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FULL PAPER

Magnetostructural characterisation of the first bimetallic assemblies derived from the anionic building block $[Cr(NCS)_6]^{3-}$ $[M(en)_3]_n$-$[\{M(en)_2\text{-}\mu\text{-}SCN\text{-}Cr(NCS)_4\text{-}\mu\text{-}NCS\}_{2n}]$ with M = Ni(II), Zn(II)†

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Two bimetallic complexes $[M(en)_3]_n[\{M(en)_2Cr(NCS)_6\}_{2n}]$ (M = Ni **1**, Zn **2**; en = ethylenediamine) have been prepared and structurally and magnetically characterised. They present a unique structure consisting of two distinct units: the catena-μ-NCS-$M(en)_2$-μ-SCN-$Cr(NCS)_4$ 1-D polymeric anion and the monomeric cations $[M(en)_3]^{2+}$. Complex **1** crystallized in the monoclinic system, space group $C2/c$, with $a = 28.330(3)$, $b = 14.256(1)$, $c = 16.013(1)$ Å, $\beta = 117.26(1)°$, $V = 5748.9(8)$ Å^3 and $Z = 4$. The crystal structure of **1** has been refined to $R1 = 0.0808$. The bridging NCS ligands occupy the rare *cis* positions in the Ni^{2+} coordination sphere and are coordinated to nickel *via* their sulfur atoms. The coordination sphere of Cr^{3+} is formed by six nitrogen atoms of the NCS ligands. The Ni–N distances vary from 2.052(5) to 2.131(5) Å, the Ni–S distances are 2.584(2) and 2.632(2) Å, whereas the Cr–N distances vary from 1.971(6) to 2.003(6) Å. A variable temperature magnetic susceptibility study of **1** has been performed over the temperature range of 4–300 K. The compound shows antiferromagnetic coupling ($J \approx -20$ cm^{-1}). This moderate antiferromagnetic interaction could be explained by the structural features related to $\mu_{\text{-N,S}}$-NCS bridged units being in *cis* positions at both metallic centres. The isostructural complex **2** exhibits magnetic behaviour that agrees well with that expected for isolated $[Cr(NCS)_6]^{3-}$ units with small inter- and/or intra-chain antiferromagnetic interactions.

Introduction

Recently, the magneto-structural correlation of heteropolynuclear complexes has been extensively studied in response to an increased demand for new optical, electrical and magnetic materials.[1] The most popular strategy in the synthesis of this type of system is based on the usage of the 'donative metal complex' with the donor groups acting as ligands towards other metal ions or coordinatively unsaturated complexes. Hexacyanometalates, $[M(CN)_6]^{n-}$, are commonly used to obtain modified Prussian blue compounds that are potential candidates for molecule-based magnets.[2] Other 'ligand complexes' are derived from oxamato,[3] oxalato[4] and oxamido.[5] The present work is focussed on the $[Cr(NCS)_6]^{3-}$ anionic block which can form bridges with different metal ions *via* the sulfur atoms. The crystallographic data of systems with this unit are very limited; the only systems investigated so far are two lanthanide complexes containing different cationic species and hexaisothiocyanatochromate(III) anions in the structure, *i.e.* $[\{Ho(L)_3(H_2O)_2\}_n][Cr(NCS)_6]_n\cdot 2nH_2O$ (L = $C_5H_4NCO_2H$, nicotinic acid),[6a] $[Ln(DMSO)_8][Cr(NCS)_6]$[6b] and a few radical cation salts with the $[Cr(NCS)_6]^{3-}$ anion.[6c]

To construct new heteronuclear systems we used the cationic constituent $[M(en)_n]^{2+}$, M = Ni **1**, Zn **2**. The number of papers on the structures of compounds with S-bonded thiocyanato ions of metals given above is relatively small. Reported cases involve only Ni(II) complexes, amongst them one is the heteropolynuclear 2-D network $[\{Cu(en)_2(Ni(en)(SCN)_3)_2\}_n]$,[7a] a few are homonuclear complexes such as the monomeric Ni(II) complex with terminal S-coordination of the thiocyanato group,[7b] two are dimeric[7c,d] and four are 1-D polymeric structures with end-to-end μ-NCS.[7e–h] Magnetic measurements of these one-dimensional systems indicated very weak ferromagnetic interactions through the NCS^- bridge. It is important to note that reported studies on heteropolynuclear thiocyanato bridge complexes are very rare.[7a,8] There are only a few papers which contain magneto-structural characterisation. Those systems studied so far include $[\{Cu(cyclam)Co(NCS)_4\}_n]$,[8a] $[\{CuLCo(NCS)_4\}_n]$ (L = *N-meso*-(5,12-Me_2-7,14-Et_2-[14]-4,11-diene-N_4)),[8b] $[\{Cu(en)_2Mn(NCS)_4(H_2O)_2\}_n]$[8c] and $[\{Co(dpa)(DMF)(\mu\text{-}SCN)_3Ag\}]_n$ [dpa = bis(2-pyridyl)amine][8d] which form one-dimensional polymeric chains. Two of them are binuclear structures[8b,e] and others[8f] are tetranuclear $(Cu–Ni)_2$ complexes. The first two 1-D complexes with macrocyclic tetraaza ligands exhibited weak magnetic interactions of different natures (antiferro- or ferro-magnetic) between Cu(II) and Co(II) through the bridging NCS^- with $J = -1.48$ and $J = 3.07$ cm^{-1}, respectively. The difference in magnetic behaviour was elucidated as the result of substitutions in the macroligand. Other polymeric heterocomplexes indicate the weak antiferromagnetic interactions between metal centres. In the case of the Cu(II)–Mn(II) system, the best fit of the J parameter ($J = -0.062$ cm^{-1}) was found for the model based on Mn(II) ··· Mn(II) coupling and a dominant zero field splitting of the Mn(II) ions. A preliminary study of the magnetic properties of reported 2-D Cu(II)–Ni(II) systems suggests ferromagnetic ordering.[7a]

In this paper we report the synthesis of two isostructural systems $[M(en)_3]_n[\{M(en)_2Cr(NCS)_6\}_{2n}]$ (M = Ni **1** or Zn **2**) giving special attention to magnetostructural studies. To the best of our knowledge this is the first report on heteropolynuclear complexes with $[Cr(NCS)_6]^{3-}$ as a building block, which is supported by the X-ray analysis.

