Antiferromagnetic ordering in a novel five-connected 3D polymer $\{Cu_2(2,5\text{-}Me_2pyz)[N(CN)_2]_4\}_n$ (2,5-Me_2pyz = 2,5-dimethylpyrazine)†

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Reaction of $Na[N(CN)_2]$ with $CuSO_4{\cdot}5H_2O$ and 2,5-Me_2pyz produced $\{Cu_2(2,5\text{-}Me_2pyz)[N(CN)_2]_4\}_n$ (2,5-Me_2pyz = 2,5-dimethylpyrazine), which is an unusual five-connected, two-fold interpenetrated network that orders antiferromagnetically at low temperature.

The use of the dicyanamide ion, $N(CN)_2^-$, as a bridging ligand for the construction of coordination polymers has received much attention recently since binary compounds of the type $M[N(CN)_2]_2$ have been found to display interesting magnetic properties.[1–6] For M = Ni[1–3] and Co,[1–4] ferromagnetic ordering occurs below 9 and 21 K, respectively. The Fe,[2] Cr,[5] and Mn[5,6] compounds undergo long-range magnetic ordering to a spin-canted antiferromagnet at low temperatures. On the other hand, for M = Cu,[3] only very weak antiferromagnetic coupling was observed down to 2 K. Apart from these binary systems, additional organic ligands were also employed in the design of new structural types and new molecule-based magnets and a number of 1D, 2D and 3D polymers has been reported.[7–23] For M = Cu(II) three compounds have been structurally characterized so far: $\{Cu[N(CN)_2]_2(ampym)_2\}_n$ (ampym = 2-aminopyrimidine), which has a 2D structure,[7] $\{Cu(pm)[N(CN)_2]_2\}_n(CH_3CN)_n$ (pm = pyrimidine), which has a 3D structure[8] and $\{Cu[N(CN)_2]_2(pyz)\}_n$ (pyz = pyrazine), which has an α-form with a 3D interpenetrating network and a β-form with a 2D sheet structure.[9] These polymers, however, exhibit only weak magnetic coupling even at low temperatures. Herein, we report the synthesis and structure of a novel 3D polymer, $\{Cu_2(2,5\text{-}Me_2pyz)[N(CN)_2]_4\}_n$ (**1**), that exhibits long-range antiferromagnetic ordering below 5 K. Antiferromagnetic ordering has also been found in the 3D Mn(II) polymer $\{Mn[N(CN)_2]_2(pyz)\}_n$.[10,11]

Reaction of $Na[N(CN)_2]$ with $CuSO_4{\cdot}5H_2O$ and 2,5-Me_2pyz in water at room temperature produced **1** as green crystals. The X-ray structure (Fig. 1) shows that each Cu(II) center adopts a distorted square pyramidal geometry and is bonded to one 2,5-Me_2pyz and four $N(CN)_2^-$ ions. The 2,5-Me_2pyz and the $N(CN)_2^-$ ligands bridge the copper centers together to produce a 3D structure (Fig. 2). One of the $Cu{-}N{\equiv}C$ units is bent with a Cu–N(5)–C(6) bond angle of 146.8(3)°, while the others are close to linear [172.6(3)–177.6(3)°]. The Cu–N(5) distance [2.177(3) Å] of the bent $Cu{-}N{\equiv}C$ unit is also significantly longer than the others [1.959(3)–1.980(3) Å]. All $C{\equiv}N$ distances [1.120(4)–1.127(4) Å], C–N_{amide} distances [1.280(4)–1.297(5) Å], C–N_{amide}–C angles [126.0(4) and 128.8(3)°] and $N_{amide}{-}C{\equiv}N$ angles [168.5(4)–173.5(4)°] are typical for this ligand. We note that **1** is an example of the rather rare five-connected coordination networks. It is also a two-fold interpenetrated network (Fig. 2) that is closely related to a recently reported heterobimetallic network found in $Cu(4,4'\text{-}bpy)_{1.5}Cr_2O_7{\cdot}H_2O$.[24] The network in **1** can be described by the connection of hexagonal layers (each hexagon is

