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Reinecke Anion Derivatives and Homobinuclear Complexes as Tectons in Designing Heteropolymetallic Systems

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Two novel Cr^{III}–Ni^{II} heteropolynuclear complexes have been obtained through a self-assembly process involving a binuclear Ni^{II} complex with a macrocyclic Robson ligand and Reinecke-type anions (*trans*-$[Cr(NCS)_4(NH_3)_2]^-$, *trans*-$[Cr(NCS)_4(4,4'\text{-bipy})_2]^-$): $[Ni_2(H_2O)_2(\text{fsal-33})\{Cr(NCS)_4(NH_3)_2\}]\cdot 2H_2O$ (**1**) and $^{1}_{\infty}[Ni_2(H_2O)_2(\text{fsal-33})\{Cr(NCS)_4(4,4'\text{-bipy})_2\}]_n\cdot n[Cr(NCS)_4(4,4'\text{-bipy})_2]$ (**2**). The compartmental ligand results from the condensation of 2,6-diformyl-4-methyl-phenol with 1,3-propanediamine. The crystal structure of **1** consists of neutral tetranuclear [CrNiNiCr] species, where each nickel ion is coordinated in one apical position by a Reinecke anion, and in the other one by an aqua ligand. The distances between the metallic centres in **1** are: Ni···Cr = 6.048 and Ni···Ni = 3.133 Å. Compound **2** contains infinite cationic chains constructed from binuclear [Ni–Ni] nodes, connected through *trans*-$[Cr(4,4'\text{-bipy})_2(NCS)_4]$ spacers, and uncoordinated *trans*-$[Cr(NCS)_4(4,4'\text{-bipy})_2]^-$ ions. The Cr^{III} and Ni^{II} ions are connected through 4,4′-bipyridine ligands arising from the Reinecke-type anion. The distance between the nickel and chromium ions within the chain is 11.252 Å. The magnetic properties of **1** have been investigated. Both Ni–Ni and Cr–Ni exchange interactions were found to be antiferromagnetic: $J_{NiNi} = -51.3\ cm^{-1}$; $J_{NiCr} = -22.7\ cm^{-1}$.

Introduction

The search for new metal-containing building blocks is of current interest in molecular magnetism and in crystal engineering. These are relatively inert anionic complexes with potentially bridging ligands, for example cyano ($[M(CN)_6]^{3-}$,[1] $[M(bipy)(CN)_4]^{-}$[2]), or oxalato complexes ($[M(C_2O_4)_3]^{3-}$, $[M(bipy)(C_2O_4)_2]^{-}$[3]), which have been widely employed to design heterospin systems with interesting magnetic properties. It is well known that the thiocyanato anion acts as a bridge between either identical or different metal ions.[4] Nevertheless, the thiocyanato complexes have rarely been used as templates in assembling heteropolynuclear complexes.[5] A very appealing complex in this respect is the anion of the Reinecke salt, $[Cr(NCS)_4(NH_3)_2]^-$, which can interact with the second metal ion through the sulfur atom. For example, a Cu^{II}–Cr^{III} heterobinuclear complex has been obtained by reacting the Reinecke anion with a cationic copper(II) complex.[6]

We are currently developing a research project aimed at obtaining heterometallic complexes with interesting structures and magnetic properties, by using homo- or heterobinuclear species as assembling cations. The basic idea of our strategy is to combine the magnetic behaviour of the assembling cation (exhibiting a ferro- or antiferromagnetic coupling between the two metal ions) with that of the anionic building-block. Beyond the individual magnetic behaviour, the two molecular entities may interact through the connecting ligands. This synthetic approach allowed us to obtain complexes with three different spin carriers: 2p-3d-4f,[7] 3d-3d′-4f[8] or high-dimensionality 3d-4f coordination polymers.[9] Apart from our interest in the classical Reinecke anion, we intend to enrich our chemical library with new building blocks, by replacing the NH_3 ligands, from the $[Cr(NCS)_4(NH_3)_2]^-$ ion, with organic molecules that can act as bridges. Such building units can be extremely versatile, having both hard and soft coordination sites (e.g. nitrogen donor atoms arising from the organic ligand and sulfur donor atoms from the isothiocyanato ligands).