Experimental

Measurements

Elemental analyses (C, H, N) were carried out with a Perkin-Elmer Analyzer Model 240. Nickel and zinc contents were determined using the AAS method. Chromium contents were

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† Non-SI units employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

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determined spectrophotometrically as CrO_4^{2-} at $\lambda = 372$ nm. IR spectra were recorded on a Perkin-Elmer FT–IR 2000 spectrophotometer in the 4000–400 cm^{-1} region using KBr discs and from 700 to 30 cm^{-1} using the polyethylene plates techniques. Electronic spectra (diffuse reflectance technique) were measured on a SPECORD M-40 (Carl Zeiss, Jena) spectrophotometer. The magnetic susceptibility measurements of complex **1** were performed in Copenhagen (Chemistry Laboratory I, H. C. Ørsted Institute) by the Faraday method in the temperature range 4–300 K at a field strength of 1.35 T. A detailed description of the instrumentation has been published elsewhere.[9] The magnetic susceptibility of complex **2** was measured between 80–300 K by the Faraday method on a balance constructed in our laboratory (Toruń, Faculty of Chemistry, Nicholas Copernicus University) at a field strength of 1.0 T. In both cases the magnetic field was calibrated with $Hg[Co(NCS)_4]$.[10] The molar susceptibilities were corrected for diamagnetism using Pascal's constants[11] (-801×10^{-6} for **1** and -798×10^{-6} cm^3 mol^{-1} for **2**). The effective magnetic moment was calculated from the equation: $\mu_{eff} = 2.828(\chi_M^{corr}T)^{1/2}$. Room temperature EPR spectra of the powder samples were recorded with an ESR Bruker Physik 418 S reflection type spectrometer in the X-band (*ca.* 9.5 GHz) with a 100 kHz modulation of the steady magnetic field. The microwave frequency was monitored with a 18 GHz microwave counter 2440 (Marconi Instruments). The magnetic field was measured with an automatic MJ-110R NMR-type magnetometer (Radiopan). X-Ray diffraction patterns of powdered samples were recorded on a HZ64/A-2 DRON-1 diffractometer using Cu-K_λ radiation, $\lambda = 0.1542$ nm.

Preparations

$K_3[Cr(NCS)_6]\cdot 4H_2O$ was prepared by the literature method.[12] Other reagents used in the syntheses were of analytical grade and were used without further purification.

$[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ 1. To an aqueous solution (20 ml) of $Ni(en)_2Cl_2$ prepared *in situ* by mixing $NiCl_2\cdot 6H_2O$ (0.5 mmol, 118.8 mg) and en (1 mmol, 60.1 mg), was added a 20 ml aqueous solution of $K_3[Cr(NCS)_6]\cdot 4H_2O$ (0.33 mmol, 194.7 mg) at room temperature. A violet precipitate was formed immediately and the whole mixture was left in a refrigerator where dark red microcrystals slowly formed. After 3 months crystals suitable for X-ray structural analysis were obtained, washed with water and air-dried. Yield: 81%. Anal. calc. for $C_{26}H_{56}N_{26}S_{12}Cr_2Ni_3$ **1**: C, 22.34; H, 4.04; N, 26.05; Ni, 12,60; Cr, 7.44. Found: C, 22.05; H, 4.38; N, 25.15; Ni, 12.94; Cr, 7.28%. IR (cm^{-1}): ν(CN) 2137, 2090vs, 2075sh, 2055sh; ν(CS) 653m; δ(NCS) 486s; ν(MN) 363vs, br; ν(CH) 2946m, 2886m; δ(NH_2) 1577s; ν(NH) 3322s, 3286s, 3246s; δ(CH_2) 1457m; δ(NMN) 216m. λ_{max} (cm^{-1}, reflectance): 12440, 12760, 17800, 24000sh, 29000br, 41000, 46000.

$[Zn(en)_3]_n[\{Zn(en)_2Cr(NCS)_6\}_{2n}]$ 2. To an aqueous solution (15 ml) of $[Zn(en)_3]SO_4$, prepared *in situ* by mixing hot solution $ZnSO_4\cdot 7H_2O$ (0.5 mmol, 143.8 mg) and en (1.5 mmol, 90.2 mg), was added 25 ml of an aqueous solution of $K_3[Cr(NCS)_6]\cdot 4H_2O$ (0.33 mmol, 194.7 mg) at room temperature. A violet precipitate formed immediately and slowly changed to red microcrystals which were collected by filtration, washed with water and left to air-dry. Yield: 79%. No monocrystals suitable for X-ray analysis were obtained. Anal. calc. for $C_{26}H_{56}N_{26}S_{12}Cr_2Zn_3$ **2**: C, 22.03; H, 3.98; N, 25.68; Zn, 13.84; Cr, 7.33. Found: C, 22.32; H, 4.51; N, 25.65; Zn, 13.88; Cr, 7.04%. IR (cm^{-1}): ν(CN) 2130sh, 2080vs, 2060sh; ν(CS) 656m; δ(NCS) 485s; ν(MN) 355vs, br; ν(CH) 2951m, 2887m; δ(NH_2) 1576s; ν(NH) 3322s, 3264s; δ(CH_2) 1457m; δ(NMN) 222m. λ_{max} (cm^{-1}, reflectance): 17800, 23500, 29500br, 42000, 46000.

