

Synthesis and Characterization of New Thiocyanato Bridged Heterobimetallic Complexes with the General Formula: $[\text{Cu}(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$

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Four new thiocyanato bridged heteropolynuclear complexes with general formula $[\text{Cu}(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$, where diamine = *N*-ethylethylenediamine (*N*-Et-en), *N*-isopropylethylenediamine (*N*-Pr^{*i*}-en), *N*-methyl-1,3-propanediamine (*N*-Me-tn), 1,3-diaminopentane (*C*-Et-tn), were prepared by treatment of corresponding cationic $[\text{Cu}(\text{diamine})_2]^{2+}$ complex with $[\text{Cr}(\text{NCS})_6]^{3-}$ in aqueous solutions. Solid products were formulated as $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$, $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ and characterized by spectroscopic methods, magnetic measurements and thermal analysis. The formation of end-to-end thiocyanato bridges between tetragonal Cu(II) and octahedral Cr(III) is evident from IR and electronic spectra. The EPR spectra measured at room temperature on solid samples show broad, symmetric signal at $g = 2.01\text{--}2.03$. Variable-temperature magnetic susceptibility measurements reveal the presence of weak antiferromagnetic interactions in $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$. Thermal decomposition after dehydration is multi-stage and yields CuO and CuCrO₂ as final products.

Key words: chromium(III), copper(II), diamine, EPR, heteropolynuclear complexes, magnetic properties, thiocyanato bridges

In recent years, heteropolynuclear complexes have been extensively studied in response to an increased demand for the new optical, electrical and magnetic materials [1–4]. So far most attention has been devoted to cyano bridged complexes generated by hexacyanometalate [1–3,5–7], octacyanometalate [8,9], tetracyanometalate [10] and nitroprusside [11] anions. Other researches especially on magnetic properties of heteropolynuclear complexes have been concerned with oxalato [12], oxamato [13], both oxamido and nitrito [14], dicyanamido [15], *etc.*, bridges. On the other hand, the literature covering heteropolynuclear complexes with thiocyanato bridges is much more scarce, although the variety of coordination modes of this anion makes it absorbing for studies on connection between structure and magnetic behaviour. At this time there are a few papers on both structure and magnetism of μ -NCS heteropolynuclear complexes [16–23]. This may be due to a difficulty in growing crystals containing this bridging ligand. In one case moderate antiferromagnetic coupling between metal centres, Ni(II)–SCN–Cr(III) ($J \approx 20 \text{ cm}^{-1}$), has been observed [17]. In the others, different bivalent or bi- with trivalent 3d group metals have been weakly coupled ferromagnetically [18,19,23] or antiferromagnetically [16,20–22]. This

weak character of the observed magnetic interactions is due to naturally structural reasons leading to a weak overlap between the involved magnetic orbitals. The large volume of the thiocyanato anions is not without significance either. Apart from those mentioned there have been characterized magnetic behaviour of several others M(II)–Cr(III), where M(II) = Cu, Ni and Co, compounds in the absence of structural data [24–29]. Continuing our interest in polynuclear complexes with thiocyanato ions as bridging ligands we now present syntheses of new four bimetallic complexes *e.g.*: [Cu(*N*-Et-en)₂]₃[Cr(NCS)₆]₂ (**1**), [Cu(*N*-Pr^{*i*}-en)₂]₃[Cr(NCS)₆]₂ · 2H₂O (**2**), [Cu(*N*-Me-tn)₂]₃[Cr(NCS)₆]₂ · H₂O (**3**) and [Cu(*C*-Et-tn)₂]₃[Cr(NCS)₆]₂ · H₂O (**4**). We report their spectroscopic, magnetic and thermal properties.

EXPERIMENTAL

Materials: K₃[Cr(NCS)₆] · 4H₂O was synthesized as described in [30]. Other reagents used *N*-ethylethylenediamine (98%), *N*-isopropylethylenediamine (98%), *N*-methyl-1,3-propanediamine (98%), 1,3-diaminopentane (98%) purchased from Aldrich Chemical Company and H₂SO₄ (98%), H₂O₂ (30%), NaOH, CuSO₄ · 5H₂O purchased from POCh Gliwice were reagent grade and used without purification.

