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Structural, Spectral, and Magnetic Properties of End-to-End Di-μ-thiocyanato-Bridged Polymeric Complexes of Ni(II) and Co(II). X-ray Crystal Structure of Di-μ-thiocyanatobis(imidazole)nickel(II)

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Thiocyanatonickel(II) and thiocyanatocobalt(II) complexes of the composition $Ni(NCS)_2(HIm)_2$ (**1**) and $Co(NCS)_2(HIm)_2$ (**2**), where HIm = imidazole, were prepared and studied. In particular, the crystal structure of $Ni(NCS)_2(HIm)_2$ was determined by X-ray methods. This compound crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 7.720(1)$ Å, $b = 5.557(1)$ Å, $c = 13.774(3)$ Å, $\beta = 102.54(3)°$, and $Z = 2$. Its structure consists of a one-dimensional polymeric chain in which nickel(II) ions are bridged by two thiocyanate groups bonding in an end-to-end fashion in a trans arrangement. The Ni···Ni distance is 5.557(1) Å. The crystal packing is determined by the intermolecular hydrogen bonds and ring-stacking interactions. From their X-ray powder-diffraction patterns and IR spectra, the complexes **1** and **2** were found to be mutually isomorphous. The coordination compounds were identified and characterized using elemental analysis, magnetic measurements, and infrared and ligand-field spectra. Both complexes are first examples of ferromagnetically coupled one-dimensional polymeric compounds with double end-to-end thiocyanate bridges. The magnetic properties of the title compounds were investigated over the 1.9–290 K temperature range. The compounds exhibit long-range magnetic ordering with T_c equal to 5.0 and 5.5 K for **1** and **2**, respectively. Their isothermal magnetization was also studied. The magnetostructural properties of the nickel(II) compound obtained are discussed and compared to those of other double end-to-end thiocyanate-bridged nickel(II) complexes.

Introduction

Structural and magnetic studies of binuclear and polynuclear complexes containing multidentate bridging ligands, in which such metal−metal interactions as magnetic coupling, energy or electron transfer, and intervalence transfer[1−3] may occur, are of considerable interest from the standpoint of inorganic and bioinorganic chemistry.[4−6] Coordination chemistry of transition-metal complexes containing pseudohalides of the type XCN (X = O, S, Se) is interesting from the structural point of view because of different modes of the ligand coordination to the metal ions. The chemistry and bonding properties of such complexes have been the subject of several reviews.[7,8] In recent years, great attention has been devoted to magnetostructural studies of polynuclear complexes of nickel(II) with pseudohalogen bridges (OCN^-, SCN^-, $SeCN^-$, N_3^-) which act as a superexchange pathway. Hence, the object of our interest was structural and magnetic studies of the title polymeric compounds.

The nickel(II) azido system has been the one most widely studied. Experimental data indicate that the most characteristic feature of the azido bridges is the relationship between

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coordination mode and magnetic behavior. Normally, the end-to-end coordination is associated with antiferromagnetic behavior and end-on coordination with ferromagnetic coupling, but there is also a possibility of ferromagnetic interaction between centers when the azido ligand binds in μ-1,3 fashion.[9] For nickel(II) compounds with end-to-end azido bridges, models to correlate the magnitude of coupling with the structure have been proposed.[9] For an end-to-end cyanate bridging ligand, ferro- or antiferromagnetic behaviors are possible, whereas for thio- and selenocyanate ones, weakly ferromagnetic coupling is always observed.[10,11]

The magnetic behavior of octahedrally coordinated dimers of nickel(II) with two end-to-end pseudohalide bridging ligands has been studied and correlated with structural parameters by different authors, and some magnetostructural trends have been summarized.[10−12] In particular, for nickel(II) pseudohalide systems (with single or double bridges), the magnetostructural correlations have been obtained by extended Hückel calculations, and a general superexchange model has been proposed.[10]

In this work, we present a synthesis and the magnetic and spectral properties of two polymeric isomorphous compounds of the formula $M(NCS)_2(HIm)_2$ (M = Co, Ni, HIm = imidazole). For the nickel(II) complex, the crystal structure has been determined. Both complexes are the first examples of ferromagnetically coupled one-dimensional polymeric compounds with a double end-to-end thiocyanate bridge. We compare the structural and magnetic properties of $Ni(NCS)_2(Him)_2$ with those of several octahedrally coordinated dimers of nickel(II) with two end-to-end NCS^- groups as a bridging ligand to determine the influence of structural parameters on the strength of exchange coupling. Unfortunately, the lack of a model for an $S = {}^3/_2$ chain system precludes theoretical analysis of the magnetic data of complex **2**.

It is interesting to underline that the conditions of formation of the thiocyanatonickel(II)[13] and thiocyanatocobalt(II)[14] complexes with imidazole derivatives and the influence of their steric properties on the stoichiometry as well as on the stereochemistry of the complexes have also been studied earlier. The results obtained show that bridging by an NCS^- group is possible if the steric conditions of the neutral ligand permit it, as it is in the case of the complexes $Co(NCS)_2(HIm)_2$ and $Ni(NCS)_2(HIm)_2$.

