VIS region they show a band at *ca.* 17400 cm$^{-1}$ assigned to the d-d transition ($^4A_{2g} \rightarrow {}^4T_{2g}$) Cr(III) of $[Cr(NCS)_6]^{3-}$ ions. The red shifts in absorption maxima of this band in comparison to this of $K_3[Cr(NCS)_6] \cdot 4H_2O$ (18040 cm$^{-1}$) may indicate small deviation from the starting symmetry of $[Cr(NCS)_6]^{3-}$. A shoulder of this band, occurring at 14000, 14500, 14500 cm$^{-1}$ for **1–3** respectively, may be attributed to the Cu(II) transitions. The shift of this shoulder to lower frequency compared with its position in $[Cu(imH)_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ (15000 cm$^{-1}$) [17] is a result of increase of steric hindrance of substituted imidazoles. It causes longer Cu–N bonds and a lower value of Dq [25]. The spectra of **4** and **5** show absorption at 17720 cm$^{-1}$ and 16520 cm$^{-1}$, respectively, which is a result of the superposition of Cr(III) and M(II) bands. The position of maxima of these bands can indicate dominant role of M(II) absorption. All complexes show shoulder at *ca.* 24000 cm$^{-1}$ that correspond to the second spin-allowed $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) Cr(III) transition. The $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) transition band expected near 32000 cm$^{-1}$ is masked by intraligand transition of $NCS^-$ ions and by the $\pi_1(imH) \rightarrow M(II)$. Next two bands observed in 41000–46000 cm$^{-1}$ region are assigned to $(NCS) \rightarrow Cr(III)$ [17,26] overlapping with $\pi_2(imH) \rightarrow M(II)$ and $\sigma(imH) \rightarrow M(II)$ LMCT absorptions [27,28], respectively.

**EPR**: EPR spectra of copper(II)–chromium(III) heterocomplexes were measured. The spectra exhibit quasi-isotropic and very broad features with g = 2.03–2.06. Their peak-to-peak widths ($\Delta B_{pp}$) and g-values are collected in Table 3. The room temperature EPR spectrum of $[Cu(1\text{-}Meim)_4]_3[Cr(NCS)_6]_2$ (**1**) complex is shown as example in Fig. 1. Such single broad lines are characteristic for systems with great concentration of paramagnetic centres and in the case of heteropolynuclear com-

**Table 1.** Selected IR vibration bands of studied complexes, cm$^{-1}$.

| Complex | $\nu$(CN) | $\delta$(NCS) | $\nu$(Cr–N) | $\nu$(M$^{II}$–N) | $\nu$(M$^{II}$–S) | $\nu$(CH) | $\delta$(CH) | imidazole ring | | |
|---|---|---|---|---|---|---|---|---|---|---|
| K$_3$[Cr(NCS)$_6$]·4H$_2$O | 2096vs | 479s | 360s, br | – | – | – | – | – | – | – |
| [Cu(1-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$ (**1**) | 2130sh 2080vs, br | 483s | 362vs, br | 281m | 248w | 3129m | 1096s | 1540s | 1420m | 657m |
| [Cu(2-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$·2H$_2$O (**2**) | 2113sh 2091vs | 483s | 361vs, br | 292m | 240w | 3126m | 1100m | 1568s | 1416m | 669m |
| [Cu(1,2-Me$_2$im)$_4$]$_3$[Cr(NCS)$_6$]$_2$·H$_2$O (**3**) | 2134sh 2088vs | 483s | 361vs, br | 294s | 227w | 3125m | 1092w | 1549m | 1415s | 651m |
| [Ni(1-Meim)$_6$]$_n$[{Ni(1-Meim)$_4$Cr(NCS)$_6$}$_{2n}$]·5nH$_2$O (**4**) | 2120sh 2082vs, br | 483s | 363vs, br | | masked | 3126m | 1092s | 1533s | 1418m | 662m |
| [Co(1-Meim)$_6$]$_n$[{Co(1-Meim)$_4$Cr(NCS)$_6$}$_{2n}$]·2nH$_2$O (**5**) | 2110sh 2084vs, br | 481s | 365vs, br | | masked | 3124m | 1094s | 1536m | 1419m | 657m |

vs – very strong, s – strong, m – medium, w – weak, br – broad, sh – shoulder.

plexes, they have been reported not only for thiocyanato bridged building blocks [17–21] but also for oxalato bridged ones [29]. In the $Cu_3Cr_2$ polynuclear complexes the total number of unpaired electrons is odd. Therefore, all electronic degeneracies could not be removed in a zero field and if relaxation time is not very short, the system should be EPR active. At room temperature, on the basis of Boltzmann's distribution, ground state and most of the excited states are thermally populated and the broad line can be considered to be caused by almost all the coupling energy levels.

