Crystal Structure and Magnetic Behaviour of a New Kind of One-dimensional Nickel(II) Thiocyanate Compound [{NiL(SCN)(μ-SCN)}$_n$] [L = bis(3-aminopropyl)methylamine]†

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The μ-thiocyanato nickel(II) one-dimensional compound, [{NiL(SCN)(μ-SCN)}$_n$] [L = bis(3-aminopropyl)methylamine] has been prepared. The crystal structure of this compound has been solved by Patterson synthesis and refined by least-squares analysis to a discrepancy factor of 0.068. The crystals are monoclinic, space group $P2_1/n$, with lattice constants a = 11.113(3), b = 16.706(4), c = 7.802(2) Å; β = 106.94(3)°. This compound represents the first structurally described nickel(II) chain in which two neighbouring nickel(II) ions are linked by only one SCN$^-$ bridging ligand. Magnetic susceptibility data, measured from 290 to 4 K, show weak ferromagnetic behaviour. These data were fitted to the de Neef equation giving the parameters J = 1.12 cm^{-1}, g = 2.16 and D = 1.72 cm^{-1}.

In recent papers we have reported the synthesis, crystal structure, magnetic behaviour and extended-Hückel molecular orbital studies of several one-dimensional nickel(II) compounds bridged by end-to-end azido ligands: [{Ni$_2$L'$_2$(μ-N$_3$)$_3$}$_n$]-[ClO$_4$]$_n$ [L' = bis(3-aminopropyl)amine] an alternating -[N$_3$-NiL-(N$_3$)$_2$]$_n$- chain[1] and [{Ni(cyclam)(μ-N$_3$)}$_n$][ClO$_4$]$_n$·nH$_2$O (cyclam = 1,4,8,11-tetraazacyclotetradecane) a homogeneous (-NiL-N$_3$-)$_n$ chain (L = cyclam),[2] which served as models for the synthesis of a series of new antiferromagnetically coupled -(NiL-N$_3$-)$_n$ chains.[3] Other potentially similar bridging ligands which can allow the formation of nickel(II) chains are cyanate or thiocyanate (or selenocyanate) anions and the first nickel(II) cyanate chain has been recently synthesised by us.[4] Focusing our attention on thiocyanate (or selenocyanate) ligands, structural data for several one-dimensional di-μ-thiocyanato and one di-μ-selenocyanato nickel(II) compound have been reported[5-8] but no magnetic studies were carried out. In contrast, [Ni(bipy)(NCS)$_2$] (bipy = 2,2'-bipyridine), reported as an infinite-chain ferromagnetic insulator has been exhaustively studied from the magnetic point of view[9] in the absence of structural data. This complex is assumed to have di-μ-thiocyanato bridges by comparison with [Ni(MeCSNH$_2$)$_2$(NCS)$_2$].[7] Some structural examples of di-μ-thiocyanato nickel(II) dinuclear complexes have also been described.[10-12] All these systems are ferromagnetically coupled. Neither dinuclear nor one-dimensional systems with only one SCN$^-$ or SeCN$^-$ bridging ligands have been previously reported. It might be interesting to compare the magnetic behaviour of these systems with those containing double SCN$^-$ bridges (ferromagnetically coupled) and analogous systems with only one azido or cyanato as bridging ligand (antiferromagnetically coupled). In an attempt to avoid the formation of di-μ-thiocyanato one-dimensional complexes, tri- or tetra-dentate ligands should be employed rather than bidentate ligands such as ethylenediamine. We now present the synthesis, crystal structure and magnetic studies of the first complex of this new type of μ-thiocyanato nickel(II) one-dimensional compound, [{NiL(SCN)(μ-SCN)}$_n$] [L = bis(3-aminopropyl)methylamine]. The -SCN-NiL-SCN- scheme is the same as that reported in the one-dimensional nickel(II) compounds bridged by the similar pseudohalide azido ligand,[2,3] which indicates that the thiocyanate anion is also a versatile bridging ligand able to give different one-dimensional nickel(II) compounds. Magnetic measurements show that [{NiL(SCN)(μ-SCN)}$_n$] is weakly ferromagnetically coupled, in contrast with the antiferromagnetism found in the similar one-dimensional nickel(II) compounds bridged by one azido ligand.[2,3]

