A 2D Thiocyanato-Bridged Copper(II)-Manganese(II) Bimetallic Coordination Polymer with Ferromagnetic Interactions

Jing-Min Shi,*[a] Wei Xu,[a] Bin Zhao,[b] Peng Cheng,*[b] Dai-Zheng Liao,[b] and Xiao-Yan Chen[b]

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The first ferromagnetic coupled, thiocyanato-bridged copper(II)-manganese(II) bimetallic 2D polymer $\{[Cu(ipa)_2]_2Mn(NCS)_6{\cdot}2H_2O\}_n$ (ipa = 1,2-propanediamine) has been synthesised and characterised by a single-crystal X-ray structure determination and variable temperature magnetic susceptibility studies.

Introduction

Recently, the field of molecular magnetism has attracted considerable attention and major advances have been made both in the theoretical description and applications of new molecular-based materials.[1] In particular, special attention has been paid to the design and construction of multi-dimensional homo- and heterometallic coordination polymers in order to undertake theoretical studies of their magnetic properties and develop high *Tc* molecular-based magnets.[2] The thiocyanate anion, which exhibits an ambidentate character with end-to-end or end-on coordination modes, can be expected to play a key role in the design of polymetallic coupling systems. A certain number of polynuclear complexes have been synthesised with discrete 1-, 2- and 3D crystal structures and some of them exhibit interesting ferromagnetic coupling properties, e.g. the 1D uniform chain complexes[3] $Co(NCS)_2(Hlm)_2$ and $Ni(NCS)_2(Hlm)_2$. The heterometallic species, however, are quite limited and show low-dimensional structures,[4–8] whereas large numbers of cyanato-bridged analogues have been reported and some exhibit interesting magnetic properties. The 1D copper(II)-manganese(II) heterometallic compound $[Cu(en)_2Mn(NCS)_4(H_2O)_2]_n$ [4] derived from $K_2[Mn(NCS)_4(H_2O)_2]$ as a precursor has also been described. The chains of Mn^{II} ($S = 5/2$) and Cu^{II} ($S = 1/2$) ions structurally ordered in an alternating manner are of intense interest as potential building blocks in the synthesis of molecular-based ferromagnetic materials.[9] In this area, the novel 2D complex $\{[Cu(ipa)_2]_2Mn(NCS)_6{\cdot}2H_2O\}_n$ was successfully constructed from a heterometallic octanuclear square lattice as a subunit and it exhibits interesting ferromagnetic coupling between adjacent Mn and Cu ions. In this species, the Cu and Mn atoms are alternately arrayed and are connected by thiocyanate bridges. To the best of our knowledge, in the reported compounds comprising SCN^- bridges, this is the first time that the octanuclear lattice of $Cu_4Mn_4C_8N_8S_8$ has been fabricated from SCN^- bridges and further assembled into a fascinating 2D structure. Remarkably, this ferromagnetic behaviour is absent for the systems containing Cu and Mn ions.

Figure 1 shows the coordination diagram for the complex with the atom numbering scheme. It indicates that the complex consists of two types of distinct building blocks, namely $Mn(NCS)_6$ and $Cu(ipa)_2(SCN)_2$. Each copper atom exhibits an elongated octahedral coordination environment: the equatorial plane is formed from four nitrogen atoms of two ipa ligands with Cu–N distances of 1.988(3) to 2.024(3) Å and the axial positions are occupied by the sulfur atoms of the thiocyanate bridges. The Cu-S separations are not identical and the two types of Cu1–S1 bonds have distances of 2.9635(16) and Cu2–S2 3.0214(16) Å which are shorter than those of other reported complexes.[10] The coordination sphere around the Mn^{2+} centre displays octahedral geometry and is completed by six N atoms from the thiocyanate ions. Four of the N atoms are from four bridging SCN^- anions with Mn–N distances of 2.185(4) to 2.218(4) Å and the other two come from two terminal SCN^- anions which occupy the remaining apical positions of the Mn centre with the Mn–N distances of 2.275(4) Å being longer than those in the equatorial plane. The symmetry elements of the crystal, namely the inversion centres, are located on the Mn and Cu atoms. This is shown clearly in Figure 1 and Figure 2. Interestingly, the equatorial planes of the Cu1 and Cu2 ions run almost parallel to that of the Mn ion with dihedral angles of 9.7°. The