Experimental Section

Physical Measurements. Metal content was determined using a Carl Zeiss Jena atomic absorption spectrophotometer. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN.

Table 1. Crystallographic Data for $Ni(NCS)_2(HIm)_2$ (**1**)

empirical formula	$C_8H_8N_6NiS_2$
fw	311.03
space group	$P2_1/n$
cryst syst	monoclinic
T, °C	20
λ, Å	0.71073
a, Å	7.720(1)
b, Å	5.557(1)
c, Å	13.774(3)
β, deg	102.54(3)
V, Å^3	576.8(2)
Z	2
D_{calcd}, g cm^{-3}	1.791(1)
μ, mm^{-1}	2.028
$R(F)^a$	0.0357
$R_w(F^2)^{a,b}$	0.093

[a] $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$, $R_w = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]\}^{1/2}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + (2F_c^2]/3$; $a = 0.0577$, $b = 0.79$.

Infrared spectra (100−4000 cm^{-1}) were recorded on a Bruker IFS 113v spectrophotometer using KBr pellets, and solid-state electronic spectra (28000−4000 cm^{-1}) on a Cary 500 spectrophotometer.

EPR spectra were recorded at X-band at room temperature, 77 K, and 4.2 K on an ESP 300E Bruker spectrometer with an ER 035 M Bruker NMR gaussmeter and a Hewlett-Packard microwave frequency counter.

Magnetic measurements of polycrystalline samples of the complexes **1** and **2** were carried out with a Quantum Design SQUID magnetometer under a magnetic field of 1 T applied over the temperature range 1.9−290 K, and under only 50 G at low temperatures ($T < 15$ K). The device was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$. The corrections for the diamagnetism (-148×10^{-6} cm^{-3} for **1** and **2**) were estimated from the Pascal constants.

Synthesis of the Complexes. $Ni(NCS)_2(HIm)_2$ (**1**). $Ni(NO_3)_2\cdot 6H_2O$ (10 mmol) dissolved in water (10 cm^3) was added to a solution of KSCN (20 mmol) in water (30 cm^3); the imidazole (20 mmol) dissolved in methanol (20 cm^3) was poured into the well-stirred aqueous solution. The resulting green solution was filtered and left to evaporate at room temperature. Green monocrystals suitable for X-ray determinations were collected after 2 weeks.

Anal. Calcd for $C_8H_8NiN_6S_2$ (%): C, 30.90; H, 2.57; N, 27.03; Ni, 18.87. Found: C, 30.76, H, 2.53, N, 27.00, Ni, 18.59.

$Co(NCS)_2(Him)_2$ (**2**). This compound was prepared according to the procedure described by Davis et al.[15] In spite of all the efforts no crystals suitable for X-ray determination were obtained.

Anal. Calcd for $C_8H_8CoN_6S_2$ (%): C, 30.87; H, 2.57; N, 27.01; Co, 18.93. Found: C, 30.28, H, 2.63, N, 26.90, Co, 18.58.

X-ray Crystallography. Diffraction data were collected with Mo Kα radiation on a Kuma KM4 four-circle diffractometer with a graphite monochromator. The crystallographic data are given in Table 1.

The X-ray intensities were corrected for Lorentz and polarization effects and extinction [$x = 0.006(3)$] but not for absorption. The structure was solved by heavy atom methods using the SHELXS-86[16] program, and refined on F by full-matrix least-squares analysis using the SHELXL-93[17] program. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen

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Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esds (in Parentheses) for Ni(NCS)$_2$(HIm)$_2$ (**1**)[a]

Coordination Polyhedron			
Ni−N(1)	2.075(3)	Ni−S(1b)	2.5985(11)
Ni−N(3)	2.038(3)	Ni···Ni′	5.557(1)
N(3)−Ni−N(1a)	90.17(11)	C(4)−N(3)−Ni	158.2(3)
N(3)−Ni−N(1)	89.83(11)	C(1)−N(1)−Ni	126.2(3)
N(3)−Ni−S(1b)	87.12(8)	C(3)−N(1)−Ni	128.7(2)
N(3)−Ni−S(1c)	92.88(8)	C(4)−S(1)−Ni″	99.57(11)
N(1)−Ni−S(1b)	90.42(8)		
N(1)−Ni−S(1c)	89.58(8)		
Imidazole			
N(1)−C(1)	1.311(5)	N(2)−C(2)	1.343(6)
N(1)−C(3)	1.363(5)	C(2)−C(3)	1.352(5)
N(2)−C(1)	1.331(5)	N(2)−H(4)	0.76(5)
C(1)−N(1)−C(3)	105.0(3)	N(2)−C(2)−C(3)	105.3(4)
C(1)−N(2)−C(2)	108.5(3)	C(2)−C(3)−N(1)	110.2(4)
N(1)−C(1)−N(2)	111.0(4)		
Thiocyanate Anion			
N(3)−C(4)	1.150(4)	N(3)−C(4)	1.150(4)
S(1)−C(4)	1.644(3)	S(1)−C(4)	1.644(3)
N(3)−C(4)−S(1)	176.8(3)	N(3)−C(4)−S(1)	176.8(3)

[a] Symmetry code: (a) $-x$, $-y$, $-z$; (b) x, $y + 1$, z; (c) $-x$, $-y - 1$, $-z$; (′) x, $y + 1$, z; (″) x, $y - 1$, z.

