Polish J. Chem., **75**, 909–914 (2001) **COMMUNICATION**

Synthesis and Properties of New Bimetallic Complexes of General Formula: $[Ni(diamine)_2]_3[Cr(NCS)_6]_2 \cdot nH_2O$

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Heteropolynuclear metal complexes have been the subject of intensive studies, because of the interest in the developing of new molecular-based magnetic materials [1–4], catalytic precursors [5] and also to understand the structure and functioning of metallobiomolecules [6,7]. In continuation of our work [8,9] regarding thiocyanato-bridged heterocomplexes consisting three-atoms pathway for exchange coupling, we report here the preparation, spectroscopic and magnetic characterization of three new bimetallic complexes: $[Ni(en)_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**1**), $[Ni(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**2**) and $[Ni(tn)_2]_3[Cr(NCS)_6]_2 \cdot 4H_2O$ (**3**), where en = ethylenediamine; 1,1-dmen = 1,1-dimethylethylenediamine; tn = 1,3-diaminopropane.

All chemicals used were reagent grade. $K_3[Cr(NCS)_6] \cdot 4H_2O$ was obtained by described procedure [10]. The new compounds were prepared in a similar manner. The appropriate diamine (2 mmol) was added to a 30 ml hot aqueous solution of $NiSO_4 \cdot 7H_2O$ (1 mmol) and formed a violet (**1**), blue (**2**) and navy blue (**3**) solution was then added dropwise to a 40 ml aqueous solution of $K_3[Cr(NCS)_6] \cdot 4H_2O$ (0.67 mmol). The dark-red (**1**), (**2**) and violet (**3**) precipitates were formed immediately. The products were collected by filtration, washed with water and left to air dry. The yields were: 62% (**1**), 73% (**2**), and 89% (**3**). All our attempts to obtain the complexes in a crystalline form failed. Analyses for C, H, N contents were carried out with a Perkin Elmer Analyser Model 240. Nickel content was determined with the AAS method. Chromium content was determined spectrophotometrically as CrO_4^{2-} at $\lambda = 372$ nm. All analyses confirmed the composition of the complexes investigated within 0.01–0.79%. 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. Thermogravimetric analyses were performed on a MOM derivatograph type OD-102. Powder diffractograms were recorded on an HZ64/A-2 DRON-1 diffractometer. Room temperature EPR spectra were recorded on an ESR Bruker Physik 418S reflection type spectrometer. Magnetic susceptibility was measured between 80–300 K by Faraday method. The elemental analyses, spectral data (IR, UV-VIS) and magnetic studies confirmed that the reactions of $[Cr(NCS)_6]^{3-}$ with the cationic $[Ni(diamine)_2]^{2+}$ complexes yielded thiocyanato-bridged complexes of given compositions.

IR spectra of **1**–**3** are quite similar (Table 1). The most intense absorption band, close to 2100 cm^{-1}, corresponds to the $\nu_{C\text{-}N}$ of the thiocyanato ligands. It is more complex than the corresponding one for $K_3[Cr(NCS)_6]$, because the appearance of split (**1**) or shoulders (**2**,**3**) above 2100 cm^{-1} and the clear components at lower frequencies of this band. This observation is in a good agreement with the existence of bridging thiocyanato ions in complexes and indicates also the presence of terminal N-bonded NCS^- [11]. The appearance of new bands assigned to $\nu_{C\text{-}S}$ further confirms the bridging nature of the NCS groups [11]. The broad band in FIR spectra at *ca*. 360 cm^{-1} is due to $\nu_{M\text{-}N}$, exhibiting few shoulders, which point to a superposition of $\nu_{Cr\text{-}N}$ and $\nu_{Ni\text{-}N}$. The expected low intensity new $\nu_{Ni\text{-}S}$ band around 200 cm^{-1} is obscured by bands of the parent complexes.

Table 1. Selected IR vibration bands of studied complexes in solid state, $[cm^{-1}]^a$.

Complex	ν(CN)	ν(CS)	δ(NCS)	ν(Cr–N) and ν(Ni–N)	ν(OH)	δ(HOH)
$K_3[Cr(NCS)_6]\cdot 4H_2O$	2096vs	820vw	479s	360s,br	3430s,br	1622m
$[Ni(en)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**1**)	2137 2090 2075sh 2055sh	748w 653m	484s	363vs,br	3443m,br	masked
$[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**2**)	2138sh 2098sh 2088sh 2076	836w 691m	484s	362vs,br	3446m,br	masked
$[Ni(tn)_2]_3[Cr(NCS)_6]_2\cdot 4H_2O$ (**3**)	2132sh 2098 2079sh 2055sh	820w 634m	484s	364vs,br	3548s	1616m

Complex	ν(CH)	$\delta(NH_2)$	ν(NH)	$\delta(CH_2)$	δ(NMN)	ring
$[Ni(en)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**1**)	2946m 2886m	1577s	3322s 3286s 3246s	1457m	216m 165m	masked
$[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**2**)	2912m,br	1571m	3251m 3189m 3119m	1460s	221sh 191m	429sh
$[Ni(tn)_2]_3[Cr(NCS)_6]_2\cdot 4H_2O$ (**3**)	2932m 2885m	1587s	3385s 3282s 3241s	1473m	187m, br	432sh

