DALTON
COMMUNICATION

Structure and magnetic properties of a novel two-dimensional thiocyanato-bridged heterometallic polymer $\{Cu(en)_2[Ni(en)(SCN)_3]_2\}_n$

Liang Shen *[a] **and Yun-Zhi Xu** [b]

[a] *Department of Chemistry, Hangzhou Teachers College, Hangzhou 310012, P.R. China*
[b] *Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China*

Received 31st August 2001, Accepted 10th October 2001

The synthesis and X-ray characterization of a novel two-dimensional network of copper(II) and nickel(II) heteronuclear complexes with two different thiocyanate groups are reported, together with a preliminary study of the magnetic properties.

The field of molecular-based magnetism has attracted considerable attention in recent years, and major advances have been made in both their theoretical description and their application as new materials.[1–3] In particular, much effort has been directed towards the design and construction of heterometallic compounds with highly ordered structures in order to provide molecular-based magnets exhibiting spontaneous magnetization.

The design of such compounds requires appropriate components, such as suitable bridging ligands between the paramagnetic centers. The thiocyanate ligand, with the ambidentate character of its 1,3-μ-SCN$^-$ or 1,1,3-μ-SCN$^-$ coordination mode,[4] is expected to play an important role in the design of extended one-, two- and three-dimensional heterometallic compounds with specific magnetic properties. There are a few reports on the crystal structures and magnetic properties of 1-D heterometallic complexes with bridging thiocyanate groups,[5] but no complexes of higher dimensionality are known. In this preliminary communication, we report the synthesis, crystal structure and magnetic properties of a new kind of heterometallic (Cu^{II} and Ni^{II}) polymeric network with thiocyanate bridges.

The starting material, $Cu(en)_2(ClO_4)_2$, was prepared according to the literature.[6] To an aqueous solution of $Cu(en)_2(ClO_4)_2$, equimolar $K_2[Ni(SCN)_4]$ in aqueous solution was added. The mixture was heated while stirring. After cooling the resulting precipitate was then filtered off. Dark blue crystals of heterometallic polymeric complex $\{Cu(en)_2[Ni(en)(SCN)_3]_2\}_n$ **1** were formed after evaporation of the filtrate.† X-Ray crystallography unequivocally confirmed the two-dimensional network structure.‡

It is a well-established criterion of infrared spectroscopy that ν_{as} (NCS) ≥ 2100 cm^{-1} indicates a thiocyanate bridge with a 1,3-μ or 1,1,3-μ bridging mode.[7] The strong ν_{as} (NCS) absorption peak at 2100 cm^{-1} in complex **1** shows the presence of 1,3-μ thiocyanate ligands. Another strong ν_{as} (NCS) peak at 2075 cm^{-1} shows the presence of non-bridging thiocyanates (Ni–NCS). The peak at 3335 cm^{-1} was assigned to a stretching vibration of the amine group in the complex. Comparing with 3400 cm^{-1} assigned to the amine group of free en, the 65 cm^{-1} shift strongly suggests coordination of the amine group in the complex.

The ORTEP view of the molecular structure of **1**, together with the atom numbering scheme, is presented in Fig. 1, while Fig. 2 shows the two-dimensional network character of the complex. The copper atom lies on an inversion centre and has an elongated octahedral environment: the equatorial positions are occupied by four nitrogen atoms from two en ligands with