Experimental

Synthesis.—The complex [{NiL(SCN)(μ-SCN)}$_n$] was prepared by mixing nickel(II) perchlorate hexahydrate (3 mmol), L (3 mmol) and ammonium thiocyanate (6 mmol) in water (75 cm^3). A blue solution was formed. From this solution blue single crystals suitable for X-ray determination were collected after a week (Found: C, 33.7; H, 6.0; N, 22.0. Calc. for $C_9H_{19}N_5NiS_2$: C, 33.8; H, 6.0; N, 21.9%).

Physical Measurements.—Infrared spectra (4000–200 cm^{-1}) were recorded from KBr pellets in a Nicolet 520 FTIR spectrophotometer. Magnetic measurements were carried out with a pendulum-type magnetometer (MANICS DSM8) equipped with an Oxford CF 1200 S helium continuous-flow cryostat working in the temperature range 300–4 K, and a Bruker B E15 electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables. Magnetization measurements were made in an MPMS (5.5 T) Quantum Design instrument (with SQUID detector).

X-Ray Data and Crystal Structure Determination.—A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Phillips PW-1100 diffractometer. Unit-cell parameters were determined from automatic centring of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: G = 10^{-4} T.

Table 1 Crystal data for [{NiL(SCN)(μ-SCN)}$_n$]

Formula	$C_9H_{19}N_5NiS_2$
Crystal system	Monoclinic
Space group	$P2_1/n$
M	320.12
a/Å	11.113(3)
b/Å	16.706(4)
c/Å	7.802(2)
β/°	106.94(3)
U/Å^3	1386(1)
Z	4
D_c/g cm^{-3}	1.534
μ(Mo-Kα)/cm^{-1}	16.71
λ(Mo-Kα)/Å	0.710 69
T/°C	25
Scan method	ω–2θ
No. of parameters refined	167
R^a	0.068
R'^b	0.073

^{a} $R(F_o) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. ^{b} $R'(F_o) = \Sigma w\|F_o| - |F_c\|/\Sigma w|F_o|$.

Table 2 Final atomic coordinates (×10^4, ×10^5 for Ni) for [{NiL(SCN)(μ-SCN)}$_n$]

Atom	X/a	Y/b	Z/c
Ni	19 530(7)	18 709(5)	20 939(11)
S(1)	5 073(2)	3 850(1)	4 988(3)
S(2)	1 513(2)	3 790(1)	−2 772(3)
N(1)	3 488(6)	2 551(4)	3 634(9)
N(2)	1 773(6)	2 749(4)	93(9)
N(3)	3 133(5)	1 257(4)	904(9)
N(4)	2 104(6)	933(4)	4 081(8)
N(5)	798(5)	2 586(4)	3 144(9)
C(1)	4 150(6)	3 085(5)	4 186(10)
C(2)	1 665(6)	3 182(5)	−1 111(10)
C(3)	3 147(10)	372(7)	809(16)
C(4)	3 355(10)	−9(6)	2 625(17)
C(5)	2 255(9)	120(6)	3 400(13)
C(6)	949(11)	863(7)	4 707(13)
C(7)	487(11)	1 629(7)	5 355(14)
C(8)	−127(8)	2 216(7)	3 886(14)
C(9)	3 198(9)	1 100(7)	5 663(12)

Table 3 Selected bond lengths (Å) and angles (°) for [{NiL(SCN)-(μ-SCN)}$_n$]