Instrumentation: Analyses for C, H, N contents were carried out with a Perkin Elmer Analyzer Model 240. Copper content was determined using the AAS method. Chromium content was determined spectrophotometrically as CrO₄²⁻ at λ = 372 nm. Thermogravimetric analyses were performed with MOM derivatograph type OD-102 under the following conditions: sample mass – 50 mg, sensitivity: DTA – 1/5 or 1/3, DTG – 1/3, TG – 50 mg, heating rate – 5 K/min, temperature range 293–1273 K, the atmosphere over the sample – air. IR spectra were recorded on a Perkin Elmer FT-IR 2000 spectrophotometer. Electronic spectra were measured on a SPECORD M-40 (Carl Zeiss, Jena) spectrophotometer. Room temperature EPR spectra were recorded on an ESR Bruker Physik 418 S reflection type spectrometer. Magnetic susceptibility was measured between 80–300 K by Faraday method. Powder diffractograms were recorded with HZ64/A-2 DRON-1 diffractometer using CuK_α, λ = 0.1542 nm. The instrumentation details and experimental conditions were described in previous papers [24,28].

Synthesis: All complexes were prepared using the similar procedure: the liquid appropriate diamine (2 mmol) was slowly added to a 30 cm³ of aqueous solution of CuSO₄ · 5H₂O (1 mmol). During mixing a violet or dark blue solution was formed. To this mixture, aqueous solution of K₃[Cr(NCS)₆] · 4H₂O (0.67 mmol in 30 cm³) was added dropwise at room temperature. The resulting precipitate was collected by filtration, washed with water and left to air dry. Only in the case of complex **2** smaller amounts of reagents and water were used, keeping the same stoichiometry. The color and yields were: violet, 90% (**1**); violet, 86% (**2**); navy-blue, 88% (**3**) and navy-blue, 92% (**4**); respectively. All complexes are air stable and insoluble in water and common organic solvents. Elemental analysis confirmed the compositions.

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 [31]. The appearance of new bands abo-

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

Complex	$\nu(\text{CN})$	$\nu(\text{CS})$	$\delta(\text{NCS})$	$\nu(\text{M-N})$	$\nu(\text{N-H})$	$\nu(\text{CH})$	$\delta(\text{NH}_2)$	$\delta(\text{CH}_2)$	$\nu(\text{O-H})$
$\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$	2096vs	820vw	479s	360s, br	–	–	–	–	3430s, br
$[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (1)	2136sh 2089vs, br	817w 777w 668sh	482s	364vs, br	3201s 3122s	2950m	1576s	1460m	–
$[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (2)	2135sh 2090vs, br	792m 669w	482s	365vs, br	3205s 3129s	2972s 2929m	1579s	1459s	3462m, br
$[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (3)	2139sh 2087vs, br	796w masked	483s	360vs, br	3206m 3131sh	2931m	1579m	1459m	3436m, br
$[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (4)	2138sh 2086vs, br	817w 670m	480s	359vs, br	3221s 3125m	2959m 2926m	1576s	1459m	3442m, br

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

at 670 cm^{-1} assigned to $\nu(\text{CS})$ further confirms the bridging nature of NCS ions on end-to-end mode [31]. The NCS^- bending vibration is observed in all analyzed spectra as a strong band at *ca.* 480 cm^{-1} .

FIR spectra show very broad band at *ca.* 360 cm^{-1} , which consists of a few shoulders due to superposition of bands arising from $\nu(\text{Cr-N})$ for both terminal and bridging thiocyanates and $\nu(\text{Cu-N}(\text{diamine}))$. In this region, spectra of Cu(II)–Cr(III) system exhibit also some bands below 300 cm^{-1} . They can be assigned to the Cu–S stretching vibrations [32]. However, this link is only tentative, because we cannot be sure that these bands arise from deformation modes, *i.e.* chelate ring and out-of-plane N–Cu–N deformations. On the other hand, $\nu(\text{Cu-S})$ bands are not observed at all, when Cu–S bond is long as in $\text{Cu}(\text{en})_2(\text{SCN})_2$ complex [33–35].

Table 2. Approximate positions of bands in electronic spectra.

Complex	Position of bands [cm^{-1}] ^{a)}	Assignments ^{b)}
$[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (1)	14000sh 18800 24000sh 30200 37000 41800	d-d (Cu) d-d (Cu, Cr) d-d (Cr) IL CT CT
$[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (2)	13500sh 17500 24000sh 30800 35000sh 41100	d-d (Cu) d-d (Cu, Cr) d-d (Cr) IL CT CT
$[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (3)	13900sh 18100 24500sh 29900 36000sh 41200	d-d (Cu) d-d (Cu, Cr) d-d (Cr) IL CT CT
$[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (4)	14000sh 18100 24000sh 32400 37000 42400	d-d (Cu) d-d (Cu, Cr) d-d (Cr) IL CT CT

^{a)}sh – shoulder, ^{b)}CT – charge transfer, IL – intra ligand.