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[a] Department of Chemistry, Shandong Normal University,
Jinan 250014, P. R. China
Fax: (internat.) +86-531-6948773
E-mail: shijingmin@beelink.com
[b] Department of Chemistry, Nankai University,
Tianjin 300071, P. R. China

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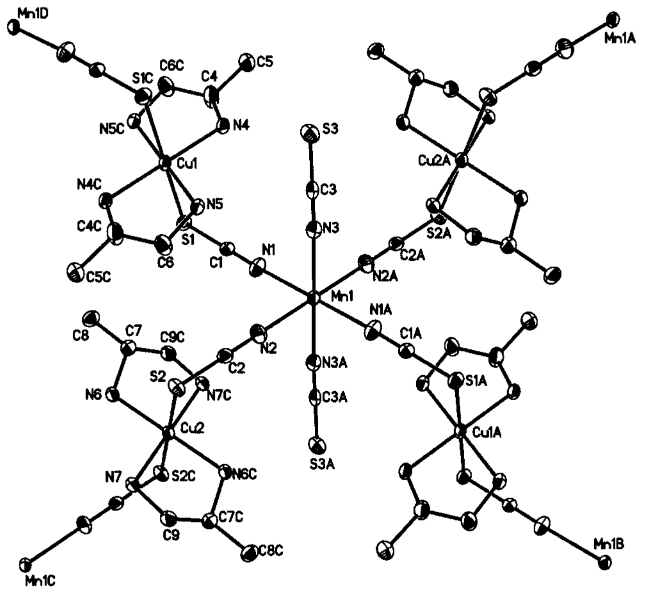

Figure 1. Diagram of the title complex with the atom numbering scheme; H atoms and water molecules are omitted for clarity

S(SCN)−Cu−N(ipa) angles, which are between 82.61(10)° and 95.99(12)°, indicate that the Cu−S bond is nearly perpendicular to the equatorial plane of the Cu ion. Each Mn ion has four Cu ions as the nearest metal centers, while the Cu ion has two Mn ions in its vicinity which is consistent with the Mn:Cu molar ratio. Adjacent Cu and Mn ions are connected through SCN^- bridges to form a 32-membered $Cu_4Mn_4C_8N_8S_8$ square lattice subunit of dimensions 9.118×10.089 Å. Mn atoms are located on the vertexes of squares and Cu atoms lie on the middle points of the edges. Importantly, the square subunits are further assembled into a 2D polymer. The distances between the neighbouring Mn···Cu pairs are 5.683 Å for Mn1···Cu1 and 5.717 Å for Mn1···Cu2.

The plot of μ_{eff} versus T is shown in Figure 3. At room temperature μ_{eff} is 7.00 μ_B which is slightly greater than the expected value for an isolated Mn ion and four Cu ions (6.86 μ_B for $g_{av} = 2$). The μ_{eff} value increases gradually with decreasing temperature from 7.00 μ_B at 300 K, reaching a maximum value of 7.32 μ_B at 5 K. This magnetic behaviour indicates ferromagnetic interactions between the $\mu_{1,3}$-NCS-bridged Mn^{II} ion and the Cu^{II} ion which is supported by the fact that the magnetic susceptibility values obey the Curie−Weiss law with a positive Weiss constant $\theta = 1.36$ K.

