Note

Crystal structure and magnetic properties of the first 1D nickel(II) complex with bridging thiocyanato ligands in *cis* position: {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$)

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Abstract

The $\mu_{N,S}$-thiocyanato nickel(II) monodimensional complex, {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) where en = ethylenediamine, has been synthesized and characterized. The crystal structure of this 1D complex has been solved by Patterson synthesis and refined by full-matrix least-squares method to a discrepancy factor of 0.046. {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) is the first structurally reported nickel(II) chain in which the neighboring nickel(II) ions are linked by thiocyanato bridging ligands in a *cis* geometry. The Ni(II) atoms present a distorted octahedral geometry. Magnetic susceptibility data, measured from 300 to 4 K show weak ferromagnetic behavior. These data were fitted to the de Neef equation, giving the parameters $J = 0.2$ cm^{-1}, $g = 2.19$ and $D = -1.8$ cm^{-1}.

Key words: Crystal structures; Magnetism; Nickel complexes; Thiocyanato complexes

Introduction

In recent papers we have reported the synthesis, crystal structure and magnetic properties of several monodimensional nickel(II) compounds bridged by end-to-end azido ligands: *catena*-($\mu_{1,3}$-N$_3$)$_3$[Ni$_2$(dpt)$_2$](ClO$_4$), an alternating chain [1], and *catena*-($\mu_{1,3}$-N$_3$)[Ni(cyclam)](ClO$_4$), a homogeneous chain [2], which served as a model for the synthesis of a series of new antiferromagnetically coupled Ni(II) chains [3]. Other potentially similar bridging ligands which may allow the synthesis and study of nickel(II) chains are the pseudohalide cyanate or thiocyanate anions. For the cyanato ligand, the first nickel(II) cyanato chain has recently been synthesized in our laboratory [4]. Focusing our attention on the thiocyanate anion, structural data for several monodimensional di-μ-thiocyanato nickel(II) compounds have been reported but without magnetic studies [5–8]. In contrast, [Ni(bipy)(NCS)$_2$] reported as an infinite-chain ferromagnetic insulator has been exhaustively studied from a magnetic point of view but structural data are not available [9]. Some structural examples of di-μ-thiocyanato nickel(II) dinuclear complexes have also been described in the literature [10–14]. All these systems are ferromagnetically coupled. The first 1D nickel(II) system with only one thiocyanato bridge in *trans* position has recently been synthesized in our laboratory [15], exhibiting a weak ferromagnetic coupling. We now present the synthesis and magnetism of another kind of 1D complex of Ni(II), {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$), also with only one thiocyanato bridge, but the consecutive thiocyanates present *cis* geometry. Magnetic measurements show that {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) is weakly ferromagnetically coupled, in contrast with the antiferromagnetism found in the similar monodimensional nickel(II) complexes bridged by azido ligands in *cis* geometry [16, 17].

Experimental

Synthesis of {catena-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$)

An aqueous solution of ethylenediamine (0.120 g, 1 mmol) was gently added to an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O (0.290 g, 2 mmol). To this solution, solid KNCS (0.097 g, 1 mmol) was added with constant stirring. No precipitate was formed. Solid KPF$_6$ (0.185 g, 1 mmol) was added with constant stirring, and the solution was allowed to stand for several days. Good purple crystals were obtained by this slow evaporation.

X-ray crystallography of {catena-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$)

A prismatic crystal (0.1×0.1×0.2) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \leq \theta \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. The structure was solved by Pat-

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terson synthesis, using the SHELXS computer program [18] and refined by full-matrix least-squares method with the SHELX76 computer program [19]. The positions of all hydrogen atoms were computed and refined with an overall isotropic temperature factor, using a riding model. Crystallographic data are given in Table 1. Final atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, respectively. The final R and R_w values were 0.046 and 0.053, respectively. Number of reflections measured: 1742 (total) and 1499 (observed). Number of parameters refined: 217.

TABLE 1. Crystallographic data for {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$)

Formula	$C_5H_{16}F_6N_5NiPS$
Formula weight	381.95
Temperature (K)	298
Space group	$Pbn2_1$
a (Å)	13.382(2)
b (Å)	13.011(2)
c (Å)	8.125(1)
V (Å^3)	1414.7(6)
Z	4
λ(Mo Kα) (Å)	0.71069
D_{calc} (g cm^{-3})	1.793
μ(Mo Kα) (cm^{-1})	16.89
R^a	0.046
R_w^b	0.053

