Synthesis, Crystal Structure and Magneto-Structural Correlation of an Unusual Thiocyanato-Bridged Nickel(II) Compound, $[Ni(\mu\text{-}NCS)(dpt)(NCS)]_2$-$[Ni(\mu\text{-}NCS)(dpt)(NCS)]_4$ [dpt = bis(3-aminopropyl)amine]

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Reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with bis(3-aminopropyl)amine (dpt) and ammonium thiocyanate produces the novel thiocyanato-bridged nickel(II) compound $[Ni(\mu\text{-}NCS)(dpt)(NCS)]_2[Ni(\mu\text{-}NCS)(dpt)(NCS)]_4$, which has been structurally characterised. The structure determination reveals that there are two different molecules in the crystal lattice; one is dinuclear and other is tetranuclear. Low-temperature magnetic measurements show that there are ferro- as well as antiferromagnetic interactions. The ferromagnetic interaction arises from the dinuclear part and the doubly bridged part of the tetranuclear unit; the antiferromagnetic interaction occurs between singly bridged nickel centres in the tetranuclear unit.

Introduction

In the last few years there has been a considerable amount work dedicated to the design and elaboration of polymetallic molecular systems with extended structures and electronic properties, mainly molecular-based magnets and inorganic materials.[1−5] The precondition for synthesising these type of materials is that the metal ions should have an unpaired electron and should be assembled in a molecule containing a bridging moiety that can propagate this electron between the paramagnetic metal centres. The pseudohalogens are very versatile ligands for making such a bridge. Amongst them, the versatility of the azido ligand as a superexchange pathway in polynuclear complexes of Cu^{II}, Ni^{II} and Mn^{II} has been well explored.[6−11] In contrast, thiocyanato-bridged polynuclear systems are not common.[12−15] Curtis et al.[16] have reported the synthesis of $[NiL(NCS)_2]$ [L = bis(2-aminoethyl)amine (dien) or bis(2-aminopropyl)amine (dpt)] and have proposed structures with one bridging thiocyanate and one N-bonded terminal thiocyanate in the *cis* position on the basis of IR spectroscopy. Vicente et al.,[12,14] however, have reported the structures and magnetic properties of two polymeric complexes, $[Ni(\mu\text{-}NCS)(L)(NCS)]_n$ [L = bis(2-aminoethyl)methylamine (medien) or bis(3-aminopropyl)methylamine (medpt)] and have observed noticeable differences in the structures upon increasing the chain length of the triamine.

Recently, our group has also reported[17−19] some novel thiocyanato-bridged nickel(II) complexes and noticed some remarkable phenomena, such as that the chain length of the linear chain triamine, the alkyl group substitution on the donor atom of the triamine and the method of preparation play a very important role when synthesising complexes with different nuclearities. Starting with $Ni(NCS)_2$ in methanol, dien gives a dimeric structure whereas aepn [(2-aminoethyl)(3-aminopropyl)amine] yields a polymeric structure.[17] On the other hand, the reaction of medpt with $Ni(NCS)_2$ in methanol gives two dimeric fragments in the unit cell,[18] while the reaction between $Ni(ClO_4)_2 \cdot 6H_2O$ and NH_4NCS generates a 1D polymeric complex.[14]

The present paper reports the synthesis, X-ray structure analysis and magneto-structural correlation of a novel thiocyanato-bridged nickel(II) compound $[Ni(\mu\text{-}NCS)(dpt)(NCS)]_2[Ni(\mu\text{-}NCS)(dpt)(NCS)]_4$. The structure determination reveals that this is a rare type of thiocyanato-bridged

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compound containing two different molecules in the crystal lattice: one is dinuclear and other is tetranuclear. Linear chain tetranuclear nickel(II) octahedral compounds are scarce in the literature.[20−21] Low-temperature magnetic measurements show that there are ferro- as well as antiferromagnetic interactions. The ferromagnetic interaction arises from the dinuclear part and the doubly bridged part of the tetranuclear unit; the antiferromagnetic interaction occurs between singly bridged nickel centres in the tetranuclear unit. To the best our knowledge this is the first report of a thiocyanato-bridged nickel(II) compound where ferro- as well as antiferromagnetic interactions are observed.

Results and Discussion

IR Spectroscopy

The compound shows two bands with medium intensity at $\tilde{\nu}$ = 3240, 3300 cm^{-1} corresponding to ν(N−H) and at $\tilde{\nu}$ = 2880, 2925 cm^{-1} assigned to the ν(C−H) stretching vibration of the triamine ligand. The occurrence of two strong peaks at 2080 and 2110 cm^{-1} in the IR spectrum, corresponding to ν(CN) stretching vibrations, suggests the presence of a bridging as well as a terminal linkage of the thiocyanate ligand. The higher frequency correlates to the bridging thiocyanate group whereas the lower frequency is assigned to a terminally bound thiocyanate ligand.[22]