Theoretically, the exchange interaction between Mn^{II} and Cu^{II} is most likely antiferromagnetic in nature because it is extremely difficult to reach strict orthogonality between the magnetic orbitals for a M(high-spin d^5)-M′(d^1) pair irrespective of the local symmetry of each.[11] Also, to the best of our knowledge, this concept has been somewhat confirmed by previously reported Mn^{II}-Cu^{II} couplings. Unexpectedly, the title compound exhibits ferromagnetic interactions and represents the first example of a Mn^{II}-Cu^{II} system. Indeed, as mentioned in the description of the structure, all the Mn−NCS−Cu angles are close to 90 degree

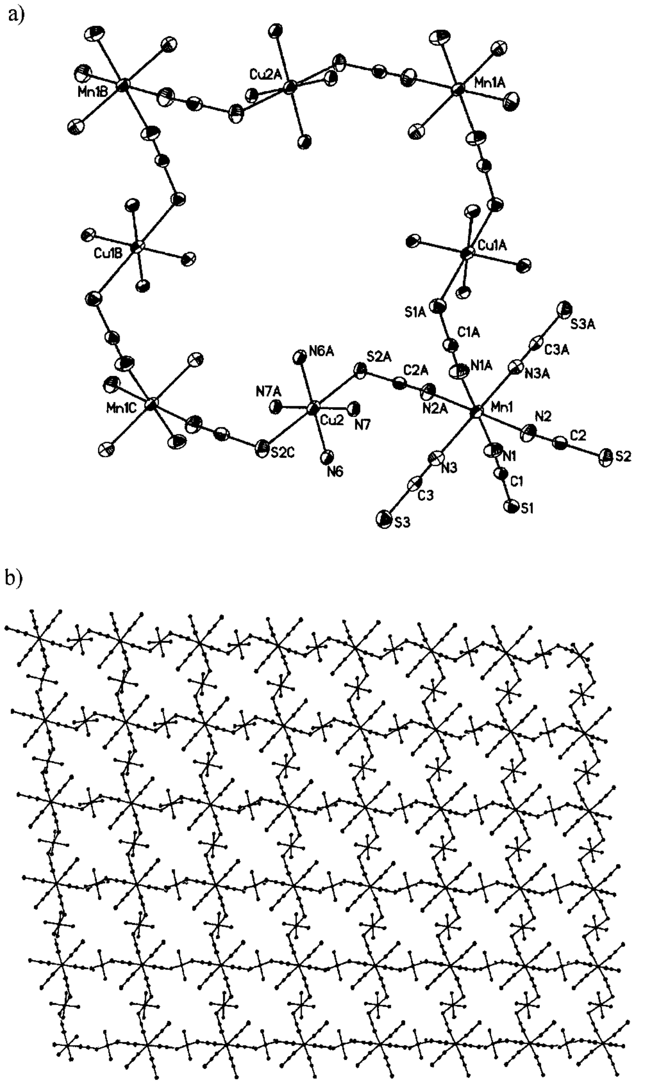

Figure 2. a) 32-membered square lattice motif of $Cu_4Mn_4C_8N_8S_8$; b) view along the [001] direction showing the 2D structure; the H atoms, C atoms in the ipa ligand and solvent molecules are omitted for clarity