N(1)–Ni	2.109(7)	S(1′)–Ni	2.553(3)
N(2)–Ni	2.109(7)	C(1)–S(1)	1.643(8)
N(3)–Ni	2.084(6)	C(2)–S(2)	1.616(7)
N(4)–Ni	2.176(6)	C(1)–N(1)	1.158(9)
N(5)–Ni	2.088(6)	C(2)–N(2)	1.164(9)
N(2)–Ni–N(1)	86.2(3)	S(1′)–Ni–N(1)	174.4(1)
N(3)–Ni–N(1)	90.5(2)	S(1′)–Ni–N(2)	88.2(1)
N(3)–Ni–N(2)	87.1(3)	S(1′)–Ni–N(3)	89.1(1)
N(4)–Ni–N(1)	95.7(2)	S(1′)–Ni–N(4)	89.9(1)
N(4)–Ni–N(2)	177.9(2)	S(1′)–Ni–N(5)	92.4(1)
N(4)–Ni–N(3)	92.0(3)	Ni–S(1)I–C(1)	100.5(1)
N(5)–Ni–N(1)	87.5(2)	Ni–N(1)–C(1)	161.5(6)
N(5)–Ni–N(2)	87.5(3)	C(2)–N(2)–Ni	174.3(6)
N(5)–Ni–N(3)	174.3(3)	N(1)–C(1)–S(1)	179.1(7)
N(5)–Ni–N(4)	93.5(3)	N(2)–C(2)–S(2)	179.5(7)

25 reflections ($8 < \theta < 12°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo-Kα radiation, using the ω–2θ scan technique. 2147 Reflections were measured in the range $2 < \theta < 25°$, 1735 of which were assumed as observed applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; no significant intensity decay was observed. Lorentz–polarization but not absorption corrections were made. The crystallographic data, conditions used for the intensity data collection, and some features of the structure are listed in Table 1. The crystal structure was solved by Patterson synthesis using the SHELXS computer program,[13] and refined by full-matrix least-squares methods, using the SHELX 76 computer programs.[14] The function minimized was $\Sigma\|F_o| - |F_c\|^2$, where $w = [\sigma^2(F_o) + 0.0031|F_o|^2]^{-1}$; f, f' and f'' values were taken from ref. 15. The position of four H atoms was located from a difference synthesis. All the H atoms were refined with an overall isotropic thermal parameter, using a riding model for eleven of these. Maximum shift/e.s.d. = 0.1, maximum and minimum peaks in final difference synthesis were 0.3 and −0.3 e Å^{-3}, respectively. Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structure.—The structure of [{NiL(SCN)-(μ-SCN)}$_n$] consists of a chain in which two neighbouring nickel(II) ions are linked by one SCN^- bridging ligand. Owing to the presence of one SCN^- terminal ligand on each Ni^{II}, the chains are neutral and are linked in the crystal only by van der Waals forces, since there are no hydrogen bonds between the chains. The structure is shown in Fig. 1, and selected bond lengths and angles are given in Table 3. In the chain, each nickel atom is octahedrally co-ordinated in which the three N atoms of L and the N atom of the non-bridging thiocyanate group define an equatorial plane around the nickel atom. The bridging thiocyanates (S atom from one, N atom from the other) co-ordinate in *trans* axial positions to this plane. Consequently, we have the same structural scheme as that previously described in $-NiL-N_3-NiL-N_3$ chains.[1–3] The Ni–S–C and Ni–N–C angles in the bridge are 100.5(1) and 161.5(6)° respectively. The Ni–N(1) and Ni–S(1′) distances are 2.109(7) and 2.553(3) Å and the Ni···Ni separation is 6.15 Å. The torsion angle Ni-SCN-Ni, assuming that the SCN is linear, is 6.7°. The structure of [{NiL(SCN)(μ-SCN)}$_n$] differs from the previously characterized di-μ-thio- or di-μ-seleno-cyanato one-dimensional structures[5–8] in that each nickel atom is bridged by only *one* thiocyanato ligand to its neighbour with one thiocyanato ligand non-bridging. From the available structural data of polynuclear di-μ-thiocyanato nickel(II) complexes reported we can see that the bridging Ni–S–C angle is practically constant (100–101.4°) but that the bridging Ni–N–C angle varies more widely (159–168.9°). Bridging Ni–N and Ni–S distances are found in the range 1.99–2.109 and 2.553–2.625 Å respectively.