Results and Discussion

The first results concerning the synthesis of new heterobimetallics using the Reinecke anion and its derivatives as building blocks are reported herein, and consist of two

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Cr^{III}–Ni^{II} heteropolynuclear complexes: $[Ni_2(H_2O)_2(fsal\text{-}33)\{Cr(NCS)_4(NH_3)_2\}]\cdot 2H_2O$ (**1**) and $^1{}_\infty[Ni_2(H_2O)_2(fsal\text{-}33)\{Cr(NCS)_4(4,4'\text{-bipy})_2\}]_n\cdot n[Cr(NCS)_4(4,4'\text{-bipy})_2]$ (**2**). Compound **1** is obtained through a self-assembly process involving the Reinecke anion and a binuclear nickel(II) cationic complex, $[Ni_2(H_2O)_2(fsal\text{-}33)]^{2+}$ (fsal-33 is a dianionic macrocyclic binucleating Schiff-base ligand obtained by condensation of 2,6-diformyl-4-methyl-phenol with 1,3-propylenediamine). Compound **2** is obtained using the same nickel(II) complex and a derivative of the Reinecke salt, *trans*-$K[Cr(NCS)_4(4,4'\text{-bipy})_2]$. This Reinecke derivative is obtained by reacting $K_3[Cr(NCS)_6]$ with 4,4′-bypiridine. Its composition and structure are confirmed by chemical analysis, and by the crystal structure of compound **2** (vide infra). The infrared spectrum displays the characteristic bands of the organic ligand, as well as the band of the isothiocyanato group (2067 cm^{-1}). The UV/Vis spectrum shows a band with a maximum at 550 nm, which is due to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. This transition occurs at lower energy (18180 cm^{-1}) than the one observed with the classical Reinecke anion, $[Cr(NCS)_4(NH_3)_2]^-$ (19610 cm^{-1}).

The crystal structures of compounds **1** and **2** have been solved. Compound **1** is a neutral tetranuclear Cr^{III}–Ni^{II}–Ni^{II}–Cr^{III} complex. The chromium and nickel ions are connected through one NCS bridge (Figure 1). The two $[Cr(NCS)_4(NH_3)_2]^-$ ions are *trans* disposed with respect to the general plane of the macrocyclic ligand enclosing the nickel ions. Each nickel ion is hexacoordinate, exhibiting an elongated octahedral geometry, with an equatorial N_2O_2 macrocyclic donor set, and the aqua ligand and the sulfur atom from the bridge coordinated in the apical positions. The Ni–N and Ni–O distances in the equatorial plane are close and vary between 2.005(2) and 2.0278(15) Å. The apical Ni–aqua and Ni–S distances are, respectively, 2.1138(18) and 2.6057(7) Å. The distances between the metallic centres are Ni···Cr = 6.048 and Ni···Ni = 3.133 Å. The Cr–N distances within the Reinecke anion vary between 1.985(2) and 2.069(2) Å. The analysis of the packing diagram (Figure 2) reveals the formation of layers through intermolecular hydrogen bond interactions established between the aqua ligand and the crystallisation water molecule [O(2)···O(3) = 2.699(3) Å], as well as between the crystallisation water molecule and one sulfur atom from an adjacent tetranuclear unit [O(3)···S(2) = 3.282(3) Å].

The IR spectrum of **1** shows two bands due to the NCS^- ligands (2066, 2104 cm^{-1}), in agreement with their different roles: terminal and bridging.

The second compound, $^1{}_\infty[Ni_2(H_2O)_2(fsal\text{-}33)\{Cr(NCS)_4(4,4'\text{-bipy})_2\}]_n\cdot n[Cr(NCS)_4(4,4'\text{-bipy})_2]$ (**2**), contains infinite cationic chains constructed from binuclear [Ni–Ni] nodes, connected through *trans*-$[Cr(NCS)_4(4,4'\text{-bipy})_2]$ spacers, and uncoordinated *trans*-$[Cr(NCS)_4(4,4'\text{-bipy})_2]^-$ ions taking over the charge of the cationic chain (Figure 3). Two chromium complexes acting as spacers are coordinated, through the 4,4′-bipy ligands, above and below the platform formed by the binuclear nickel complex [Ni–N(4,4′-bipy) = 2.139(16) Å] (Figure 3). The equatorial nickel–ligand distances fall in the range 2.008(16)–2.034(15) Å. The sixth coordination site at the nickel ions is occupied by an aqua ligand [Ni–O = 2.241(16) Å]. The intranode Ni···Ni distance is 3.09 Å. The shortest Ni···Cr distance within the chain is 11.25 Å. As far as the chromium building blocks are concerned, the metal ions exhibit an almost perfect octahedral stereochemistry. The Cr–N(NCS) distances (ave, 1.98 Å) are slightly shorter than the Cr–N(4,4′-bipy) ones (ave, 2.08 Å). Selected bond lengths and angles for compounds **1** and **2** are collected in Table 1.