Table 1 Crystallographic data for $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ **1**

Chemical formula	$C_{26}H_{56}N_{26}S_{12}Cr_2Ni_3$
Formula weight	1397.82
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	28.330(3)
b/Å	14.256(1)
c/Å	16.013(1)
β/°	117.26(1)
V/Å^3	5748.9(8)
Z	4
D_{calc}/g cm^{-3}	1.615
T/K	293(2)
μ(Mo-Kα)/mm^{-1}	1.816
Reflections collected	25691
Independent reflections	8790
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0808, 0.1721

Table 2 X-Ray powder diffraction data for **1** and **2**

1		2	
d/Å	I/I_0 (%)	d/Å	I/I_0 (%)
10.572	34	10.593	30
7.211	55	7.312	49
6.508	52	6.736	38
6.378	70	6.534	41
6.264	47	6.341	57
5.603	41	5.503	34
5.314	37	5.256	34
4.966	54	5.034	39
4.250	100	4.190	100
4.127	48	4.113	40
3.917	81	3.905	74
3.794	76	3.842	64
3.765	75	3.783	63
3.197	50	3.179	45
2.992	48	2.978	51
2.616	50	2.632	49
2.552	49	2.547	42

X-Ray crystallography

A dark red prismatic crystal (0.26 × 0.16 × 0.15 mm) of $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ **1** was used in the diffraction experiment. The X-ray data were collected at 293(2) K by the ω–2θ method with a Kuma KM4CCD Sapphire diffractometer using Mo-Kα radiation, $\lambda = 0.71073$ Å. A total number of 52260 observations were collected, of which 8790 were unique, $R_{int} = 0.099$. The structure was solved by direct methods and refined with full-matrix least-squares against F^2 using SHELX97[13] to $R1 = 0.0808$, $wR2 = 0.172$ and $S(F^2) = 1.037$ [$I > 2\sigma(I)$]. No extinction correction was applied. The shape-based absorption correction was calculated using Kuma software (CrysAlis CCD and CrysAlis RED version 1.1.67 (2000) by Kuma Diffraction Instruments, Wrocław, Poland), the maximum and minimum transmission being 0.83443 and 0.72989. The riding model for the hydrogen atoms was applied during the refinement. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[14] The geometry of the reported compound was compared to other complexes using the Cambridge Structural Database.[15] Crystal data are summarised in Table 1.

CCDC reference number 178388.

See http://www.rsc.org/suppdata/dt/b2/b200979j/ for crystallographic data in CIF or other electronic format.

Results and discussion

General and spectroscopic properties

X-Ray diffraction patterns of **1** and **2** (Table 2), as well as almost identical IR spectra indicate that these complexes have the same 1-D network structures.

Both IR spectra exhibit intense absorption at about 2090 cm^{-1}, which is characteristic for the presence of thiocyanato ligands and attributed to ν(CN). The components of this band such as a split at 2137 cm^{-1} **1**, shoulder at 2130 cm^{-1} **2** and clear shoulders at lower frequencies, indicate the differences in the interaction of NCS^- ions with the adjacent molecules in the crystal lattice. The vibrations occurring above 2100 cm^{-1} are characteristic for NCS bridge formation, whereas the lower frequency bands indicate the terminal N-bonded NCS^-.[16] The band appearing at *ca.* 650 cm^{-1}, assigned to ν(CS), also proves the presence of thiocyanato bridges. The reflectance spectrum of **1** is highly complicated. It shows, respectively, sharp bands at 12440 and 12760 cm^{-1}, intense absorption at 17800, a shoulder at 24000, a broad band at 29000 and a band at 41000 cm^{-1}. This is a result of the superposition of the spectra of $[Cr(NCS)_6]^{3-}$ (with bands at 18040, 23500, 31000br, 42640 in $K_3[Cr(NCS)_6]\cdot 4H_2O$), the octahedral NiN_6 chromophore and the *cis*-distorted octahedral NiN_4S_2 chromophore.[17] The reflectance spectrum of **2** is much simpler due to the presence of Zn^{2+} in place of Ni^{2+}, and is similar to that of the parent chromium(III) complex. It shows bands at 17800, 23500, 29500 and 42000 cm^{-1}. The clear red shift of the band corresponding to the $^4A_{2g} \longrightarrow {}^4T_{2g}$ chromium(III) transition indicates deviation from the starting symmetry of $[Cr(NCS)_6]^{3-}$ and is evidence for the formation of a bimetallic network. Additionally, the spectra of **1** and **2** show a band at *ca.* 46000 cm^{-1} due to the presence of the ethylenediamine ligands. The compounds are stable in air and insoluble in most organic and inorganic solvents.

