

Spectroscopic, Magnetic and Thermal Properties of New Thiocyanato Bridged Complexes of the Type $[M(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$, where $M = \text{Cu}(\text{II}), \text{Ni}(\text{II})$

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Heteropolynuclear complexes of the type $[M(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$, where diamine = *N*-methylethylenediamine (*N*-Me-en), 1,2-diaminopropane (pn); $M = \text{Ni}(\text{II}), \text{Cu}(\text{II})$ have been prepared by reacting $[\text{Cr}(\text{NCS})_6]^{3-}$ with the corresponding cationic $[M(\text{diamine})_2]^{2+}$ complex in an aqueous solution. They have been characterized by elemental analysis, IR, UV-VIS, EPR, variable temperature magnetic susceptibility and thermal analysis. Spectroscopic studies reveal thiocyanato bridges between $M(\text{II})$ – $\text{Cr}(\text{III})$ centres. The parameters determined from temperature dependence on magnetic susceptibility (80–300 K) indicate moderate antiferromagnetic interactions for $\text{Ni}(\text{II})$ – $\text{Cr}(\text{III})$ and negligibly small or very weak ones for $\text{Cu}(\text{II})$ – $\text{Cr}(\text{III})$ systems. Magnetic studies suggest also presence of diamagnetic $\text{Ni}(\text{II})$ ions in the structure of $\text{Ni}(\text{II})$ –pn– $\text{Cr}(\text{III})$ complex. Thermal analysis shows higher thermal stability of $\text{Ni}(\text{II})$ – $\text{Cr}(\text{III})$ than $\text{Cu}(\text{II})$ – $\text{Cr}(\text{III})$ compounds. The process of thermal decomposition after dehydration is multistage and yields $\text{NiO} + \text{NiCr}_2\text{O}_4$ and $\text{CuO} + \text{CuCrO}_2$ as final products, respectively.

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

Considerable attention has been devoted in recent years to the study of heteronuclear complexes in which bridging ligands act as a superexchange pathway. This interest has been caused by a concern to understand various phenomena connected with magnetism and, on the other hand, by search for new, better materials, which can be used in optics and electronics [1–3]. So far, the most known polymetallic coupling systems are cyano complexes generated by hexacyanometalate anions [4,5]. To them belongs 3D $[\text{Mn}(\text{en})_3][\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$, which shows the highest magnetic phase-transition temperature ($T_C = 69 \text{ K}$) among structurally characterized molecular-based magnets to this date [6]. Oxalato [7], oxamato [8] and dithiooxalato [9] complexes have also been the subject of intensive study. In our work we focus on thiocyanato compounds obtained by usage hexaisothiocyanatochromate(III) anion as a template. The thiocyanato ions belong to ligands, which can coordinate to metals in the terminal and bridging modes. This ability is a cause of intriguing structural diversity. The polymeric homonuclear thiocyanato complexes especially of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ have been widely explored [10–13]. Published results on magnetic studies indicate that position of the bridges in the coordination polyhedra have a large influence

on efficiency to mediate magnetic interactions [14]. The available information on thiocyanato bridged heteronuclear polymeric systems is very limited. There are only a few papers that present structural data [15–21] and several others describing magnetic behaviour without structural data [22–28]. Most of the magneto-structurally characterized complexes indicate only very weak ferro- or antiferromagnetic interaction ($J = -1.48 \div +3.07 \text{ cm}^{-1}$). The low values of coupling constant indicate poor overlap of the magnetic orbitals, what is a result of *trans* position thiocyanato ions at the metal centres [16,19,20]. Different magnetic behaviour was observed for $[\text{Ni}(\text{en})_3]_n[\{\text{Ni}(\text{en})_2\text{Cr}(\text{NCS})_6\}_{2n}]$, where thiocyanato bridges occupy the *cis* position. It exhibits moderate antiferromagnetic interactions between Ni(II)–Cr(III) ($J \sim 20 \text{ cm}^{-1}$) [15]. In view of the limited literature on heteropolynuclear thiocyanato systems, more examples of this type of compound are needed to uncover the relations between molecular structure and magnetism. As a continuation of our work along this line, we report here the synthesis, spectroscopic, magnetic and thermal properties of the new thiocyanato bridging systems such as: $[\text{Ni}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**2**), $[\text{Cu}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**3**) and $[\text{Cu}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (**4**).