Description of the Structure

The structure determination of the title complex reveals that there are two crystallographically independent molecules in the unit cell. One part of the complex is a dimer and other part is a tetramer (Figure 1). In the dimeric fragment two nickel atoms (Ni1 and its symmetry related counterpart) are bridged by two thiocyanate ligands in an end-to-end fashion; the other two thiocyanate groups exist as terminal ligands. The coordination polyhedron around the Ni1 atom in the dimeric fragment is best described as a distorted octahedron with an N_5S donor set. The three nitrogen atoms (N7, N8 and N9) from the triamine dpt ligand and one nitrogen atom (N1*; * =1 − *x*, 1 − *y*, 1 − *z*) from one of the bridging thiocyanate groups define the equatorial plane for Ni1 atom. The equatorial Ni1−N bond lengths are in the range 2.059(5)−2.114(4) Å (Table 1). The axial position is occupied by S1 [Ni1−S1, 2.577(2) Å] and N2 [Ni1−N2, 2.106(4) Å] from the bridging and terminal thiocyanate ligand, respectively. The Ni1 atom deviates from the mean plane by 0.008(2) Å and the maximum deviation of any equatorial atom (N1*) from the mean plane is 0.011(2) Å.

In the tetrameric part, the asymmetric unit comprises two nickel atoms (Ni2 and Ni3) with different coordination environments. The geometry around the Ni2 centre in the tetrameric part is distorted octahedral with an NiN_6 chromophore. The Ni2 atom is linked to Ni3 centre by only one bridging thiocyanate ligand. The other two terminal thiocy-

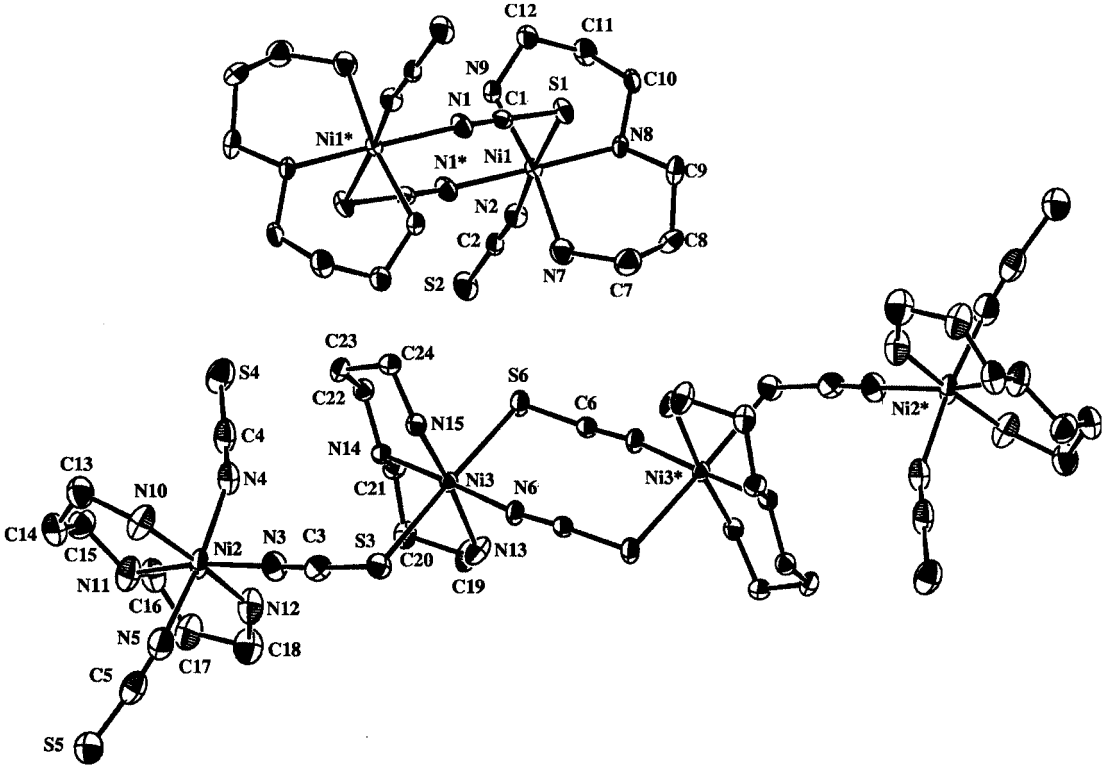


Figure 1. ZORTEP plot with atom labelling scheme of $[Ni(\mu_{N,S}\text{-NCS})(dpt)(NCS)]_2[Ni(\mu_{N,S}\text{-NCS})(dpt)(NCS)]_4$ (thermal ellipsoids are drawn at 50% probability for all non-hydrogen atoms)

Table 1. Selected bond lengths (Å) and angles (°) for [Ni(μ-NCS)(dpt)(NCS)]$_2$[Ni(μ-NCS)(dpt)(NCS)]$_4$