Infrared Spectroscopy.—The IR spectrum of [{NiL(SCN)-(μ-SCN)}$_n$] shows three bands in the region 2050–2150 cm^{-1}, which can be assigned according to Curtis[16] as: 2125vs [$\nu(CN)_{bridging}$], 2089vs and 2108vs cm^{-1} [$\nu(CN)_{terminal}$]. According to Curtis, the presence of a doublet in the 'terminal' thiocyanate region, as well as a band in the 'bridging' region, suggests that the two *N*-bonded thiocyanate ions are in a *cis* arrangement. The present structure confirms this hypothesis.

Magnetic Measurements.—The molar magnetic susceptibility *vs.* T of [{NiL(SCN)(μ-SCN)}$_n$] is plotted in Fig. 2. The $\chi_M T$ value is approximately constant (1.25 cm^3 K mol^{-1}) in the temperature range 300–60 K, but below 50 K it increases slightly, to reach a maximum of 1.40 cm^3 K mol^{-1} at 15 K. Below this maximum, $\chi_M T$ decreases slightly down to 4 K. This behaviour indicates a weak intramolecular ferromagnetic coupling and weak intermolecular antiferromagnetic coupling at low temperature. The experimental data were fitted in the interval 290–25 K by the empirical relation proposed by de Neef[17] for $S = 1$ ferromagnetic chains [equation (1)] where $\chi(0, D)$ and $\bar{\chi}(J, 0)$ are defined by equations (2) and (3).

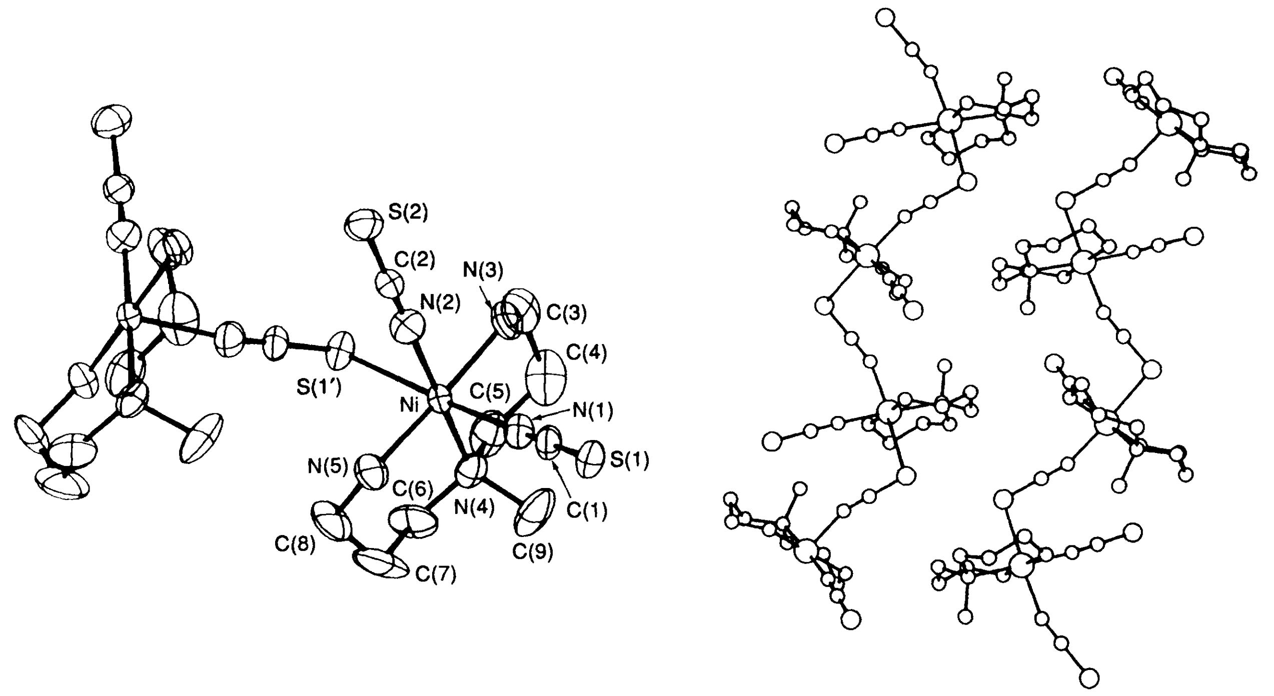

Fig. 1 Atom labelling scheme and cell packing for [{NiL(SCN)(μ-SCN)}$_n$]