**Table 2.** Approximate positions of bands in electronic spectra.

| Complex | Position of bands [cm$^{-1}$][a] | Assignments[b] |
|---|---|---|
| [Cu(1-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$ (**1**) | 14000sh | d-d (Cu) |
| | 17400br | d-d (Cu, Cr) |
| | 24000sh | d-d (Cr) |
| | 31000br | CT, IL |
| | 41440 | CT |
| | 45600sh | CT, IL |
| [Cu(2-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$·2H$_2$O (**2**) | 14500sh | d-d (Cu) |
| | 17400br | d-d (Cu, Cr) |
| | 24000sh | d-d (Cr) |
| | 31000 | CT, IL |
| | 41200 | CT |
| | 45600 | CT, IL |
| [Cu(1,2-Me$_2$im)$_4$]$_3$[Cr(NCS)$_6$]$_2$·H$_2$O (**3**) | 14000sh | d-d (Cu) |
| | 17500br | d-d (Cu, Cr) |
| | 24880sh | d-d (Cr) |
| | 31300 | CT, IL |
| | 41300 | CT |
| | 45500 | CT, IL |
| [Ni(1-Meim)$_6$]$_n$[{Ni(1-Meim)$_4$Cr(NCS)$_6$}$_{2n}$]·5nH$_2$O (**4**) | 17720 | d-d (Ni, Cr) |
| | 24000 | d-d (Ni, Cr) |
| | 31000br | CT, IL |
| | 41300 | CT |
| | 45400sh | CT |
| | 48000sh | IL |
| [Co(1-Meim)$_6$]$_n$[{Co(1-Meim)$_4$Cr(NCS)$_6$}$_{2n}$]·2nH$_2$O (**5**) | 16520br | d-d (Co) |
| | 18000sh | d-d (Co, Cr) |
| | 24000sh | d-d (Cr) |
| | 30000br | CT, IL |
| | 41000sh | CT |
| | 46000sh | CT |
| | 48300 | IL |

[a]sh – shoulder, [b]CT – charge transfer, IL – intra ligand.

**Table 3.** EPR parameters for copper(II)–chromium(III) complexes.

| Complex | g$_{iso}$ | ΔB$_{pp}$ [mT] |
|---|---|---|
| [Cu(1-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$ (**1**) | 2.031 | 32 |
| [Cu(2-Meim)$_4$]$_3$[Cr(NCS)$_6$]$_2$·2H$_2$O (**2**) | 2.057 | 30 |
| [Cu(1,2-Me$_2$im)$_4$]$_3$[Cr(NCS)$_6$]$_2$·H$_2$O (**3**) | 2.060 | 39 |