Ni1−S1	2.577(2)	Ni1−N2	2.106(4)
Ni1−N7	2.096(6)	Ni1−N8	2.114(4)
Ni1−N9	2.059(5)	Ni1−N1i[a]	2.105(4)
Ni2−N5	2.078(7)	Ni2−N10	2.075(7)
Ni2−N11	2.291(7)	Ni2−N12	2.022(7)
Ni2−N3	2.082(5)	Ni2−N4	2.133(6)
Ni3−N6	2.086(4)	Ni3−S3	2.667(2)
Ni3−S6	2.522(2)	Ni3−N15	2.062(4)
Ni3−N13	2.027(5)	Ni3−N14	2.117(4)
S1−Ni1−N2	175.66(11)	N3−Ni2−N4	89.9(2)
S1−Ni1−N7	90.49(15)	N3−Ni2−N11	168.3(2)
S1−Ni1−N8	87.45(12)	S3−Ni3−S6	175.62(5)
S1−Ni1−N9	90.94(13)	S3−Ni3−N6	83.70(11)
S1−Ni1−N1i[a]	92.46(13)	S6−Ni3−N13	96.12(15)
N2−Ni1−N7	88.85(19)	S6−Ni3−N14	88.83(11)
N2−Ni1−N8	88.32(15)	S6−Ni3−N15	92.90(11)
N2−Ni1−N9	90.35(18)	N6−Ni3−N13	85.97(19)
N1i−Ni1−N2[a]	91.79(16)	N6−Ni3−N14	178.26(18)
N7−Ni1−N8	94.45(19)	N6−Ni3−N15	88.66(17)
N7−Ni1−N9	171.31(18)	N13−Ni3−N14	92.55(19)
N1i−Ni1−N7[a]	86.52(19)	N13−Ni3−N15	169.67(18)
N8−Ni1−N9	94.18(16)	N14−Ni3−N15	92.66(17)
N1i−Ni1−N8[a]	179.02(19)	S3−Ni3−N14	95.28(11)
N1i−Ni1−N9[a]	84.85(16)	S3−Ni3−N15	85.43(11)
N3−Ni2−N12	88.8(2)	S3−Ni3−N13	85.21(15)
N4−Ni2−N5	173.7(3)	S6−Ni3−N6	92.22(11)
N4−Ni2−N10	92.1(2)	Ni1−S1−C1	102.54(18)
N4−Ni2−N11	91.9(2)	Ni3−S3−C3	104.5(2)
N4−Ni2−N12	89.6(3)	Ni3−S6−C6	102.24(19)
N5−Ni2−N10	83.7(3)	Ni1i−N1−C1[a]	163.7(4)
N5−Ni2−N11	84.0(3)	Ni1−N2−C2	165.2(3)
N5−Ni2−N12	94.4(3)	N10−Ni2−N11	96.5(2)
N10−Ni2−N12	175.9(3)	N11−Ni2−N12	79.7(3)
N3−Ni2−N5	95.1(2)	N3−Ni2−N10	95.0(2)
Ni2−N3−C3	176.5(5)	Ni2−N4−C4	155.8(6)
Ni2−N5−C5	161.9(7)	Ni3−N6−C6ii[a]	157.0(4)
S1−C1−N1	178.2(5)	S2−C2−N2	178.8(5)
S3−C3−N3	176.0(6)	S4−C4−N4	176.7(8)
S5−C5−N5	173.7(8)	S6−C6−N6	176.4(5)

[a] Symmetry code: i = 1 − x, 1 − y, 1 − z; ii = 3 − x, 2 − y, 1 − z.

anate groups are attached in a *cis* position to each other. The two nitrogen atoms (N4 and N5) [Ni2−N4, 2.133(6) Å; Ni2−N5, 2.078(7) Å] from the two pendent thiocyanate groups and other two nitrogen atoms (N10, N12) [Ni2−N10, 2.075(7) Å; Ni2−N12, 2.022(7) Å] (Table 1) form the equatorial plane around Ni2. One nitrogen atom (N3) [Ni2−N3, 2.082(5) Å] of the singly bridging thiocyanate ligand and a second nitrogen atom (N11) [Ni2−N11, 2.291(7) Å] of the triamine are in a *trans* axial position around Ni2. The maximum deviation of Ni2 from the mean plane formed by the four equatorial nitrogen atoms is 0.077(3) Å and the maximum deviation of any equatorial atom (N10) from the mean plane is 0.011(3) Å. In the case of Ni3 all the ligated thiocyanate groups are involved in bridging: two of them are attached to its symmetry related counterpart Ni3* and the other to Ni2. The coordination environment around Ni3 is pseudo-octahedral with an NiN_4S_2 chromophore. The two sulfur atoms (S6, S3) [Ni3−S6, 2.522(2) Å; Ni3−S3, 2.667(2) Å] from thiocyanate groups and N13 and N15 [Ni3−N13, 2.027(5) Å; Ni3−N15, 2.062(4) Å] (Table 1) from the triamine ligand define the equatorial plane around Ni3. The *trans* axial sites are occupied by N14 and N6 [Ni3−N14, 2.117(4) Å; Ni3−N6, 2.086(4) Å] of the triamine ligand and the bridging thiocyanate group, respectively. The maximum deviation of Ni3 from the mean plane formed by the four equatorial atoms is 0.088(2) Å and the maximum deviation of any equatorial atom (S3) from the mean plane is 0.005(2) Å.

