

Short Communication

Crystal Structure of $[\text{Ni}(\text{CTH})(\text{NCS})_2]$ with Linearly and Nonlinearly Coordinated Isothiocyanate Groups

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One of the main challenges in the field of magnetic molecular materials is the design and synthesis of molecular-based ferromagnets. A useful strategy for achieving such ferromagnets has been to build tridimensional (3D) poly-metallic systems in which all the interactions between nearest neighbours are ferromagnetic.¹ A good example of this is the bimetallic $\text{Cr}^{\text{III}}-\text{Ni}^{\text{II}}$ polymer reported by Verdaguer *et al.*, in which the orthogonality of the magnetic orbitals centred on Cr^{III} and Ni^{II} ions gives rise to ferromagnetic interaction.² In an attempt to prepare 3D heterobimetallic Ni–Cr compounds of this type, we have used the complexes $[\text{Cr}(\text{NCS})_6]\text{K}_3$ as precursor and $[\text{Ni}(\text{CTH})(\text{ClO}_4)_2]$ with *meso*-CTH as counterpart (CTH = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclo-tetradecane). The former contains six potential donor atoms for other metal ions, whereas in the latter the Ni^{II} ion has two empty axial coordination sites. However, when we allowed water solutions of $[\text{Cr}(\text{NCS})_6]\text{K}_3$ and $[\text{Ni}(\text{CTH})(\text{ClO}_4)_2]$ to react by slow diffusion, we obtained pink crystals of a compound with empirical formula $[\text{Ni}(\text{CTH})(\text{NCS})_2]$. This paper deals with the synthesis and crystal structure of this new complex, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclo-tetradecane-*N,N',N'',N'''*-*trans*-bis(isothiocyanato-*N*)nickel(III).

Results and discussion

The structure contains two discrete, non-equivalent monomeric $[\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)(\text{NCS})_2]$ units (Fig. 1). In both units the metal ion occupies the inversion centre and has a distorted octahedral NiN_6 environment, with Ni–N distances 2.081(6)–2.139(6) Å (Fig. 2). Four N atoms of the macrocyclic CTH ligands are chelated to the nickel(II)

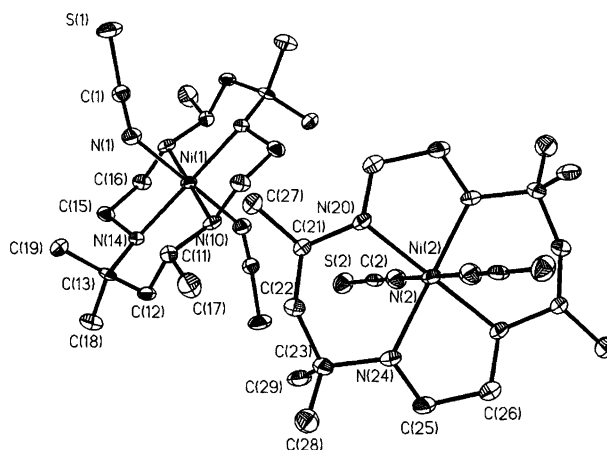


Fig. 1. Structural view and numbering scheme for $[\text{Ni}(\text{CTH})(\text{NCS})_2]$.

atom in a planar NiN_4 arrangement, and the octahedral coordination is completed by the N atoms of two NCS^- ions in *trans* position. The two $[\text{Ni}(\text{CTH})]^{2+}$ moieties are closely similar: the corresponding Ni–N distances and N–Ni–N angles are almost identical, bond lengths and

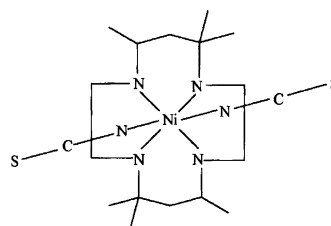


Fig. 2.

Table 1. Crystal data and structure determination summary for [Ni(CTH)(NCS)₂].