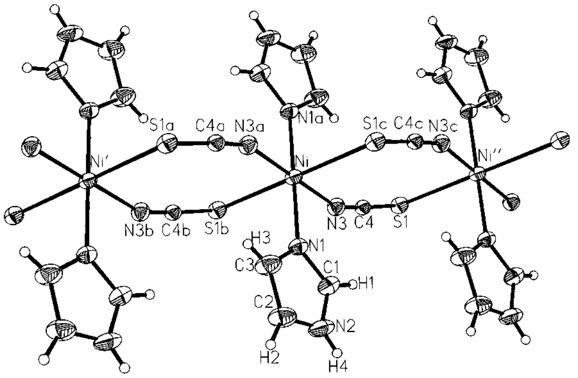

Figure 1. Molecular structure of Ni(NCS)$_2$(HIm)$_2$ (**1**) showing the atomic numbering. Displacement ellipsoids are draw at the 40% probability level.

atoms of the imidazole molecule were found from difference Fourier synthesis and refined with isotropic thermal parameters.

Results and Discussion

The obtained compounds are formulated as M(NCS)$_2$(HIm)$_2$, with M = Co, Ni and HIm = imidazole. The IR spectra of the two compounds are very similar with respect to band positions, shapes, and relative intensities, indicating a very similar structure for the two compounds. X-ray powder patterns also suggest that both complexes are structurally isomorphous.

Crystal Structure of Ni(NCS)$_2$(HIm)$_2$ (1). The crystallographic parameters are summarized in Table 1. The most important bond lengths and angles are listed in Table 2.

Figure 1 shows the structure and the labeling scheme of the Ni(II) complex. As it can be seen from Figure 1, the structure is a one-dimensional polymeric chain. Each Ni(II) ion is connected with the two adjacent metal ions by two NCS bridges, creating a polymeric chain along the *b* axis, in which the Ni···Ni distance within the chain is 5.557(1) Å. The Ni atom lies at a center of symmetry surrounded by six symmetrically related atoms, namely, two nitrogen ones from HIm ligands and two from thiocyanate anions, and, more loosely, two sulfur atoms from the bridging NCS groups, so that the polyhedron can be described as a distorted octahedron, symmetrically elongated along the Ni−S direction. The length of the Ni−S bond, being 2.5985(11) Å, is greater compared with those of the Ni−N bonds, which are 2.038(3) and 2.075(3) Å, which causes a significant distortion of the coordination polyhedron around the Ni(II) ion. The valence angles in the octahedron differ from 90° by a maximum of 2.9°. The geometry of the coordination polyhedron about the Ni(II) ion is given in Table 2. The values observed for the Ni−N and Ni−S distances are comparable with those found in other octahedral Ni(II) complexes.[18−20] Moreover, the Ni−N distance involving the NCS group is shorter than the other, involving the nitrogen atom of the HIm ligand. The eight-membered ring formed by two nickel atoms and two bridging thiocyanates is nonplanar, with the nickel atoms displaced 0.612(4) Å above and below the plane determined by the two coplanar thiocyanate groups. The NCS group shows a small distortion [176.8(3)°] from linearity, as is usually observed. The imidazole ring is planar within 0.004(3) Å. The dihedral angle between the plane of the HIm ring and the coordination plane around Ni(II) is 12.1(3)°. The molecular packing is shown in Figure 2.

Every polymeric chain of each of the complexes is linked to other ones by the N(2)−H(4)···S(1) [N(2)···S(1) ($-x + 1$, $-y - 1$, $-z$) 3.381(3) Å; H(4)···S(1) 2.63(5) Å; ∠N(2)−H(4)···S(1) 168(5)°] hydrogen bonds arising from the interaction of the imidazole NH and the S atom from an NCS group. These bonds form a double linkage joining adjacent molecules along *a*, and thereby generating a chain of hydrogen bonds in the *x* direction.

On the other hand, there is a stacking interaction between an imidazole ring of the molecule placed at x, y, z and that of the molecule placed at $-x + 1$, $-y$, $-z$. Both imidazole rings are parallel. The mean distance between their planes is 3.2 Å, the shortest contact being between the C(1) and N(2) atoms of adjacent imidazole rings (3.213(5) Å). Another intermolecular interaction in this crystal is between an imidazole ring of the molecule located at (x, y, z) and that of another at ($-x + {}^1/_2$, $y + {}^1/_2$, $-z - {}^1/_2$). The rings are not coplanar, and the angle between them is 45.5° [the shortest distance between them is 3.493(6) Å].

Apart from that, two short contacts between the N(3) from the NCS group and C(1) and C(3) from an imidazole ring were found in the molecule. The C(1)···N(3) and C(3)···N(3) distances are shorter than the van der Waals radii [3.018(5) and 3.111(5) Å, respectively].