The Ni−S−C, Ni−N−C and N−C−S angles in the bridge are 102.2(2)−104.5(3) Å, 157.0(4)−176.5(5) Å and 176.0(6)−178.2(5) Å, respectively. The Ni−N−C angle in the nonbridging thiocyanate group is 155.8(9)−166.9(5) Å. The Ni···Ni separation in the dimeric fragment is 5.736(9) Å and in the tetrameric fragment Ni2···Ni3 and Ni3···Ni3* are 5.998(2) and 5.682(3) Å, respectively. Weak intra- and intermolecular H-bonding (Table 2) results in a 1D supramolecular network lying on the *ab* plane (Figure 2). These H-bonding interactions are responsible for the overall conformation and stability of the crystal lattice.

Table 2. Hydrogen bonding interactions (Å,°) for [Ni(μ-NCS)(dpt)(NCS)]$_2$[Ni(μ-NCS)(dpt)(NCS)]$_4$

D−H···A[a]	D−H	H···A	D···A	D−H···A
N7−H7A···S6^{i}	0.90	2.865	3.696(6)	154.25
N15−H15A···S2^{ii}	0.90	2.711	3.500(6)	146.90

[a] Symmetry code: (i) =2 − x, 1 − y, 1 − z; (ii) = 3 − x, 1 − y, 1 − z.

Magnetic Measurements

Taking into account that there are two independent molecular entities — one dinuclear and the other tetranuclear — a plot of the magnetic data in the 200−2 K range is shown in Figure 3 as $\chi_M T$ vs. T for a molecular weight corresponding to six nickel(II) atoms. At 200 K, the $\chi_M T$ value is equal to 7.047 cm^3·mol^{-1}·K, a value that would be expected for six isolated nickel(II) ions with local S = 1 spins. $\chi_M T$ increases smoothly as T is lowered, reaching a maximum value of 7.35 cm^3·mol^{-1}·K at 22 K. From this temperature down to 2 K there is a clear and abrupt decrease of $\chi_M T$, reaching a minimum of 3.9147 cm^3·mol^{-1}·K at 2 K. These features are indicative of global weak ferromagnetic interactions between nickel(II) ions in the dinuclear and/or in the tetranuclear species present in the crystal, followed by a contribution of zero-field splitting, D, and antiferromagnetic coupling between the dinuclear and tetranuclear systems. Variable-temperature susceptibility data for a dinuclear moiety could be analysed using the isotropic Ginsberg [23] model from the Hamiltonian

$$H = -2JS_1S_2 - D(S_{1z}^2 + S_{2z}^2) - g\beta H(S_1 + S_2) - z'J'S\{S\}$$

where J is the intradimer exchange parameter, D the single-ion zero-field splitting and $z'J'$ the quantity for effective interdimer exchange; it is assumed that $g_x = g_y = g_z = g$. As previously indicated by Ginsberg, the parameters D and $z'J'$ are very strongly correlated with each other, but are

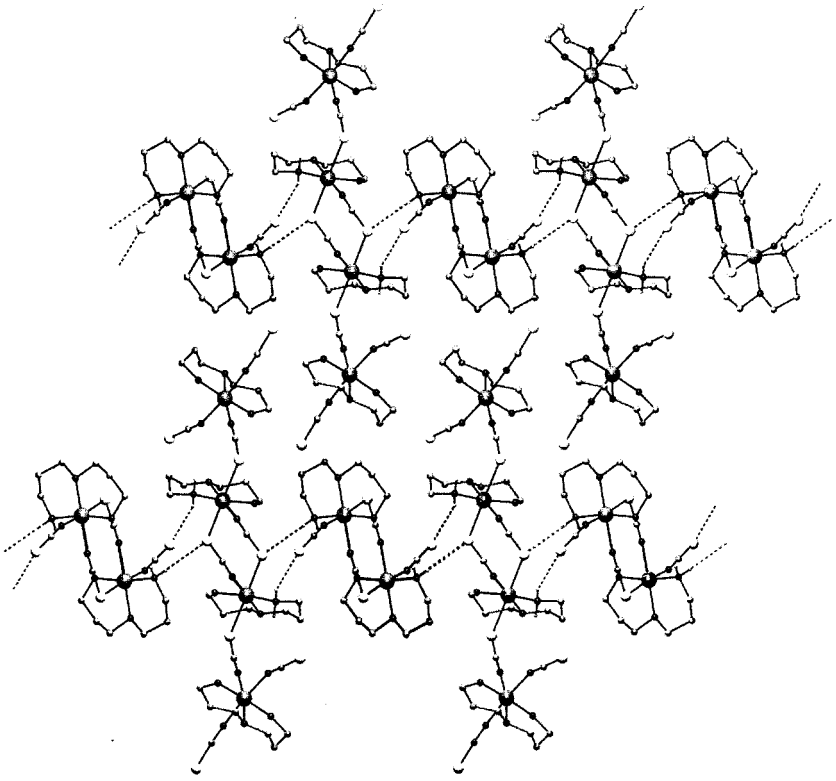


Figure 2. View of infinite one-dimensional H-bonded polymeric network of $[Ni(\mu_{N,S}\text{-}NCS)(dpt)(NCS)]_2[Ni(\mu_{N,S}\text{-}NCS)(dpt)(NCS)]_4$ (for clarity only relevant hydrogen atoms are shown)