Compound	[Ni(CTH)(NCS) ₂]
Formula	C ₁₈ H ₃₆ N ₆ NiS ₂
Formula mass	459.36
Space group	<i>P</i> 1 (No. 2)
Wavelength, (MoK α)/Å	0.71073
Crystal system	Triclinic
Temperature/K	193(2)
<i>a</i> /Å	8.049(2)
<i>b</i> /Å	9.134(2)
<i>c</i> /Å	15.488(3)
α /°	94.22(3)
β /°	97.53(3)
γ /°	92.97(3)
<i>V</i> /Å ³	1123.6(4)
<i>Z</i>	2
<i>F</i> (000)	492
<i>D</i> _c /g cm ⁻³	1.358
μ /cm ⁻¹	10.65
Crystal size/mm	0.15 × 0.12 × 0.10
Scan mode	$\omega/2\theta$
θ_{\max} /°	26.50
Weights	$[\sigma^2(F_o^2) + (0.0991P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$
No. of independent reflections	3878
No. of observed reflections	2279 [$F > 4\sigma(F)$]
No. of variables	250
<i>R</i>	7.59
<i>wR</i>	17.49

angles in the CTH ligands are not markedly different, the five-membered chelate rings assume a *gauche* conformation and the six-membered rings adopt a *chair* conformation.

The two independent isothiocyanate ions are practically linear, and bond lengths of the ions do not differ significantly. However, there is a difference in the axial orientation of the *trans*-isothiocyanato-*N* ions. In unit **2** the NCS–Ni–NCS arrangement is almost linear and perpendicular to the NiN₄ plane, with an Ni(2)–N(2)–C(2) angle of 174.5(6)°, whereas in unit **1** the Ni(1)–N(1)–C(1) angle is 143.1(6)° and the whole NCS⁻ is bent away from the axial position, thus avoiding close contact with the surrounding molecules. There are no contact distances shorter than 3.5 Å between NCS⁻ ions and the non-H atoms of neighbouring molecules. Thus NCS⁻ ions do not participate in intermolecular hydrogen-bond formation, and the monomers are bound together only by van der Waals forces.

A difference in inclination of the two NCS groups has been observed previously in this type of complex. The complex [Ni(*as*-Et₂en)₂(NCS)₂]³ (where *as*-Et₂en is *N,N*-diethylethylenediamine), which also contains two non-equivalent monomeric units, exhibits Ni–N–CS angles of 162.8(2) and 171.3(3)°. Likewise, in [Ni(L³)(NCS)₂]⁴ (with L³ standing for 1,4,8,11-tetraazacyclotetradecane), the inclination of the NCS groups ranges from 156 to 168° for the four crystallographically independent molecules. In these cases, the difference in the Ni–N–CS angles may be a consequence of intermolecular interactions. However, in our case, where there are no close

Table 2. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters (in Å² × 10³) for [Ni(CTH)(NCS)₂].

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq)
Ni(1)	5000	5000	0	26(1)
Ni(2)	5000	10000	5000	30(1)
S(1)	1985(3)	8000(3)	-1843(2)	57(1)
S(2)	7149(3)	6117(2)	3167(1)	45(1)
N(1)	2869(8)	5798(7)	-756(4)	40(2)
N(2)	6095(8)	8375(7)	4243(4)	39(2)
N(10)	4110(7)	5557(6)	1176(4)	33(1)
N(14)	4043(7)	2788(6)	-111(4)	28(1)
N(20)	3235(7)	10368(7)	3944(4)	35(1)
N(24)	3422(7)	8479(7)	5521(4)	36(1)
C(1)	2467(9)	6680(8)	-1215(5)	35(2)
C(2)	6562(9)	7457(8)	3798(5)	32(2)
C(11)	2476(8)	4810(8)	1260(5)	33(2)
C(12)	2611(9)	3152(8)	1181(4)	33(2)
C(13)	2506(9)	2331(7)	276(5)	30(2)
C(15)	4112(9)	2218(7)	-1021(5)	34(2)
C(16)	5817(7)	2818(6)	-1286(4)	37(2)
C(17)	1898(7)	5286(6)	2127(4)	56(2)
C(18)	2526(10)	680(9)	417(5)	48(2)
C(19)	917(9)	2635(9)	-315(5)	41(2)
C(21)	2160(9)	9058(8)	3571(4)	33(2)
C(22)	1176(9)	8451(8)	4265(5)	38(2)
C(23)	2026(9)	7522(8)	4970(5)	36(2)
C(25)	4562(9)	7721(8)	6157(5)	41(2)
C(26)	5803(10)	8875(9)	6669(5)	49(2)
C(27)	926(10)	9406(9)	2791(5)	46(2)
C(28)	715(9)	7085(9)	5538(5)	46(2)
C(29)	2683(10)	6146(8)	4552(5)	44(2)

