NJC
Letter

A new 1D bimetallic thiocyanate-bridged copper(II)–cobalt(II) compound†

Giancarlo Francese,[a] Sylvie Ferlay,[a] Helmut W. Schmalle[b] and Silvio Decurtins[a]*

[a] *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. E-mail: Silvio.Decurtins@iac.unibe.ch*

[b] *Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

Received (in Strasbourg, France) 5th October 1998, Revised m/s received 21st December 1998, Accepted 21st December 1998

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

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-,[3–5] 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)[10] derivatives. 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 CH_3CN–EtOH solution containing cyclam (1.53 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (1.53 mmol) to 10 ml of an alcoholic solution (1.53×10^{-2} M) of $K_2[Co(NCS)_4]$ (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 in the region near 2000 cm^{-1} (2107 and 2073 cm^{-1}), which correspond to the $\nu_{as}(NCS)$ 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 as 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 sulfur atoms from thiocyanate ligands, which are also coordinated to cobalt(II) ions. These sulfur 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

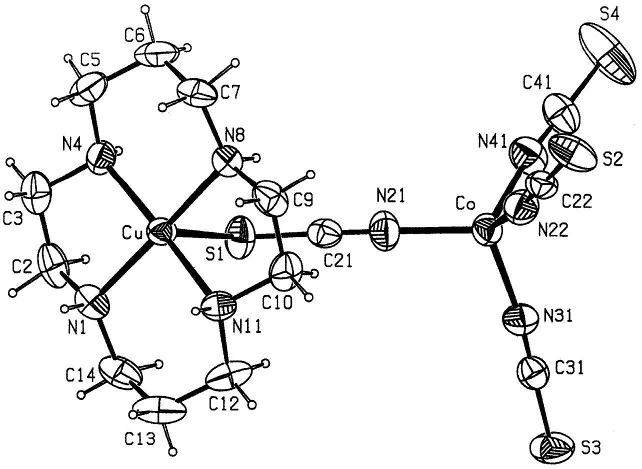

Fig. 1 ORTEP drawing of the $[Cu(cyclam)][Co(NCS)_4]$ molecules. Thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary size. Selected bond lengths [Å] and angles [°]: Cu—N8 2.004(3), Cu—N1 2.014(3), Cu—N4 2.020(3), Cu—N11 2.025(3), Cu—S1 2.891(3), Cu—S2 3.160(3), Co—N21 1.951(4), Co—N41 1.951(4), Co—N31 1.955(3), Co—N22 1.976(3), S1—C21 1.625(4), C21—N21 1.152(5), S2—C22 1.634(4), C22—N22 1.141(5), S3—C31 1.625(4), C31—N31 1.155(5), S4—C41 1.612(5), N1—C2 1.479(5), N1—C14 1.488(5), C2—C3 1.491(7), C3—N4 1.480(5), C41—N41 1.138(6), N4—C5 1.486(5), C5—C6 1.498(7), C6—C7 1.514(7), C7—N8 1.476(5), N8—C9 1.491(5), C9—C10 1.482(6), C10—N11 1.478(5), N11—C12 1.480(5), C12—C13 1.509(7), C13—C14 1.504(7). N8—Cu—N1 177.18(13), N1—C2—C3 107.9(3), N8—Cu—N4 94.31(13), N4—C3—C2 108.8(4), N1—Cu—N4 85.57(13), N41—C41—S4 178.5(5), N8—Cu—N11 85.88(12), C31—N31—Co 172.5(3), N1—Cu—N11 94.10(13), C3—N4—C5 113.2(3), N4—Cu—N11 177.11(14), C3—N4—Cu 107.2(3), S1—Cu—S2 169.96(12), C5—N4—Cu 117.6(3), N21—Co—N41 114.1(2), N4—C5—C6 111.7(4), N21—Co—N31 107.9(2), C5—C6—C7 115.2(4), N41—Co—N31 105.8(2), N8—C7—C6 111.3(3), N21—Co—N22 109.8(2), C7—N8—C9 113.0(3), N41—Co—N22 103.8(2), C7—N8—Cu 117.9(2), N31—Co—N22 115.44(14), C9—N8—Cu 107.6(2), N21—C21—S1 179.3(3), C10—C9—N8 108.6(3), C21—N21—Co 171.8(3), N11—C10—C9 108.7(3), N22—C22—S2 178.7(4), C12—N11—C10 113.2(3), C22—N22—Co 169.7(3), C12—N11—Cu 117.7(3), N31—C31—S3 178.8(4), C10—N11—Cu 105.9(2), C31—N31—Co 172.5(3), N11—C12—C13 111.9(4), C2—N1—C14 113.2(3), C12—C13—C14 114.7(4), C2—N1—Cu 106.9(3), N1—C14—C13 111.9(3), C14—N1—Cu 117.3(3).