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

The electronic spectra (Table 2) for solid samples exhibit a broad, asymmetric band in the visible region, making it difficult to identify the band maximum accurately. It is an effect of superposition of Ni(II) and Cr(III) bands. The clear shift of the first spin-allowed d-d (Ni, Cr) bands to a higher frequency in **2**, in comparison with those in **1** and **3**, can be explained by changes in the Ni(II) chromophore, coming from the differences of the steric interactions between appropriate diamine and axial thiocyanato ligands [12]. An interesting feature in the spectrum of **1** is the presence of two sharp low-energy bands at *ca*. 12400 and 12800 cm^{-1}, which can be attributed to the mixed spin allowed $^3B_{1g} \rightarrow {}^3E_g$ and spin forbidden $^3B_{1g} \rightarrow {}^1A_1$, $^3B_{1g} \rightarrow {}^1B_1$ Ni(II) transitions [13] with the intensity gain of the latter, originating from exchange coupling in the complex [14].

Table 2. Approximate positions of bands in electronic spectra.

Complex[a]	Position of bands $[cm^{-1}]$[b]	Assignments[c]
$[Ni(en)_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**1**)	12400	SF (Ni)
	12800	SF (Ni)
	18160	d-d (Ni, Cr)
	29000br	d-d (Ni, Cr); IL (NCS)
	40000	CT
	43850	CT
$[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ (**2**)	13600sh	SF (Cr)
	21000br	d-d (Ni, Cr)
	30000br	IL (NCS)
	41000	CT
	46900	CT
$[Ni(tn)_2]_3[Cr(NCS)_6]_2 \cdot 4H_2O$ (**3**)	18120br	d-d (Ni, Cr)
	24000sh	d-d (Ni, Cr)
	30000br	IL (NCS)
	40400br	CT
	46000sh	CT

a) spectra recorded in nujol mulls; b) sh – shoulder, br – broad; c) SF – spin-forbidden, CT – charge transfer, IL – intra ligand.

Thermal behaviour is presented in Table 3. The dehydration occurs in one endothermic step for **1** and **2** and in two endothermic steps for **3**. In **3** the temperatures of consecutive steps of this process in conjunction with the result of TG analysis may indicate a loss of three hydrated water molecules in the first step and one water molecule in the next one. Complexes **1** and **2** melt at 179 and 183°C respectively, whereas compound **3** decomposes at about 200°C without prior melting. The decomposition after dehydration runs in five steps in air. It is parallel for **1** and **2** and different for **3** in view of effects on DTA curves attendant the successive stages. Total decomposition occurs at *ca*. 830°C and leads finally to a mixture of $NiCr_2O_4$ and NiO in 1:2 ratio, identified on the basis of powder diffractograms and analysis of TG curves.

Table 3. Results of thermal analysis, in air.

Process	Dehydration	1st stage of decom- position	2nd stage of decom- position	3rd stage of decom- position	4th stage of decom- position	5th stage of decom- position
Heat effect	endothermic	exothermic	strong exothermic	endothermic	endothermic	endothermic
Complex	$[Ni(en)_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ (**1**)					
T_{max} [°C][a]	64	300	390	545	580	768
Dehydration: weight loss on TG curve – %calc./found: 1.3/1.5 Final products (at 820°C): $NiCr_2O_4 + 2NiO$ (%calc./found: 27.7/29)						
Complex	$[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ (**2**)					
T_{max} [°C][a]	82	305	442	562	618	800
Dehydration: weight loss on TG curve – %calc./found: 1.2/1.0 Final products (at 840°C): $NiCr_2O_4 + 2NiO$ (%calc./found: 25.0/25.5)						
Complex	$[Ni(tn)_2]_3[Cr(NCS)_6]_2{\cdot}4H_2O$ (**3**)					
Process	Dehydration	1st stage of decom- position	2nd stage of decom- position	3rd stage of decom- position	4th stage of decom- position	5th stage of decom- position
Heat effect	endothermic	endothermic	exothermic	strong exothermic	endothermic	endothermic
T_{max} [°C][a]	90 178	256	330	440	592	800
Dehydration: weight loss on TG curve – %calc./found: 4.8/4.8 Final products (at 850°C): $NiCr_2O_4 + 2NiO$ (%calc./found: 25.2/27.8)						

a) on DTG curves.