The electronic spectra of complexes were measured in nujol mulls and their data are listed in Table 2. In general all compounds absorb in a broad band in the $13000\text{--}19000\text{ cm}^{-1}$ regions with a clear evidence of a shoulder on the low-frequency side. This result indicates a superposition of Cr(III) and Cu(II) bands in this range. The band, which exhibits maximum between $17800\text{--}18800\text{ cm}^{-1}$, was assigned to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ Cr(III) transition. It overlaps with ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ Cu(II) transitions [36]. The position of this band is comparable to the one defined for octahedral $[\text{Cr}(\text{NCS})_6]^{3-}$ ion [36] and tetragonal $\text{Cu}(\text{diamine})_2\text{X}_2$ complexes [37–39]. A shoulder of the main band, occurring at *ca.* 14000 cm^{-1} , may be attributed to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ Cu(II) transition. The definite separation between copper(II) d-d transitions is evi-

dence of reduction of tetragonal distortion due to coordination of thiocyanato ions in axial position by copper(II) in heteropolynuclear complexes [37]. A similar effect was observed for copper(II) complexes with the same CuN_4S_2 chromophore, *eg.* $\text{Cu}(\text{NH}_3)_4(\text{SCN})_2$ [40] and $\text{Cu}(\text{en})_2(\text{SCN})_2$ [38]. In the later, however, this effect is clearly seen only at low temperature spectrum. The second spin-allowed ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ Cr(III) transition is weaker than the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transition and appears at 24000 cm^{-1} as a weak band or shoulder. Intraligand transition of thiocyanato ions is observed at *ca.* 30000 cm^{-1} . Others bands observed in $35000\text{--}42400\text{ cm}^{-1}$ regions are assigned to LMCT absorptions, according to the previous reports on the similar or parent compounds. Thus, the $\sigma(\text{N}) \rightarrow \text{Cu}(\text{II})$ and $(\text{NCS}) \rightarrow \text{Cr}(\text{III})$ transitions occur at *ca.* $35000\text{--}40000\text{ cm}^{-1}$ for Cu(II) bis(diamine) complexes [36] and at 42740 cm^{-1} for $[\text{Cr}(\text{NCS})_6]^{3-}$ [41], respectively.

EPR and magnetic studies: The EPR line shape and width of solid state substances depend on the type and strength of interaction existing in the crystal lattice. EPR spectra of complexes exhibit quasi-isotropic and very broad features with $g = 2.012\text{--}2.032$. Their peak-to-peak widths (ΔB_{pp}) and g -values are collected in Table 3. The room temperature EPR spectrum of **2** is shown as example in Fig. 1. Such broad lines are characteristic of systems with a great concentration of paramagnetic centers and in the case of heteropolynuclear complexes, they have been reported not only for thiocyanato bridged building blocks [24–28] but also for oxalato bridged ones [42]. 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 3. EPR parameters for copper(II)–chromium(III) complexes.

Complex	g_{iso}	ΔB_{pp} [mT]
$[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (1)	2.031	39
$[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (2)	2.032	40
$[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (3)	2.012	54
$[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (4)	2.018	28

Generally, copper(II) bis-diamine complexes give axial or nearly axial EPR spectra [40]. On the contrary, EPR spectrum of $\text{K}_3[\text{Cr}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$ complex shows unsymmetrical line with $g = 1.995$ and $\Delta B_{\text{pp}} = 18\text{ mT}$. 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 exists through thiocyanato bridges [43]. A more detailed analysis of the spectra is impossible due to the broadness of the signal.

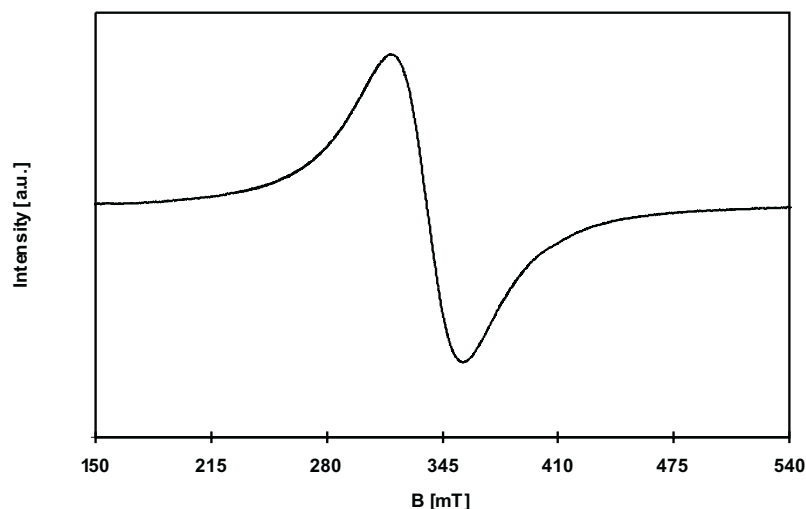


Figure 1. EPR spectrum of $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (**2**) at room temperature (powder, 9.5625 GHz).

