A new 1D bimetallic thiocyanate bridged Copper (II) Cobalt (II) compound

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The crystal structure of the first one-dimensional heterometallic compound containing thiocyanate as bridging ligands $\{[\text{Cu}(\text{cyclam})][\text{Co}(\text{NCS})_4]\}_n$, has been determined, together with a preliminary study of the magnetic properties.

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In recent years, the field of molecular magnetism has attracted considerable attention, both for theoretical reasons, and with a view to developing new materials for magneto-optic devices [1]. In particular, special attention has been paid to the design and construction of one-dimensional, metal ion containing molecular compounds (both homo and heterometallic) in order to undertake theoretical studies of their magnetic properties [2]. The design of such materials requires appropriate components, such as suitable bridging ligands between the magnetic centres. The thiocyanate ligand, with the ambidentate ability of its “end-to-end” coordination mode, seems to play an important role in the design of extended one-[3][4][5], two- [6] and three-dimensional [3][7] copper(II) compounds with specific magnetic properties. Other extended homometallic compounds, in which the metals are bridged by the thiocyanate ligand, include nickel(II) [8], manganese(II) [9] and cobalt(II) derivatives [10]. However, there is no information in the literature about infinite heterometallic copper(II) containing networks with thiocyanate as a bridging ligand. Only recently the crystal structures and magnetic properties of tetranuclear heterometallic compounds have been reported [11], but no compounds of higher dimensionality are known. In this preliminary communication, we report the synthesis, crystal structure and magnetic properties of the first bimetallic cobalt(II)-copper(II) one-dimensional complex **1**. Compound **1** was prepared by carefully adding 40 ml of a 1:1 CH₃CN/EtOH solution containing cyclam (1.53 mmol) and Cu(ClO₄)₂ · 6H₂O (1.53 mmol) to 10 ml of an alcoholic solution (1.53.10⁻² M) of K₂[Co(NCS)₄] (1.53 mmol) [12]. The solution was left in air to evaporate and deep-blue single-crystals appeared after several days[†]. The infrared spectrum[‡] of **1** exhibits two bands

[†] *Anal.* Calc. for C₁₄H₂₄N₈S₄CoCu : C, 30.29; H, 4.36; N, 20.18. Found : C, 29.60; H, 4.40; N, 19.75.

[‡] The infra-red spectrum was recorded on a Bio-Rad IR.FT spectrophotometer, in the 4000 - 250 cm⁻¹ range, using pressed KBr pellets containing 1% in mass of the sample.

in the region near 2000 cm^{-1} (2107 and 2073 cm^{-1}), which correspond to the ν_{as} (NCS) stretching mode, resulting from a combination of four effects: (i) the presence of bridging thiocyanate ligands (Co-NCS-Cu); (ii) the presence of non-bridging thiocyanate ligands (Co-NCS); (iii) the distorted octahedral copper(II) environment and (iv) the tetrahedral environment of cobalt(II). It is therefore difficult to assign unambiguously both bands, in accordance with earlier discussions in the literature [13].

The molecular structure[§] of **1** is presented in Fig. 1 with an ORTEP view of the molecule, together with the atomic labeling scheme, while Fig. 2 shows the one-dimensional character of the compound, and especially the coordination geometry around the metallic ions. Each copper(II) atom is bound to two sulphur atoms from thiocyanate ligands which are also coordinated to cobalt(II) ions. These sulphur atoms lie in the axial positions of a deformed octahedron around the copper(II), the equatorial plane being filled with the four nitrogen atoms of the cyclam ligand. The cobalt(II) atom possesses two bridging and two non-bridging thiocyanate ligands, each attached to the metal by the nitrogen atom, giving rise to a deformed tetrahedral environment around the cobalt(II) centre. Both molecular building blocks possess two points of connectivity; as such, they assemble as a 1:1 complex consisting