EXPERIMENTAL

Materials: $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$ was synthesized as described in [29]. Other reagents used, *i.e.* *N*-methylethylenediamine (95%), 1,2-diaminopropane (99%), purchased from Aldrich Chemical Company; HNO_3 (65%), H_2O_2 (30%), NaOH , $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 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. Nickel and copper contents were determined using the AAS method. Chromium content was determined spectrophotometrically as CrO_4^{2-} at $\lambda = 372 \text{ nm}$. 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 (Ni_3Cr_2 complexes) or in nujol mulls (Cu_3Cr_2 complexes) were measured with the spectrophotometer SPECORD M-40 (Carl Zeiss, Jena) within the range $11000 \div 50000$ or $12000 \div 48000 \text{ cm}^{-1}$, respectively. Thermogravimetric analyses were performed with MOM derivatograph type OD-102 under the following conditions: sample mass – 50 mg, sensitivity: DTA – $1/3 \div 1/10$, DTG – $1/3$, TG – 50 mg, heating rate – 5 K/min, temperature range 293–1273 K, the atmosphere over the sample – air, reference substance – $\alpha\text{-Al}_2\text{O}_3$. 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 $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant [30]. Powder diffractograms were recorded with HZ64/A-2 DRON-1 diffractometer using $\text{CuK}\alpha$, $\lambda = 0.1542 \text{ nm}$.

Synthesis: The complexes were prepared in a similar manner. The appropriate diamine (2 mmol) was added to a 15 ml aqueous solution of appropriate metals sulphate (1 mmol). During mixing dark blue (**1**), blue (**3**) and violet (**4**) solutions were formed. Each mixture was added dropwise to a 30 ml solution of $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$ (0.67 mmol). A violet (**1**), blue (**3**) and pink (**4**) precipitates were formed immediately. The products were collected by filtration, washed with water and left to air dry. The yields were 90% (**1**), 90% (**2**), 83% (**3**) and 82% (**4**). 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 presented in Table 1. The most relevant IR features are associated with the NCS^- ions. The broad and split band in the region $2150\text{--}2000\text{ cm}^{-1}$ corresponds to the CN stretching mode. Profile of the band indicates the presence of bridging and N-bonded thiocyanato groups. As pointed out in the literature, the shoulder at the higher frequency ($>2100\text{ cm}^{-1}$) can be assigned to bridging ions [31]. The further confirmation of existence of NCS bridges is new, weak band at *ca.* 668 cm^{-1} observed in spectra of **1**, **2** and **3** and arising from $\nu(\text{CS})$. In spectrum of **4** it is masked by band from rocking NH_2 . The NCS^- bending vibration appears in all analysed spectra as a strong band at *ca.* 480 cm^{-1} . The complex nature of this band confirms differences in mode of bound thiocyanato ions. FIR spectra show very broad band at *ca.* 360 cm^{-1} , which consists of a few shoulders due to superposition of bands from $\nu(\text{Cr}\text{--}\text{NCS})$ and $\nu(\text{M(II)}\text{--}\text{N})$. In this region, spectra of Ni(II)–Cr(III) systems exhibit also bands at 227 and 225 cm^{-1} for **1** and **2**, respectively. They can be assigned to the Ni–S stretching vibrations. Bands attributed to Cu–S stretching vibrations were not found probably because of considerable length of Cu–S bond, also noticed by others [32,33]. Hydrated complexes, *i.e.* **1–3** show bands of water molecules in the region $3463\text{--}3420\text{ cm}^{-1}$ arising from stretching vibrations. Band from bending vibrations is observed only for **1** as a shoulder at 1613 cm^{-1} . In the others spectra it is obscured by band from $\delta(\text{NH}_2)$.