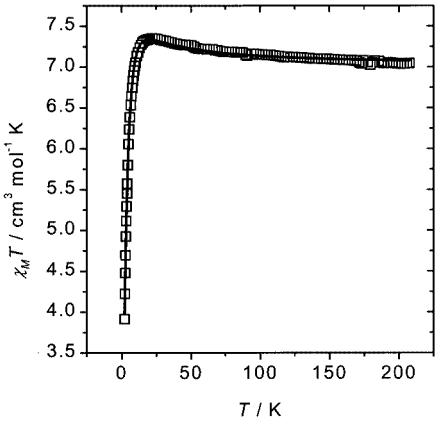
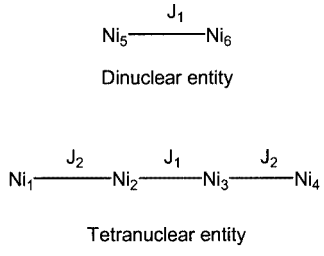


Figure 3. $\chi_M T$ vs. T plot for $[Ni(\mu_{N,S}\text{-}NCS)(dpt)(NCS)]_2[Ni(\mu_{N,S}\text{-}NCS)(dpt)(NCS)]_4$ [considering a molecular weight of 1836.58 corresponding to six nickel(II) centres]; the solid line corresponds to the best fit

The spin-Hamiltonian for all these tetranuclear nickel(II) complexes can easily be solved applying Kambe's method,[29] although for the linear systems a full diagonalization method is required and, seemingly, has never used for this kind of complex. The topological spin-scheme for this system is represented in Scheme 1.



Scheme 1

only weakly correlated with g and J, therefore it is impossible to calculate D and $z'J'$ values accurately. Unfortunately, there is no mathematical expression which allows a fit of the tetranuclear part. The tetranuclear nickel(II) complexes reported in the literature are either planar, rhomboidal, cubanes or have square (cyclic) cores;[24−27] one zig-zag tetranuclear nickel(II) complex is known where two terminal nickel(II) atoms are in a square-planar geometry and thus show a diamagnetic behaviour.[28]

In this scheme, taking into account the structure, we assume that the coupling constants between the nickel(II) ions in the dinuclear entity (Ni1−Ni1*) and the central part (Ni3−Ni3*) of the tetranuclear entity (J_1) are the same. In both these cases, the two nickel(II) ions are linked by two thiocyanate bridges, although the terminal nickel(II) ions are linked to the central ones by only a thiocyanate bridge in the tetranuclear entity. Following this scheme, the ther-

mal variation of the $\chi_M T$ product was analysed using the following anisotropic Hamiltonian:

$$H = -2J_1(S_2S_3 + S_5S_6) - 2J_2(S_1S_2 + S_3S_4) + D(S_{1z}^2 + S_{2z}^2 + S_{3z}^2 + S_{4z}^2 + S_{5z}^2 + S_{6z}^2)$$

This Hamiltonian takes into account the interactions of one tetramer unit and one dimer unit at the same time. In order to remove the over-parametrization we have assumed some simplifications. Firstly, both exchange pathways through two end-to-end thiocyanate bridging ligands are associated to the same parameter, J_1, and secondly all single-ion parameters are identical (all single-ion anisotropies, D_i, are equal and collinear and all nickel(II) atoms have the same isotropic g value).

Evaluation of the susceptibility curve was performed with the MAGPACK programs package.[30−31] This efficient computing program allows the solution of the full spin-Hamiltonian by a numerical procedure and the calculation of the magnetic properties of spin clusters of arbitrary nuclearity, topology and anisotropy. Least-squares fitting of the magnetic data was accomplished with an adapted version of the function-minimization program MINUIT.[32] Using this conditions the best set of parameters is the following: $J_1 = +2.73$ cm^{-1}, $J_2 = -1.27$ cm^{-1}, $D = 3.12$ cm^{-1} and $g = 2.16$ ($R = 3.1 \times 10^{-3}$).