[§] Crystal data for **1** : $\text{C}_{14}\text{H}_{24}\text{N}_8\text{S}_4\text{CoCu}$, $M = 555.12 \text{ g mol}^{-1}$, monoclinic, space group $P 2_1/c$, $a = 8.568(2) \text{ \AA}$, $b = 14.463(3) \text{ \AA}$, $c = 18.562(4) \text{ \AA}$, $\beta = 96.62(3)^\circ$, $V = 2284.8(9) \text{ \AA}^3$, $Z = 4$, $D_c = 1.614 \text{ Mg/m}^3$, $\mu = 2.040 \text{ mm}^{-1}$, $T = 296(2) \text{ K}$. Of 5845 reflections collected [Enraf-Nonius CAD-4, MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$)], 5488 unique reflections were used for the Patterson interpretation routine of SHELXS-97 [G.M. Sheldrick, *Acta Cryst.*, **A46** (1990) 467.]. Refinement was carried out using full-matrix least-squares techniques, with SHELXL-97 [G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen : Göttingen, Germany, 1997]. Hydrogen atomic positions were calculated at

of an infinite helical bimetallic chain running along the *b*-axis, in which the copper(II) and cobalt (II) atoms alternate, as shown in Fig. 2.

Figures 1 and 2

Bond lengths in the planar cyclam ligand and Cu-N distances (see Table 3 in supplementary material) are in accordance with the ones found in the literature for similar copper(II) complexes [14]. The Cu-S axial distances are equal to 2.891(3) Å and 3.160(3) Å respectively for Cu-S(1) and Cu-S(2). These distances are close to the ones found in other complexes in which the sulphur atoms adopt the axial positions of a distorted octahedron around copper(II) [15]. The S(1)-Cu-S(2) angle is equal to 169.96(12)°. The Co-N distances are in agreement with those found in the literature for other cobalt(II) thiocyanato complexes [16]. The thiocyanato groups are almost linear with a mean value of the N-C-S angles of 178.8(4)°. The Co-N-C linkages are bent with angles varying from 169.7(3)° to 172.5(3)°. These structural features have already been observed in other thiocyanato-containing metal complexes [17]. The S-C average distance of 1.625(13) Å and C-N average distance of 1.145 (9) Å, are in accordance with the values given in the literature [18].

The CoCo, CuCu and CoCu distances within the chain are equal to 7.619 (3) Å, 10.254 (3) Å and 6.909 (3) Å respectively. The CoCo, CuCu and CoCu distances between the chains are equal to 7.701 (3) Å, 7.472 (3) Å and 6.361 (2) Å respectively. The chains are aligned parallel with respect to each other in the crystal structure.

Magnetic susceptibility data on the polycrystalline sample were collected with a MPMS Quantum Design SQUID magnetometer in the temperature range of 260 – 1.7 K at a field of 1000 G. The sample holder was a quartz tube. The data were corrected for the experimentally determined diamagnetism of the sample holder, whilst the diamagnetic contribution from the

distances of 0.93 Å and were fixed by using a riding model in the refinement. R = 0.0465

sample was calculated from Pascal's constants. The magnetic behaviour is presented in Fig. 3. The room temperature $\chi_M T$ value ($1.95 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), is slightly lower than the value expected for isolated copper(II) and cobalt(II) ions ($2.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, assuming $g = 2$ for copper(II) and cobalt(II)). Upon cooling from room temperature, the $\chi_M T$ values decrease slowly until 30 K and sharply below 15 K. This feature could be explained by a weak antiferromagnetic interaction between the metallic centres probably together with an antiferromagnetic coupling between the chains. This must be confirmed by the fit of the experimental data to an adapted law. Because of non-compensation of spins of copper(II) ($S = \boxed{}\frac{1}{2}$) and cobalt(II) ($S = \boxed{}\frac{1}{2}$) and from a physical point of view, the compound is expected to behave as a ferrimagnetic chain at temperatures below 1K. Further magnetic measurements at very low temperatures ($T < 1 \text{ K}$) should allow us to confirm this behaviour.

Figure 3

The experimental susceptibility data were analysed by an expression derived by Drillon *et al.* [19] which is valid for bimetallic alternating ferrimagnetic chains with quantum-classical spins. This expression is derived for $S = \boxed{}\frac{1}{2}$ quantum spins like the spin of Copper (II), alternating with a classical spin, spin of Cobalt (II) in our case :

$$\boxed{} \quad (1)$$

with $\boxed{}$

where N_A is the Avogadro constant, β is the Bohr magneton, k_B is the Boltzmann constant, and J is the exchange coupling constant. The best fit gave a g value of 2.42 (1) for cobalt(II)

and $R'(\text{all data}) = 0.1436$ with 346 parameters.

and 2.12 (1) for copper(II), and a J value of -1.48 (3) cm^{-1} (coefficient of determination $r^2 = 0.9996$), as indicated by the solid curve in Fig. 3. Attempt to introduce the mean field theory in this equation, in order to determine the interaction between the chains, failed.