The electronic spectra are given in Table 2. It can be noted that the spectra within the appropriate systems Ni(II)–Cr(III) and Cu(II)–Cr(III) are similar in profile. In VIS region the all spectra exhibit a broad, asymmetric band at *ca.* 18000 cm^{-1} , which is an effect of superposition of M(II) and Cr(III) bands. A shoulder of this band occurring at *ca.* 13900 cm^{-1} for **3** and **4** can be attributed to the Cu(II) transition. Especially interesting is low-energy part of spectra **1** and **2** because of presence of two, sharp bands at *ca.* 12700 and 13500 cm^{-1} . They can be attributed to spin forbidden Ni(II) and/or Cr(III) transitions, where gain of intensity is a result of coupling of magnetic centres. The similar effect was previously reported for Cr(III)–Mn(II) system with hydroxo and acetate bridges [34]. All complexes (**1–4**) show band or shoulder at *ca.* 24000 cm^{-1} that correspond to the second spin-allowed ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ Cr(III) transition. The ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition band expected near 32000 cm^{-1} is masked by broad band of intraligand transition of NCS^- ions. Next bands observed in $37600\text{--}42400\text{ cm}^{-1}$ region of spectra of **1**, **2** and **4** are assigned to $(\text{NCS}) \rightarrow \text{Cr(III)}$ [35] overlapping with $\sigma(\text{N}) \rightarrow \text{M(II)}$ LMCT absorptions [36,37], respectively. They are separated in spectrum of **3**, where band at 37600 cm^{-1} is due to $\sigma(\text{N}) \rightarrow \text{M(II)}$ LMCT absorptions whereas band at 42000 cm^{-1} arises from $(\text{NCS}) \rightarrow \text{Cr(III)}$.

EPR and magnetic studies: EPR spectra of **3** and **4** exhibit quasi-isotropic and very broad features with $g \sim 2.02$. Their peak-to-peak widths (ΔB_{pp}) and g -values are collected in Table 3. The room temperature EPR spectrum of **4** is shown as an example in Figure 1. Such broad lines are characteristic of systems with a great concentration of paramagnetic centres and in the case of heteropolynuclear complexes,

Table 1. Selected IR vibrations bands of studied complexes, cm^{-1} .

Complex	$\nu(\text{CN})$	$\delta(\text{NCS})$	$\nu(\text{Cr-N})$ $\nu(\text{M}^{\text{II}}-\text{N})$	$\nu(\text{NH})$	$\delta(\text{NH}_2)$	$\nu(\text{CH})$	$\delta(\text{CH}_2)$
$\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$	2096 vs	479 s	360 s, br	–	–	–	–
$[\text{Ni}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 4\text{H}_2\text{O}$ (1)	2141 w, sh 2085 vs, br	483 s	363 vs, br	3281 sh 3245 s	1577 m	2944 m 2885 m	1458 m
$[\text{Ni}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (2)	2140 sh 2082 vs, br	479 s	363 vs, br	3315 m 3242 s 3113 m	1579 s	2966 m 2877 m	1458 m
$[\text{Cu}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (3)	2132 sh 2089 vs, br	482 s	363 vs, br	3224 s 3131 s	1578 s	2943 m	1468 m
$[\text{Cu}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (4)	2133 w, sh 2089 vs, br	481 s	363 vs, br	3303 s 3227 vs	1578 s	2967 m	1456 s