$$\chi(J, D) = \chi(J, 0) + \chi(0, D) + (1/3kT)g^2\mu_B{}^2\Sigma_{i,j}b_{i,j}J^iD^j/\{(3kT)^{i+j}(i+j)!\} - 2g^2\mu_B{}^2/3kT \quad (1)$$

$$\chi(0, D) = 2g^2\mu_B{}^2/kT(2 + e^{-D/kT}) \quad (2)$$

$$\chi(J, 0) = g^2\mu_B{}^2\Sigma_{i>1}[d_iJ^{i-1}(kT)^i]/(3^ii!) \quad (3)$$

The numerical values of b_{ij} and d_i are given in ref. 17. As has been pointed out by Dupas and Renard [18] the uncertainty of the extrapolation given in the de Neef equation increases with decreasing temperature. Minimization of the agreement factor R leads to an intrachain coupling constant $J = 1.12$ cm^{-1}, $g = 2.16$ and $D = 1.72$ cm^{-1} with $R = 7.5 \times 10^{-5}$. On the other hand, the $z'J'$ parameter (magnetic interaction between the chains) was assumed to be negligible. It must be pointed out that, as usual in the fit of ferromagnetic systems data, both D and $z'J'$ values are correlated. Under these conditions attempts to determine the D values appear meaningless, at least in the high-temperature zone. In the low-temperature zone (decreasing χ_MT) it is impossible to use the de Neef formula owing to the antiferromagnetic intermolecular interactions. For this reason we have attempted to fit the experimental results without D and the values so obtained are $J = 1.16$ cm^{-1} and $g = 2.16$. In order to rationalize these results, magnetization isotherm measurements *vs.* applied field were carried out at 15 and 2 K up to 51 kG. The normalized plots of $M/N\beta$ *vs.* H/T at the two temperatures are shown in Fig. 3. Even at the highest field attained the complex was not fully saturated at 2 K ($M/N\beta = 1.88$). This behaviour can suggest large single-ion anisotropy.[9,19] For all these reasons, we can state that the value of J is actually very low, although the value of D could be different and higher than 0.1 cm^{-1}. At 15 K the complex follows Brillouin behaviour with $S > 1$ (1.10) owing to weak ferromagnetic interactions within the chain (Fig. 3). The g value of 2.16, is the same as obtained applying the de Neef formula assuming $D = 0$ in the high temperature region. At 2 K the magnetization measurements clearly separate from the Brillouin formula[20] (Fig. 3) assuming the same S and g values obtained at 15 K (paramagnetic regions). This fact may indicate a long-range antiferromagnetic order at low temperature (metamagnetism).

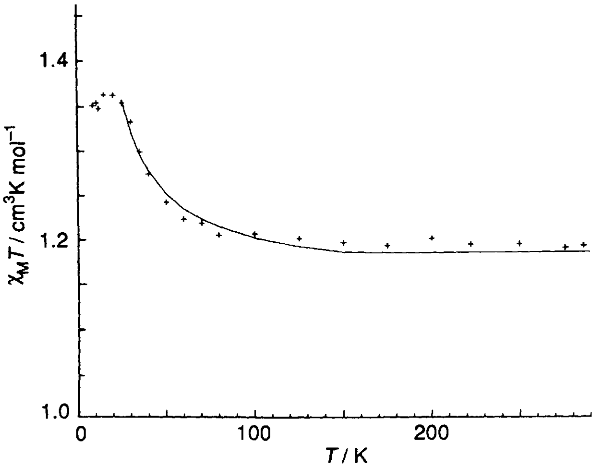

Fig. 2 Magnetic susceptibility plots of a polycrystalline sample of [{NiL(SCN)(μ-SCN)}$_n$]. The solid line shows the best fit with the de Neef equation (see text)