This very weak character of the antiferromagnetic interaction is due to intrinsic structural features and especially to the large distance between the copper (II) and cobalt (II) centres which leads to a poor overlap of the magnetic orbitals.

In conclusion, this work presents the synthesis, crystal structure and preliminary magnetic characterisation of the first bimetallic chain containing thiocyanate as bridging ligands. The weak antiferromagnetic interaction observed between the magnetic centres could finally reveal a heterometallic ferrimagnetic chain at low temperatures.

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Figure Captions

Figure 1 ORTEP drawing of the $[\text{Cu}(\text{cyclam})][\text{Co}(\text{NCS})_4]$ molecules. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary size.

Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Cu—N(8) 2.004(3), Cu—N(1) 2.014(3), Cu—N(4) 2.020(3), Cu—N(11) 2.025(3), Cu—S(1) 2.891(3), Cu—S(2) 3.160(3), Co—N(21) 1.951(4), Co—N(41) 1.951(4), Co—N(31) 1.955(3), Co—N(22) 1.976(3), S(1)—C(21) 1.625(4), C(21)—N(21) 1.152(5), S(2)—C(22) 1.634(4), C(22)—N(22) 1.141(5), S(3)—C(31) 1.625(4), C(31)—N(31) 1.155(5), S(4)—C(41) 1.612(5), N(1)—C(2) 1.479(5), N(1)—C(14) 1.488(5), C(2)—C(3) 1.491(7), C(3)—N(4) 1.480(5), C(41)—N(41) 1.138(6), N(4)—C(5) 1.486(5), C(5)—C(6) 1.498(7), C(6)—C(7) 1.514(7), C(7)—N(8) 1.476(5), N(8)—C(9) 1.491(5), C(9)—C(10) 1.482(6), C(10)—N(11) 1.478(5), N(11)—C(12) 1.480(5), C(12)—C(13) 1.509(7), C(13)—C(14) 1.504(7).

N(8)—Cu—N(1) 177.18(13), N(1)—C(2)—C(3) 107.9(3), N(8)—Cu—N(4) 94.31(13), N(4)—C(3)—C(2) 108.8(4), N(1)—Cu—N(4) 85.57(13), N(41)—C(41)—S(4) 178.5(5), N(8)—Cu—N(11) 85.88(12), C(31)—N(31)—Co 172.5(3), N(1)—Cu—N(11) 94.10(13), C(3)—N(4)—C(5) 113.2(3), N(4)—Cu—N(11) 177.11(14), C(3)—N(4)—Cu 107.2(3), S(1)—Cu—S(2) 169.96 (12), C(5)—N(4)—Cu 117.6(3), N(21)—Co—N(41) 114.1(2), N(4)—C(5)—C(6) 111.7(4), N(21)—Co—N(31) 107.9(2), C(5)—C(6)—C(7) 115.2(4), N(41)—Co—N(31) 105.8(2), N(8)—C(7)—C(6) 111.3(3), N(21)—Co—N(22) 109.8(2), C(7)—N(8)—C(9) 113.0(3), N(41)—Co—N(22) 103.8(2), C(7)—N(8)—Cu 117.9(2), N(31)—Co—N(22) 115.44(14), C(9)—N(8)—Cu 107.6(2), N(21)—C(21)—S(1) 179.3(3), C(10)—C(9)—N(8) 108.6(3), C(21)—N(21)—Co, 171.8(3), N(11)—C(10)—C(9), 108.7(3), N(22)—C(22)—S(2) 178.7(4), C(12)—N(11)—C(10) 113.2(3), C(22)—N(22)—Co 169.7(3), C(12)—N(11)—Cu 117.7(3), N(31)—C(31)—S(3) 178.8(4), C(10)—N(11)—Cu 105.9(2), C(31)—N(31)—Co 172.5(3), N(11)—C(12)—C(13) 111.9(4), C(2)—N(1)—C(14) 113.2(3), C(12)—C(13)—C(14) 114.7(4), C(2)—N(1)—Cu 106.9(3), N(1)—C(14)—C(13) 111.9(3), C(14)—N(1)—Cu 117.3(3).