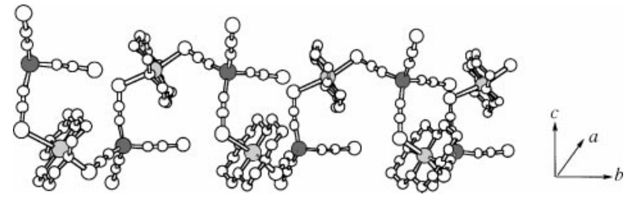

Fig. 2 A perspective view of the chain of $\{[\mathrm{Cu(cyclam)}][\mathrm{Co(NCS)_4}]\}_n$, running along the *b* axis. Black circles indicate cobalt(II) atoms and grey circles indicate copper(II) atoms.

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 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.

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) and 3.160(3) Å, respectively, for Cu—S1 and Cu—S2. These distances are close to the ones found in other complexes in which the sulfur atoms adopt the axial positions of a distorted octahedron around copper(II).[15] The S1—Cu—S2 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 Co ··· Co, Cu ··· Cu and Co ··· Cu distances within the chain are equal to 7.619(3), 10.254(3) and 6.909(3) Å, respectively. The Co ··· Co, Cu ··· Cu and Co ··· Cu distances between the chains are equal to 7.701(3), 7.472(3) 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 Oe. 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 sample was calculated from Pascal's constants. The magnetic behaviour is presented in Fig. 3. The room temperature $\chi_M T$ value (1.95 $\mathrm{cm^{-3}\ mol^{-1}\ K}$), is slightly lower than the value expected for isolated copper(II) and cobalt(II) ions [2.25 $\mathrm{cm^{-3}\ mol^{-1}\ K}$, assuming $g = 2$ for copper(II) and cobalt(II)]. Upon cooling from room temperature, the $\chi_M T$ values decrease slowly down to 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 the non-compensation of spins of copper(II) ($S = \frac{1}{2}$) and cobalt(II) ($S = \frac{3}{2}$) and from a physical point of view, the compound is expected to behave as a ferrimagnetic chain at temperatures below 1 K. Further magnetic measurements at very low temperatures ($T < 1$ K) should allow us to confirm this behaviour.

The experimental susceptibility data were analysed by an expression derived by Drillon and co-workers[19] that is valid for bimetallic alternating ferrimagnetic chains with quantum classical spins. This expression is derived for $S = \frac{1}{2}$ quantum spins like the spin of copper(II), alternating with a classical spin, the spin of cobalt(II) in our case:

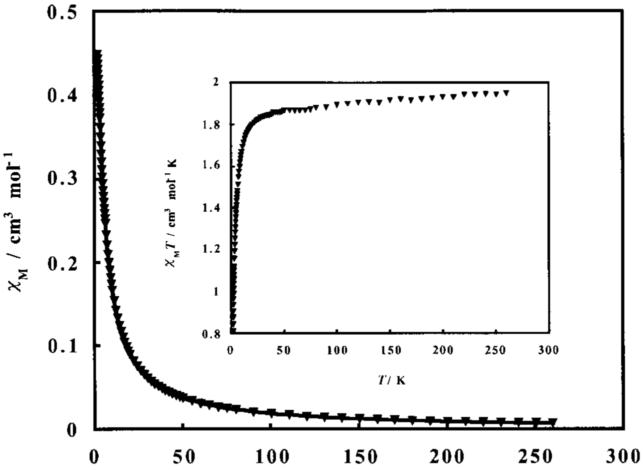

Fig. 3 Thermal dependence of the molar susceptibility χ_M for $\{[\mathrm{Cu(cyclam)}][\mathrm{Co(NCS)_4}]\}_n$ in a 1000 Oe applied field. The solid line shows the best fit using eqn. (1). Insert shows the thermal dependence of the product of the molar susceptibility χ_M and temperature under the same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

$$\chi_M = \frac{N_A g_{Cu}^2 \beta^2}{4 k_B T} \left[r^2 \frac{3a(a^2+2)\sinh a - 6a(a+\sinh a)\cosh a + 3(a^2+1)\sinh^2 a + a^2(a^2+3)}{3a^3(a+\sinh a)} - 2\mathrm{r} \frac{a\cosh a - \sinh a}{a^2} + \frac{\sinh a}{a} \right] \quad (1)$$

with

$$r = \frac{2 g_{Co} S_{Co}}{g_{Cu}} \quad \text{and} \quad a = -\frac{J S_{Co}}{k_B T}.$$

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 2.12(1) for copper(II), and a J value of $-1.48(3)$ $\mathrm{cm^{-1}}$ (coefficient of determination $r^2 = 0.9996$), as indicated by the solid curve in Fig. 3. Attempts to introduce 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 characterization 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.

Acknowledgements

We express our gratitude to Dr. Marc Drillon for helpful discussions concerning the magnetic data and to the Swiss National Science Foundation for financial support through Project No. 20-45750.95.

Notes and references

† *Non-SI units employed*: 10^4 G = 1 T; 1 Oe = 79.6 A $\mathrm{m^{-1}}$.

‡ Anal. calcd for $C_{14}H_{24}N_8S_4CoCu$: C, 30.29; H, 4.36; N, 20.18. Found: C, 29.60; H, 4.40; N, 19.75.

§ The infrared spectrum was recorded on a Bio-Rad IR.FT spectrophotometer, in the 4000–250 cm^{-1} range, using pressed KBr pellets containing 1% by mass of the sample.

¶ Crystal data for **1**: $C_{14}H_{24}N_8S_4CoCu$, $M = 555.12$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 8.568(2)$, $b = 14.463(3)$, $c = 18.562(4)$ Å, $\beta = 96.62(3)°$, $U = 2284.8(9)$ $Å^3$, $Z = 4$, $D_c = 1.614$ Mg m^{-3}, $\mu = 2.040$ mm^{-1}, $T = 296(2)$ K. Of 5845 reflections collected [Enraf-Nonius CAD-4, MoK_α radiation ($\lambda = 0.71073$ Å)], 5488 unique reflections were used for the Patterson interpretation routine of SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*., *Sect. A*, 1990, **46**, 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 distances of 0.93 Å and were fixed by using a riding model in the refinement. $R = 0.0465$ and R'(all data) = 0.1436 with 346 parameters. CCDC reference number 440/089. See http://www.rsc.org/suppdata/nj/1999/267/ for crystallographic files in .cif format.

1 See for example: P. Day, *Science*, 1993, **261**, 431; J. S. Miller and A. J. Epstein, *Angew. Chem*., *Int. Ed. Engl*., 1994, **33**, 385; D. Gatteschi, *Adv. Mater*., 1994, **6**, 635; O. Kahn, *Adv. Inorg. Chem*, 1996, **43**, 179.