contacts between molecules, the source of the difference is not apparent.

In the title compound with *meso*-CTH and in [Cu(ClO₄)(μ -L)Ni(CTH)](ClO₄)·H₂O with *rac*-CTH (H₂L is α,ω -bis((1,3-dimethyl-5-nitrosouracil-6-yl)amino)propane),⁵ the macrocycle acts as a tetradentate ligand in an octahedral environment; however, the geometry of the ligand differs in the two compounds. As mentioned above, in the title compound the four coordinating N atoms of CTH in **1** and **2** are exactly in the plane owing to symmetry, leading to a *trans* occupation of thiocyanates.

Table 3. Bond lengths (in Å) for [Ni(CTH)(NCS)₂].^a

Ni(1)–N(10)	2.082(5)	N(20)–C(26) ²	1.487(9)
Ni(1)–N(14)	2.111(5)	N(24)–C(25)	1.490(9)
Ni(1)–N(1)	2.139(6)	N(24)–C(23)	1.514(9)
Ni(2)–N(20)	2.081(6)	C(11)–C(17)	1.519(8)
Ni(2)–N(24)	2.109(6)	C(11)–C(12)	1.521(9)
Ni(2)–N(2)	2.123(6)	C(12)–C(13)	1.530(9)
S(1)–C(1)	1.635(8)	C(13)–C(19)	1.523(10)
S(2)–C(2)	1.637(8)	C(13)–C(18)	1.539(9)
N(1)–C(1)	1.145(9)	C(15)–C(16)	1.567(8)
N(2)–C(2)	1.156(9)	C(21)–C(27)	1.523(10)
N(10)–C(11)	1.475(9)	C(21)–C(22)	1.534(10)
N(10)–C(16) ¹	1.479(8)	C(22)–C(23)	1.544(10)
N(14)–C(15)	1.474(8)	C(23)–C(28)	1.516(10)
N(14)–C(13)	1.498(8)	C(23)–C(29)	1.522(10)
N(20)–C(21)	1.475(9)	C(25)–C(26)	1.516(10)

^a Symmetry transformations used to generate equivalent atoms: ¹ $-x+1, -y+1, -z$; ² $-x+1, -y+2, -z+1$.