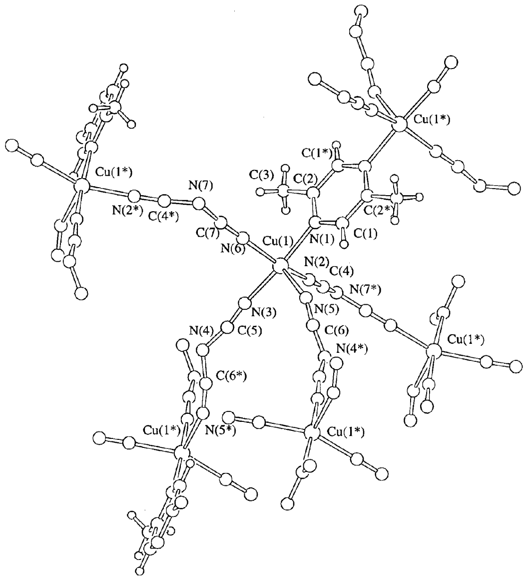

Fig. 1 The coordination environment of Cu in **1**. Selected bond lengths (Å) and angles (°) Cu(1)–N(1) 2.057(2); Cu(1)–N(2) 1.980(3); Cu(1)–N(3) 1.959(3); Cu(1)–N(5) 2.177(3); Cu(1)–N(6) 1.976(3); N(4)–C(5) 1.280(4); N(4)–C(6*) 1.285(4); N(5)–C(6) 1.123(4); N(6)–C(7) 1.126(4); N(7)–C(4*) 1.297(5); N(2)–C(4) 1.120(4); N(7)–C(7) 1.283(5); N(3)–C(5) 1.127(4); N(1)–Cu(1)–N(2) 87.60(10); N(1)–Cu(1)–N(3) 172.2(1); N(1)–Cu(1)–N(5) 95.05(10); N(1)–Cu(1)–N(6) 89.07(10); N(2)–Cu(1)–N(3) 89.3(1); N(2)–Cu(1)–N(5) 102.7(1); N(2)–Cu(1)–N(6) 155.1(1); N(3)–Cu(1)–N(5) 92.6(1); N(3)–Cu(1)–N(6) 90.7(1); N(5)–Cu(1)–N(6) 102.1(1); Cu(1)–N(1)–C(2) 121.8(2); Cu(1)–N(1)–C(1) 120.1(2); Cu(1)–N(2)–C(4) 175.2(3); Cu(1)–N(3)–C(5) 172.6(3); Cu(1)–N(5)–C(6) 146.8(3); Cu(1)–N(6)–C(7) 177.6(3); C(4*)–N(7)–C(7) 126.0(4); C(5)–N(4)–C(6*) 128.8(3); N(2)–C(4)–N(7*) 173.5(4); N(3)–C(5)–N(4) 168.5(4); N(4*)–C(6)–N(5) 169.3(4); N(6)–C(7)–N(7) 173.3(4).

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† Electronic supplementary information (ESI) available: plot of the temperature dependence of the ac susceptibility (Fig. S1). See http://www.rsc.org/suppdata/nj/b1/b111012h/

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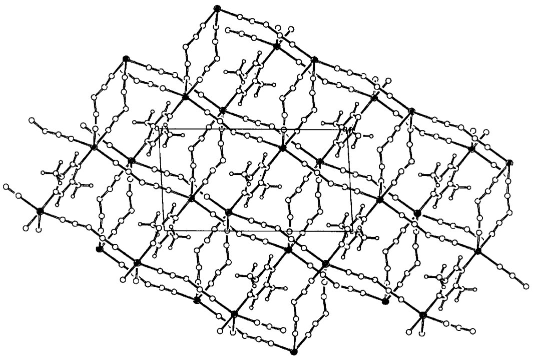

Fig. 2 A view along the *b* axis showing the 2-fold interpenetrated network of **1**. Filled circles refer to Cu atoms.

defined by four Cu–dicyanamide–Cu and two Cu–Me_2pyz–Cu edges) joined by dicyanamide bridges. The stacking of the hexagonal layers is ABAB..., which is different from the AAA... pattern in Cu(4,4′-bpy)$_{1.5}$$Cr_2O_7$·$H_2O$. Other examples of five-connected networks include two Ag(I) polymers, [Ag(pyz)$_2$][Ag_2(pyz)$_5$]$(PF_6)_3$·2G (G = CH_2Cl_2, $CHCl_3$ and CCl_4)[25] and [Ag(tcm)(pyz)] (tcm = tricyanomethanide),[26] and two lanthanum coordination networks, [La_4L_{10}(CH_3OH)$_{10}$-Cl_3]Cl(BPh_4)$_8$·22CH_3OH and [$LaL_{2.5}$(CH_3OH){$Ph_2B(OMe)_2$}]-(BPh_4)$_2$·4.5CH_3OH (L = 4,4′-bipyridine-*N*,*N*′-dioxide).[27]