Magneto-Structural Correlations

The number of nickel(II) complexes with one or two bridging thiocyanate ligands is very limited. The magnetic data and the main structural parameters of these complexes, along with the title complex, are gathered in Tables 3 and 4. The J values found for the two systems with double end-to-end bridging thiocyanate ligand agree perfectly with those reported in the literature for the same kind of linkage. As can be seen from Table 3 the structural parameters are also very similar. However, the single thiocyanate bridging ligand in the tetrameric entity causes an antiferromagnetic coupling, while the other three complexes reported so far are ferromagnetically coupled. Comparing Tables 3 and 4 it is easy to realize that when there are two bridging thiocyanate ligands, J is always positive and greater than the values reported when there is only one thiocyanate ligand. On the other hand, the Ni−S−C and Ni−N−C angles are very different in the tetrameric entity from the other three complexes (Table 4). It has been postulated that these angles are the most important features for the character of the exchange coupling constant;[33] the Ni2−N3−S3−Ni3 torsion angle is −4.8°. It has been reported that, with the very similar OCN^- ligand, the effect of this torsion angle is similar to that reported for the azido bridging ligand: the maximum of the antiferromagnetic component corresponds to a torsion of 180° (or 0°), with a value close to zero for $J_{antiferro}$ (accidental orthogonality) for a torsion angle of 90°.[33] According to this idea, it is not surprising to find that other metal complexes with end-to-end bridging thiocyanate ligands show antiferromagnetic coupling. The $2J$ value for a dinuclear copper(II) complex is −148.2 cm^{-1},[34] and for some similar manganese(II) complexes the J values are −0.15 cm^{-1} and −2.5 cm^{-1}.[35−36]

New efforts are necessary for synthesising new complexes with this kind of structure in order to analyze their magnetic properties. This goal will not be easy, though, because there is a spontaneous tendency for four nickel(II) ions to give cubane-like or square-planar complexes.[24−27]

Table 3. Main structural and magnetic parameters for dinuclear nickel(II) complexes with double thiocyanate bridging bond

Compound[a]	Ni−S−C (°)	Ni−N−C (°)	Ni−N (Å)	Ni−S (Å)	J (cm^{-1})	Ref.
$[Ni_2(tren)_2(\mu\text{-}NCS)_2](BPh_4)_2$	100.0	167	2.04	2.61	2.4	[43]
$[Ni_2(terpy)(NCS)_2(\mu\text{-}NCS)_2]$	100.0(8)	159(2)	1.99	2.62	4.9	[44]
$[Ni_2(ibn)_3(NCS)_2(\mu\text{-}NCS)_2]$	100.7	165.2	2.06	2.55	4.3	[45]
	105.8	142.4	2.10	2.64		
$[Ni_2(ibn)_4(\mu\text{-}NCS)_2](PF_6)_2$	96.2	166.7	1.92	2.83	6.3	[45]
$[Ni_2(en)_4(\mu\text{-}NCS)_2]I_2$	100.0	167.0	2.04	2.61	4.5	[46,47]
dinuclear entity (*)	102.54	163.74	2.11	2.57	2.73	[b]
tetranuclear entity (*)	102.24	157.00	2.08	2.66	2.73	[b]

[a] (tren = 2,2′,2′′-triaminotriethylamine; terpy = 2,2′:6′,2′′-terpyridine; ibn = 1,2-diamino-2-methylpropane; en = 1,2-diaminoethane). [b] This work.

Table 4. Main structural and magnetic parameters for polymeric and polynuclear nickel(II) complexes with single thiocyanate bridging bond

Compound[a]	Ni−S−C(°)	Ni−N−C(°)	Ni−N (Å)	Ni−S(Å)	J (cm^{-1})	Ref.
$[Ni(medien)(NCS)(\mu\text{-}NCS)]_n$	100.24	167.5	2.04	2.66	0.96	[12]
$[Ni(en)_2(\mu\text{-}NCS)]_n(PF_6)_n$	100.8	171.5	2.10	2.62	0.2	[13]
$[Ni(medpt)(NCS)(\mu\text{-}NCS)]_n$	100.5	161.5	2.11	2.55	1.16	[14]
Tetranuclear entity	104.50	176.50	2.08	2.66	−1.27	[b]

[a] medien = bis(2-aminoethyl)methylamine; en = 1,2-diaminoethane; medpt = bis(3-aminopropyl)methylamine. [b] This work.

Experimental Section

Materials: High purity (98%) bis(3-aminopropyl)amine (dpt) was purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals used were of AR grade.

Physical Measurements: Elemental analysis (C, H and N) was performed using a Perkin−Elmer 240C elemental analyser. IR spectra (4000−400 cm^{-1}) were taken using Nicolet Magna-IR 750 spectrometer series-II. Variable temperature (2−208 K) magnetic susceptibility measurements on polycrystalline sample was carried out with a Quantum Design SQUID magnetometer. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants.

Synthesis of [Ni(μ-NCS)(dpt)(NCS)]$_2$[Ni(μ-NCS)(dpt)(NCS)]$_4$: A methanolic solution (5 mL) of dpt (1 mmol) was added to an aqueous solution (15 mL) of $Ni(ClO_4)_2·6H_2O$ (1 mmol). Solid NH_4SCN (2 mmol) was then added slowly with constant stirring. The resulting solution was kept in a $CaCl_2$ desiccator and after a few days a blue crystalline complex separated out. This was dissolved in ethanol and filtered and the filtrate was kept in an open atmosphere. After some days blue single crystals suitable for X-ray diffraction were obtained. Yield ca. 80%. $C_8H_{17}N_5NiS_2$ (306.1): calcd. C 31.40, N 22.89, H 5.56, Ni 19.18; found C 31.40, N 22.88, H 5.54, Ni 19.20. IR: ν(NH_2), 3240, 3300 cm^{-1}; ν(CH_2), 2880, 2925 cm^{-1}; ν(CN), 2080, 2120 cm^{-1}.