The magnetic properties of complex **1** have been investigated. The $\chi_M T$ versus T curve is represented in Figure 4. The room temperature value of the $\chi_M T$ product (5.30 $cm^3 mol^{-1} K$) is slightly lower than the one corresponding to the four uncoupled metal ions (5.7 $cm^3 mol^{-1} K$). By lowering the temperature, $\chi_M T$ continuously decreases, reaching 0.19 $cm^3 mol^{-1} K$ at 2 K.

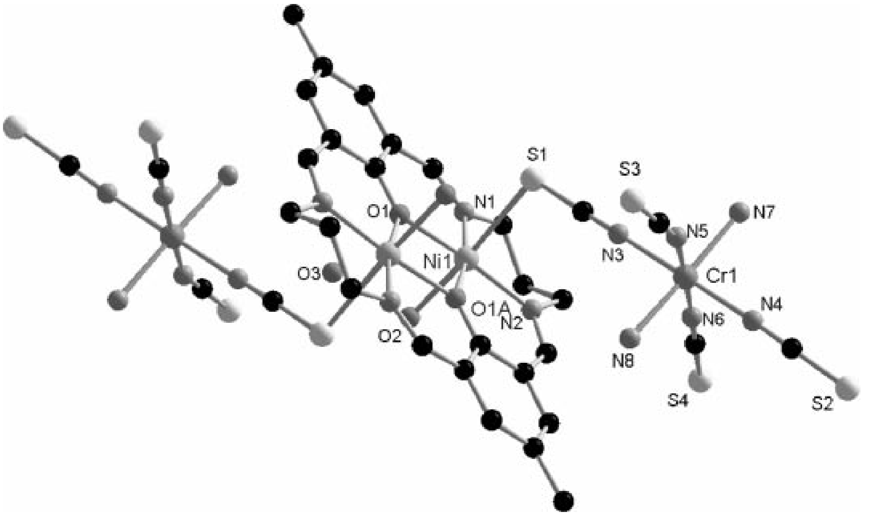

Figure 1. Perspective view of the tetranuclear complex **1**.