The variable-temperature magnetic susceptibility χ_M for a collection of small crystals of **1** was measured between 1.8 and 300 K (Fig. 3). The magnetic susceptibility above 15 K obeys the Curie–Weiss law with a Weiss constant, $\theta = -3.1$ K, and a Curie constant, $C = 0.432$ cm^3 mol^{-} K. The C value corresponds to $g = 2.15$, $S = 1/2$ for a Cu^{2+} ion. The negative Weiss constant indicates antiferromagnetic interaction between copper ions. χ_M increases as the temperature is lowered, reaching a sharp maximum at *ca.* 8.8 K, suggesting antiferromagnetic ordering. The Neel temperature, T_N, of **1** was determined from the plot of $d(\chi_M T)/dT$ *vs.* T at 5.0 K, shown in the inset of Fig. 3.[28] The in-phase component of the ac susceptibility (χ') is frequency independent and also shows a maximum around 8–9 K, while the out-of-phase component (χ'') is zero, in accordance with antiferromagnetic ordering (Fig. S1, ESI).

The field dependence of the magnetization for **1** at different temperatures is shown in Fig. 4. The magnetization below T_N increases very slowly with increasing field in the beginning due to antiferromagnetic ordering, it then increases more rapidly as it undergoes a transition from an antiferromagnet to a spin-flop state at a rather high transition field of around 50–70 kOe, depending on the temperature.[29] The magnetization value at 1.88 K is only 0.16 Nβ at 70 kOe, far from the saturation value of 1.1 Nβ for one Cu^{2+} ion with $g = 2.15$, again consistent with antiferromagnetic ordering. The ordering temperature T_N of a 3D antiferromagnet (AFM) should be just slightly less than $T(\chi_{max})$.[30] In the case of **1**, the ratio of $T_N/T(\chi_{max})$ is only 0.57, suggesting that the antiferromagnet possesses low-dimensional characters, although the connection between the double-layers in **1** through 2,5-Me_2pyz could make a crucial contribution to the magnetic ordering.

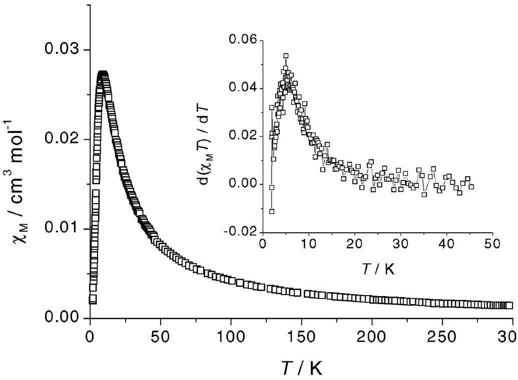

Fig. 3 Temperature dependence of the molar magnetic susceptibility χ_M for **1**. Inset: $d(\chi_M T)/d(T)$ *vs.* T.

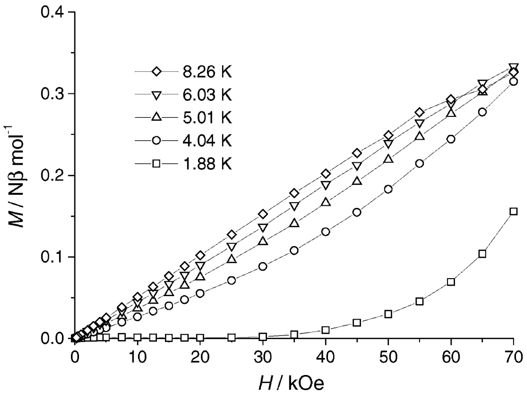

Fig. 4 Field dependence of the magnetization of **1** at various temperatures.

In conclusion, we have described an unusual five-connected 3D structure that orders antiferromagnetically at low temperature. Our work here suggests that five-connected networks constructed from paramagnetic metal centres could have novel magnetic properties, and hence more work should be done in this area.

Experimental

Synthesis

2,5-Me_2pyz (108 mg, 1.0 mmol) was added to an aqueous solution (20 mL) containing $CuSO_4$·5H_2O (250 mg, 1.0 mmol) and Na[N$(CN)_2$] (178 mg, 2.0 mmol). Slow evaporation of the pale blue solution gave green needle-shaped crystals (yield; 188 mg, 75%). Anal. calcd for $CuN_7C_7H_4$: C, 33.67; H, 1.61; N, 39.27%. Found: C, 33.61; H, 1.66; N, 39.35%. IR (KBr/cm^{-1}) ν_{CN}: 2200vs, 2260vs, 2317s, 2348s.