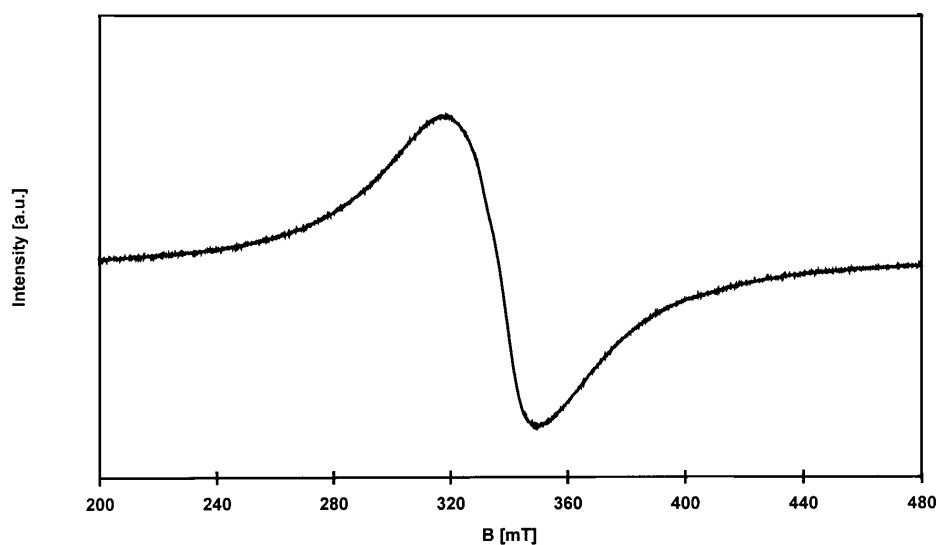**Figure 1.** EPR spectrum of $[Cu(1-Meim)_4]_3[Cr(NCS)_6]_2$ at room temperature (powder, 9.5674 GHz).

Nondiluted copper(II) complexes with substituted imidazoles give a typical axial or nearly axial EPR spectra with resolved hyperfine structure in the low-field part of spectrum [30,31]. On the contrary, EPR spectrum of $K_3[Cr(NCS)_6] \cdot 4H_2O$ complex shows unsymmetrical line with g = 1.995 and $\Delta B_{pp}$ = 18 mT. So, it is clear that spectra of the heteropolynuclear complexes studied are not the superposition of the spectra of parent Cu(II) and Cr(III) complexes. Therefore, interaction between metal ions through thiocyanato bridges exists [32]. A more detailed analysis of the spectra is impossible due to the broadness of the signal.

**Table 4.** Parameters from the Curie-Weiss law and magnetic moments for chromium(III)–M(II) complexes.

| Complex | $\chi_{dia} \cdot 10^6$ $(cm^3 \cdot mol^{-1})$ | Curie contant $(cm^3 \cdot mol^{-1} \cdot K)$ | Weiss constant (K) | $\mu_{eff}$ (B.M.) RT/LNT |
|---|---|---|---|---|
| $[Cu(1-Meim)_4]_3[Cr(NCS)_6]_2$ **(1)** | −1019 | 4.94 | −7 | 6.25/6.02 |
| $[Cu(2-Meim)_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ **(2)** | −1045 | 5.17 | −1 | 6.46/6.32 |
| $[Cu(1,2-Me_2im)_4]_3[Cr(NCS)_6]_2 \cdot H_2O$ **(3)** | −1174 | 5.00 | − | Const. 6.35±0.06 |
| $[Ni(1-Meim)_6]_n[\{Ni(1-Meim)_4Cr(NCS)_6\}_{2n}] \cdot 5nH_2O$ **(4)** | −1174 | 7.10 | −1 | Const. 7.55±0.05 |
| $[Co(1-Meim)_6]_n[\{Co(1-Meim)_4Cr(NCS)_6\}_{2n}] \cdot 2nH_2O$ **(5)** | −1138 | 11.1 | −14 | 9.77/9.22 |

**Magnetic studies**: The molar susceptibilities were corrected for diamagnetism using Pascal's constants and temperature independent paramagnetism. The effective magnetic moments were calculated from $\mu_{\text{eff}} = 2.828 \, (\chi_{\text{M}}^{\text{corr}} \cdot T)^{1/2}$. The temperature dependencies of magnetic susceptibilities obey the Curie-Weiss law, *i.e.* $\chi_{\text{M}}^{\text{corr}} = C/(T - \theta)$. The best fitted values of the Curie (C) and Weiss constant ($\theta$) are given in Table 4. Among copper(II)–chromium(III) heteropolynuclear complexes **1** and **2** possess a negative Weiss constant, whereas for **3** Weiss constant is very close to 0, and the complex equally obeys the Curie law. The room-temperature magnetic moments have approximately the expected spin-only value for five noninteracting ions (S = 1/2, 1/2, 1/2, 3/2, 3/2) with g = 2, which is 6.24 B.M. However, the negative value for $\theta$ and the decrease in the effective magnetic moment at liquid nitrogen temperature for $[Cu(1\text{-Meim})_4]_3[Cr(NCS)_6]_2$ (**1**) and $[Cu(2\text{-Meim})_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ (**2**) complexes may be caused by a weak antiferromagnetic interaction between metal ions [33]. Effective magnetic moment for **3** is nearly constant down to liquid nitrogen temperature and indicates that magnetic interactions in this temperature range are negligible.