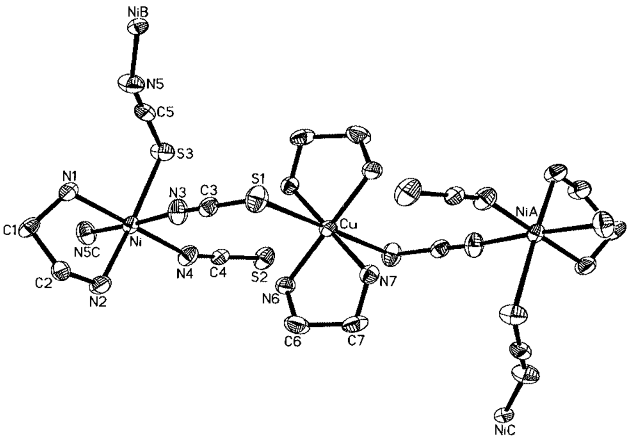

Fig. 1 An ORTEP[15] view of complex **1** with atom labels, showing 40% probability displacement ellipsoids. Selected bond distances (Å) and angles (°): Cu–N(6) 2.018(2), Cu–N(7) 2.017(2), Cu–S(1) 3.071(1), Ni–N(1) 2.077(2), Ni–N(2) 2.081(2), Ni–N(3) 2.086(3), Ni–N(4) 2.043(2), Ni–N(5C) 2.080(3), Ni–S(3) 2.575(1); N(6)–Cu–N(7) 84.32(9), N(6)–Cu–S(1) 92.86(7), N(7)–Cu–S(1) 88.58(7), N(1)–Ni–N(2) 82.76(9), N(1)–Ni–N(3) 89.51(10), N(1)–Ni–N(4) 178.80(11), N(1)–Ni–N(5C) 88.28(11), N(1)–Ni–S(3) 93.78(7), N(2)–Ni–N(3) 90.17(10), N(2)–Ni–N(4) 97.26(9), N(2)–Ni–N(5C) 91.96(11), N(2)–Ni–S(3) 176.53(6), N(3)–Ni–S(3) 90.01(8), N(3)–Ni–N(4) 91.69(10), N(3)–Ni–N(5C) 176.72(11), N(4)–Ni–S(3) 86.20(8), N(4)–Ni–N(5C) 90.52(11), N(5C)–Ni–S(3) 87.71(8). Symmetry transformations used to generate equivalent atoms: (A) $-x, -y + 1, -z$; (B) $x, -y + 3/2, z - 1/2$; (C) $x, -y + 3/2, z + 1/2$.

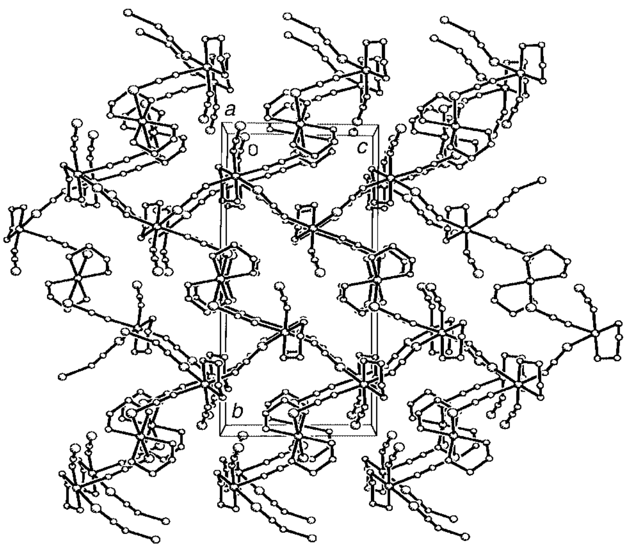

Fig. 2 View of the packing diagram of polymeric **1** showing the two-dimensional network.

DOI: 10.1039/b107865h

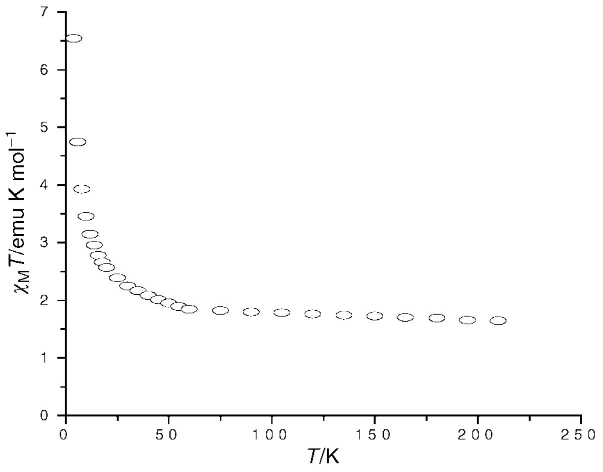

Fig. 3 Magnetic data for the $\{Cu(en)_2[Ni(en)(SCN)_3]_2\}_n$ crystalline sample at 210–4 K.