Infrared Spectra. The interest in the IR spectra of the compounds studied comes mainly from the bands due to the thiocyanate group. The position of the bands corresponding

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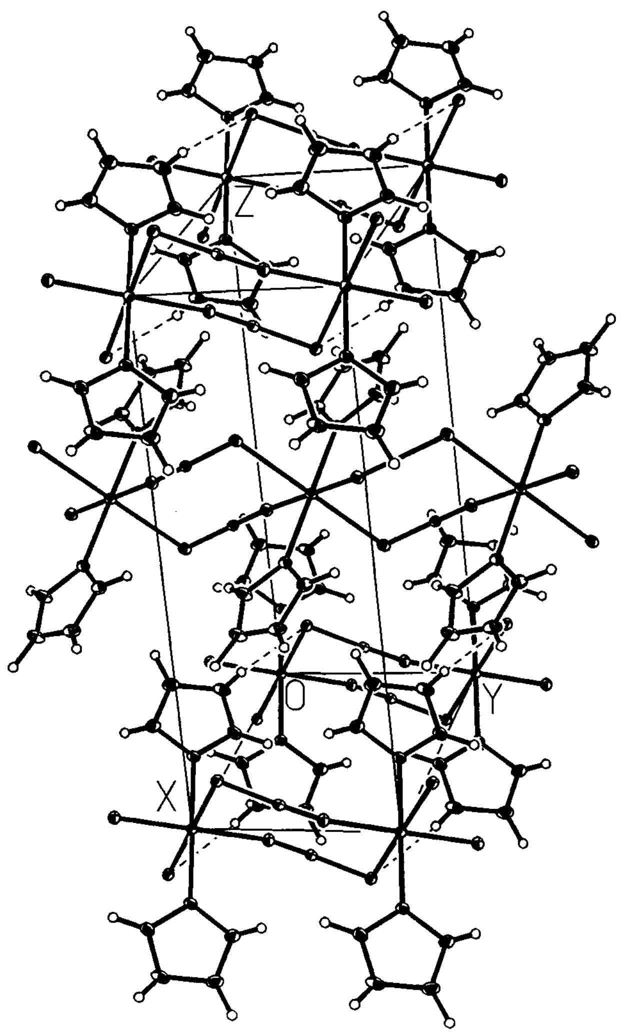

Figure 2. Crystal packing of Ni(NCS)$_2$(HIm)$_2$ (**1**) showing hydrogen bonds (dashed lines).

to the stretching frequency (CN) of this group can be used for characterization of the mode of coordination to the metal ions. The ν(CN) of a bridging thiocyanate is usually found to be above 2100 cm^{-1}.[21] In the case of the Ni(II) and Co(II) complexes studied here, the stretching frequency ν(CN) occurs at 2121 and 2114 cm^{-1}, respectively. Such high frequencies of these vibrations suggest the presence of end-to-end NCS bridges, and they are in the range usually observed for polymeric pseudooctahedral ML$_2$(NCS)$_2$ complexes.[21] Moreover, since this band for both complexes is single, their NCS bridging groups are equivalent. In addition, for cis isomers of both polymeric compounds with double thiocyanate bridges, both infrared modes of ν(CN) should be active in a non-centrosymmetric M(II) environment.[21] Thus, since no bands assignable as both components of ν(CN) were observed, both Ni(NCS)$_2$(HIm)$_2$ (**1**) and Co(NCS)$_2$(HIm)$_2$ (**2**) are trans isomers. The bands corresponding to the stretching frequency ν(CS) appear at 769 cm^{-1} for both complexes. The bands belonging to the deformation frequency δ(NCS) were found as doublets at 468 and 472 cm^{-1} and at 466 and 472 cm^{-1} for the Ni(II) and Co(II) complexes, respectively. The above bands are consistent with a bridging thiocyanate anion. These assignments were made on the basis of an observation that the stretching frequency ν(CS) in a bridging thiocyanate group is lower than in a terminal one,[22] and that a bridging NCS group gives rise to a splitting of the δ(NCS) band.[23] The presented structure of **1** confirms this hypothesis.

The bands found in the far IR region at 288 and 271 cm^{-1} can be assigned to the nickel− and cobalt−nitrogen stretching modes ν(M−NCS), respectively,[24−26] whereas the bands at 253 and 260 cm^{-1} observed in the spectra of the Co(II) and Ni(II) compounds, respectively, can be attributed to the stretching frequency ν(M−N(HIm)).[27] The values of ν(M−N(HIm)) obtained here were observed at lower frequencies than those of the metal−isothiocyanate stretching mode of tetrahedral complexes, thus confirming an octahedral polymeric structure.[13,14,26] Similar trends for M−N(HIm) frequencies have been observed previously for monomeric (tetrahedral) and polymeric (octahedral) Co(py)$_2$X$_2$ (X = Cl, Br) complexes.[28] The bands at 210 and 208 cm^{-1} were assigned to the Co−SCN and Ni−SCN stretching modes, respectively.