Table 4. Bond angles (in °) for [Ni(CTH)(NCS)₂].^a

N(10)–Ni(1)–N(14)	95.2(2)	C(15)–N(14)–Ni(1)	106.4(4)	N(14)–C(13)–C(18)	109.0(5)
N(10)–Ni(1)–N(14) ¹	84.8(2)	C(13)–N(14)–Ni(1)	121.8(4)	C(19)–C(13)–C(18)	110.1(6)
N(10)–Ni(1)–N(1) ¹	87.2(2)	C(21)–N(20)–C(26) ²	116.3(6)	C(12)–C(13)–C(18)	106.8(6)
N(14)–Ni(1)–N(1) ¹	84.6(2)	C(21)–N(20)–Ni(20)	114.6(4)	N(14)–C(15)–C(16)	107.7(5)
N(10)–Ni(1)–N(1)	92.8(2)	C(26) ² –N(20)–Ni(2)	105.4(4)	N(10) ¹ –C(16)–C(15)	108.3(5)
N(14)–Ni(1)–N(1)	95.4(2)	C(25)–N(24)–C(23)	116.3(6)	N(20)–C(21)–C(27)	111.5(6)
N(20)–Ni(2)–N(24) ²	85.1(2)	C(25)–N(24)–Ni(2)	105.1(4)	N(20)–C(21)–C(22)	110.4(6)
N(20)–Ni(2)–N(24)	94.9(2)	C(23)–N(24)–Ni(2)	123.4(4)	C(27)–C(21)–C(22)	109.0(6)
N(20)–Ni(2)–N(2)	91.8(2)	N(1)–C(1)–S(1)	176.7(7)	C(21)–C(22)–C(23)	120.9(6)
N(24)–Ni(2)–N(2)	94.6(2)	N(2)–C(1)–S(2)	177.6(7)	N(24)–C(23)–C(28)	109.2(6)
N(20)–Ni(2)–N(2) ²	88.2(2)	N(10)–C(11)–C(17)	111.1(5)	N(24)–C(23)–C(29)	111.7(6)
N(24)–Ni(2)–N(2) ²	85.4(2)	N(10)–C(11)–C(12)	109.8(5)	C(28)–C(23)–C(29)	109.5(6)
C(1)–N(1)–Ni(1)	143.1(6)	C(17)–C(11)–C(12)	109.9(6)	N(24)–C(23)–C(22)	108.0(6)
C(2)–N(2)–Ni(2)	174.5(6)	C(11)–C(12)–C(13)	119.7(6)	C(28)–C(23)–C(22)	107.5(6)
C(11)–N(10)–C(16) ¹	115.6(5)	N(14)–C(13)–C(19)	111.0(6)	C(29)–C(23)–C(22)	110.7(6)
C(11)–N(10)–Ni(1)	114.1(4)	N(14)–C(13)–C(12)	107.9(5)	N(24)–C(25)–C(26)	107.9(6)
C(16) ¹ –N(10)–Ni(1)	106.5(4)	C(19)–C(13)–C(12)	111.8(6)	N(20) ² –C(26)–C(25)	109.4(6)
C(15)–N(14)–C(13)	116.4(5)				

^a See Table 3.

In the reference compound, one of the N atoms of the macrocycle is out of the plane of the other three, offering a *cis* position for the fifth and sixth coordinating atoms. This also leads to a larger diversity in Ni–N(CTH) bond lengths, e.g. from 2.077(5) to 2.169(6) Å.

Experimental

Synthesis and analyses. [Cr(NCS)₆]K₃ and [Ni(CTH)]-(ClO₄)₂ were prepared by literature methods.^{6,7} Crystals of [Ni(CTH)(NCS)₂] were obtained by slow diffusion of a water solution of [Cr(NCS)₆]K₃ (0.3 mmol, 0.155 g) into a water solution of [Ni(CTH)](ClO₄)₂ (1 mmol, 0.54 g). The crystals were filtered off and air-dried. Calc. for C₁₈H₃₆N₆NiS₂: C, 47.1; H, 7.9; N, 18.3; Ni, 12.8; S, 14.0%. Anal. Found: C, 46.7; H, 8.3; N, 17.8; Ni, 12.9; S, 13.7%.

Crystallography. A light-pink crystal of dimensions 0.15 × 0.12 × 0.10 mm was selected for data collection at 193(2) K with a Rigaku AFC7S diffractometer using monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined from a least-squares fit of the setting angles of 21 reflections with 2θ in the range 7–20°. A total of 4113 reflections (3878 independent) were recorded in the range $5 < 2\theta < 53^\circ$. The intensities of three check reflections monitored every 200 reflections showed only a statistical variation, of $\pm 2\%$. The data were corrected for Lorentz and polarization effects and for absorption ($0.63 < T < 1.00$) using ψ -scan methods.⁸ The structure was solved by direct methods⁹

and refined on F^2 by a full-matrix least-squares technique.¹⁰ In the final refinement, all non-H atoms were anisotropically refined and H atoms isotropically refined. All hydrogen atoms were placed in calculated positions. The displacement parameters of H-atoms were $1.5 \times$ that of the host atom. In the final refinement of 3865 reflections the data converged at $R = 0.076$ [$F > 4\sigma(F)$]. Crystal parameters and refinement results are summarized in Table 1, while atomic coordinates, bond lengths and angles are listed in Tables 2–4.

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