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Synthesis, Spectroscopy and Magnetism of New μ-Thiocyanato Polynuclear Copper(II)-Chromium(III) Complexes

by **L. Dobrzańska**[1], **G. Wrzeszcz**[1*], **A. Grodzicki**[1] and **F. Rozpłoch**[2]

[1]*Department of Chemistry, Gagarina 7,* [2]*Institute of Physics, Grudziądzka 5/7,*
Nicholas Copernicus University, 87-100 Toruń, Poland

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New heteropolynuclear complexes with general formula $[Cu(diamine)_2]_3[Cr(NCS)_6]_2 \cdot nH_2O$, where diamine = N,N′-dimethylethylenediamine (1,2-dmen), N,N-dimethylethylenediamine (1,1-dmen), N,N′-diethylethylenediamine (1,2-deen), N,N-diethylethylenediamine (1,1-deen), 1,3-diaminopropane (tn) were obtained by reactions of $[Cr(NCS)_6]^{3-}$ with the corresponding cationic Cu(II) complexes: $[Cu(diamine)_2]^{2+}$ and characterized by spectroscopic methods and magnetic measurements. The formation of end-to-end thiocyanato bridges between tetragonal Cu(II) and pseudo-octahedral Cr(III) is evident from IR and UV-VIS spectra by appearance of new components of ν(CN) band and shifts in the absorption maxima assigned to copper d-d transitions in comparison with corresponding mononuclear complexes. The EPR spectra measured at room temperature on solid samples show broad, symmetric signal at $g = 2.02–2.03$. Variable-temperature magnetic susceptibility measurements reveal the presence of weak antiferromagnetic interactions in $[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ and $[Cu(tn)_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$.

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

The increase of interest in heteropolynuclear complexes, which can be observed in the last decade, is connected on the one hand with the occurring of this type of systems in biological structures such as active sites of metal enzymes, on the other it is a result of the search for materials with interesting magnetic properties and the willingness to find out how a structural-magnetic correlation takes place. Hence such a broad range of metals (mainly first-row transition metals) and bridging ligands used: from imidazolate used for the preparation of models of bimetallic centres [1–3] to hydroxo and azide (cyanide) anions [4,5], which are efficient mediators for magnetic interactions between metal centres. The literature presenting these compounds, especially heteropolynuclear complexes with thiocyanato bridges is very limited, although the variety of coordination modes of this anion makes it absorbing for studies of connection between structure and magnetic behaviour. The majority of characterized compounds with μ-NCS are homopolynuclear systems of Cu(II) and Ni(II) with asymmetric a end-to-end coordination fashion and a weak magnetic exchange interaction

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[*] Author for correspondence.

(anti- and ferromagnetic), or a virtual lack of coupling [6–9]. This weak character of the observed magnetic interactions is due to naturally structural reasons, leading to a weak overlap between the magnetic orbitals involved. The large volume of the thiocyanato anions is not without significance either. Distinctive magnetic features presented $[Cu(NCS)(\mu\text{-}NCS)(Hmpto)(H_2O)]_{2n}$ (Hmpto = 4*H*,7*H*-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine), where the strong antiferromagnetic coupling between the copper centres ($J = 74.1\ cm^{-1}$) is a result of occupying equatorial position by both the N and S donor groups of two symmetric bridges in the coordination polyhedra about the metal centres [10]. It is the only described example of a compound with symmetric end-to-end coordination mode.

At this time there exist three papers on the structure of μ-NCS heteropolynuclear complexes. This may be due to the difficulty in growing crystals containing this bridging ligand [11–13]. Two of these compounds are 1D chains of Cu(II)–Mn(II) and Cu(II)–Co(II) and show weak antiferromagnetic interactions. The next one is tetranuclear complex of the type $(Cu\text{–}Ni)_2$, where coupling constant Cu–NCS–Ni is very small, but positive and may indicate ferromagnetic interactions. Apart from those mentioned, there have been characterized magnetic behaviour of several others Cu(II)–Cr(III), Ni(II)–Cr(III) compounds in the absence of structural data [14–17]. Continuing our interest in polynuclear complexes with thiocyanato ions as bridging ligands, we now present five syntheses of bimetallic complexes *e.g.*: $[Cu(1,2\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$, $[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$, $[Cu(1,2\text{-deen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$, $[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$, $[Cu(tn)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$. We describe their spectroscopic and magnetic properties.