Figure 2 A perspective view of the chain of $\{[\text{Cu}(\text{cyclam})][\text{Co}(\text{NCS})_4]\}_n$, running along the b -axis. Black ions indicate cobalt(II) atoms and grey ions indicate copper(II) atoms.

Figure 3 Thermal dependence of the molar susceptibility χ_M for $\{[\text{Cu}(\text{cyclam})][\text{Co}(\text{NCS})_4]\}_n$ in a 1000 Oe applied field. The solid line shows the best fit using Eq. (1). Insert shows the thermal dependence of the product of the molar susceptibility χ_M and the temperature under the same conditions.

Figures

Figure 1

Figure 2

Figure 3

Supplementary material

Table S1. Crystal data and structure refinement for $\{(\text{Co}(\text{NCS})_4)(\text{Cu}(\text{cyclam}))\}_n$.

Empirical formula	$\text{C}_{14}\text{H}_{24}\text{N}_8\text{S}_4\text{CoCu}$
Formula weight	555.12 g mol^{-1}
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	$a = 8.568(2)$ Å $b = 14.463(3)$ Å $c = 18.562(4)$ Å $\alpha = 90^\circ$ $\beta = 96.62(3)^\circ$ $\gamma = 90^\circ$
Volume	$2284.8(9)$ Å ³
Z	4
Density (calculated)	1.614 Mg/m^3
Absorption coefficient	2.040 mm^{-1}
F(000)	1136
Crystal size	0.38 x 0.13 x 0.09 mm
Theta range for data collection	1.79 to 27.96 deg.
Index ranges	$0 \leq h \leq 11, 0 \leq k \leq 19, -24 \leq l \leq 24$
Reflections collected	5845
Independent reflections	5488 [$R_{\text{(int)}} = 0.0395$]
Absorption correction	Numerical
Max. and min. transmission	0.8486 and 0.7286
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5488 / 0 / 346
Goodness-of-fit on F^2	0.978
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465, w_{R2} = 0.1003$
R indices (all data)	$R_1 = 0.1436, w_{R2} = 0.1244$
Largest diff. peak and hole	0.718 and -0.656 e.Å^{-3}

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\{(\text{Co}(\text{NCS})_4)(\text{Cu}(\text{cyclam}))\}_n$.

	x	y	z	U(eq)
Cu	4111(1)	2584(1)	537(1)	32(1)
Co	694(1)	-861(1)	1974(1)	38(1)
S(1)	2027(1)	1066(1)	89(1)	49(1)
C(21)	1655(4)	435(3)	773(2)	36(1)
N(21)	1376(4)	-11(3)	1256(2)	50(1)
S(2)	3904(2)	-579(1)	4215(1)	59(1)
C(22)	2736(4)	-602(2)	3454(2)	37(1)
N(22)	1901(4)	-629(2)	2929(2)	47(1)
S(3)	-4829(1)	-530(1)	1725(1)	64(1)
C(31)	-2932(5)	-651(3)	1852(2)	39(1)
N(31)	-1587(4)	-753(2)	1945(2)	47(1)
S(4)	1613(2)	-4036(1)	1762(1)	101(1)
N(1)	2888(4)	3389(2)	-213(2)	40(1)
C(2)	3211(6)	3042(3)	-931(2)	51(1)
C(3)	4923(6)	2832(3)	-888(2)	51(1)
C(41)	1296(5)	-2938(3)	1775(2)	51(1)
N(41)	1106(5)	-2160(3)	1783(2)	56(1)
N(4)	5350(4)	2193(2)	-274(2)	37(1)
C(5)	7074(5)	2073(3)	-97(3)	52(1)
C(6)	7461(5)	1418(3)	523(3)	55(1)
C(7)	7112(5)	1774(3)	1254(2)	47(1)
N(8)	5404(3)	1834(2)	1294(2)	46(1)
C(9)	5010(5)	2146(3)	2017(2)	46(1)
C(10)	3310(5)	2365(3)	1956(2)	45(1)
N(11)	2940(4)	3033(2)	1358(2)	38(1)
C(12)	1237(5)	3217(4)	1194(3)	56(1)
C(13)	896(6)	3889(4)	574(3)	63(1)
C(14)	1184(5)	3517(3)	-155(3)	51(1)

$U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Bond lengths [Å] and angles [°] for {(Co(NCS)₄)(Cu(cyclam))}_n.