In the Ni_3Cr_2 polynuclear complex the total number of unpaired electrons is even. Therefore, all electronic degeneracies should be removed in a zero field and the system should be usually EPR silent [15]. As expected, **1** and **3** do not exhibit any EPR signal. A different behaviour is observed for $[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ (**2**) complex. It shows unusual magnetic (*vide infra*) and EPR behaviour. The room temperature EPR spectrum of **2**, shown in Fig. 1, exhibits two lines, first at low field with $g = 3.90$, and a second very broad feature with $g = 2.010$ and peak-to-peak width (ΔB_{pp}) equal *ca.* 38 mT. Such broad lines are characteristic of systems with a great concentration of paramagnetic centres. On the other hand, zero field splitting parameter(s) should be small to render EPR lines observable. In this case, low-field EPR line arises from $\Delta M_s = \pm 2$ forbidden transition, whereas line with $g \sim 2$ arises from $\Delta M_s = \pm 1$ allowed transition [15]. Different behaviour of **2**, in comparison with **1** and **3**, is most probably due to a drastic change in the network structure of $[Ni(diamine)_2]_3[Cr(NCS)_6]_2{\cdot}nH_2O$, when two methyl substituents are introduced into one ethylenediamine nitrogen. Influence of substituents on the structure have been reported for similar complexes, *i.e.* $[Ni(L)_2]_3[M(CN)_6]_2{\cdot}nH_2O$, where L = en or N-methylethylenediamine and M = Fe or Co [1]. So, EPR behaviour of studied heterocomplexes is quite different from the parent Ni(II) and Cr(III) complexes. Therefore, the metal ions cannot be considered as non-interacting [15].

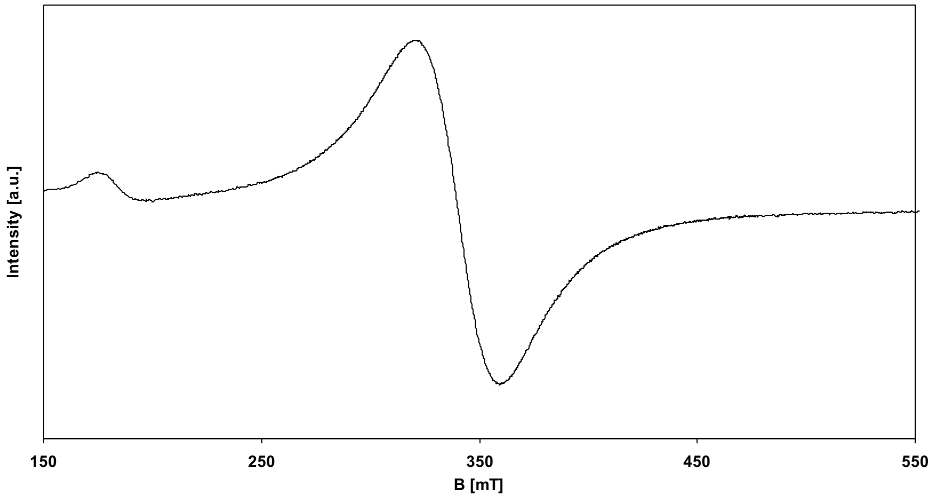

Figure 1. EPR spectrum of $[Ni(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ at room temperature (powder, 9.5753 GHz).

Magnetic properties of obtained heterocomplexes were studied down to liquid nitrogen temperature. The molar susceptibilities were corrected for diamagnetism using Pascal's constants. The effective magnetic moments were calculated from $\mu_{eff} = 2.828\ (\chi_M^{corr}{\cdot}T)^{1/2}$. The temperature dependencies of magnetic susceptibilities obey the Curie-Weiss law, *i.e.* $\chi_M^{corr} = C/(T-\theta)$. The best fitted values of the Curie (C) and Weiss constant (θ) are given in Table 4. All complexes studied possess a negative Weiss constant. The room-temperature effective magnetic moment of **3** has approximately the expected spin-only value for five noninteracting ions (with S = 1, 1, 1, 3/2, 3/2), which is 7.35 B.M. However, the negative value for θ and the decrease in the effective magnetic moment at liquid nitrogen temperature may be caused by an antiferromagnetic interaction between metal ions [16]. Antiferromagnetic interaction in $[Ni(en)_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ (**1**) is significantly larger than that in **3** and also observed for analogous Cu(II)–Cr(III) heterocomplex [8]. Magnetic interaction in **2** is quite different. The effective magnetic moment for **2** is nearly constant down to liquid nitrogen temperature, but is considerably below spin-only value and indicates drastic changes in the network structure of Ni_3Cr_2 polynuclear complex. It could be connected with the introduction of methyl substituents into diamine ligand. So, different pathways for magnetic interaction probably exist in **2** compared with those in **1** and **3**.

The exact structure is unknown, but considering the data given above, we can propose a polymeric structure for the compounds prepared, with thiocyanato bridges between octahedral nickel(II) and octahedral chromium(III).

Table 4. Parameters from the Curie-Weiss law and magnetic moments for nickel(II)-chromium(III) heterocomplexes.

Complex	$\chi_{dia}\cdot10^6$	Curie constant	Weiss constant	$\mu_{eff.}$ [B.M.]	
	[cm^3·mol^{-1}]	[cm^3·K·mol^{-1}]	[K]	LNT	RT
$[Ni(en)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**1**)	–771	7.39	–71	5.51	6.88
$[Ni(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (**2**)	–900	3.87	–2	5.49	5.56
$[Ni(tn)_2]_3[Cr(NCS)_6]_2\cdot 4H_2O$ (**3**)	–881	7.44	–23	6.84	7.43

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