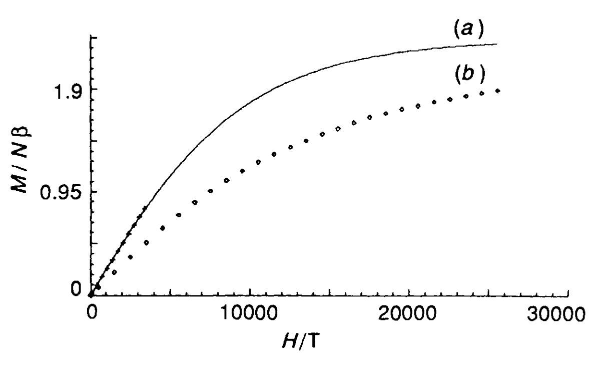

Fig. 3 Magnetization isotherms at 15 and 2 K up to 51 kG for [{NiL(SCN)(μ-SCN)}$_n$]. The solid line shows the best fit with the Brillouin formula (see text)

Finally, in order to clarify the ferromagnetic coupling found in [{NiL(SCN)(μ-SCN)}$_n$] extended-Hückel molecular orbital

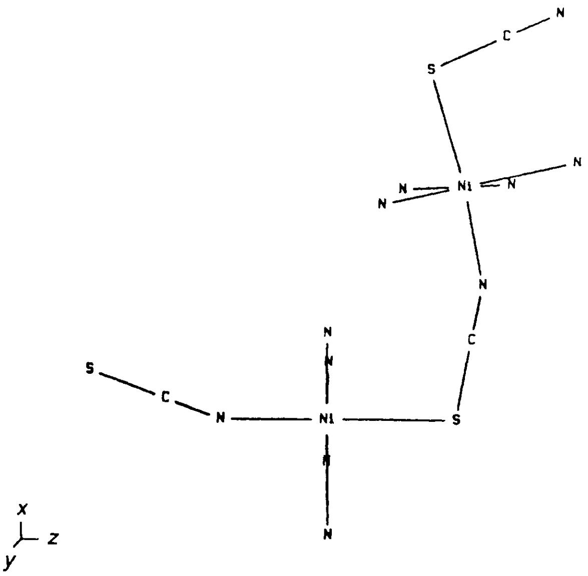

Fig. 4 Dimeric fragment model of $[\{NiL(SCN)(\mu\text{-}SCN)\}_n]$ used in extended-Hückel molecular orbital calculations

calculations were performed by means of the CACAO program,[21] on a dimeric fragment modelled as shown in Fig. 4 keeping bond distances and angles similar to those of the actual structure. Owing to the ferromagnetic behaviour for these geometries, accidental orthogonality should be found in the corresponding molecular orbitals. According to our calculations, the $xy + xy$ and $xy - xy$ combinations of the two nickel(II) ions are completely degenerate and the two $z^2 - z^2$, $z^2 + z^2$ combinations are almost of the same energy. Taking into consideration the qualitative character of the extended-Hückel calculations, these values do not have quantitative sense but can indicate that we have, as assumed, nearly orthogonal orbitals. The weak character of this ferromagnetism can be explained as due to the large volume of the thiocyanate anion. Indeed, according to the Kahn[22] theory, when we have extended bridging ligands (non-monoatomic) each magnetic orbital is delocalized over a large number of bridge atoms, the overlap density is spread over the whole bridge and the self-repulsion of this overlap density ($\propto j_F$) remains weak. On the other hand, if the molecular orbitals are not strictly orthogonal, J_{AF} can diminish the final ferromagnetic behaviour. Ginsberg *et al.*,[12] applying the Goodenough–Kanamori rules,[23] effectively showed for Ni–NCS and Ni–SCN angles of 180 and 90° respectively that strict orthogonality is achieved and the complexes should be ferromagnetic. The angles observed in this work are very close to these ideal values.

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