The EPR spectra measured at room temperature on polycrystalline samples of **1** and **2** show extremely different behaviour. $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ **1** does not show any EPR signals, which could be due either to relaxation, or alternatively, zero field splitting effects (*vide infra*). $[Zn(en)_3]_n[\{Zn(en)_2Cr(NCS)_6\}_{2n}]$ **2** shows a quasi-isotropic and very broad feature with $g \approx 2.0$ and a peak-to-peak width (ΔB_{pp}) equal *ca.* 28 mT. Such a broad line is characteristic of a system with a high concentration of paramagnetic centres. On the other hand, the zero field splitting parameter should be very small or equal to zero for a nearly octahedral $[Cr(NCS)_6]^{3-}$ unit in a bimetallic chain. Thus, the EPR line observed is due to the spin transitions $|3/2,-3/2> \longrightarrow |3/2,-1/2>$, $|3/2,-1/2> \longrightarrow |3/2,1/2>$ and $|3/2,1/2> \longrightarrow |3/2,3/2>$ of the spin ground state $S = 3/2$.

Crystal structure

The crystal data and refinement details for **1** are summarised in Table 1 and selected bond lengths and angles are shown in Table 3.

The perspective view of the asymmetric unit of the structure, which corresponds to half of the chemical unit, with its numbering scheme, is shown in Fig. 1.

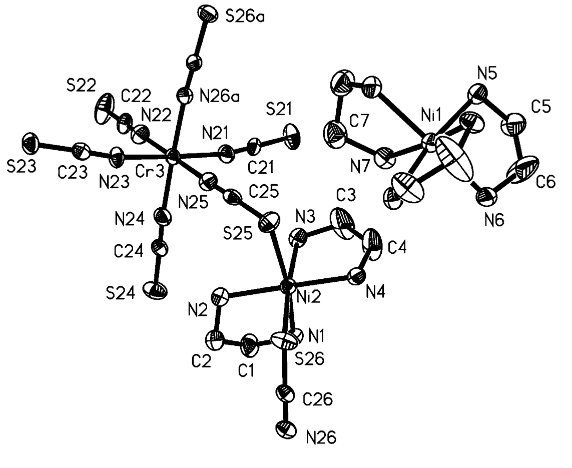

Fig. 1 Perspective drawing of the asymmetric unit of complex **1** with the atom numbering scheme. For clarity the thermal ellipsoids are displayed at 30% probability and hydrogen atoms are omitted.

Table 3 Selected bond lengths (Å) and angles (°) for $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ **1**

Ni(2)–N(4)	2.052(5)	Cr(3)–N(23)	1.980(5)
Ni(2)–N(2)	2.076(5)	Cr(3)–N(25)	1.996(6)
Ni(2)–N(1)	2.103(5)	Cr(3)–N(26)#2	1.997(6)
Ni(2)–N(3)	2.112(5)	Cr(3)–N(24)	2.003(6)
Ni(2)–S(26)	2.584(2)	Ni(1)–N(5)	2.119(5)
Ni(2)–S(25)	2.632(2)	Ni(1)–N(7)	2.123(5)
Cr(3)–N(22)	1.971(6)	Ni(1)–N(6)	2.131(5)
Cr(3)–N(21)	1.978(5)		
C(25)–S(25)–Ni(2)	93.2(2)	N(2)–Ni(2)–N(3)	98.3(2)
C(26)–S(26)–Ni(2)	105.1(2)	N(1)–Ni(2)–N(3)	92.3(2)
C(22)–N(22)–Cr(3)	173.1(5)	N(4)–Ni(2)–S(26)	89.83(15)
C(23)–N(23)–Cr(3)	170.0(6)	N(2)–Ni(2)–S(26)	88.79(17)
S(26)–Ni(2)–S(25)	81.79(6)	N(1)–Ni(2)–S(26)	95.36(16)
N(21)–C(21)–S(21)	179.4(6)	N(3)–Ni(2)–S(26)	170.25(16)
N(22)–C(22)–S(22)	179.0(7)	N(4)–Ni(2)–S(25)	89.26(16)
N(23)–C(23)–S(23)	178.9(6)	N(2)–Ni(2)–S(25)	90.23(17)
N(24)–C(24)–S(24)	179.1(6)	N(1)–Ni(2)–S(25)	172.12(16)
N(25)–C(25)–S(25)	177.4(5)	N(3)–Ni(2)–S(25)	91.42(16)
N(26)–C(26)–S(26)	179.8(6)	N(5)#1–Ni(1)–N(7)#1	91.9(2)
N(4)–Ni(2)–N(2)	178.6(2)	N(5)–Ni(1)–N(6)	81.8(2)
N(4)–Ni(2)–N(1)	98.1(2)	N(7)–Ni(1)–N(6)	92.6(2)
N(2)–Ni(2)–N(1)	82.3(2)	N(5)#1–Ni(1)–N(5)	170.8(3)
N(4)–Ni(2)–N(3)	83.1(2)	N(5)–Ni(1)–N(7)#1	95.1(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$; #2 $x, -y, z - 1/2$.

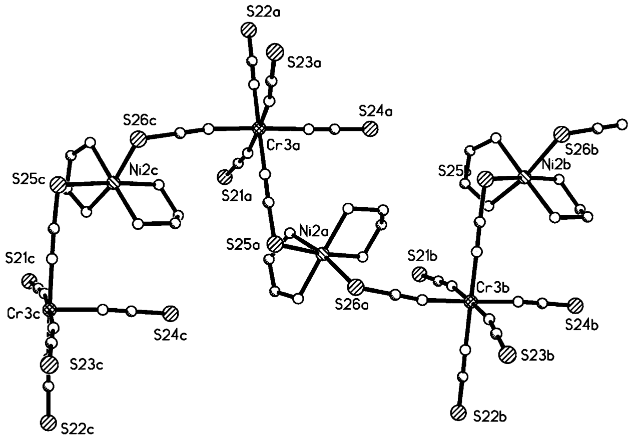

Fig. 2 View of the 1-D anionic chain for complex **1**.