2 O. Kahn, *Molecular Magnetism*, VCH Press, Weinheim, Germany, 1993.

3 G. De Munno, G. Bruno, F. Nicolò, M. Julve and J. A. Real, *Acta Crystallogr*., *Sect. C*, 1993, **49**, 457; M. Julve, M. Verdaguer, G. De Munno, J. A. Real and G. Bruno, *Inorg. Chem*., 1993, **32**, 795; P. C. Healy, C. Pakawatchai, R. I. Papasergio, V. A. Patrick and A. H. White, *Inorg. Chem*., 1984, **23**, 3769.

4 J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quiros and E. R. T. Tiekink, *Inorg. Chem*., 1997, **36**, 4988.

5 J. Ribas, C. Diaz, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 1995, **231**, 229.

6 S. Ferlay, G. Francese, H. W. Schmalle and S. Decurtins, *Inorg. Chim. Acta*, in press.

7 M. B. Hursthouse, K. J. Izod, M. A. Mazid and P. Thornton, *Polyhedron*, 1990, **9**, 535.

8 R. Vincente, A. Escuer, J. Ribas and X. Solans, *J. Chem. Soc*., *Dalton Trans*., 1994, 259; M. Montfort, C. Bastos, C. Diaz, J. Ribas and X. Solans, *Inorg. Chim. Acta*, 1994, **218**, 185; A. Escuer, S. Kumar, F. Mautner and R. Vicente, *Inorg. Chim. Acta*, 1998, **269**, 313.

9 J. N. McElearny, L. L. Balagot, J. A. Muir and R. D. Spence, *Phys. Rev. B*, *Condens. Mater*., 1979, **19**, 306.

10 J. Lu, T. Paliwala, S. Lim, C. Yu, T. Niu and A. J. Jacobson, *Inorg. Chem*., 1997, **36**, 923; F. Lloret, G. De Munno, M. Julve, J. Cano, R. Ruiz and A. Caneschi, *Angew. Chem*, *Int. Ed. Engl*., 1998, **37**, 135.

11 J. Ribas, C. Diaz, R. Costa, J. Tercero, X. Solans, M. Font-Bardia and H. Stoeckli-Evans, *Inorg. Chem*., 1998, **37**, 233.

12 M.-C. Chow and T. C. W. Mak, *Aust. J. Chem*., 1992, **43**, 1307.

13 R. A. Bailey, S. L. Kosak, T. W. Michelson and W. N. Mills, *Coord. Chem. Rev*., 1971, **6**, 407.

14 P. A. Tasker and L. Sklar, *J. Crystallogr. Mol. Struct*., 1975, **5**, 329; X. Chen, G. Lay, R. D. Willet, T. Howks, S. Molnar and K. Brewer, *Acta Crystallogr*., *Sect. C*, 1996, **52**, 1924.

15 M. Kabesova, R. Boca, M. Melnik, D. Valigura and M. Dunaj-Jurco, *Coord. Chem. Rev*., 1995, **140**, 115.

16 J. S. Wood and R. K. McMullan, *Acta Crystallogr*., *Sect. C*, 1984, **40**, 1803.

17 A. Sedov, J. Kozisek, M. Kabesova, M. Dunaj-Jurco, J. Kazo and J. Garaj, *Inorg. Chim. Acta*, 1983, **75**, 73; F. H. Cano, S. Garcia-Blanco and A. Guerrero-Laverat, *Acta Crystallogr*., *Sect. B*, 1976, **32**, 1526; M. Nardelli, A. Gasparri, A. Musati and A. Manfedotti, *Acta Crystallogr*, 1966, **21**, 910.

18 H. van Rooyen and J. C. A. Boeyens, *Acta Crystallogr*., *Sect. B*, 1975, **31**, 2933.

19 J. Curély, R. Georges and M. Drillon, *Phys. Rev. B*, 1986, **33**, 6243.

Letter 9/00125E