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

TABLE 2. Final atomic coordinates (×10000) of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) (Ni and S×100000)

	x/a	y/b	z/c	B_{eq}^{a}
Ni	11250(5)	11680(5)	0	2.62(3)
S	10488(13)	−8408(14)	−2134(23)	3.42(6)
P	3181(2)	−1146(1)	4785(3)	4.03(8)
N(1)	290(5)	1086(5)	2188(8)	3.70(26)
N(2)	2094(6)	1153(5)	−2055(10)	4.12(28)
N(3)	2482(5)	1040(5)	1292(11)	3.50(28)
N(4)	1107(4)	2796(4)	114(11)	3.74(22)
N(5)	−195(5)	1384(5)	−1288(9)	3.86(26)
C(1)	248(6)	−984(5)	−1749(9)	3.16(25)
C(2)	3096(8)	1341(7)	−1491(16)	5.56(47)
C(3)	3265(6)	773(7)	137(17)	5.46(38)
C(4)	71(7)	3108(6)	−253(14)	4.95(37)
C(5)	−344(7)	2479(6)	−1653(15)	5.01(37)
F(1)	2699(23)	−1278(24)	3018(31)	4.74(63)
F(2)	3292(22)	64(12)	4603(25)	9.12(108)
F(2)′	2189(14)	−1089(37)	−4326(25)	15.30(200)
F(3)	3770(20)	−2164(17)	4970(46)	9.91(129)
F(3)′	2827(46)	−2205(25)	5123(50)	21.72(302)
F(4)	3850(22)	−703(29)	6344(53)	12.46(208)
F(4)′	3536(19)	−1016(17)	6579(20)	6.76(93)
F(5)	3975(24)	−616(28)	3695(37)	11.73(185)
F(5)′	4192(14)	−1442(42)	4063(49)	14.28(230)
F(6)	2368(16)	−324(14)	4905(23)	8.36(87)
F(6)′	2599(31)	−1561(34)	3237(44)	9.04(188)

$^aB_{eq} = 8\pi^2/3U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$

TABLE 3. Selected bond lengths and angles for {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$)

S–Ni	2.621(2)	N(4)–Ni	2.120(5)
N(1)–Ni	2.102(6)	N(5)–Ni	2.072(6)
N(2)–Ni	2.114(7)	C(1)–S	1.656(7)
N(3)–Ni	2.104(6)	C(1)*–N(1)	1.132(14)
N(1)–Ni–S	89.1(2)		
N(2)–Ni–S	87.8(2)		
N(2)–Ni–N(1)	173.3(3)		
N(3)–Ni–S	89.3(2)		
N(3)–Ni–N(1)	91.9(3)		
N(3)–Ni–N(2)	82.2(3)		
N(4)–Ni–S	176.9(2)		
N(4)–Ni–N(1)	90.5(3)		
N(4)–Ni–N(2)	92.9(3)		
N(4)–Ni–N(3)	93.8(3)		
N(5)–Ni–S	93.9(2)		
N(5)–Ni–N(1)	88.9(3)		
N(5)–Ni–N(2)	97.2(3)		
N(5)–Ni–N(3)	176.7(3)		
N(5)–Ni–N(4)	83.0(2)		
C(1)–S–Ni	100.8(2)		
Ni–N(1)–C(1)*	171.5(3)		
S–C(1)–N(1)*	179.1(4)		

Physical measurements

Magnetic measurements were carried out with a pendulum-type magnetometer MANICS-DSM8, equipped with a TBT continuous-flow helium cryostat working in the temperature range 300–4 K, and a Bruker electromagnet. The instrument was calibrated by a magnetization measurement of a standard ferrite. Diamagnetic corrections were estimated from Pascal Tables.

Results and discussion

The molecular structure of the complex {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) together with the atom labelling scheme, is shown in Fig. 1, and the view of the crystal packing, down the c axis is shown in Fig. 2. The structure of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) consists of helicoidal chains parallel to the c axis, each chain is surrounded by four others. PF_6^- ions occupy interchain sites located between the closest chains. In each chain two neighboring Ni(II) ions are linked by one NCS^- bridging ligand. Consecutive thiocyanato bridging ligands are in a *cis* arrangement: this is the first chain in which the thiocyanate ion takes this configuration. In the chain, each nickel(II) is octahedrally coordinated by four N atoms of two ethylenediamine ligands, one N atom of one bridging thiocyanato ligand and one S atom of the other bridging thiocyanato ligand in *cis*

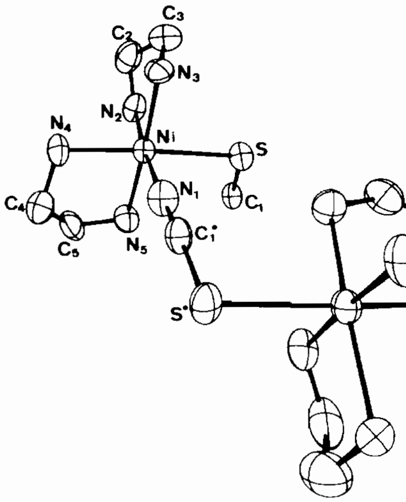

Fig. 1. Structure of the cationic part of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) and the atom labelling scheme.