EXPERIMENTAL

Materials: $K_3[Cr(NCS)_6]\cdot 4H_2O$ was synthesized as described in [18]. Other reagents used, *i.e.* N,N′-dimethylethylenediamine (99%), N,N-dimethylethylenediamine (95%), N,N′-diethylethylenediamine (95%), N,N-diethylethylenediamine (99%), 1,3-diaminopropane (99%) purchased from Aldrich Chemical Company; H_2SO_4 (98%), H_2O_2 (30%), NaOH, $CuSO_4\cdot 5H_2O$ 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 CrO_4^{2-} at $\lambda = 372$ nm. The water content of studied complexes was determined from thermogravimetric analyses performed on a MOM derivatograph type OD-102. 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.

Synthesis: All complexes were prepared using the following procedure: to a 30 ml aqueous solution of $CuSO_4\cdot 5H_2O$ (249.7 mg, 1 mmol) was added the appropriate diamine (2 mmol). The resulting deep-blue solution was added dropwise to a 40 ml aqueous solution of $K_3[Cr(NCS)_6]\cdot 4H_2O$ (395.2 mg, 0.67 mmol) at room temperature. The resulting precipitate was collected by filtration, washed with water and left to air dry. Yields: 66–90%. Results of elemental analyses for $[Cu(1,2\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$ (Calcd: C, 28.10; H, 4.85; N, 21.85; Cr, 6.76; Cu,12.39. Found: C, 28.26; H, 4.94; N, 21.67; Cr, 5.97; Cu, 13.10%). $[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$, (Calcd: C, 27.78; H, 4.92; N, 21.60; Cr, 6.68; Cu, 12.25. Found: C, 27.80; H, 5.01; N, 21.46; Cr, 7.04; Cu, 12.13%). $[Cu(1,2\text{-deen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$, (Calcd: C, 33.78; H, 5.79; N, 19.69; Cr, 6.09; Cu, 11.17. Found: C, 33.65; H, 5.68; N, 19.75; Cr, 6.09; Cu, 11.36%). $[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$, (Calcd: C, 33.78; H, 5.79; N, 19.69; Cr, 6.09; Cu, 11.17. Found: C, 33.74; H, 6.25; N, 19.50; Cr, 6.24; Cu, 11.34%). $[Cu(tn)_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ (Calcd: C, 24.47; H, 4.38; N, 22.83; Cr, 7.06; Cu, 12.95. Found: C, 24.64; H, 4.43; N, 22.97; Cr, 6.44; Cu, 12.95%).

RESULTS AND DISCUSSION

Spectroscopic properties: The most important bands in the IR spectra of complexes for structural diagnosis are those, which correspond to vibrations of thiocyanato groups. Selected IR data are summarized in Table 1. All heteropolynuclear complexes show a strong, broad band attributed to ν(CN) with shoulder above 2100cm^{-1}. This result is a combination of the following effects: formation of thiocyanato bridges connected with decrease in symmetry about the $[Cr(NCS)_6]^{3-}$ entities and distortion octahedral copper(II) environment, and the presence of non-bridging thiocyanato ligands (Cr–NCS). The appearance of new bands about 670 cm^{-1} assigned to ν(CS) further confirms the bridging nature of NCS ions on end-to-end mode [19]. FIR spectra show the very broad band at *ca*. 360 cm^{-1} with shoulders due to superposition of bands arising from ν(Cr–NCS) and ν(Cu–N(diamine)) vibrations. In this region spectra exhibit also bands at 246, 277 and 248 cm^{-1} for $[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$, $[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$ and $[Cu(tn)_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$ complexes, respectively. They can be assigned to the Cu–S stretching vibrations [20].