The structure consists of the $[Ni(1)(en)_3]^{2+}$ cations and the polymeric anions formed by $[(SCN)Cr(3)(NCS)_5Ni(2)(en)_2]$ chemical units. The two thiocyanate ions N(25)–C(25)–S(25) and N(26)–C(26)–S(26) form the bridges between the alternating Ni(2) and Cr(3) ions along the anionic chain (Fig. 2). This type of binuclear Ni(II)–Cr(III) compound has not been characterised by X-ray methods before. The bridging NCS ligands are positioned along the axis of the Cr–N bond, but the Ni–S–C angle of 90° is found for both isothiocyanate links, Ni(2)–S(25)–C(25) and Ni(2)–S(26)–C(26) being 93.2(2) and 105.1(2)°, respectively. Consequently, the anionic chains formed by the alternating $[Cr(NCS)_6][Ni(en)_2]$ motif are not linear.

The bridging interactions formed by the NCS ligands in the polymeric component of the crystal lattice are similar to those reported in the homonuclear complexes Ni[bis(3-aminopropyl)-methylamine](SCN)(μ-SCN)[7g] or $[Ni(Medien)(NCS)_2]$.[7f] In complex **1** only the unbranched chains are formed. These chains are not linear because of the *cis* position of the bridging thiocyanates in the coordination sphere of both Ni(2) and Cr(3). Such a geometry of the anionic chain is different from that reported for the Cu(II)–Mn(II) bimetallic compound,[8c] where the bridging thiocyanates are positioned axially in the coordination sphere of the Mn(II) central ion.

The $[Ni(1)(en)_3]^{2+}$ cation is positioned on the crystallographic two-fold axis. Because of the special position of the central ion, the N(5)–C(5)–C(6)–N(6) ligand has its two-fold related

Table 4 Details of the H-bonds found in **1**

D–H	d(D–H)/Å	d(H $\cdots$ A)/Å	∠DHA/°	d(D $\cdots$ A)/Å	A	[Symmetry]
N1–H1B	0.900	3.010	125.67	3.610	S21	$[-x + 1/2, y + 1/2, -z + 3/2]$
N2–H2B	0.900	2.684	166.19	3.565	N24	
N3–H3A	0.900	2.725	165.49	3.603	S22	$[-x + 1/2, y + 1/2, -z + 3/2]$
N4–H4A	0.900	2.867	149.94	3.673	S23	$[-x, -y, -z + 1]$
N4–H4B	0.900	2.602	168.70	3.489	S21	$[-x + 1/2, y + 1/2, -z + 3/2]$
N5–H5A	0.900	2.597	159.58	3.455	N24	$[x, -y, z - 1/2]$
N5–H5B	0.900	2.846	142.35	3.601	S23	$[-x, y + 1, -z + 1/2]$
N6–H6B	0.900	2.876	151.90	3.695	S23	$[-x, -y, -z + 1]$
N7–H7A	0.900	2.776	168.69	3.663	S24	$[x, -y, z - 1/2]$
N7–H7B	0.900	2.526	166.76	3.408	S23	$[-x, -y, -z + 1]$

equivalent coordinated to the same central ion, while the ligand formed by the N(7) and C(7) atoms is built up with two symmetry related halves. The Ni(1)–N distances vary from 2.119(5) to 2.131(5) Å and the N–Ni(1)–N angles are between 80.9(3) and 95.1(2)° and 170.8(3) and 172.8(2)°. Each of the five-membered chelate rings formed by the en ligands reveal the half-chair conformation. The corresponding asymmetry parameters[18] are $\Delta C_2^{C5,C6} = 4.7^0$ and $\Delta C_2^{C7,C7\#} = 0^0$ with the symmetry axes running through the Ni(II) ion and intersecting C(5)–C(6) and C(7)–C(7) $[-x, y, -z + 1/2]$ bonds, respectively. The zero value observed for the latter corresponds to the crystallographic two-fold axis relating two halves of this ligand. The en ligands reveal significant conformational disorder manifested in the values of anisotropic displacement parameters larger that those of other atoms.

The coordination sphere of the $Ni(2)^{2+}$ cation consists of two ethylenediamine bidentate ligands and two NCS ligands coordinated *via* their sulfur atoms. The asymmetry parameters calculated for the chelate rings reveal their half-chair conformation, with the two-fold axes running through the Ni(II) ion and intersecting the C(1)–C(2) and C(3)–C(4) bonds. The corresponding $\Delta C_2^{C1,C2} = 8.5°$ and $\Delta C_2^{C3,C4} = 0.7°$, for N(1)–C(1)–C(2)–N(2) and N(3)–C(3)–C(4)–N(4) ligands, respectively. The coordination sphere is an octahedron with two isothiocyanates in *cis* positions. Such a position of the bridging isothiocyanato ligands is unique among similar binuclear systems. The deformation of the octahedral environment of Ni(2) corresponds to the local C_2 symmetry with the non-crystallographic two-fold axis bisecting the S–Ni–S angle. The Ni(2)–N and Ni(2)–S distances vary from 2.052(5) to 2.112(5) Å and from 2.584(2) to 2.632(2) Å, respectively. The S(26)–Ni(2)–S(25) angle is 81.8(1)°, while the other angles within the coordination sphere are between 82.3(2) and 98.3(2)° and 170.3(2) and 178.6(2)°.