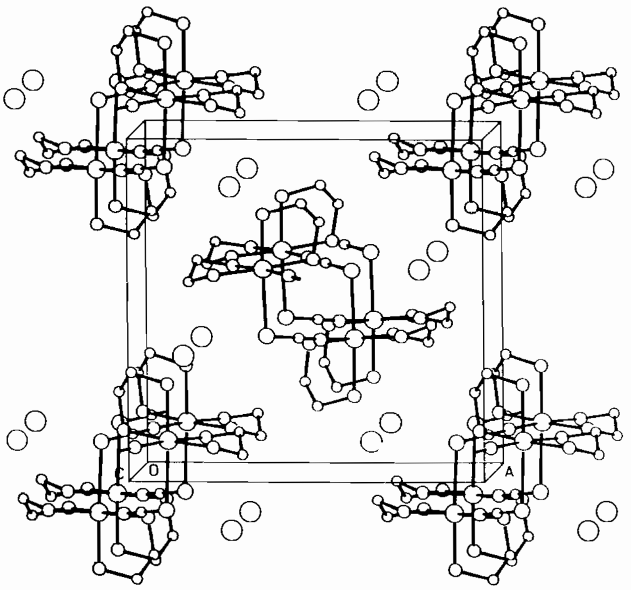

Fig. 2. View of the crystal packing, down the *c* axis of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$). PF$_6^-$ ions are shown by a sphere.

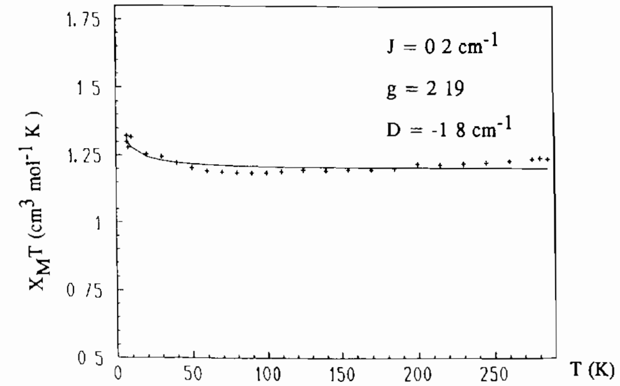

Fig. 3. Magnetic susceptibility plot of a polycrystalline sample of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$). $\chi_M T$ in cm^3 mol^{-1} K. Solid line shows the best fit with the de Neef equation.

position to the former NCS ligand. The Ni-S-C and Ni-N-C angles in the bridge are 100.8 and 171.5°, respectively. The Ni-N(1) and Ni-S distances are 2.102 and 2.621 Å, respectively. From the ensemble of structural data of the polynuclear di-μ-thiocyanato Ni(II) complexes reported [5–8, 10–14] we can see that the bridging Ni-S-C angle is practically constant (100–101.4°) and the bridging Ni-N-C angle varies over a wide range (159–169°). The bridging Ni-N and Ni-S distances are found in the range 1.99–2.11 and 2.55–2.63 Å, respectively.

The $\chi_M T$ versus T of {*catena*-($\mu_{N,S}$-NCS)[Ni(en)$_2$]}(PF$_6$) is plotted in Fig. 3. The $\chi_M T$ value is approximately constant (1.25 cm^3 mol^{-1} K) in the range 300–60 K, but below 50 K it increases slightly to reach a maximum of 1.33 cm^3 mol^{-1} K at 4 K. This behavior indicates a weak intramolecular ferromagnetic coupling. The experimental data were fitted by the empirical relation proposed by de Neef [20] for the $S=1$ ferromagnetic chains. The minimization of the agreement factor R leads to the following parameters: $J=0.2$ cm^{-1}, $g=2.19$ and $D=-1.83$ cm^{-1}. As indicated by de Neef, at low temperature there is uncertainty in the fitted parameters. It must be pointed out that in ferromagnetic systems [21] the D parameter and the possible intermolecular $z'J'$ interaction are strongly correlated. In the de Neef formula these intermolecular interactions are not considered. Consequently in these conditions attempts to determine the D value accurately appear difficult. For this reason we have applied the same de Neef formula assuming $D=0$: the magnetic parameters do not show significant variations ($J=0.16$ cm^{-1}, $g=2.19$). This result (weak ferromagnetic coupling in the new 1D system) agrees with those previously reported [10, 12, 13] for this kind of polynuclear nickel(II) complex, in which the thiocyanato bridging ligand always creates weak ferromagnetic coupling.

Supplementary material

Tables of anisotropic thermal parameters, all interatomic bond distances and angles and final hydrogen coordinates are available from the authors on request.

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