Table 1. Selected infrared and electronic spectral data.

Complex	ν(CN)	ν(CS)	δ(NCS)	ν(Cr–N) ν(Cu–N)	d-d transitions
$K_3[Cr(NCS)_6] \cdot 4H_2O$	2096vs	820vw	479s	360s,br	18440 24200sh
$[Cu(1,2\text{-dmen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$	2139sh 2090vs, br	668m 822w	482s	367vs, br	13800sh 18000 23800sh
$[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$	2135sh 2097vs, br	669w masked	484s	368vs, br	14000sh 18200
$[Cu(1,2\text{-deen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$	2135sh 2089vs, br	669m 817m	482s	364vs, br	13600sh 18000 23600sh
$[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2 \cdot H_2O$	2131sh 2089vs, br	668m masked	484s	369vs, br	14000sh 17800
$[Cu(tn)_2]_3[Cr(NCS)_6]_2 \cdot 2H_2O$	2136sh 2082vs, br	657m masked	480s	364vs, br	14000sh 18100 24000sh

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

The electronic spectra of complexes were measured in nujol mulls and their data are listed in Table 1. All spectra are dominated by the bands of six-fold chromium(III) chromophore. The small, but not negligible shifts in the absorption maxima in comparison with those for $K_3[Cr(NCS)_6]\cdot 4H_2O$ indicate deviation from starting $[Cr(NCS)_6]^{3-}$ symmetry. In addition to the bands due to a nearly octahedral chromium(III) centre a shoulder attributable to the copper(II) d-d transition is observed. Its red shift in relation to bands occurring in corresponding compounds of copper(II) with CuN_4S_2 chromophore (showing significantly tetragonal distortion) is an evidence of stronger coordination of thiocyanato ions in axial position by copper(II) in heteropolynuclear complexes [21–23]. A similar effect was observed in the paper presenting the crystal structure and spectral properties of $[Cu(en)_2Mn(NCS)_4(H_2O)_2]_n$, where it has been shown that Cu-S bond in this complex is shorter by about 0.2 Å than the one in $Cu(en)_2(SCN)_2$ [13].

EPR and magnetic studies: The EPR line shape and the 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 = 2.020–2.032. Their peak-to-peak widths (ΔB_{pp}) and g-values are collected in Table 2.

Table 2. EPR parameters for Cu(II)–Cr(III) complexes.

Complex	g_{iso}	ΔB_{pp} [mT]	Comments
$[Cu(1,2\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$	2.020	26	symmetric line, nearly Lorentzian shape
$[Cu(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$	2.027	37	symmetric line, Lorentzian shape
$[Cu(1,2\text{-}deen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$	2.026	38	symmetric line, mixed shape
$[Cu(1,1\text{-}deen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$	2.032	38	symmetric line, Lorentzian shape
$[Cu(tn)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$	2.030	45	symmetric line, Lorentzian shape

The room temperature EPR spectrum of $[Cu(1,1\text{-}dmen)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$ complex is shown as example in Fig. 1. Such broad lines are characteristic of systems with a great concentration of paramagnetic centres. Generally, copper(II) bis-diamine complexes give axial or nearly axial EPR spectra [24]. On the contrary, EPR spectrum of $K_3[Cr(NCS)_6]_2\cdot 4H_2O$ complex shows unsymmetrical line with g = 1.995 and ΔB_{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 [25]. The molar susceptibilities were corrected for diamagnetism using Pascal's constants and temperature independent paramagnetism equal to 60×10^{-6} cm^3/mol for copper(II) ion. 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 3. The $[Cu(1,1\text{-}deen)_2]_3[Cr(NCS)_6]_2\cdot H_2O$ and $[Cu(tn)_2]_3\,[Cr(NCS)_6]_2\cdot 2H_2O$ complexes possess a negative Weiss constant, whereas for others complexes the Weiss constants are very close to 0, and the complexes equally obey Curie law. The