The six NCS ligands are coordinated to the $Cr(3)^{3+}$ ion *via* their N atoms and form an almost ideal octahedral environment. The Cr(3)–N distances are between 1.971(6) and 2.003(6) Å, while the N–Cr–N angles vary from 88.3(2) to 92.5(2)° and from 178.0(2) to 179.0(2)°, respectively. The bridging NCS(25) and NCS(26) isothiocyanates occupy *cis* positions in the coordination sphere. The N(25)–Cr(3)–N(26) angle of 88.3(2)° between these ligands is the smallest in the coordination sphere of Cr(III) due to isothiocyanato interactions with the adjacent Ni(2) ions in the anionic chain.

The vast network of hydrogen bonds is responsible for the interactions between the polymeric anion and the complex cations. In particular the $[Ni(en)_3]^{2+}$ cation is positioned in the kink of the polymeric chain between two adjacent $[Cr(NCS)_6]$ groups. Most of the NCS sulfur atoms not coordinated to Ni(II) participate in the network of hydrogen bonds between adjacent polymeric anionic chains or between the anionic chain and the $[Ni(en)_3]^{2+}$ cations. Details of the H-bonds are presented in Table 4.

Magnetic properties

The magnetic behaviour of **1** is presented in Fig. 3a, in a $\chi_M T$ *vs.* T plot, χ_M being the corrected molar magnetic susceptibility per Ni_3Cr_2 unit.

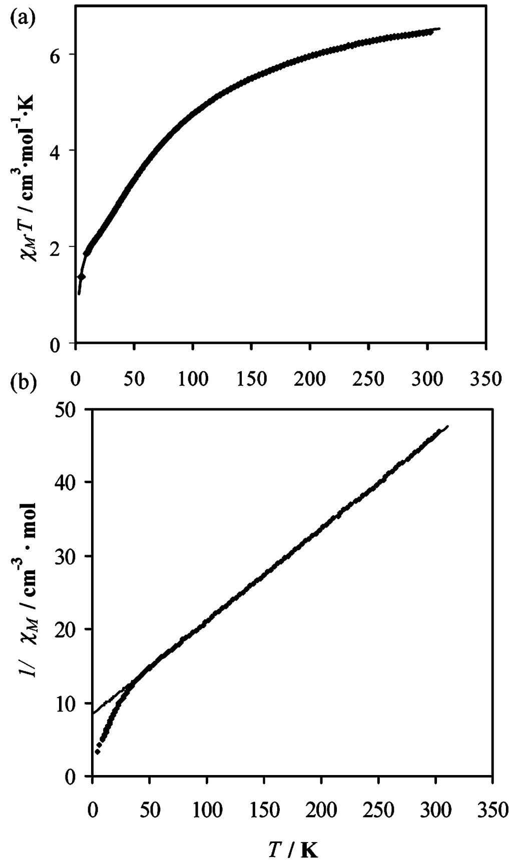

Fig. 3 Temperature dependence of $\chi_M T$ (a) and $1/\chi_M$ (b) for complex **1**. The solid line represents the fit discussed in the text (a) and the theoretical Curie–Weiss plot (b).

At room temperature, the $\chi_M T$ value is 6.45 cm^3 K mol^{-1} (7.18 μ_B), below that expected for uncoupled S = 1, 1, 1, 3/2 and 3/2 spins (6.75 cm^3 K mol^{-1} for $g_{Ni} = g_{Cr} = 2$). It is likely that we have an antiferromagnetic coupling occurring already at room temperature and therefore $\chi_M T$ is lower than the calculated value. When the temperature is lowered, $\chi_M T$ continuously decreases, slowly at first and then more rapidly after *ca.* 100 K to 1.37 cm^3 K mol^{-1} (3.31 μ_B) at 4.4 K. The temperature dependencies of magnetic susceptibilities above 40 K obey the Curie–Weiss law, *i.e.* $\chi_M^{corr} = C/(T - \theta)$. The $1/\chi_M$ *vs.* T plot (Fig. 3b) gives Curie and Weiss constants, C and θ, of 7.91 cm^3 K mol^{-1} and −66.6 K, respectively. These results are indicative of the occurrence of moderate antiferromagnetic coupling between metallic centres, probably together with an antiferromagnetic coupling between the chains and/or cations and chains. Because of the non-compensation of spins of nickel(II) (S = 1) and chromium(III) (S = 3/2) and from a physical point of view, the compound is expected to behave as a ferrimagnetic chain at low temperature. In this case the minimum of $\chi_M T$ is expected at a definite temperature. Below the critical temperature $\chi_M T$ should diverge but if the interchain interactions couple the chains in an antiparallel fashion, as is most often the case, then the divergence of $\chi_M T$ is stopped with a maximum of $\chi_M T$ occurring just above the critical temperature. If this interchain interaction is large, the minimum in $\chi_M T$ can be hidden.[19] Additionally, complex **1** is more complicated because of isolated cationic moieties, which should follow Curie behaviour with $S = 1$. Therefore, the magnetic susceptibility is given by eqn. (1):

$$\chi_M = \chi_{cation} + \chi_{chain} \qquad (1)$$

with

$$\chi_{cation} = \frac{Ng^2_{cat.}\mu_B^2}{3kT}S(S+1)$$

Several quantitative approaches to the magnetic susceptibility of ordered bimetallic chains have been presented.[19] The $(AB)_N$ ring chain technique with quantum (or quantum-classical) spins S_A and S_B does not apply because the problem becomes intractable very rapidly.[20] In spite of this preliminary calculations have been performed for $N = 2$. The nearest neighbours coupling constant, J, lies within the range −19 to −23 cm^{-1} and its value depends on several factors such as the range of considered temperatures, the molecular field, TIP and fixed parameters.