Bonds			
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Cu-N(8)	2.004(3)	C(5)-C(6)	1.498(7)
Cu-N(1)	2.014(3)	C(5)-H(51)	1.02(4)
Cu-N(4)	2.020(3)	C(5)-H(52)	0.91(5)
Cu-N(11)	2.025(3)	C(6)-C(7)	1.514(7)
Co-N(21)	1.951(4)	C(6)-H(61)	1.00(4)
Co-N(41)	1.951(4)	C(6)-H(62)	0.92(4)
Co-N(31)	1.955(3)	C(7)-N(8)	1.476(5)
Co-N(22)	1.976(3)	C(7)-H(71)	1.00(4)
S(1)-C(21)	1.625(4)	C(7)-H(72)	0.98(4)
C(21)-N(21)	1.152(5)	N(8)-C(9)	1.491(5)
S(2)-C(22)	1.634(4)	N(8)-H(8)	0.794(3)
C(22)-N(22)	1.141(5)	C(9)-C(10)	1.482(6)
S(3)-C(31)	1.625(4)	C(9)-H(91)	0.92(3)
C(31)-N(31)	1.155(5)	C(9)-H(92)	0.97(4)
S(4)-C(41)	1.612(5)	C(10)-N(11)	1.478(5)
N(1)-C(2)	1.479(5)	C(10)-H(101)	0.93(4)
N(1)-C(14)	1.488(5)	C(10)-H(102)	0.97(5)
N(1)-H(1)	0.81(4)	N(11)-C(12)	1.480(5)
C(2)-C(3)	1.491(7)	N(11)-H(11)	0.79(3)
C(2)-H(21)	0.98(3)	C(12)-C(13)	1.509(7)
C(2)-H(22)	0.96(4)	C(12)-H(121)	1.11(5)
C(3)-N(4)	1.480(5)	C(12)-H(122)	0.94(5)
C(3)-H(31)	0.85(4)	C(13)-C(14)	1.504(7)
C(3)-H(32)	0.98(5)	C(13)-H(131)	0.94(4)
C(41)-N(41)	1.138(6)	C(13)-H(132)	0.89(4)
N(4)-C(5)	1.486(5)	C(14)-H(141)	1.10(4)

N(4)-H(4)	0.73(4)	C(14)-H(142)	0.92(5)
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Angles