Table 4. Magnetic data for studied heterobimetallic complexes.

Complex	$\chi_{\text{dia}} \cdot 10^6$ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	Curie constant ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$)	Weiss constant (K)	μ_{eff} (B.M.) RT/LNT
$[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (1)	-897	4.76	-	const. 6.20 ± 0.03
$[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (2)	-994	4.95	-10	6.25/6.09
$[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (3)	-910	5.21	-	const. 6.48 ± 0.05
$[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (4)	-981	5.06	-13	6.27/6.05

The molar susceptibilities were corrected for diamagnetism using Pascal's constants and temperature independent paramagnetism equal to $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ for copper(II) ion. 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 $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**4**) complexes possess of negative Weiss constant, whereas for others complexes Weiss constant are very close to 0, and the complexes equally obey the Curie law. The room-temperature effective magnetic moments of chromium(III)–copper(II) heteropolynuclear complexes have approximately the expected spin-only value for five noninteracting ions (with $S = 1/2, 1/2, 1/2, 3/2, 3/2$), which is 6.24 B.M. However, the negative value for θ and the decrease in the effective magnetic moment at liquid nitrogen temperature for **2** and **4** complexes may be caused by a weak antiferromagnetic interaction between metal ions through thiocyanato bridges [44]. Similar effect has been observed for Cu_3Cr_2 thiocyanato bridged bimetallic complexes with *N,N*-diethylethylenediamine and 1,3-diaminopropane [25].

Effective magnetic moments for others complexes are nearly constant down to liquid nitrogen temperature and indicate that magnetic interactions in this temperature range are negligible.

Thermal analysis: Results of thermal analysis are presented in Table 5. Thermal decomposition curves of **1** is shown as example in Fig. 2.

Table 5. Results of thermal analysis, in air.

Complex	Heat effect	Temperature [K] ^{a)}			Weight loss on TG [%]		Detached molecule or final products
		T _i	T _m	T _f	found	calcd.	
[Cu(<i>N</i> -Et-en) ₂] ₃ [Cr(NCS) ₆] ₂ (1)	endo	448	493	533	8		
	exo	533	593	658	26		
	exo ^{b)}	658	763	848	31		
	endo	898	978	1003	4		
	endo	1003	1053	1078	10		
	endo	1123	1173	1253	4	75.4	2CuCrO ₂ + CuO
[Cu(<i>N</i> -Pr ^{<i>l</i>} -en) ₂] ₃ [Cr(NCS) ₆] ₂ · 2H ₂ O (2)	endo	308	353	408	2	2.2	2H ₂ O
	endo	408	433	478	3		
	endo	478	493	498	5		
	exo	498	593	643	27		
	exo ^{b)}	643	773	898	24		
	endo	933	998	1023	5		
	endo	1023	1058	1093	7		
	endo	1178	1253	1273	4	77.2	2CuCrO ₂ + CuO
[Cu(<i>N</i> -Me-tn) ₂] ₃ [Cr(NCS) ₆] ₂ · H ₂ O (3)	endo	313	343	418	1	1.2	H ₂ O
	endo	418	463	488	3		
	endo	488	523	543	5		
	exo	543	623	728	36		
	exo ^{b)}	728	768	848	9		
	endo	928	993	1008	4		
	endo	1008	1038	1068	10		
	endo	1148	1188	1233	3	75.7	2CuCrO ₂ + CuO
[Cu(<i>C</i> -Et-tn) ₂] ₃ [Cr(NCS) ₆] ₂ · H ₂ O (4)	endo	313	368	418	1	1.1	H ₂ O
	endo	423	453	473	2		
	endo	473	483	533	8		
	exo	523	588	668	29		
	exo ^{b)}	668	753	858	20		
	endo	913	983	998	8		
	endo	998	1038	1053	6		
	endo	1153	1168	1253	3	76.9	2CuCrO ₂ + CuO

^{a)}T_i – initial temperature, T_m – maximum temperature, T_f – final temperature; ^{b)}strong effect.