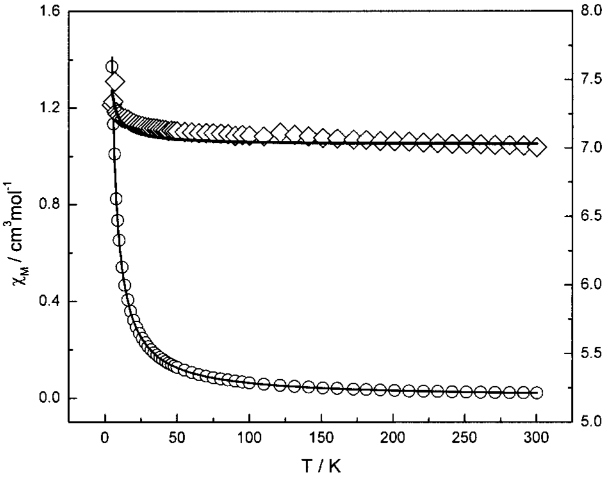

Figure 3. Plots of χ_M (diamonds) and μ_{eff} (circles) versus T

and the S atom is in the apical position of the Cu^{II} centre. Therefore, the small spin density of the d_{z^2} type orbital of the Cu^{II} centre interacts with that of the $d_{x^2-y^2}$ type magnetic orbital of the Mn^{II}. This situation occurs because of strict orthogonality and results in a ferromagnetic contribution. On the other hand, the $3d^5$ electrons of the Mn^{II} display a sphere-type distribution, thus partial overlapping of the magnetic orbitals of the Cu^{II} and Mn^{II} ions inevitably occurs which causes an antiferromagnetic contribution to the Cu^{II} and Mn^{II} system. The two kinds of interactions conflict in an antagonistic process but the ferromagnetic contribution may predominate, however, and this should be responsible for the ferromagnetic coupling between Cu^{II} and Mn^{II}.

Taking into account the complex magnetic treatment for multi-dimensional systems containing paramagnetic centres, only approximate models were employed to fit the experimental data so far obtained. In this context, the pentanuclear Mn-Cu_4 system was considered as the smallest repeat unit in order to analyse the magnetic properties of the 2D structure. Equation (2) was obtained based on an isotropic Hamiltonian presented as in Equation (1) with interactions between Cu ions neglected due to the long distance between them.

$$\hat{H} = -2J\hat{S}_{Mn}(\hat{S}_{Cu1} + \hat{S}_{Cu2} + \hat{S}_{Cu3} + \hat{S}_{Cu4}) \qquad (1)$$

$$\chi_M = Ng^2\beta^2 A/4k_BT + TIP \qquad (2)$$

$A = 165 + 84\exp(-9J/kT) + 35\exp(-16J/kT) + 10\exp(-21J/kT) + 252\exp(-5J/kT) + 105\exp(-12J/kT) + 30\exp(-17J/kT) + 70\exp(-10J/kT)$

$B = 5 + 4\exp(-9J/kT) + 3\exp(-16J/kT) + 2\exp(-21J/kT) + \exp(-24J/kT) + 12\exp(-5J/kT) + 9\exp(-12J/kT) + 6\exp(-17J/kT) + 6\exp(-10J/kT)$

where J is the Heisenberg exchange constant between adjacent Mn^{II} and Cu^{II} ions, S_{Mn} and S_{Cu} are spin operators corresponding to Mn and Cu, respectively, and the temperature-independent paramagnetism TIP = 3.0×10^{-4}. The theoretical model gave a good fitting of the experimental results. The agreement factor $R = 5.8\times10^{-4}$ [R was defined as $R = \Sigma(\chi_{obsd.} - \chi_{calcd.})^2/(\chi_{obsd.})^2$], $g = 2.04$ and $J = 0.13$ cm^{-1}. The sign and magnitude of the J value suggest that weaker ferromagnetic coupling exists between adjacent Cu^{II} and Mn^{II} centres bridged by SCN^- anions.

To further support the nature of the interaction provided by the temperature dependence of the magnetisation, the field dependence of the magnetisation for the complex was measured in a field of 0−50 kOe at 7 K. The experimental values of M for the title compound were compared with those calculated by the Brillouin function corresponding to an $S = 9/2$ spin state with $g = 2$ (Figure 4). The plot of M vs. H approaches the Brillouin curve based on $S = 9/2$, although experimental values do not reach a magnetic saturation value of 9. This behaviour confirms that the ground state of $S = 9/2$ results from ferromagnetic interactions between the Mn and Cu ions of the pentanuclear system.