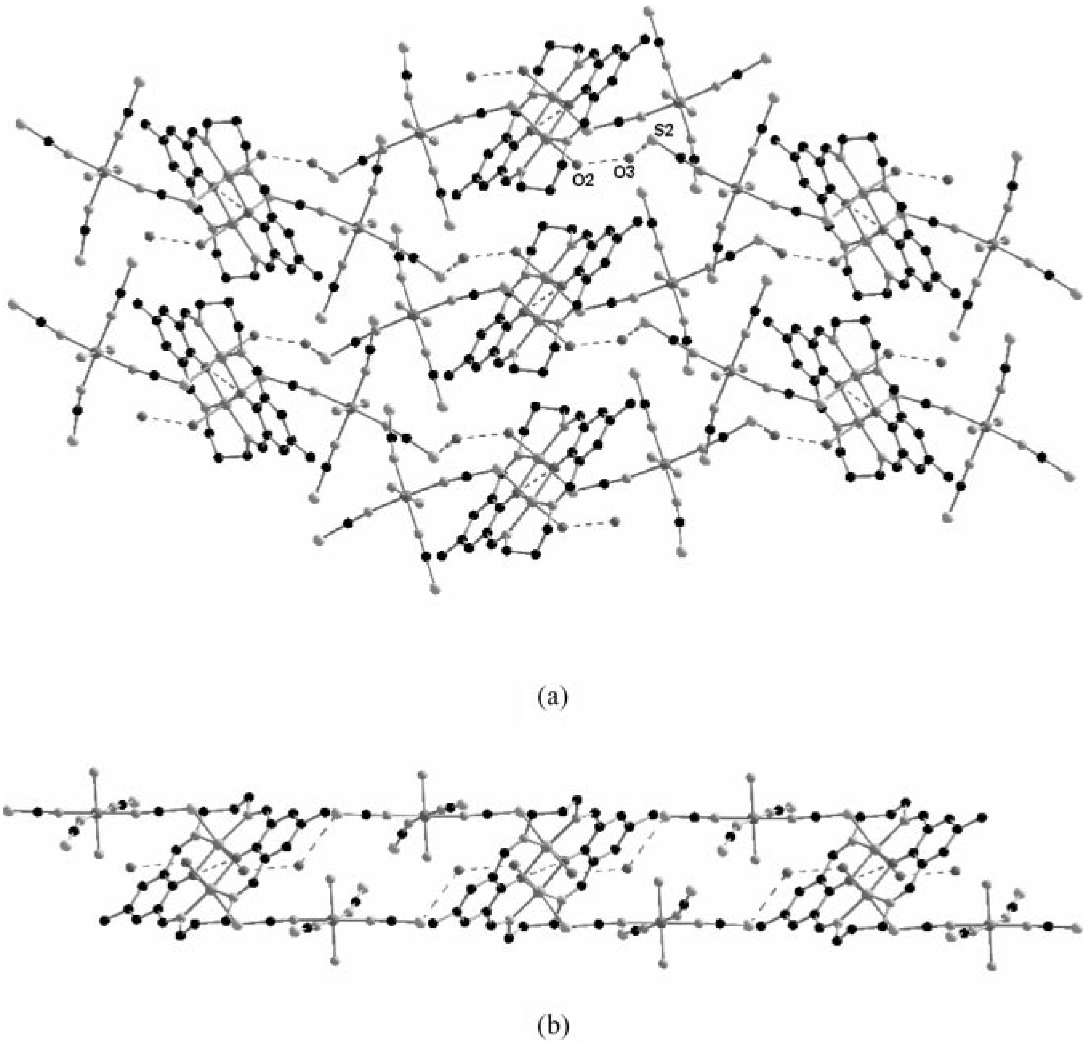

Figure 2. Packing diagram for crystal **1**, showing the formation of the supramolecular layers: a) view along the crystallographic *a* axis; b) side view.

For the centrosymmetric [CrNiNiCr] complex the energies of the low-lying spin states are obtained by using the isotropic Hamiltonian:

$\boldsymbol{H} = -J_{\mathrm{CrNi}}(\boldsymbol{S}_{\mathrm{Cr1}}\boldsymbol{S}_{\mathrm{Ni1}} + \boldsymbol{S}_{\mathrm{Ni2}}\boldsymbol{S}_{\mathrm{Cr2}}) - J_{\mathrm{NiNi}}\boldsymbol{S}_{\mathrm{Ni1}}\boldsymbol{S}_{\mathrm{Ni2}}$

The full matrix diagonalisation technique was employed to reproduce the experimental data. The best fit to the data led to:

$J_{\mathrm{NiCr}} = -22.7\ \mathrm{cm}^{-1}$; $J_{\mathrm{NiNi}} = -51.3\ \mathrm{cm}^{-1}$; $g_{\mathrm{Ni}} = 2.2$ (fixed); $g_{\mathrm{Cr}} = 1.98$; $R = 2.6\times10^{-4}$ {R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{\mathrm{obsd}}(i) - (\chi_M T)_{\mathrm{calcd.}}(i)]^2/\Sigma_i[(\chi_M T)_{\mathrm{obsd.}}(i)]^2$}.