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

they have been reported not only for thiocyanato bridged building blocks [23–28], but also for oxalato [38] and dicyanamide [39] bridged ones. 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 ^{a)} [cm^{-1}]	Assignments ^{b)}
[Ni(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·4H ₂ O (1)	12760	SF (Ni, Cr)
	13520	SF(Ni, Cr)
	18000	d-d (Ni, Cr)
	24000	d-d (Cr)
	29500	IL(NCS)
	42000	CT
	46800	CT or IL
[Ni(pn) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (2)	12700	SF (Ni, Cr)
	13500	SF(Ni, Cr)
	17800	d-d (Ni, Cr)
	24000 sh	d-d (Cr)
	28000 br	IL(NCS)
	42400	CT
	48500	CT or IL
[Cu(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (3)	13900 sh	d-d (Cu)
	18480	d-d (Cu, Cr)
	24000 sh	d-d (Cr)
	29900	IL
	37600	CT
	42000	CT
[Cu(pn) ₂] ₃ [Cr(NCS) ₆] ₂ (4)	13920 sh	d-d (Cu)
	18640	d-d (Cu, Cr)
	24000 sh	d-d (Cr)
	30000	IL
	41700	CT

^{a)}sh – shoulder, br – broad, ^{b)}SF – spin forbidden, CT – charge transfer, IL – intra ligand.

Table 3. EPR parameters for complexes.

Complex	g_{iso}	ΔB_{pp} [mT]
[Ni(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·4H ₂ O (1)		EPR silent
[Ni(pn) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (2)	~2.1	~90
[Cu(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (3)	2.021	20
[Cu(pn) ₂] ₃ [Cr(NCS) ₆] ₂ (4)	2.015	19

Generally, copper(II) bis-diamine complexes give axial or nearly axial EPR spectra [40]. On the contrary, EPR spectrum of $K_3[Cr(NCS)_6] \cdot 4H_2O$ complex shows an 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, interacting between metal ions exists through thiocyanato bridges [41]. A more detailed analysis of the spectra is impossible due to the broadness of the signal.

Because of the even total number of unpaired electrons, nickel(II)–chromium(III) heterocomplex **1** is EPR silent as expected, although, in the spectrum of complex **2**, a very broad, weak and ill defined signal at $g \sim 2.1$ appears.

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

Complex	$\chi_{\text{dia}} \cdot 10^6$ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	Curie constant ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	Weiss constant (K)	μ_{eff} (B.M.) RT/LNT
$[Ni(N\text{-Me-en})_2]_3[Cr(NCS)_6]_2 \cdot 4H_2O$ (1)	–881	6.95	–71	6.82/5.51
$[Ni(pn)_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (2)	–842	5.54	–29	6.42/5.70
$[Cu(N\text{-Me-en})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (3)	–842	4.78	–	Const. 6.21 \pm 0.03
$[Cu(pn)_2]_3[Cr(NCS)_6]_2$ (4)	–829	4.63	–2	6.11/6.00