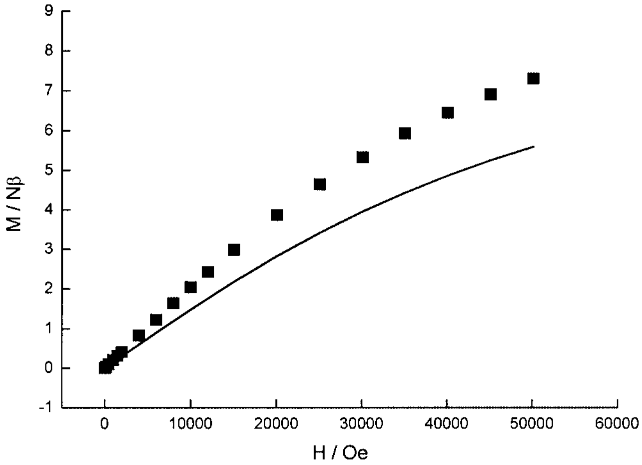

Figure 4. Plot of M versus H (squares) and the Brillouin curve for four independent Cu^{II} ions and one Mn^{II} ion

In conclusion, a novel 2D heterometallic polymer has been assembled from 32-membered $Cu_4Mn_4C_8N_8S_8$ square lattices as subunits fabricated from SCN anions bridges. It shows a fascinating topological motif which is relatively rare in SCN-bridged complexes. Magnetic studies revealed intriguing ferromagnetic couplings between adjacent Cu^{II} and Mn^{II} ions which is the first report of such a phenomenon in Cu^{II}-Mn^{II} systems.

Experimental Section

General: Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000−500 cm^{-1} region using KBr discs. C, H and N elemental analyses were carried out on a Perkin−Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 1 kOe in the temperature range of 5−300 K on a SQUID magnetometer. The data were corrected for magnetisation of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

Synthesis of the Complex: All chemicals were of analytical grade and were used without further purification. $Cu(ipa)_2(ClO_4)_2$ (ipa = 1,2-propanediamine) (0.1949 g, 0.58 mmol) and $Na_4Mn(NCS)_6\cdot9H_2O$ (0.4199 g, 0.64 mmol) were each dissolved in H_2O (10 mL), the two solutions were mixed together and the resultant mixture stirred for a few minutes. Purple single crystals were obtained after the resultant solution was allowed to stand at room temperature for several days. Yield: 0.2027 g (81%). $C_{18}H_{44}Cu_2MnN_{14}O_2S_6$ (863.05): calcd. Cu, 14.73, Mn, 6.37, C 25.05, H 5.14, N 22.73; found Cu, 14.28, Mn, 5.93, C 25.37, H 5.58, N 23.15%. The IR spectrum shows a characteristic strong and sharp absorption peak for the NCS^- groups at 2084 cm^{-1} and the sharp peaks due to the NH and NH_2 groups appear at 3462, 3305 and 1583 cm^{-1}.

X-ray Crystallographic Analysis of the Complex:[12] A single-crystal of dimensions 0.15 × 0.12 × 0.08 mm was selected and subsequently glued to the tip of a glass fibre. The determination of the crystal structure at 25 °C was carried out on a Bruker Smart-1000 CCD X-ray diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Corrections for *Lp* factors were applied and all nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier map and refined isotropically using a riding model with displacement parameters. The programs for structure solution and refinement were SHELXS-97[13] (Sheldrick, 1990) and SHELXL-97[14] (Sheldrick, 1997), respectively. The crystal belongs to the triclinic space group $P\bar{1}$ with $a = 9.118(5)$, $b = 10.089(5)$, $c = 11.434(6)$ Å, $\alpha = 74.652(7)$, $\beta = 66.775(7)$, $\gamma = 72.358(8)$°, $V = 908.4(8)$ Å^3, $Z = 1$, empirical formula $C_{18}H_{44}Cu_2MnN_{14}O_2S_6$, molecular mass 863.05, $D_c = 1.578$ g·cm^{-3}, $F(000) = 445$, θ range 2.49−26.36°, index ranges $-11 \leq h \leq 11$, $-12 \leq k \leq 8$, $-14 \leq l \leq 14$. A total of 5076 reflections were collected, 3574 were independent ($R_{int} = 0.0238$) and 2422 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final refinement including hydrogen atoms converged to $R = 0.0453$, $wR = 0.0979$, $(\Delta\rho)_{max.} = 0.644$ eÅ^{-3}, $(\Delta\rho)_{min} = -0.579$ eÅ^{-3}.

Acknowledgments

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[12] CCDC-199138 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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