Although nickel(II)–chromium(III) heteropolynuclear complex **4** shows a small negative Weiss constant, magnetic moment is nearly constant down to liquid nitrogen temperature and from mathematical point of view (the same agreement factor) complex equally obeys the Curie law with C = 7.06 $cm^3 \cdot K \cdot mol^{-1}$. It indicates that magnetic interactions, even if operate, are very weak. The magnetic moments have approximately the expected spin-only value for five noninteracting ions (S = 1, 1, 1, 3/2, 3/2) with g = 2, which is 7.35 B.M. Magnetic behaviour of this complex is quite different from some thiocyanato bridged Ni(II)–diamine–Cr(III) complexes [19,21], where moderate antiferromagnetic interactions operate. It could be connected with presence of four bulky substituted ligands in coordination sphere of nickel(II) in anionic chain of **4**, in contradiction to only two diamine chelate rings in the others. So, Ni–S bonds are probably longer and pathways for magnetic interactions are much less efficient.

Cobalt(II)–chromium(III) heteropolynuclear complex **5** shows a negative Weiss constant. Magnetic moment continuously decreases down to liquid nitrogen temperature. It indicates that antiferromagnetic interaction between metal ions exists. The magnetic moments have somewhat higher values than expected spin-only value for five noninteracting ions (S = 3/2, 3/2, 3/2, 3/2, 3/2) with g = 2, which is 8.66 B.M. Because of $^4T_{1g}$ ground state for octahedral Co(II) there is a considerable orbital contribution to the effective magnetic moment.

**Thermal analysis**: Results of thermal analysis are presented in Table 5. Complexes **3**, **4**, **5** are stable up to about 358 K, whereas **2** to 413 K, where dehydration takes place. Decomposition occurs immediately after dehydration for **2–5** compounds and at about 433 K for **1**. It runs in a few separate steps. For all complexes the temperatures of the first two steps are very similar and are connected with the exothermic DTA peaks. The strong exothermic effect, observed for second step, can be compared with the third step of $K_3[Cr(NCS)_6] \cdot 4H_2O$ pyrolysis that occurs at 718 K with a similarly strong exothermic effect. Further heating caused further gradual decrease in we-

ight due to endothermal decomposition. It occurs in two separate steps for **1–4** and in one step for **5**. As the samples **3–5** are heated to temperatures over 763 K, the mass of the samples increases by *ca*. 0.5–1%. It is probably connected with partial oxidation of previously formed $S^{2-}$ ions to $SO_4^{2-}$, which was unambiguously stated for $Cu_3[Cr(NCS)_6]$ and $Cd_3[Cr(NCS)_6]_2 \cdot 8H_2O$ [34].