At first glance, the antiferromagnetic nature of the interaction between $\mathrm{Cr^{III}}$ and $\mathrm{Ni^{II}}$ is surprising, this pair of ions, both in octahedral stereochemistry, being a classical example of orthogonality of the magnetic orbitals leading to a ferromagnetic coupling. One of the most important factors influencing the sign and the magnitude of the exchange interaction is the bridging angle; more precisely, in our case, the Ni(1)–S(1)–C(13) one [106.03(8)°]. For a $[\mathrm{M_AXM_B}]$ single bridge system, the ferromagnetic interaction arising from the strict orthogonality of the magnetic orbitals is maximal for a linear $\mathrm{M_A}$–X–$\mathrm{M_B}$ linkage.[10,11] By decreasing the $\mathrm{M_A}$–X–$\mathrm{M_B}$ angle, the ferromagnetic interaction decreases also, being finally dominated by the antiferromagnetic one. For example, recent calculations for a related compound, containing the Ni–NC–Cr motif,[11] have shown that the ferromagnetic interaction between $\mathrm{Ni^{II}}$ and $\mathrm{Cr^{III}}$ ions through a single cyanide bridge is weakened with the bending at the cyanide bridge, becoming antiferromagnetic for values of $\alpha \leq 148°$.

For compound **1**, the deviation from linearity is very important and consequently the relatively strong antiferromagnetic interaction between $\mathrm{Ni^{II}}$ and $\mathrm{Cr^{III}}$, because of the overlap of the magnetic orbitals, is not surprising. A [NiCr] thiocyanato-bridged cationic coordination polymer, –catena-μ-NCS–Ni(en)$_2$-μ-SCN–Cr(NCS)$_4$–, has recently been described.[5c] The values of the Ni–S–C angles were 93.2 and 105.1° and, accordingly, favoured an antiferromagnetic interaction ($J = -19.9\ \mathrm{cm}^{-1}$). As far as the Ni–Ni exchange interaction is concerned, it falls in the range already observed with several other nickel complexes with the same ligand: $\mathrm{Ni^{II}_2L(H_2O)_2(ClO_4)_2}$ ($J = -61\ \mathrm{cm}^{-1}$),[10] $\mathrm{Ni^{II}_2L(py)_2(BF_4)_2}$ (py = pyridine) ($J = -46\ \mathrm{cm}^{-1}$)[12] and

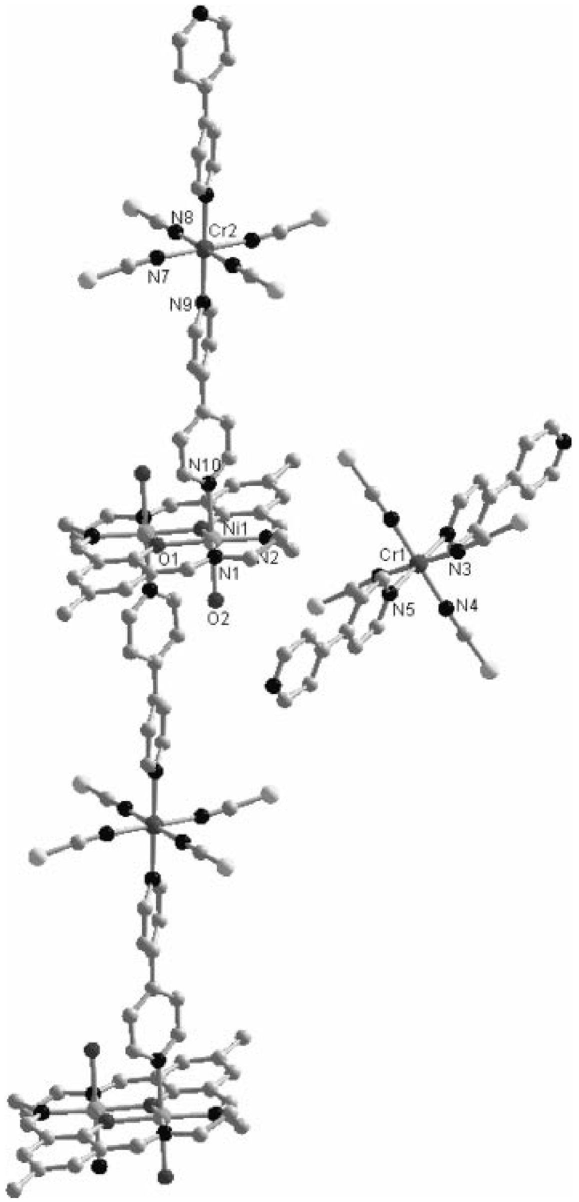

Figure 3. Perspective view of the cationic chain and of the complex anion in **2**, along with the atom-numbering scheme.