Ligand Field Spectra. The electronic spectrum of the Ni(NCS)$_2$(HIm)$_2$ (**1**) complex is characteristic of a six-coordinated, tetragonally distorted environment of an Ni(II) ion. The ligand-field spectrum shows bands at 16260 cm^{-1} (ν_2) and 7480 cm^{-1} (ν_1), and two additional weaker bands at 13150 cm^{-1} and 12130 cm^{-1}. The ratio ν_2/ν_1 for the present complex is 2.17, which is outside the usual range for octahedral complexes (1.5−1.7), characterizing thereby the complex to be tetragonally distorted. Assuming a tetragonal model (D_{4h}), it is possible to assign the observed bands to the transitions $^3B_{1g} \rightarrow {}^3E_g$ (7480 cm^{-1}) and $^3B_{1g} \rightarrow {}^3B_{2g}$ (12130 cm^{-1}). The remaining bands (16260 and 13150 cm^{-1}) may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3A_{2g}$, respectively. The ν_3 band ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in O_h symmetry) is not observed, probably masked by strong UV absorption. The value of the parameter Dt, which is directly related to the tetragonal distortion along the z axis, was calculated[29,30] to be +531 cm^{-1}. It is evident from the calculated values of Dq^{xy} (1213 cm^{-1}) and Dq^{z} (283 cm^{-1}) that the field strength along the z axis is much weaker than along the xy plane. The calculated average value[31] Dq is 905 cm^{-1}.

The assumption about the octahedral coordination of Co(NCS)$_2$(HIm)$_2$ (**2**), and thus the bridging function of the NCS group, is supported by absorption at 8700 cm^{-1}, corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$ transition, and at 19210 cm^{-1}

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with a shoulder at 17260 cm^{-1}, corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ one. The spectrochemical parameters *Dq* and *B* were calculated using a known method[32] and are equal to 950 and 745 cm^{-1}, respectively.

In comparison with other Co(II) complexes containing thiocyanate and imidazole derivatives with an octahedral configuration,[14] a decrease in the parameter *B* for the $Co(NCS)_2(HIm)_2$ (**2**) compound is probably caused by an increased nephelauxetic effect in consequence of a Co−S coordination originating from the bridge-bonding of the NCS group.

The values of *Dq* determined for the Co(II) and Ni(II) complexes are in good agreement with those expected for isomorphous nickel and cobalt compounds.[32]

Magnetic Properties of the Complexes $Ni(NCS)_2(HIm)_2$ (1) and $Co(NCS)_2(HIm)_2$ (2). The nickel(II) compound does not exhibit an X-band EPR spectrum, and the cobalt(II) compound shows no lines at room temperature and only broad single lines at 77 K (with a shoulder in low field about 2000 G) and 4.2 K.

The magnetic behavior of the complexes **1** and **2** is shown in Figure 3 in the form of $\chi_M T$ versus T (χ_M being the magnetic susceptibility per mole of metal atoms). The values of $\chi_M T$ at room temperature are 1.26 (**1**) and 3.6 cm^3 mol^{-1} K (**2**). The former is as expected for a magnetically isolated spin triplet (1.21 cm^3 mol^{-1} K for $S = 1$ with $g = 2.20$), whereas the latter lies above that calculated for a spin quartet (1.875 cm^3 mol^{-1} K for $S = {}^3/_2$ with $g = 2.0$), but it agrees with the values observed for octahedral cobalt(II) complexes with a significant first-order orbital contribution to the magnetic moment. In both cases, the $\chi_M T$ values follow a quasi Curie law from room temperature to 40 K. At lower temperatures, they increase sharply to reach a maximum of 155 cm^3 mol^{-1} K at 4.0 K (**1**) and of 160 cm^3 mol^{-1} K at 5.0 K (**2**), and further they decrease abruptly to 95 (**1**) and 67 cm^3 mol^{-1} K (**2**) at 1.9 K. This behavior of **1** and **2** is typical of an overall ferromagnetic coupling, as confirmed by magnetization measurements at low temperatures for both complexes (see Figure 4). The decrease of $\chi_M T$ in the very low temperature range is due to the saturation of magnetization as shown by the field cooled (FC) curves for **1** and **2** in Figure 4. Both compounds exhibit a three-dimensional magnetic ordering with the values of T_c equal to 5.0 (**1**) and 5.5 K (**2**), these values being determined from the field cooled magnetization (FCM) and zero field cooled magnetization (ZFCM) (see Figure 4), as well as ac measurements (see Figure 4, insets). Neither frequency nor amplitude dependence was observed for in-phase and out-of-phase signals. Finally, the field dependence of the magnetization at 1.9 K for **1** and **2** (Figure 5) provides additional evidence of the occurrence of a ferromagnetic coupling in both compounds although no saturation of magnetization was reached up to 5 T. At 1.9 K, complex **2** exhibit a hysteresis loop of a soft magnet (Figure 5, inset **2**), the values of the remanent magnetization and coercive field being 1.0 μ_B and 110 G, respectively. In the case of complex **1**, no hysteresis was detected under our experimental conditions (see Figure 5, insert **1**).