Cu–N distances of 2.017(2) to 2.018(2) Å and the axial positions are occupied by the sulfur atoms from the bridging thiocyanate ligands. The bond distances of Cu–S, 3.071(1) Å, are shorter than the sum of the van der Waals radii of the Cu and S atoms (3.4 Å)[8] and similar to the values found in other complexes in which the sulfur atoms adopt an axial position in a distorted octahedron around copper(II).[9] The reported Cu–S(SCN) distance is 3.27(1) Å in $Cu(en)_2(SCN)_2$,[10] much longer than that of the present complex.

The nickel ion is octahedrally coordinated by two N atoms of one ethylenediamine ligand, two N atoms and one S atom of three bridging thiocyanate ligands and one N atom of the terminal thiocyanate ligand. The bridging Ni–S–C angle is 99.47(10)°, which is in close agreement with the values observed (100–101.4°) in other complexes.[11] The Ni–N–C angles in the two bridges are 157.5(3)° and 174.3(2)° for Ni–N(5C)–C(5C) and Ni–N(3)–C(3), respectively, this angle decreases when the thiocyanate ligand is non-bridging: 155.4(2)° for Ni–N(4)–C(4). These structural features have been observed in other thiocyanate-containing metal complexes.[12] Ni–N–C angles deviate from 180° expected for the sp hybrid orbital of the N atom. Although the Ni–N(4)–C(4) angle of 155.4(2)° implies less overlap between the sp hybrid orbital of N(4) and the atomic orbital of Ni(II), the Ni–N(4) distance [2.043(2) Å] is apparently shorter than the Ni–N(3) distance [2.086(3) Å]. This fact might suggest the existence of an electrostatic interaction between the metal and coordinated atoms as reported elsewhere.[13]

Two kinds of SCN^- anions, 1,3-μ bridging SCN^- and terminal SCN^-, exist in the complex. The 1,3-μ-SCN^- ligands bridge the adjacent Cu(II), Ni(II) and Ni(II), Ni(II) atoms to form a two-dimensional network structure. The distances between adjacent Ni–Cu and Ni–Ni, bridged by 1,3-μ-SCN^-, are 5.375(1) and 5.878(1) Å, respectively. The thiocyanate groups in this complex are almost linear with a mean value of the N–C–S angles of 178.4(3)°. The C–N average distance of 1.148(4) Å and C–S average distance of 1.633(3) Å in the SCN^- moiety show the normal structure of the thiocyanate in the complex.

Variable-temperature magnetic susceptibility data on the crystalline sample were collected with a Quantum Design MPMS-5SP SQUID magnetometer in the temperature range of 210–4 K. The experimental susceptibilities were corrected for diamagnetism of the constituent atoms (Pascal's tables). The magnetic behavior is presented in Fig. 3, in the form of $\chi_M T$ *versus* T. Upon cooling from 210 K, $\chi_M T$ increases gradually until about 25 K, then abruptly to reach a maximum of 6.53 emu K mol^{-1} at 4 K. The maximum $\chi_M T$ value is larger than the value expected for $S_T = 5/2$ of ferromagnetically coupled $CuNi_2$ (4.38 emu K mol^{-1}). This fact suggests ferromagnetic ordering within the two-dimensional network. The magnetic properties of this complex will be studied further.

Acknowledgements

We express our gratitude to Dr Xun Xu for determination of the magnetic data and to the National Natural Science Foundation of China for financial support through Project No. 29973036.