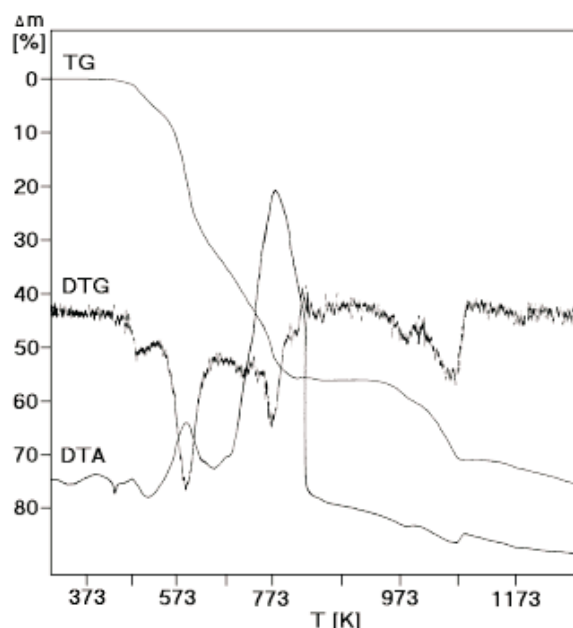


Figure 2. Thermal decomposition curves of $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (**1**).

Dehydration starts at about 323 K. Water molecules are lost in a one step process, which is connected with the dissociation of water molecules that are not bonded directly to the metal ion but *via* the hydrogen-bond network in the crystal lattice. The dehydration has the characteristic DTG and DTA curves, which indicate that this process is very slow because it is stretched over 100 K. Complex **1** melts at 431 K with the beginning of decomposition, whereas for others complexes decomposition occurs immediately after dehydration. Decomposition is very similar for all studied chromium(III)–copper(II) heterometallic complexes and runs in a few separate steps. The first two (or only one for **1**) endothermic steps are probably connected with the loss and/or decomposition of diamine ligands, according to the previous TG-FTIR study on the similar $[\text{Ni}(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2$ compounds [45]. In a subsequent exothermic step decomposition at the chromium center also takes place. The strong exothermic effect, observed for fourth step (third for **1**), can be compared with the $\text{K}_3[\text{Cr}(\text{NCS})_6]$ pyrolysis that occurs at somewhat lower temperature, 718 K, with a similarly strong exothermic effect. As the samples **3** and **4** are heated to temperatures over 800 K, the mass of the samples increases by *ca.* 0.5%. It is probably connected with partial oxidation of previously formed S^{2-} ions to SO_4^{2-} , which was unambiguously stated for $\text{Cu}_3[\text{Cr}(\text{NCS})_6]$ and $\text{Cd}_3[\text{Cr}(\text{NCS})_6]_2 \cdot 8\text{H}_2\text{O}$ [46]. Further heating caused further gradual decrease in weight due to endothermal decomposition. It occurs in three separate steps for **1–4** complexes. The temperature of total decomposition takes place at *ca.* 1250 K and finally leads to the mixtures of CuO and CuCrO_2 in 1:2 ratio, which is 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 [47].

CONCLUSIONS

The examination of the infrared spectra of obtained compounds support the hypothesis of existence of both bridging and terminal thiocyanato ions and consequently their heteropolynuclear structure. Although, superposition of Cu(II) and Cr(III) d-d bands occurs in the electronic absorption spectra, they agree well with tetragonal – CuN_4S_2 and octahedral – CrN_6 chromophores. The parameters determined from the temperature dependence of magnetic susceptibility indicate weak antiferromagnetic interactions in $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**4**), which can be transmitted through thiocyanato bridges. Other compounds such as $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$ (**1**) and $[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ (**3**) show no net interaction in the measured temperature range, but this does not exclude existence of thiocyanato bridges [18, 20, 21]. Studies down to liquid helium temperature could give 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 Cu(II) ions through bridging NCS ions. The exact structure is unknown. However, on the basis of the obtained results and recently reported [48], crystal structures of similar composition of Cu_3Cr_2 complexes with bridging cyanide ions, it is possible to predict that **1–4** compounds have polynuclear structures, *i.e.* they consist of two distinct ionic units, where one is cation, *e.g.* $[(\text{diamine})_2\text{Cu-SCN-Cr}(\text{NCS})_4\text{NCS-Cu}(\text{diamine})_2]^+$ and the other is anion, *e.g.* $[(\text{SCN})_5\text{Cr-NCS-Cu}(\text{diamine})_2]^-$. Ions can also form one-dimensional (1D) polymeric chains, *e.g.* $[\{((\text{diamine})_2\text{Cu-SCN})_2\text{Cr}(\text{NCS})_4\}_n]^{n+}$ and $[\{\text{SCN-Cr}(\text{NCS})_4\text{NCS-Cu}(\text{diamine})_2\}_n]^{n-}$. Structures with higher dimensionalities, *e.g.* 2D or 3D are also possible [2].

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