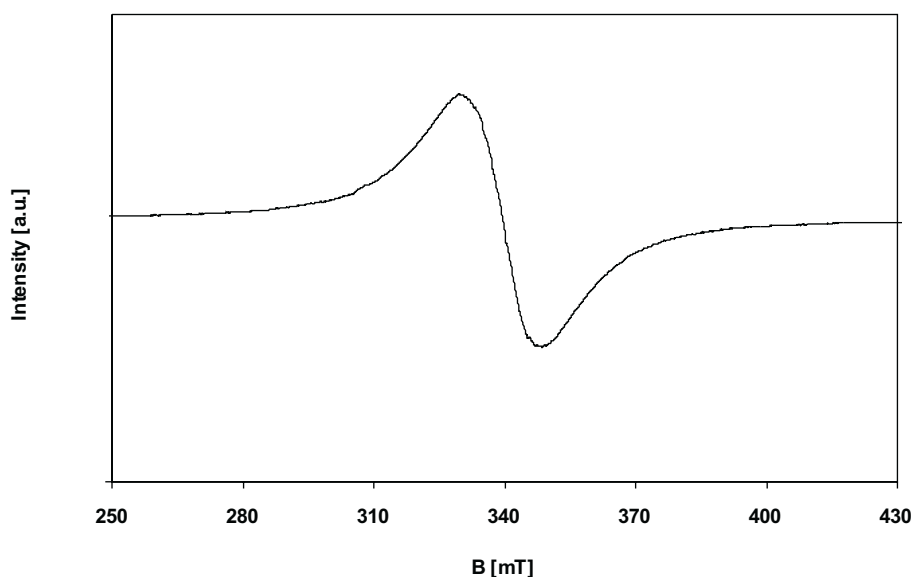


Figure 1. X-band (9.5759 GHz), room temperature EPR spectrum of powder sample of $[Cu(pn)_2]_3[Cr(NCS)_6]_2$ (**4**).

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 (θ) are given in Table 4. The $[\text{Ni}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (**4**) complexes possess a negative Weiss constant, whereas for $[\text{Cu}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**3**) complex the Weiss constant is very close to 0, and the complex equally obeys the Curie law.

At room temperature the magnetic moments for nickel(II)–chromium(III) complexes have their values below the expected spin-only value for five noninteracting ions ($3 \times S = 1$ and $2 \times S = 3/2$) with $g = 2$, which is 7.35 B. M. The negative value for θ and the decrease in the effective magnetic moment with decreasing of the temperature for **1** and **2** complexes is a result of antiferromagnetic interaction between metal ions through thiocyanato bridges [42]. Magnetic behaviour of complex **1** is quite similar to that of $[\text{Ni}(\text{en})_3]_n \{ \text{Ni}(\text{en})_2 \text{Cr}(\text{NCS})_6 \}_{2n}$, where moderate antiferromagnetic interactions operate ($J \sim 20 \text{ cm}^{-1}$) [15]. Thus, we could suppose existence of similar antiferromagnetic pathways through *cis* positioned thiocyanato bridges. Magnetic behaviour of complex **2** is quite different from that of complex **1** and some other thiocyanato bridged Ni(II)–diamine–Cr(III) complexes [25]. Antiferromagnetic interactions are probably weaker. The different steric effects and structural differences could be connected with the position of methyl group in diamine ligands from coordinated N atom in **N-Me-en** ligand to chelate chain C atom in **pn** ligand. So, Ni–S bonds are probably longer and pathways for magnetic interactions are much less efficient. In addition, in complex **2** one or two nickel(II) ion(s) should be diamagnetic because of low room temperature magnetic moment. Such rather unexpected behaviour has been recently reported for $(\text{NiL})_3[\text{M}(\text{NCS})_6]_2$ complexes, where $\text{M} = \text{Fe}, \text{Cr}$ and $\text{L} = 5,6,12,13\text{-Me}_4\text{-}[14]\text{-}4,11\text{-dieneN}_4$ [43]. It is only possible when one assumes that one or two nickel(II) ions are low spin five coordinated and terminal species connected with chromium(III) complex through only one thiocyanato bridge.

The room-temperature effective magnetic moments of copper(II)–chromium(III) heteropolynuclear complexes have approximately the expected spin-only value for five noninteracting ions ($3 \times S = 1/2$ and $2 \times S = 3/2$), which is 6.24 B.M. Effective magnetic moments for **3** are nearly constant down to liquid nitrogen temperature and indicate that magnetic interactions in this temperature range are negligible. However, the negative value for θ and the decrease in the effective magnetic moment at liquid nitrogen temperature for $[\text{Cu}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (**4**) complex may be caused by a very weak antiferromagnetic interaction between metal ions [42].