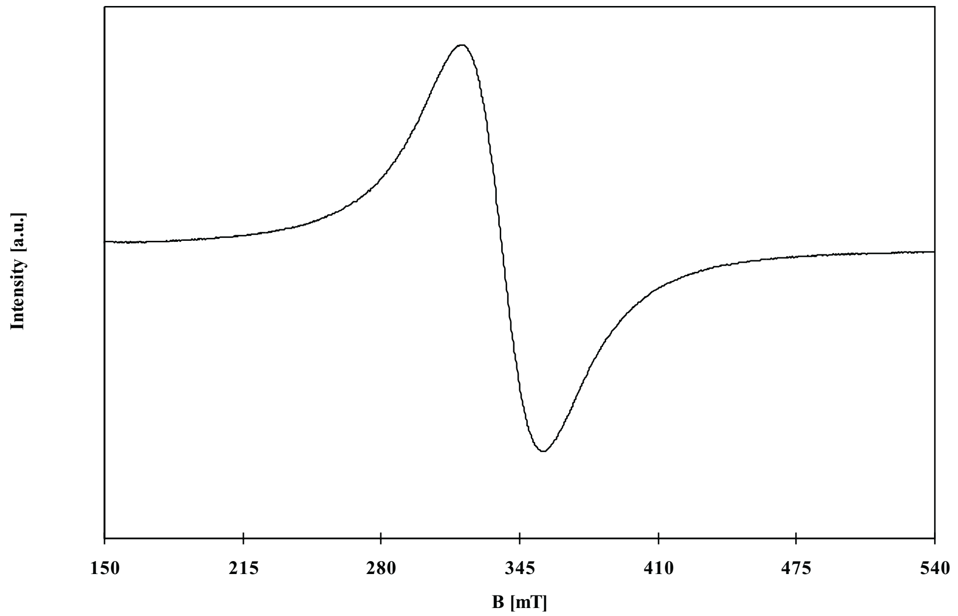

Figure 1. EPR spectrum of $[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2{\cdot}2H_2O$ at room temperature (powder, 9.5567 GHz).

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 $[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2{\cdot}H_2O$ and $[Cu(tn)_2]_3[Cr(NCS)_6]_2{\cdot}2H_2O$ complexes may be caused by a weak antiferromagnetic interaction between metal ions [26]. Effective magnetic moments for other complexes are nearly constant down to liquid nitrogen temperature and indicate that magnetic interactions in this temperature range are negligible. The exact structure is unknown, but considering the data given above and recently reported [27] crystal structure of similar composition Cu_3Cr_2 complex with bridging cyanide ions, it is possible to predict that prepared compounds have polynuclear structures, *i.e.* they consist two distinct ionic units, where one is cation, *e.g.* $[(diamine)_2CuSCNCr(NCS)_4NCSCu(diamine)_2]^+$ and the other is anion, *e.g.* $[Cr(NCS)_5NCSCu(diamine)_2]^-$. Ions can also form polymeric chains, *e.g.* $[\{((diamine)_2CuSCN)_2Cr(NCS)_4\}_n]^{n+}$ and $[\{SCNCr(NCS)_4NCSCu(diamine)_2\}_n]^{n-}$.

Table 3. Magnetic properties of Cu(II)–Cr(III) complexes.