$Ni^{II}_2L(H_2O)_2Cl_2$ (J = –72 cm^{-1}).[13] In the similar cyano-bridged [CrNiNiCr] complex, the value of the J_{NiNi} parameter is –44.6 cm^{-1}.[11]

The functionalisation of the Reinecke anion, by replacing the NH_3 groups with potentially bridging ligands, as illustrated by compound **2**, opens interesting perspectives in crystal engineering. Various solid-state architectures can be thus constructed through the selective interaction of the hard (N) and soft (S) donor atoms with appropriate transition-metal ions. Two different metal ions (one hard, the other soft) can be employed simultaneously in order to obtain new solid-state architectures. Moreover, compound **2** illustrates how the building-block approach can be combined with the node-and-spacer approach, to design extended structures.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**.

1		**2**	
Ni(1)–N(1)	2.0230(19)	Ni(1)–N(1)	2.029(7)
Ni(1)–N(2)	2.005(2)	Ni(1)–N(2)	2.009(7)
Ni(1)–O(1)	2.0263(15)	Ni(1)–O(1)	2.019(5)
Ni(1)–O(1)	2.0278(15)	Ni(1)–O(2)	2.241(7)
Ni(1)–O(2)	2.1138(18)	Ni(1)–N(10)	2.140(6)
Ni(1)–S(1)	2.6057(7)	Cr(1)–N(3)	2.002(8)
Cr(1)–N(3)	2.017(2)	Cr(1)–N(4)	1.969(9)
Cr(1)–N(4)	1.987(2)	Cr(1)–N(5)	2.084(7)
Cr(1)–N(5)	1.993(2)	Cr(2)–N(7)	1.989(8)
Cr(1)–N(6)	1.985(2)	Cr(2)–N(8)	1.991(6)
Cr(1)–N(7)	2.069(2)	Cr(2)–N(9)	2.079(6)
Cr(1)–N(8)	2.059(2)		
		N(1)–Ni(1)–N(10)	91.9(3)
N(1)–Ni(1)–O(1)	91.16(7)	N(1)–Ni(1)–O(2)	85.2(3)
N(1)–Ni(1)–O(2)	89.86(8)	N(2)–Ni(1)–O(1)	169.1(2)
N(1)–Ni(1)–S(1)	85.35(6)	N(2)–Ni(1)–N(1)	98.8(3)
N(2)–Ni(1)–N(1)	99.21(8)	N(2)–Ni(1)–N(10)	94.0(3)
N(2)–Ni(1)–O(1)	169.63(7)	N(2)–Ni(1)–O(2)	87.1(3)
N(2)–Ni(1)–O(2)	90.02(8)	N(10)–Ni(1)–O(2)	177.0(3)
N(2)–Ni(1)–S(1)	92.73(6)	O(1)–Ni(1)–N(1)	90.7(2)
O(1)–Ni(1)–O(2)	89.99(7)	O(1)–Ni(1)–N(10)	90.9(2)
O(1)–Ni(1)–S(1)	88.10(5)	O(1)–Ni(1)–O(2)	88.5(2)
O(2)–Ni(1)–S(1)	174.80(6)	N(3)–Cr(1)–N(5)	91.0(3)
N(3)–Cr(1)–N(7)	89.49(9)	N(4)–Cr(1)–N(3)	89.1(3)
N(3)–Cr(1)–N(8)	89.48(9)	N(4)–Cr(1)–N(5)	89.6(3)
N(4)–Cr(1)–N(5)	91.06(9)	N(7)–Cr(2)–N(8)	91.7(3)
N(4)–Cr(1)–N(3)	177.17(9)	N(7)–Cr(2)–N(9)	89.0(3)
N(4)–Cr(1)–N(8)	91.13(9)	N(8)–Cr(2)–N(9)	90.5(2)
N(4)–Cr(1)–N(7)	90.01(9)		
N(5)–Cr(1)–N(3)	91.73(9)		
N(5)–Cr(1)–N(8)	87.00(10)		
N(5)–Cr(1)–N(7)	90.63(10)		
N(6)–Cr(1)–N(4)	89.63(9)		
N(6)–Cr(1)–N(5)	178.16(10)		
N(6)–Cr(1)–N(3)	87.60(9)		
N(6)–Cr(1)–N(8)	91.29(10)		
N(6)–Cr(1)–N(7)	91.07(10)		
N(8)–Cr(1)–N(7)	177.38(10)		