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	5th stage of decomposition
Heat effect	endothermic	endothermic	exothermic	strong exothermic	endothermic	endothermic
Complex	[Ni(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·4H ₂ O (1)					
T _{max} [K] ^a	369	553	593	711	893 ^b	1073
Dehydration: weight loss on TG curve – % calc./found: 4.8/5.1						
Final products (at 1233 K): NiCr ₂ O ₄ + 2NiO (% calc./found: 25.2/28)						
Complex	[Ni(pn) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (2)					
T _{max} [K] ^a	335	555	577	713	873 ^b	1093
Dehydration: weight loss on TG curve – % calc./found: 1.3/1.4						
Final products (at 1193 K): NiCr ₂ O ₄ + 2NiO (% calc./found: 26.1/28)						
Complex	[Cu(<i>N</i> -Me-en) ₂] ₃ [Cr(NCS) ₆] ₂ ·H ₂ O (3)					
T _{max} [K] ^a	353	473	593	733	993	1063
Dehydration: weight loss on TG curve – % calc./found: 1.2/1.4						
Final products (at 1213 K): 2CuCrO ₂ + CuO (% calc./found: 25.6/26)						
Complex	[Cu(pn) ₂] ₃ [Cr(NCS) ₆] ₂ (4)					
T _{max} [K] ^a	–	493	593	753	993	1043
Final products (at 1248 K): 2CuCrO ₂ + CuO (% calc./found: 26.1/24)						

^a) on DTG curve, ^b) additional exothermic peak appears before stronger endothermic one.

Thermal analysis: Results of thermal analysis are presented in Table 5. The dehydration occurs in one endothermic step for **1–3**. For **1** it is connected with the loss of four molecules of water and decomposition of crystal lattice. It can indicate the presence of hydrogen-bond network in the structure. The complexes **2**, **3** and **4** decompose with melting at about 463, 434 and 457 K, respectively. The process of decomposition is complicated and runs in five separate steps for all complexes. During the first three steps about 55% of the loss in the mass samples is observed. The first endothermic step is connected with decomposition of diamine ligands. This process takes place at a higher temperature for Ni(II)–Cr(III) systems than for Cu(II)–Cr(III) (the difference is about 60 K). The next two exothermic steps are due to the decomposition of the thiocyanato groups. The maximal speeds of the third very strong effect related to oxidation S^{2–} ions to SO₄^{2–} occur between 711–753 K [44]. It can be compared with the third step of K₃[Cr(NCS)₆]·4H₂O pyrolysis that occurs at 718 K with a similarly strong exothermic effect. A slight increase of the samples mass (1–2%) observed during heating over 773 K could be connected with the aforementioned oxidation. Further heating induced a further gradual decrease in weight, corresponding with

endothermic peak on the DTA curves. For **1** and **2** the peak is a result of overlapping of exo- and endothermic effects. It corresponds to decomposition of MSO_4 to MO [44]. The last endothermic effect might be the result of a recrystallisation of chromium compounds. Finally, decomposition leads to the mixtures of products presented in Table 5, which are evident from the analysis of TG curves and the powder diffractograms. The lines observed for the final products correspond to those reported in Powder Diffraction File [45].

CONCLUSIONS

This and our prior studies [15,23–28] demonstrate that anionic complex $[\text{Cr}(\text{NCS})_6]^{3-}$ is an ideal building block to form the new group of heteronuclear thiocyanato bridged compounds. The formation of NCS bridges in presented complexes is evident from IR spectra. It has been confirmed by results of other studies, such as EPR and the temperature dependence of magnetic susceptibility. Comparison of the magnetic properties of Ni_3Cr_2 complexes (**1**) and (**2**) with those of the corresponding Cu_3Cr_2 complexes (**3**) and (**4**), has shown antiferromagnetic interaction for the first ones and weakly antiferromagnetic or negligibly small for the last ones. Magnetic data have also indicated differences in structure of Ni_3Cr_2 complexes. The $[\text{Ni}(\text{N-Me-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 4\text{H}_2\text{O}$ (**1**) seems to have octahedral coordination environment around the Ni(II) atoms, whereas some of the Ni(II) ions in $[\text{Ni}(\text{pn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**2**) are probably low spin five coordinated complexes. The exact structure is unknown, but on the basis of spectroscopic and magnetic properties we have assumed a network construction with thiocyanato bridges between metal(II) and chromium(III) centres in all studied compounds.

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