N(8)-Cu-N(1)	177.18(13)	C(7)-C(6)-H(61)	111(3)
N(8)-Cu-N(4)	94.31(13)	C(5)-C(6)-H(62)	107(3)
N(1)-Cu-N(4)	85.57(13)	C(7)-C(6)-H(62)	106(2)
N(8)-Cu-N(11)	85.88(12)	H(61)-C(6)-H(62)	110(4)
N(1)-Cu-N(11)	94.10(13)	N(8)-C(7)-C(6)	111.3(3)
N(4)-Cu-N(11)	177.11(14)	N(8)-C(7)-H(71)	106(2)
N(21)-Co-N(41)	114.1(2)	C(6)-C(7)-H(71)	108(2)
N(21)-Co-N(31)	107.9(2)	N(8)-C(7)-H(72)	110(3)
N(41)-Co-N(31)	105.8(2)	C(6)-C(7)-H(72)	112(3)
N(21)-Co-N(22)	109.8(2)	H(71)-C(7)-H(72)	110(3)
N(41)-Co-N(22)	103.8(2)	C(7)-N(8)-C(9)	113.0(3)
N(31)-Co-N(22)	115.44(14)	C(7)-N(8)-Cu	117.9(2)
N(21)-C(21)-S(1)	179.3(3)	C(9)-N(8)-Cu	107.6(2)
C(21)-N(21)-Co	171.8(3)	C(7)-N(8)-H(8)	116.5(3)
N(22)-C(22)-S(2)	178.7(4)	C(9)-N(8)-H(8)	99.7(3)
C(22)-N(22)-Co	169.7(3)	Cu-N(8)-H(8)	99.8(2)
N(31)-C(31)-S(3)	178.8(4)	C(10)-C(9)-N(8)	108.6(3)
C(31)-N(31)-Co	172.5(3)	C(10)-C(9)-H(91)	113(2)
C(2)-N(1)-C(14)	113.2(3)	N(8)-C(9)-H(91)	111(2)
C(2)-N(1)-Cu	106.9(3)	C(10)-C(9)-H(92)	109(3)
C(14)-N(1)-Cu	117.3(3)	N(8)-C(9)-H(92)	105(3)
C(2)-N(1)-H(1)	107(3)	H(91)-C(9)-H(92)	110(3)
C(14)-N(1)-H(1)	108(3)	N(11)-C(10)-C(9)	108.7(3)
Cu-N(1)-H(1)	103(3)	N(11)-C(10)-H(101)	111(2)
N(1)-C(2)-C(3)	107.9(3)	C(9)-C(10)-H(101)	109(3)
N(1)-C(2)-H(21)	107(2)	N(11)-C(10)-H(102)	104(3)
C(3)-C(2)-H(21)	107(2)	C(9)-C(10)-H(102)	116(3)
N(1)-C(2)-H(22)	110(2)	H(101)-C(10)-H(102)	108(4)
C(3)-C(2)-H(22)	113(2)	C(12)-N(11)-C(10)	113.2(3)
H(21)-C(2)-H(22)	113(3)	C(12)-N(11)-Cu	117.7(3)
N(4)-C(3)-C(2)	108.8(4)	C(10)-N(11)-Cu	105.9(2)
N(4)-C(3)-H(31)	108(3)	C(12)-N(11)-H(11)	110(3)

C(2)-C(3)-H(31)	109(3)	C(10)-N(11)-H(11)	109(3)
N(4)-C(3)-H(32)	110(3)	Cu-N(11)-H(11)	101(3)
C(2)-C(3)-H(32)	116(3)	N(11)-C(12)-C(13)	111.9(4)
H(31)-C(3)-H(32)	104(4)	N(11)-C(12)-H(121)	103(3)
N(41)-C(41)-S(4)	178.5(5)	C(13)-C(12)-H(121)	116(3)
C(41)-N(41)-Co	169.8(4)	N(11)-C(12)-H(122)	106(3)
C(3)-N(4)-C(5)	113.2(3)	C(13)-C(12)-H(122)	110(3)
C(3)-N(4)-Cu	107.2(3)	H(121)-C(12)-H(122)	109(4)
C(5)-N(4)-Cu	117.6(3)	C(12)-C(13)-C(14)	114.7(4)
C(3)-N(4)-H(4)	103(4)	C(12)-C(13)-H(131)	107(3)
C(5)-N(4)-H(4)	110(4)	C(14)-C(13)-H(131)	115(3)
Cu-N(4)-H(4)	105(4)	C(12)-C(13)-H(132)	102(3)
N(4)-C(5)-C(6)	111.7(4)	C(14)-C(13)-H(132)	107(3)
N(4)-C(5)-H(51)	105(2)	H(131)-C(13)-H(132)	110(4)
C(6)-C(5)-H(51)	115(2)	N(1)-C(14)-C(13)	111.9(3)
N(4)-C(5)-H(52)	106(3)	N(1)-C(14)-H(141)	109(2)
C(6)-C(5)-H(52)	106(3)	C(13)-C(14)-H(141)	108(2)
H(51)-C(5)-H(52)	112(4)	N(1)-C(14)-H(142)	102(3)
C(5)-C(6)-C(7)	115.2(4)	C(13)-C(14)-H(142)	118(3)
C(5)-C(6)-H(61)	108(3)	H(141)-C(14)-H(142)	107(4)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\{(\text{Co}(\text{NCS})_4)(\text{Cu}(\text{cyclam}))\}_n$.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	33(1)	38(1)	27(1)	2(1)	3(1)	8(1)
Co	34(1)	40(1)	38(1)	6(1)	2(1)	-1(1)
S(1)	61(1)	41(1)	46(1)	1(1)	11(1)	-15(1)
C(21)	26(2)	34(2)	49(2)	-3(2)	-1(2)	-1(2)
N(21)	46(2)	51(2)	52(2)	15(2)	4(2)	-8(2)
S(2)	67(1)	45(1)	57(1)	-11(1)	-24(1)	15(1)
C(22)	37(2)	31(2)	44(2)	0(2)	5(2)	5(2)
N(22)	39(2)	58(2)	44(2)	5(2)	3(2)	2(2)
S(3)	33(1)	47(1)	111(1)	-2(1)	9(1)	-1(1)
C(31)	43(2)	30(2)	44(2)	-2(2)	5(2)	-1(2)
N(31)	38(2)	50(2)	53(2)	4(2)	3(2)	4(2)
S(4)	149(1)	39(1)	95(1)	2(1)	-63(1)	-5(1)
N(1)	45(2)	32(2)	39(2)	-3(1)	-7(2)	-3(2)
C(2)	78(3)	40(2)	32(2)	5(2)	-3(2)	-7(2)
C(3)	71(3)	46(2)	37(2)	4(2)	12(2)	-9(2)
C(41)	53(3)	47(2)	47(2)	6(2)	-15(2)	-3(2)
N(41)	61(2)	44(2)	61(2)	2(2)	6(2)	7(2)
N(4)	43(2)	34(2)	37(2)	-1(1)	12(1)	-3(2)
C(5)	41(2)	57(3)	62(3)	-9(2)	24(2)	0(2)
C(6)	35(2)	44(2)	87(3)	-9(2)	14(2)	12(2)
C(7)	34(2)	45(2)	59(3)	0(2)	-5(2)	12(2)
N(8)	36(2)	32(2)	32(2)	-1(1)	1(1)	0(1)
C(9)	60(3)	46(2)	30(2)	2(2)	-3(2)	10(2)
C(10)	60(2)	49(2)	28(2)	-7(2)	12(2)	-2(2)