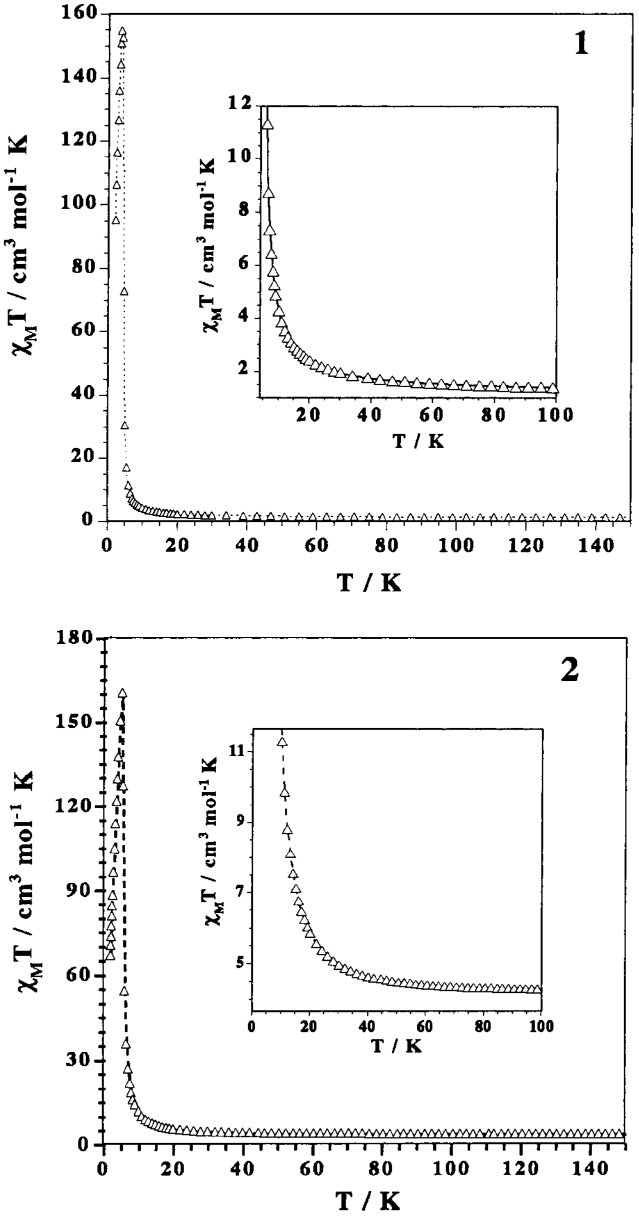

Figure 3. Plot of $\chi_M T$ versus T for complexes **1** and **2**. Experimental data are represented by triangles while the dotted line is an eye guide only. The solid line in the inset for **1** is the best-fit curve down to 12 K through the De Neef equation (see text). The inset for **2** is for comparison only.

Experimental data for complex **1** were fitted up to 10 K to the De Neef expression[33] based upon the Hamiltonian of the equation

$$H = -2J \sum_{i=1} (S_i \cdot S_{i+1}) - D \sum_{i=1} [(S_{iz})^2 - {}^2/_3] \qquad (1)$$

where the nickel atom is assumed to be magnetically isotropic and $2J$ is the intrachain magnetic coupling. The best-fit parameters obtained by the least-squares fit through eq 1 are as follows: $2J = 8.0$ cm^{-1}, $D = 0.2$ cm^{-1}, $g = 2.18$ and R

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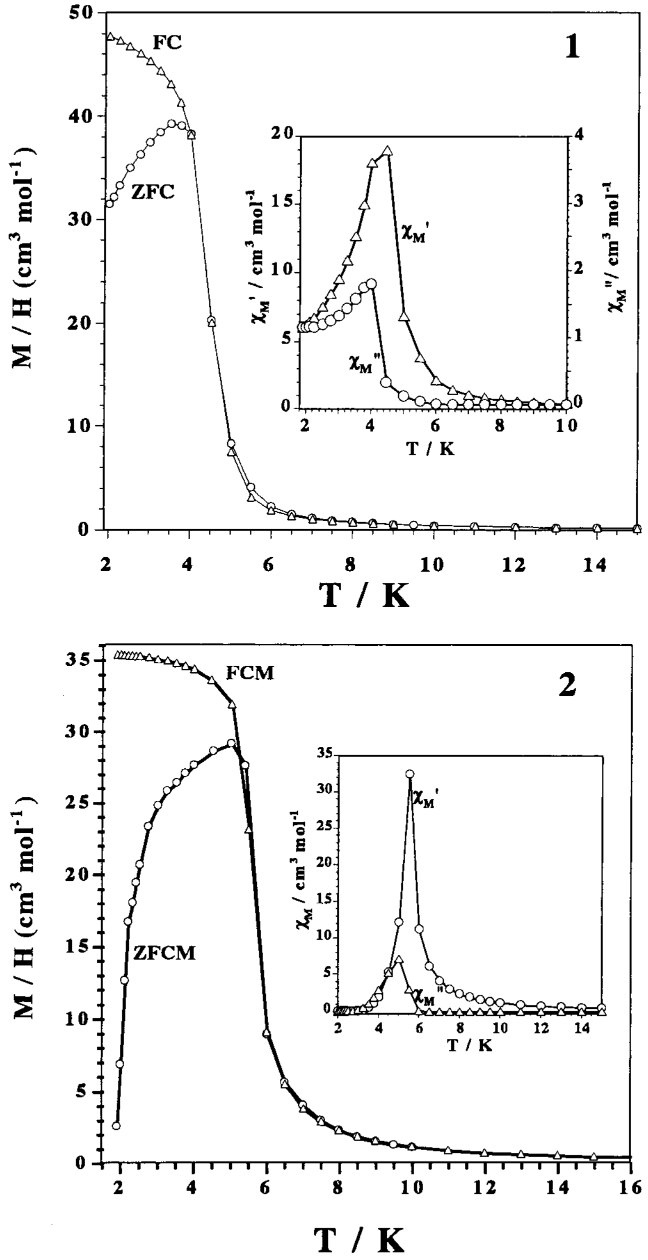