Notes and references

† Preparation of **1**. A 10 ml aqueous solution of $K_2[Ni(SCN)_4]$ (370 mg, 1 mmol) was added to a 10 ml aqueous solution of $Cu(en)_2(ClO_4)_2$ (380 mg, 1 mmol). The resulting solution was stirred for half an hour at 60 °C. After cooling the blue precipitate was filtered off. The filtrate was evaporated at room temperature, and dark blue crystals of heterometallic polymeric complex $\{Cu(en)_2[Ni(en)(SCN)_3]_2\}_n$ **1** were formed. Calc. for $C_{14}H_{32}N_{14}S_6CuNi_2$: C, 21.68; H, 3.85; N, 25.81; found: C, 21.83; H, 4.16, N, 25.47%. IR(KBr pellet/cm^{-1}): 3335, 2100, 2075, 1585, 1450, 1320, 1275,1092, 1045, 775,700, 640, 502, 465 and 425.

‡ Crystal data for **1**. $C_{14}H_{32}N_{14}S_6CuNi_2$, $M = 769.86$, monoclinic, space group $P2(1)/c$; 0.48 × 0.40 × 0.40 mm; $a = 7.472(2)$, $b = 21.770(7)$, $c = 9.297(2)$ Å, $\beta = 96.01(1)°$, $V = 1504.0(7)$ Å^3, $Z = 2$, $F(000) = 790$, $D_c = 1.700$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 2.389 mm^{-1}. The intensity data were collected at 296(2) K on a Siemens P4 diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL software,[14] with 2613 unique absorption corrected reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.0275$ and $wR = 0.0663$ for 2111 observed reflections with $[I > 2\sigma(I)]$. CCDC reference number 154232. See http://www.rsc.org/suppdata/dt/b1/b107865h/ for crystallographic data in CIF or other electronic format.

1 P. Day, *Science*, 1993, **261**, 431; J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385; O. Kahn, *Molecular Magnetism*, VCH, New York, 1993; O. Kahn, *Adv. Inorg. Chem.*, 1996, **43**, 179.

2 A. J. Blake, W. S. Li, V. Lippolis and M. Schröder, *Chem. Commun.*, 1997, 1943; M. Munakata, L. P. Wu, M. Yamanoto, T. Kuroda-Sowa and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1995, 3215.

3 W. R. Entley and G. S. Girolami, *Science*, 1995, **268**, 397; S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701; O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **271**, 49.

4 H. Krautscheid, N. Emig, N. Klaassen and P. Seringer, *J. Chem. Soc., Dalton Trans.*, 1998, 3071; M. A. S. Goher, Q. C. Yang and T. C. W. Mak, *Polyhedron*, 2000, **19**, 615.

5 H. Z. Kou, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, G. L. Wang, X. K. Yao and H. G. Wang, *Can. J. Chem.*, 1998, **76**, 1102; J. L. Zuo, H. K. Fun, K. Chinnakali, X. Z. You and C. M. Che, *New J. Chem.*, 1998, **22**, 923; G. Francese, S. Ferlay, H. W. Schmalle and S. Decurtins, *New J. Chem.*, 1999, **23**, 267.

6 T. W. Hambley, G. A. Lawrance, M. Maeder and E. N. Wilkes, *J. Chem. Soc., Dalton Trans.*, 1992, 1283.

7 G. A. V. Albada, R. A. G. DeDraaff, G. A. Haasnoot and J. Reedjik, *Inorg Chem.*, 1984, **23**, 1404.

8 L. Pauling, *The nature of chemical bonds*, 3rd edn., Cornell University Press, Ithaca, 1960, p. 260.

9 J. Ribas, C. Diaz, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 1995, **231**, 229; K. Vicent, A. Esouer, E. Penalba, X. Solans and M. Font-Badia, *Inorg. Chim. Acta*, 1997, **255**, 7; S. Ferlay, G. Francese, H. W. Schmsall and S. Decurtins, *Inorg. Chim. Acta*, 1998, **286**, 108.

10 B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 1145.

11 M. Monfort, C. Bastos, C. Diaz and J. Ribas, *Inorg. Chim. Acta*, 1994, **218**, 185.

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

13 L. Shen, D. Xu, J. G. Liu and Y. Z. Xu, *J. Coord. Chem.*, 2001 in press.

14 G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data, version 5.0, Siemens Analytical X-Ray Instruments, Madison, WI, 1994 .

15 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976 .