Complex	$\chi_{dia}\cdot10^6$ ($cm^3\ mol^{-1}$)	Curie constant ($cm^3\ mol^{-1}\ K$)	Weiss constant (K)	μ_{eff} (B.M.) RT/LNT
$[Cu(1,2\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$	–913	4.92	–	const. 6.30 ± 0.05
$[Cu(1,1\text{-dmen})_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$	–926	4.89	–	const. 6.28 ± 0.03
$[Cu(1,2\text{-deen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$	–1056	4.89	–	const. 6.29 ± 0.05
$[Cu(1,1\text{-deen})_2]_3[Cr(NCS)_6]_2\cdot H_2O$	–1056	4.99	–6	6.30/6.11
$[Cu(tn)_2]_3[Cr(NCS)_6]_2\cdot 2H_2O$	–855	5.06	–13	6.27/5.96

REFERENCES

1. Costes J-P. and Fernandez-Garcia M.I., *Inorg. Chim. Acta*, **173**, 247 (1990).
2. Chungplang V. and Wilson L.J., *J. Chem Soc*., *Chem. Commun*., 1760 (1985).
3. Davis W., Dewan J.C. and Lippard S.J., *Inorg. Chem*., **20**, 2928 (1981).
4. Zhong Z.J., Matsumoto N., Okawa H. and Kida S., *Inorg. Chem*., **30**, 436 (1991).
5. Ohba M. and Okawa H., *Coord. Chem. Rev*., **198**, 312 (2000).
6. Ferlay S., Francese G., Schmalle H.W. and Decurtins S., *Inorg. Chim. Acta*, **286**, 108 (1999).
7. Diaz C., Ribas J., Sanz N., Solans X. and Font-Bardia M., *Inorg. Chim. Acta*, **286**, 169 (1999).
8. Ribas J., Diaz C., Solans X. and Font-Bardia M., *Inorg. Chim. Acta*, **231**, 229 (1995).
9. Vicente R., Escuer A., Ribas J. and Solans X., *J. Chem. Soc*., *Dalton Trans*., 259 (1994).
10. Navarro J.A.R., Romero M.A., Salas J.M., Quiros M. and Tiekink E.R.T., *Inorg. Chem*., **36**, 4988 (1997).
11. Francese G., Ferlay S., Schmalle H.W. and Decurtins S., *New J. Chem*., 267 (1999).
12. Ribas J., Diaz C., Costa R., Tercero J., Solans X., Font-Bardia M. and Stoeckli-Evans H., *Inorg.Chem*., **37**, 233 (1998).
13. Kou H-Z., Liao D-Z., Cheng P., Jiang Z-H., Yan S-P., Wang G-L., Yao X-K. and Wang H-G., *Can. J. Chem*., **76**, 1102 (1998).
14. Smékal Z., Březina F., Šindelář Z. and Klička R., *Trans. Met. Chem*., **22**, 299 (1997).
15. Dobrzańska L., Wrzeszcz G., Grodzicki A. and Rozpłoch F., *Polish J. Chem*., **74**, 199 (2000).
16. Dobrzańska L., Wrzeszcz G., Grodzicki A. and Rozpłoch F., *Polish J. Chem*., **74**, 1017 (2000).
17. Dobrzańska L., Wrzeszcz G., Grodzicki A. and Rozpłoch F., *Polish J. Chem*., **75**, 909 (2001).
18. Schlessinger G.G., *Inorganic Laboratory Preparations*, Chemical Publishing Company, NY, 1962, p.89.
19. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, J. Wiley & Sons, NY, 1997, pp. 116–121, 269.
20. Forster D. and Goodgame D.M.L., *Inorg. Chem*., **4**, 715 (1965).
21. Lever A.B.P. and Mantovani E., *Inorg. Chim. Acta*, **5**, 429 (1971).
22. Lever A.B.P. and Mantovani E., *Inorg. Chem*., **10**, 817 (1971).
23. Procter I.M., Hathaway B.J. and Nicholls P., *J. Chem. Soc. (A)*, 1678 (1968).
24. Hathaway B.J. and Billing D.E., *Coord. Chem. Rev*., **5**, 143 (1970).
25. Kahn O., *Struct. Bond*., **68**, 89 (1987).
26. O'Connor C.J., *Progr. Inorg. Chem*., **29**, 203 (1982).
27. Fu D.G., Chen J., Tan X.S., Jiang L.J., Zhang S.W., Zheng P.J. and Tang W.X., *Inorg. Chem*., **36**, 220 (1997).