N(11)	38(2)	38(2)	39(2)	-9(2)	4(1)	13(2)
C(12)	36(2)	73(3)	60(3)	-19(2)	11(2)	13(2)
C(13)	40(2)	64(3)	80(3)	-20(3)	-8(2)	23(2)
C(14)	42(2)	45(2)	61(3)	1(2)	-17(2)	12(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\{(\text{Co}(\text{NCS})_4)(\text{Cu}(\text{cyclam}))\}_n$.

	x	y	z	U(iso)
H(1)	3320(5)	3890(3)	-160(2)	51(13)
H(4)	4990(6)	1760(3)	-410(2)	63(15)
H(8)	4929	1362	1258	45(12)
H(11)	3390(4)	3500(2)	1460(19)	29(10)
H(21)	2660(4)	2450(2)	-1009(19)	33(10)
H(22)	2880(5)	3490(3)	-1300(2)	52(12)
H(31)	5440(5)	3330(3)	-800(2)	45(12)
H(32)	5300(5)	2590(3)	-1330(2)	62(14)
H(51)	7520(5)	2730(3)	-20(2)	61(13)
H(52)	7420(6)	1800(3)	-490(3)	73(15)
H(61)	6900(5)	820(3)	400(2)	63(13)
H(62)	8530(5)	1320(3)	560(2)	48(12)
H(71)	7510(5)	2420(3)	1310(2)	41(11)
H(72)	7600(5)	1390(3)	1660(2)	60(13)
H(91)	5300(4)	1710(2)	2368(17)	20(8)
H(92)	5610(5)	2710(3)	2120(2)	59(13)
H(101)	3080(5)	2610(3)	2390(2)	51(12)
H(102)	2610(5)	1850(3)	1830(2)	63(14)
H(121)	720(6)	2520(4)	1110(3)	89(17)
H(122)	910(6)	3470(3)	1620(3)7	8(16)
H(131)	1450(5)	4440(3)	710(2)	59(14)

H(132)	-140(5)	3980(3)	560(2)	58(13)
H(141)	590(4)	2840(3)	-231(19)	37(10)
H(142)	860(6)	3870(4)	-560(3)	78(16)