Figure 4. Temperature dependence of the field cooled (FC, △) and zero field cooled (ZFC, ○) *M*/*H* quotient for complexes **1** and **2**. The insets show the temperature dependence of both the in-phase (χ_M') and out-of-phase (χ_M'') components of the ac molar magnetization at 1 G for both complexes.

$= 1.2 \times 10^{-5}$, where *R* is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\sum_i[(\chi_M T)_{obs}(i)]^2$. As shown in the inset of Figure 3 for **1**, the calculated curve matches very well the magnetic data from room temperature to temperatures a few degrees above the critical ones. At lower temperatures, long-range magnetic ordering accounts for a deviation from one-dimensional magnetic behavior of **1**. The absence of a model for an $S = {}^3/_2$ chain system precludes theoretical analysis of the magnetic data of complex **2**. Nevertheless, in light of the magnetostructural data reported above, the occurrence of ferromagnetic coupling in this compound is impossible.

The origins of ferromagnetic coupling observed in double end-to-end thiocyanate bridged nickel(II) complexes have been analyzed by different authors. In his earlier work,[34] Ginsberg follows the valence-bond theory applying the Goodenough−Kanamori[35] rules or Anderson's expanded orbital theory.[36] Within this context and with idealized Ni−N−C and Ni−S−C angles of 180° and 90°, respectively, the overlap between the $d_{x^2-y^2}$ and d_{z^2} magnetic orbitals of the octahedral nickel(II) ions is zero. So, the occurrence of ferromagnetic coupling for this type of complex would be due to the orthogonality of the magnetic orbitals involved. In 1974, an analysis of the available magnetostructural studies concerning pseudohalide-bridged nickel(II) com-

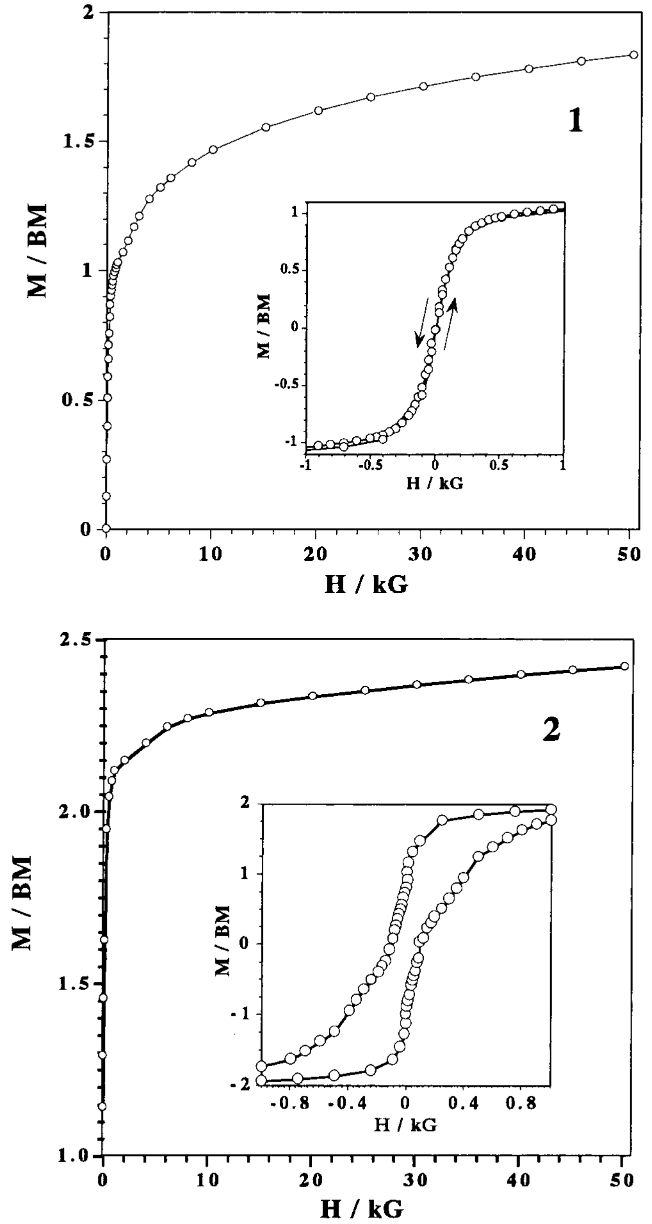

Figure 5. Field dependence of the dc molar magnetization (○) for **1** and **2** at 1.9 K. The inset shows the magnetic hysteresis loop at 1.9 K. The solid line is an eye quide.