To extend the explanation of the magnetic behaviour of **1** we used a classical spin approach. An analytical expression for such a system has been derived by Drillon *et al.*:[21]

$$\chi_{chain} = \frac{4N\mu_B^2}{3kT}\left[g^2\frac{1+u}{1-u}+\delta^2\frac{1-u}{1+u}\right] \qquad (2)$$

where $g = (g^e_{Ni} + g^e_{Cr})/2$, $\delta = (g^e_{Ni} - g^e_{Cr})/2$ and $u = \coth(J^e/kT) - (kT/J^e)$.

The effective parameters are related to the actual parameters through: $g^e_{Ni} = g_{Ni}[S_{Ni}(S_{Ni} + 1)]^{1/2}$, $g^e_{Cr} = g_{Cr}[S_{Cr}(S_{Cr} + 1)]^{1/2}$ and $J^e = J_{NiCr}[S_{Ni}(S_{Ni} + 1)S_{Cr}(S_{Cr} + 1)]^{1/2}$.

Taking into consideration the possibility of chain-to-chain and chain to cation interactions occurring in the crystal lattice, a correction for the molecular field was taken into account:

$$\chi'_M = \frac{\chi_M}{1-[\chi_M(2zJ'/Ng^2\mu_B^2)]} \qquad (3)$$

Least-squares fitting of experimental magnetic data to eqn. (3) gives the values: $J = -19.9$ cm^{-1}, $g_{cat.} = 2.361$, $g_{Ni} = 2.166$, $g_{Cr} = 2.095$, $zJ' = -1.63$ cm^{-1} and $R = 1.42 \times 10^{-5}$ where R is the factor defined as $R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\Sigma(\chi_M T)_{obs}{}^2$. In this fitting, the contribution of the zero field splitting of nickel(II) was ignored. This assumption is probably true for octahedral $[Ni(en)_3]^{2+}$ but for *cis*-distorted $[Ni(en)_2(SCN)_2]$ units in chain it is certainly not. At low temperatures there are also others effects which have an effect on magnetic properties, *e.g.* the quantum nature of the spins and saturation effects.[21] In spite of that, as shown in Fig. 3a, the fit may be considered good. The zJ' value is probably overestimated due to the above mentioned factors. However, taking into account experimental susceptibilities only above 17 K by using eqn. (1), *i.e.* without molecular field and with fixed $g_{Cr} = 2.0$ (a more resonable value), a best fit was obtained with parameters: $J = -23.4$ cm^{-1}, $g_{cat.} = 2.148$, $g_{Ni} = 2.335$ and $R = 9.05 \times 10^{-6}$. Both fits give similar results, but extrapolation of the latter shows a minimum at *ca.* 14 K and divergence below this temperature on the $\chi_M T$ curve. It is clear that interchain interactions can also play a part. To explain this we synthesized analogous complex **2** with diamagnetic Zn^{2+} instead of paramagnetic Ni^{2+}. Complex **2** follows Curie–Weiss behaviour from room temperature down to liquid nitrogen temperature, corresponding to $C = 1.78$ cm^3 K mol^{-1} and $\theta = -1.9$ K. The product $\chi_M T$ decreases very smoothly when the complex cools down, 1.78 cm^3 K mol^{-1} (3.78 μ_B) and 1.74 cm^3 K mol^{-1} (3.73 μ_B) per mole of Cr at room and liquid nitrogen temperature, respectively. The $\chi_M T$ value is close to that expected for $S = 3/2$ (1.88 cm^3 K mol^{-1} for $g_{Cr} = 2$). However, the negative value for θ and the small decrease in $\chi_M T$ at liquid nitrogen temperature for complex **2** may be caused by weak antiferromagnetic interactions between chromium(III) ions.[22] This result supports the existence of inter- and intrachain antiferromagnetic interactions in $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ **1**.

The magnetic properties will mainly depend upon the nature of the magnetic orbitals of the metal ions interacting with each other and the bridge angle.[19] The angles formed by the thiocyanato ligand and the Cr and Ni atoms, which determine the magnetic properties of **1**, are Cr–N–C = 170.0 and 173.1°, Ni–S–C = 93.2 and 105.1°, S–Ni–S = 81.79°, and N–Cr–N = 88.3°. The Cr ··· Ni, Cr ··· Cr and Ni ··· Ni distances within the chain are equal to 5.442 and 5.984 Å, 10.526 and 8.511 Å, respectively. Although, the local symmetry of the chromium site is close to O_h and that of the nickel is C_2, the whole symmetry of the Cr ··· Ni binuclear bridging units is very low close to C_s. The three unpaired electrons around Cr(III) in an octahedral surrounding occupy the t_{2g}-type magnetic orbitals transforming as a′ (xy) and a″ (xz and yz). In the Ni(II) ion with two unpaired electrons, magnetic orbitals transform as a′ ($x^2 - y^2$ and z^2). Both of these may overlap with one of the three chromium magnetic orbitals. This provides an antiferromagnetic contribution that is dominant.[19] The SCN bridge has for its highest filled molecular orbitals two σ and four π orbitals.[23] Assuming an idealized geometry with linear thiocyanato bridges, Cr–N–C–S (x-axis), and a 90° C–S–Ni angle (y-axis), the pathways for antiferromagnetic coupling are $a'_{Cr}\|\pi_y\|a'_{Ni}$ and $a'_{Cr}\|\pi_z\|a'_{Ni}$, where the notation $\|$ symbolizes overlapping.