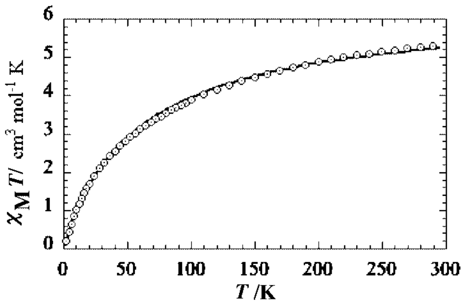

Figure 4. χT vs T diagram for complex **1**. The solid line corresponds to the best fit.

Experimental Section

Synthesis: $K[Cr(NCS)_4(4,4'\text{-bipy})_2]$ was prepared by refluxing a *i*PrOH solution of $K_3[Cr(NCS)_6]$ and 4,4′-bipy (in a 1:2.5 ratio) for 6 h, and isolation of the red solid appeared by cooling. IR (KBr): $\tilde{\nu}$ = 2067 (vs), 1597 (m), 1409 (m), 1218 (m), 1065 (m), 807 (m), 628 (m) cm^{-1}.

Compounds **1** and **2** were obtained by reacting the binuclear nickel(II) complex $[Ni_2(fsal\text{-}33)Cl_2]\cdot 2H_2O$[14] (in 1:1 EtOH/water solution) with, respectively, $NH_4[Cr(NCS)_4(NH_3)_2]$ (in H_2O) and $K[Cr(NCS)_4(4,4'\text{-bipy})_2]$ (in EtOH), in a 1:2 ratio. In both cases, light red precipitates formed and were isolated by filtration and dried. The first one was dissolved in pure methanol and allowed to evaporate slowly, generating orange needle-like crystals of **1** suitable for X-ray diffraction studies. In the second case, red single crystals of **2** were obtained by dissolving the precipitate in DMF, followed by slow diffusion of ethanol into the resulting solution. Characteristic IR bands due to the NCS ligands (KBr pellets) – **1**: 2066, 2104 cm^{-1}; **2**: 2062 cm^{-1}.

Physical Techniques: The IR spectra (KBr pellets) were recorded with a BIO-RAD FTS 135 spectrophotometer. The electronic spectra (diffuse reflectance technique) were recorded with a UV4 UNICAM spectrophotometer with MgO as a reference.

Magnetic measurements were carried out with a MPMS-5S (Quantum Design) SQUID magnetometer. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

Crystallography: Crystal **1** was measured at 183 K with a Bruker AXS SMART diffractometer (Mo-K_α radiation monochromator). Data for crystal **2** were collected at 293 K with a Stoe-IPDS imaging plate system operating with a Mo-K_α X-ray tube with a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. Calculations were performed using the SHELX-97 crystallographic software package. The crystallographic data and other pertinent information are collected in Table 2.

CCDC-283332 (for **1**) and CCDC-283333 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data and structure refinement parameters for compounds **1** and **2**.

	1	2
Empirical formula	$C_{32}H_{46}Cr_2N_{16}Ni_2O_6S_8$	$C_{72}H_{58}Cr_2N_{20}Ni_2O_4S_8$
M	1228.75	1745.28
Temperature [K]	183	293
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	9.5752(3)	11.3113(13)
b [Å]	8.7100(3)	13.2258(13)
c [Å]	30.2624(10)	15.9098(17)
α [°]	90.00	80.927(12)
β [°]	91.5870(10)	82.556(13)
γ [°]	90.00	89.067(13)
V [$Å^3$]	2522.92(14)	2330.5(4)
Z	2	1
$\rho_{(calcd)}$ [$Mg\,m^{-3}$]	1.617	1.244
μMo [mm^{-1}]	1.543	0.856
$F(000)$	1260	894
Gof (for F^2)	1.035	0.831
Final R, wR [$I > 2\sigma(I)$]	0.0319, 0.0776	0.0732, 0.1822
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ [$e\,Å^3$]	1.009 and –0.350	1.101 and –0.508

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