Reaction Scheme:

$6Ni(ClO_4)_2·6H_2O + 12NH_4SCN + 6dpt = [Ni(μ\text{-}NCS)(dpt)(NCS)]_2[Ni(μ\text{-}NCS)(dpt)(NCS)]_4 + 12NH_4ClO_4 + 36H_2O$

Crystal-Data Collection and Refinement: A suitable single crystal of the title complex was mounted on a Rigaku AFC 7 diffractometer. The unit cell parameters and crystal orientation matrix were determined by least square refinement of 25 accurately centred reflections. Intensity data were collected in the ω-2θ scan mode using graphite-monochromated Mo-$K_α$ radiation. The crystal and instrument stabilities were monitored with a set of three standard reflections measured at a regular interval; in all cases no significant variations were found. The intensity data were corrected for Lorentz and polarisation effects[37] and an empirical absorption correction based on ψ-scans (T_{min}/T_{max} 0.678/0.968) was also employed. A total of 5865 reflections ($2.1 < θ < 27.5°$) were measured and all of them were assumed observed applying the condition $I > 2σ(I)$. The structure was solved by a Patterson synthesis and followed by successive Fourier and difference-Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97, with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in fixed calculated positions. At convergence the final residuals were $R = 0.045$; $wR = 0.122$. The final difference Fourier map showed a maximum and minimum peak height of 0.54 e·Å^{-3} and −0.39 e·Å^{-3} respectively, with no chemical significance. Complex neutral atom scattering factors[38] were used throughout. All calculations were carried out using the SHELXS-86,[39] SHELXL-97,[40] PLATON 99[41] and ZORTEP[42] programs. Crystal data are summarised in Table 5. Selected bond lengths and angles are listed in Table 1. Possible hydrogen bonds are displayed in Table 2.

Table 5. Crystal data and details of the structure determination for [Ni(μ-NCS)(dpt)(NCS)]$_2$[Ni(μ-NCS)(dpt)(NCS)]$_4$

Chemical formula	$C_{24}H_{51}N_{15}S_6Ni_3$
Molecular weight	918.29
T (K)	293(2)
λ (Å) (Mo-$K_α$)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	7.680(10)
b (Å)	15.134(2)
c	18.719(4)
α (°)	70.550(10)
β (°)	81.540(10)
γ (°)	87.280(10)
V (Å^3)	2029.2(6)
Z	1
$ρ_{cal}$ (mg m^{-3})	1.503
μ (mm^{-1}) (Mo-$K_α$)	1.725
F(000)	960
Crystal size (mm)	0.50 × 0.40 × 0.20
θ range (°)	2.1−27.5
Reflections collected	5865
Reflections observed [$I > 2σ(I)$]	5865
$R(F)$[a]	0.0445
$wR(2)$	0.1221

[a] $R = ||F_o| - |F_c||/|F_o|$; $Rw = [\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]^{1/2}$.

CCDC-180314 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] *Magnetic Molecular Materials* (Eds.: D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio), NATO ASI Series, No. E198; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1991**.
[2] O. Kahn, *Adv. Inorg. Chem.* **1995**, *43*, 179−259.
[3] J. S. Miller, A. J. Epstein, W. M. Reiff, *Science* **1988**, *240*, 40−47.
[4] D. Gatteschi, *Adv. Mater.* **1994**, *6*, 635−645.
[5] *Magnetism: A Supramolecular Function* (Ed.: O. Kahn), NATO ASI Series, No. C484; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1996**.
[6] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezema, T. Rojo, *Coord. Chem. Rev.* **1999**, *193−195*, 1027.
[7] L. K. Thompson, S. S. Tandon, *Comments Inorg. Chem.* **1996**, *18*, 125−144.
[8] P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. Ray Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147−5150.
[9] T. K. Maji, P. S. Mukherjee, G. Mostafa, T. Mallah, J. Cano-Boquera, N. Ray Chaudhuri, *Chem. Commun.* **2001**, 1012.
[10] F. A. Mautner, R. Cortes, L. Lezema, T. Rojo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 96−98.
[11] J. Ribas, M. Monfort, R. Costa, X. Solans, *Inorg. Chem.* **1993**, *32*, 695−699.
[12] A. Escuer, S. B. Kumar, F. Mautner, R. Vicente, *Inorg. Chim. Acta* **1998**, *269*, 313−316.
[13] M. Monfort, C. Bastos, C. Diaz, J. Ribas, *Inorg. Chim. Acta* **1994**, *218*, 185−188.
[14] R. Vicente, A. Escuer, J. Ribas, X. Solans, *J. Chem. Soc., Dalton Trans.* **1994**, 259.
[15] R. Vicente, A. Escuer, E. Peñalba, X. Solans, M. Font-Bardía, *Inorg. Chim. Acta* **1997**, *255*, 7−12.
[16] N. F. Curtis, Y. M. Curtis, *Aust. J. Chem.* **1966**, *19*, 1423−1430.
[17] A. Mondal, C. Pariya, N. Ray Chaudhuri, N. P. Nayak, A. K. Mukherjee, A. Ghosh, *Polyhedron* **1997**, *16*, 39−45.