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Table 3. Selected Magnetostructural Data for Double End-to-End Thiocyanato-Bridged Nickel(II) Complexes

compd[a]	nuclearity	Ni−N−C, deg	Ni−S−C, deg	Ni−N, Å	Ni−S, Å	J, cm^{-1}	D, cm^{-1}	d,[b] Å	ref
$[Ni_2(en)_4(\mu\text{-}NCS)_2]I_2$	dimer	167.0	100.0	2.04	2.61	4.5	−3.3	0.05	38
$[Ni_2(tren)_2(\mu\text{-}NCS)_2](BPh_4)_2$	dimer	167	100	2.04	2.61	2.4	−0.4	0.05	37[c]
$[Ni_2(terpy)_2(NCS)_2(\mu\text{-}NCS)_2]\cdot 2H_2O$	dimer	159.0	100.0	2.04	2.62	4.9	−4.3	0.56	11
$[Ni_2(2\text{-}mepn)_3(NCS)_2(\mu\text{-}NCS)_2]$	dimer	165.2	100.7	2.06	2.55	4.3	−20	0.84	12
		142.4	105.8	2.10	2.64			0.42	
$[Ni_2(2\text{-}mepn)_4(NCS)_2(\mu\text{-}NCS)_2](PF_6)_2$	dimer	166.7	96.2	1.93	2.83	6.3	−2.0	0.16	12
$[Ni(Him)_2(\nu\text{-}NCS)_2]$ (**1**)	chain	158.2	99.5	2.03	2.59	4.0	0.2	0.61	*d*

[a] Abbreviations used for the ligands: en = ethylenediamine, tren = tris(2-aminoethyl)amine, terpy = 2,2′:6′2″-terpyridine, 2-mepn = 1,2-diamino-2-methylpropane, and HIm = imidazole. [b] d = Ni to mean $(NCS)_2$ plane distance. [c] Not fully characterized. [d] This work.

plexes led Hendrickson to assume that two structural factors are responsible for the magnetic behavior they exhibit: (i) the deviation from planarity of the $Ni_2(NCX)_2$ bridging skeleton and (ii) the symmetry and the energy, of the bridged molecular orbitals.[37] For the former, he pointed out that it is less important, while for the latter, he pointed out that the antiferromagnetic coupling is enhanced when a mirror plane perpendicular to the metal−metal vector occurs within the $Ni_2(NCX)_2$ unit. Finally, extended Hückel calculations by Ribas et al.[12] have shown that, when going from planarity to a chairlike geometric conformation, the molecular orbitals of the $Ni_2(NCX)_2$ unit are always practically degenerate (suggesting thus a possibility of ferromagnetic coupling). This agrees with the previous Hendrickson's assumption, which was established with very limited data, when going from planarity to a chairlike geometry of the $Ni_2(NCS)_2$ unit. In any case, an inspection of the magnetostructural data of the double end-to-end thiocyanate-bridged nickel(II) complexes studied, which are listed in Table 3, shows that (i) the magnetic coupling is always weakly ferromagnetic; (ii) it is not necessary to have the Ni−N−C and Ni−S−C angles very close to 180° and 90°, respectively, for quasi-orthogonality of the molecular orbitals; and (iii) the value of the magnetic coupling of **1** correlates well with those observed in the parent complexes in spite of presenting the greatest deviation from planarity.

We would like to finish the present contribution by pointing out that complex **1** is the first example of a ferromagnetically coupled nickel(II) chain with end-to-end thiocyanate bridges which exhibits a long-range magnetic ordering (T_c = 5.0 K). Most likely, it is the hydrogen bonds which link the chains to each other and the ring-stacking interactions that provide an exchange pathway for this magnetic ordering. Finally, the number of examples gathered in Table 3 is to be increased in the near future with an aim of establishing a correlation between the J value and the relevant structural parameters, as it has recently been done for μ-oxalato[39] and μ-azido[40] compounds.

Conclusions

In this work, we have reported two novel, from the point of view of structural and magnetic properties, compounds of the formula $Ni(NCS)_2(HIm)_2$ and $Co(NCS)_2(HIm)_2$. The research presented shows that, in one-dimensional polymeric compounds of Ni(II) and Co(II) with double end-to-end thiocyanate bridges, ferromagnetic exchange is produced. On the basis of IR spectroscopy, the existence of trans isomers for both complexes has been concluded, as confirmed by the crystal-structure determination of **1**. The ligand-field spectrum of **1** is consistent with a tetragonally elongated octahedral geometry. This geometry is also proposed for the Co(II) compound, as both complexes have been found to be mutually isomorphous.

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Supporting Information Available: Crystallographic data for **1** in CIF format. Figures 1S and 2S showing the crystal packing and a fragment of the structure of **1**, respectively. Figure 3S showing the X-ray powder diffraction patterns of **1** and **2** in order to corroborate the isomorphism of both complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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