X-Ray crystallography

Single crystals of complex **1** suitable for X-ray crystallographic studies were mounted in glass capillaries. Diffraction data were collected at room temperature on a Bruker AXS SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects as well as absorption. The structure was solved by direct methods (SHELXS86)[31] and expanded using Fourier techniques (DIRDIF94).[32] The structure was refined by full-matrix least squares using the teXsan crystallographic software package. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystal data for **1**. $CuN_7C_7H_4$, $M = 249.7$, monoclinic, $P2_1/n$ (no.14), $a = 7.417(1)$, $b = 9.686(1)$, $c = 13.661(1)$ Å, $\beta = 93.30(1)°$, $u = 979.8(2)$ Å^3, $Z = 4$, μ(Mo-Kα) = 22.05 cm^{-1}, $D_c = 1.693$ g cm^{-3}, $F(000) = 496$, $T = 298$ K, 6072 reflections measured, 2300 unique ($R_{int} = 0.021$), final $R_1 = 0.035$ for 1898 reflections with $I > 1.50\sigma(I)$, $wR_2 = 0.045$.

CCDC reference number 171329. See http://www.rsc.org/suppdata/nj/b1/b111012h/ for crystallographic data in CIF or other electronic format.

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References

1 J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552.
2 M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515.
3 S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439.
4 P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray and D. J. Price, *Chem. Commun.*, 1999, 177.
5 J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 2552.
6 J. L. Manson, C. R. Kmety, F. Palacio, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 2001, **13**, 1068.
7 G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2000, **298**, 221.
8 I. Riggio, G. A. van Albada, D. D. Ellis, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2001, **313**, 120.
9 P. Jensen, S. R. Batten, G. D. Fallon, D. C. R. Hockless, B. Moubaraki, K. S. Murray and R. Robson, *J. Solid State Chem.*, 1999, **145**, 387.
10 J. L. Manson, C. D. Incarvito, A. L. Rheingold and J. S. Miller, *J. Chem. Soc., Dalton Trans.*, 1998, 3705.
11 J. L. Manson, Q.-Z. Huang, J. W. Lynn, H. J. Koo, M. H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyriou and J. S. Miller, *J. Am. Chem. Soc.*, 2001, **123**, 162.
12 S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray and A. Ziebell, *J. Chem. Soc., Dalton Trans.*, 2000, 3829.
13 B.-W. Sun, S. Gao, B.-Q. Ma, D.-Z. Niu and Z.-M. Wang, *J. Chem. Soc., Dalton Trans.*, 2000, 4187.
14 B.-W. Sun, S. Gao, B.-Q. Ma and Z.-M. Wang, *New J. Chem.*, 2000, **24**, 953.
15 A. Claramunt, A. Escuer, F. A. Mautner, N. Sanz and R. Vicente, *J. Chem. Soc., Dalton Trans.*, 2000, 2627.
16 S. R. Marshall, C. D. Incarvito, J. L. Manson, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 2000, **39**, 1969.
17 J. L. Manson, A. M. Arif and J. S. Miller, *J. Mater. Chem.*, 1999, **9**, 979.
18 B.-W. Sun, S. Gao, B.-Q. Ma and Z.-M. Wang, *Inorg. Chem. Commun.*, 2001, **4**, 72.
19 J. L. Manson, J. A. Schlueter, U. Geiser, M. B. Stone and D. H. Reich, *Polyhedron*, 2001, **20**, 1423.
20 P. Jensen, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2000, 793.
21 I. Dasna, S. Golhen, L. Ouahab, O. Peña, J. Guillevic and M. Fettouhi, *J. Chem. Soc., Dalton Trans.*, 2000, 129.
22 J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold and J. S. Miller, *J. Solid State Chem.*, 1999, **145**, 369.
23 S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987.
24 L. Pan, N. Ching, X. Huang and J. Li, *Chem. Commun.*, 2001, 1064.
25 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew Chem., Int. Ed. Engl.*, 1995, **34**, 1895.
26 S. R. Batten, B. F. Hoskins and R. Robson, *New J. Chem.*, 1998, **22**, 173.
27 D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schröder, *J. Am. Chem. Soc.*, 2001, **123**, 3401.
28 M. E. Fisher, *Proc. R. Soc. London, Ser. A*, 1960, **254**, 66; M. E. Fisher, *Philos. Mag.*, 1962, **7**, 1731.
29 B.-Q. Ma, H.-L. Sun, S. Gao and G. Su, *Chem. Mater.*, 2001, **13**, 1946.
30 G. C. DeFotis, E. D. Remy and C. W. Scherrer, *Phys. Rev. B*, 1990, **41**, 9074.
31 G. M. Shedrick, SHELXS86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.
32 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, 1994.