The Cr ··· Ni, Cr ··· Cr and Ni ··· Ni distances between the chains are equal to 6.696, 8.646 and 8.170 Å, respectively. The closest distances between $Ni_{cat.} \cdots Ni_{cat.}$, $Ni_{cat.} \cdots Ni_{chain}$ and $Ni_{cat.} \cdots Cr_{chain}$ are equal to 8.359, 8.006 and 5.984 Å, respectively. The hydrogen bonds (see above) are responsible for the interactions between the anionic chains and chains and $[Ni(en)_3]^{2+}$ cations.

It is interesting to compare the relationship between the structures and magnetic properties for known 1-D thiocyanato bridged heterobimetallic complexes. These are listed in Table 5. Because no information has been found concerning other μ-$_{N,S}$-NCS bridged Cr–Ni systems only a tentative correlation is given. The $[\{Co(dpa)(DMF)(\mu\text{-}SCN)_3Ag\}]_n$[8d] complex strongly deviates from the others which is due to different structure which consist three different thiocyanato bridges between diamagnetic Ag(I) and paramagnetic Co(II). Both $[\{Cu(cyclam)Co(NCS)_4\}_n]$[8a] and $[\{CuLCo(NCS)_4\}_n]$[8b] complexes have nearly linear S–Cu–S motifs but different Cu–S–C angles and packing in the crystal lattice, which give small antiferromagnetic and ferromagnetic interactions between Cu(II) and Co(II), respectively. In the $[\{Cu(en)_2Mn(NCS)_4(H_2O)_2\}_n]$[8c] complex with both '*trans*' S–Cu–S and N–Mn–N chain motifs Cu(II) ··· Mn(II) interaction is negligible and a weak antiferromagnetic interaction between Mn(II) ions with a zero field splitting of the single Mn(II) ions predominates.

Obviously, more structural and magnetic data are required to establish the relationship between the structures and magnetic properties of 1-D thiocyanato bridged bimetallic assemblies.

Conclusion

The stabilisation of the co-ordination sphere around one metal

Table 5 Magnetic and structural parameters for μ-$_{\mathrm{N,S}}$-thiocyanato bridged 1-D heterobimetallic complexes

Complex[a]	M–S/Å	M′–N[b]/Å	M–S–C/°	M′–N–C/°	S–M–S/°	J[c]/cm^{-1}	Intrachain M–M′/Å	Interchain M–M′/Å	Ref.
[{Cu(cyclam)-Co(NCS)$_4$}$_n$]	2.891 3.160	1.951	111.89	171.8	169.96	−1.48	6.909	6.361	8*a*
[{CuLCo(NCS)$_4$}$_n$]	2.984	1.957	97.89	[d]	*trans*[d]	3.07	5.935	[d]	8*b*
[{Cu(en)$_2$Mn(NCS)$_4$-(H$_2$O)$_2$}$_n$]	3.065	2.166	94.3	172.9	179.97	−0.22 or −0.062[e]	6.096	6.200	8*c*
[{Co(dpa)(DMF)-(NCS)$_3$Ag}$_n$]	2.698 2.523	2.108–2.205[f]	[d]	[d]	91.90–123.35[f]	[g]	5.398	[d]	8*d*
[Ni(en)$_3$]$_n$[{Ni(en)$_2$-Cr(NCS)$_6$}$_{2n}$]	2.632 2.584	1.996 1.997	93.2 105.1	177.4 170.7	81.79	−19.9	5.442 5.984	6.696 6.706	This work

[a] Ligand abbreviations, L = *N*-*meso*-(5,12-Me$_2$-7,14-Et$_2$-[14]-4,11-dieneN$_4$), dpa = bis(2-pyridyl)amine. [b] Distance for N atom of thiocyanato bridges only. [c] Based on the spin Hamiltonian $H = -J\Sigma S_A \cdot S_B$. [d] Value not reported. [e] Interaction between Mn(II) ions *via* the NCS–Cu–SCN pathway. Value of J depends on model considered. [f] Three distances and six angles because of three different thiocyanato ligands. [g] No model of interactions given. $C = 2.55$ cm^3 K mol^{-1} and $\theta = -17.2°$ from the Curie–Weiss law.

ion by using an inert [Cr(NCS)$_6$]$^{3-}$ complex has led to the preparation of two new 1-D compounds, [Ni(en)$_3$]$_n$[{Ni(en)$_2$-Cr(NCS)$_6$}$_{2n}$] **1** and [Zn(en)$_3$]$_n$[{Zn(en)$_2$Cr(NCS)$_6$}$_{2n}$] **2**, with thiocyanato bridges. As far as the authors are aware, **1** represents not only the first structurally characterised Cr–NCS–Ni system exhibiting intermetallic connections through thiocyanato bridges but also one of the few examples of a μ-$_{\mathrm{N,S}}$-NCS bridged one-dimensional heterobimetallic compound. The magnetic behaviour of **1** has been explained as a sum of cationic and anionic parts. The former shows simple Curie behaviour of the nickel(II) ion with $S = 1$, whereas the latter was treated as a Heisenberg linear chain with classical spin, $S_{\mathrm{Ni}} = 1$ and $S_{\mathrm{Cr}} = 3/2$, alternation. This magnetic behaviour is consistent with the structural features related to μ-$_{\mathrm{N,S}}$-NCS bridged units being in *cis* positions at both metallic centres.

Compound **2**, with diamagnetic Zn^{2+} instead of the paramagnetic Ni^{2+} of **1**, shows magnetic behaviour which agrees well with that expected for isolated [Cr(NCS)$_6$]$^{3-}$ units with very weak inter- and/or intra-chain antiferromagnetic interactions.

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