[18] A. K. Mukherjee, N. P. Nayak, A. Mondal, N. Ray Chaudhuri, *Acta Crystallogr., Sect. C* **1999**, *55*, 365−368.
[19] N. P. Nayak, A. K. Mukherjee, A. Mondal, N. Ray Chaudhuri, *Acta Crystallogr., Sect. C* **1998**, *54*, 208−210.
[20] S. Y Lai, T. W. Lin, Y. H. Chen, C. C. Wang, G. H. Lee, M.H. Yang, M. K. Leung, S. M. Peng, *J. Am. Chem. Soc.* **1999**, *121*, 250−251.
[21] S. Uozumi, H. Furutachi, M. Ohba, H. Okawa, D. E. Fenton, K. Shindo, S. Murata, D. J. Kitko, *Inorg. Chem.* **1998**, *37*, 6281−6287.
[22] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, p 271−275, Wiley- Interscience, New York, **1978**.
[23] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **1972**, *11*, 2884−2891.
[24] K. S. Murray, *Adv. Inorg. Chem.* **1995**, *43*, 261−358 and references therein.
[25] M. A. Halcrow, J-S. Sun, J. C. Huffman, G. Christou, *Inorg. Chem.* **1995**, *34*, 4167−4177.
[26] C. S. Campos-Fernández, R. Clérac, K. R. Dunbar, *Angew. Chem. Int. Ed.* **1999**, *38*, 3477−3479.
[27] C. J. Matthews, K. Avery, Z. Xu, L. K. Thompson, L. Zhao, D. O. Miller, K. Biradha, K. Poirier, M. J. Zaworotko, C. Wilson, A. E. Goeta, J. A. K. Howard, *Inorg. Chem.* **1999**, *38*, 5266−5276.
[28] M. Mikuriya, K. Nakadera, T. Kotera, *Chem. Lett.* **1993**, 637.
[29] K. Kambe, *J. Phys. Soc. Jpn.* **1950**, *5*, 48−51.
[30] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, *Inorg. Chem.* **1999**, *38*, 6081−6088.
[31] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, S. Tsukerblat, *J. Comput. Chem.* **2001**, *22*, 985−991.
[32] F. James and M. Roos, *MINUIT Program, a System for Function-Minimization and Analysis of the Parameter Errors and Correlations Comput. Phys. Commun.* **1975**, *10*, 345.
[33] A. Escuer, R. Vicente, M. S. El Fallah, X. Solans, M. Font-Bardía, *J. Chem. Soc., Dalton Trans.* **1996**, 1013.
[34] J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quirós, E. R. T. Tiekink, *Inorg. Chem.* **1997**, *36*, 4988−4991.
[35] E. J. Laskowski, D. N. Hendrickson, *Inorg. Chem.* **1978**, *17*, 457−470.
[36] B. W. Dockum, G. A. Eisman, E. H. Witten, W. M. Reiff, *Inorg. Chem.* **1983**, *22*, 150−156.
[37] A. C. T. North, D. C. Philips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1986**, *24*, 351.
[38] *International Tables for Crystallography*, Vol. C., Tables 4.2.6.8 and 6.1.1.4, **1992**.
[39] G. M. Sheldrick, SHELXS-86, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany, **1986**.
[40] G. M. Sheldrick, SHELXL-97, *Program for the Solution of Crystal Structure*, University of Gottingen, Germany,**1997**.
[41] A. L. Spek, PLATON99, *Molecular Geometry Program*, **1999**, University of Utrecht, The Netherlands.
[42] L. Zsolani, ZORTEP. *A Program for the Presentation of Thermal Ellipsoids*, University Heidelberg, Germany, **1994**.
[43] D. M. Duggan, D. N. Hendrickson, *Inorg. Chem.* **1974**, *13*, 2929−2940.
[44] T. Rojo, R. Cortés, L. Lezama, M. I. Arriortua, K. Urtiaga, G. Villeneuve, *J. Chem. Soc., Dalton Trans.* **1991**, 1779.
[45] M. Monfort, J. Ribas, X. Solans, *Inorg. Chem.* **1994**, *33*, 4271.
[46] A. P. Ginsberg, R. C. Sherwood, R. W. Brookes, R. L Martin, *J. Am. Chem. Soc.* **1971**, *93*, 5927−5928.
[47] A. E. Shvelasvili, M. A. Porai-Koshity, A. S. Antsyshkins, *J. Struct. Chem. (Engl. Transl.)* **1969**, *10*, 552−557.

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