**Table 5.** Results of thermal analysis, in air.

| Process | Dehydration | 1st stage of decomposition | 2nd stage of decomposition | 3rd stage of decomposition | 4th stage of decomposition |
|---|---|---|---|---|---|
| Heat effect | endothermic | exothermic | strong exothermic | endothermic | endothermic |
| Complex | $[Cu(1\text{-}Meim)_4]_3[Cr(NCS)_6]_2$ (**1**) | | | | |
| $T_{max}$ [K][a] | – | 613 | 753 | 993 | 1051 |
| Final products (at 1213 K): $2CuCrO_2 + CuO$ (% calc./found: 19.0/19) | | | | | |
| Complex | $[Cu(2\text{-}Meim)_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ (**2**) | | | | |
| $T_{max}$ [K][a] | 413 | 613 | 763 | 1013 | 1063 |
| Dehydration: weight loss on TG curve – % calc./found: 1.8/2 | | | | | |
| Final products (at 1213 K): $2CuCrO_2 + CuO$ (% calc./found: 18.6/21) | | | | | |
| Complex | $[Cu(1,2\text{-}Me_2im)_4]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**3**) | | | | |
| $T_{max}$ [K][a] | 353 | 623 | 733 | 968 | 1008 |
| Dehydration: weight loss on TG curve – % calc./found: 0.8/1 | | | | | |
| Final products (at 1198 K): $2CuCrO_2 + CuO$ (% calc./found:17.3/17.0) | | | | | |
| Complex | $[Ni(1\text{-}Meim)_6]_n[\{Ni(1\text{-}Meim)_4Cr(NCS)_6\}_{2n}] \cdot 5H_2O$ (**4**) | | | | |
| $T_{max}$ [K][a] | 358 | 593 | 737 | 858 | 1055 |
| Dehydration: weight loss on TG curve – % calc./found: 4.1/4 | | | | | |
| Final products (at 1163 K): $NiCr_2O_4 + 2NiO$ (% calc./found: 17.0/14) | | | | | |
| Complex | $[Co(1\text{-}Meim)_6]_n[\{Co(1\text{-}Meim)_4Cr(NCS)_6\}_{2n}] \cdot 2H_2O$ (**5**) | | | | |
| $T_{max}$ [K][a] | 351 | 633 | 733 | – | 1093 |
| Dehydration: weight loss on TG curve – % calc./found: 1.7/2 | | | | | |
| Final products (at 1133 K): $CoCr_2O_4 + 2CoO$ (% calc./found: 17.4/17) | | | | | |

[a]on DTG curve.

The temperature of total decomposition of **1–3** complexes is about 40 K higher than that of **4, 5** complexes and finally leads to the mixtures of products presented in Table 5, which are evident from the analysis of TG curves and the final powder diffractograms. The lines observed for final products correspond to those reported in Powder Diffraction File [35].

## CONCLUSIONS

The examination of the infrared spectra of obtained compounds may support the hypothesis of existence of both bridging and terminal thiocyanato ions and consequently their heteropolynuclear structure. Electronic absorption spectra may confirm differences in composition Cu(II)–Cr(III) and M(II)–Cr(III) (M = Ni, Co) complexes but they are difficult to interpret because of superposition of M(II) and Cr(III) d-d bands. The parameters determined from the temperature dependence on magnetic susceptibility indicate weak antiferromagnetic interactions in $[Cu(1\text{-Meim})_4]_3[Cr(NCS)_6]_2$ **(1)**, $[Cu(2\text{-Meim})_4]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ **(2)** and $[Co(1\text{-Meim})_6]_n[\{Co(1\text{-Meim})_4Cr(NCS)_6\}_{2n}] \cdot 2nH_2O$ **(5)**, which can be transmitted through thiocyanato bridges. Other compounds such as $[Cu(1,2\text{-Me}_2im)_4]_3[Cr(NCS)_6]_2 \cdot H_2O$ **(3)** and $[Ni(1\text{-Meim})_6]_n[\{Ni(1\text{-Meim})_4Cr(NCS)_6\}_{2n}] \cdot 5nH_2O$ **(4)** show no net interaction in the measured temperature range, but this does not exclude the existence of thiocyanato bridges [12–14]. Studies down to liquid helium temperature are highly desirable to cast further light on these findings. The changes in the EPR spectra of obtained complexes, compared to parent complexes, prove the interactions between Cr(III) and M(II) ions through bridging NCS ions. In spite of our endeavors, we did not manage to grow single crystals for X-ray diffraction. Thus, the exact structure is unknown. However, on the basis of the obtained results and recently reported [6,36] crystal structures of similar composition of $M_3Cr_2$ complexes with bridging cyanide ions, it is possible to predict that **1–3** compounds have polynuclear structures. Tendency to form octahedral complexes by Ni(II) and Co(II) ions with 1-methylimidazole [30] causes a difference in composition between $M_3Cr_2$ (M = Ni, Co) and $Cu_3Cr_2$ complexes. Structure of the similar constitution as in **4** and **5**, *i.e.* M : L : Cr : NCS = 3 : 14 : 2 : 12, was found for $[M(en)_3]_n[\{M(en)_2Cr(NCS)_6\}_{2n}]$, where M = Ni, Zn and L = $^1/_2$ en [21]. Therefore, a similar structure could be also possible.

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