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A new Co(II) coordination solid with mixed oxygen, carboxylate, pyridine and thiolate donors exhibiting canted antiferromagnetism with $T_C \approx 68$ K

Simon M. Humphrey,†[a] Antonio Alberola,[a] Carlos J. Gómez García[b] and Paul T. Wood*[a]

Received (in Cambridge, UK) 13th January 2006, Accepted 23rd February 2006
First published as an Advance Article on the web 8th March 2006
DOI: 10.1039/b600347h

Reaction of Co(II) chloride with the sodium salt of 2-mercaptonicotinic acid in water at 200 °C results in the formation of $Co_4(2\text{-mna})_4(H_2O)$, which orders as a canted antiferromagnet at 68 K.

The synthesis of new metal–organic coordination polymers continues to attract a great deal of interest since such materials have been shown to exhibit highly desirable solid-state properties such as magnetism,[1] nanoporosity,[1,2] second-harmonic generation[3] and show promise for use in molecular electronics.[4] They may also be doped with other metals to produce active heterogeneous catalysts.[5] In particular, materials that have thermally-accessible magnetically bistable states have the potential to be utilized in data storage on the molecular level.[6] One of the major obstacles impeding progress in this area is the very low temperatures at which magnetic ordering occurs.[6,7] Extensive study of Prussian blue derivatives has produced materials which order above room temperature.[8] Good metal–ligand orbital overlap is expected to increase the strength of magnetic exchange due to a greater degree of spin delocalisation onto the bridging ligand.[9] Thiolate ligands are attractive candidates for such an approach, but success has previously been limited due to the ease of disulfide formation for such ligands. We have recently shown that hydrothermal synthesis is an effective way of preparing thiolate networks whilst minimising the possibility of disulfide formation,[10] presumably due to the inherently reducing nature of high temperature water. The thiolate-mediated magnetic exchange in these materials is still relatively weak, presumably as a result of unfavorable M–S–M bridging angles. However, we now report strong superexchange and weak ferromagnetism due to spin canting in a highly complex and dense coordination solid containing 5- and 6-coordinate Co^{II}, $[Co_4(2\text{-mna})_4(OH_2)]$ (**1**) (2-mna = 2-mercaptonicotinate, $(NC_5H_3(S)(CO_2)\text{-}2,3)^{2-}$) (Fig. 1). Spherical clusters of very fine branched (fern leaf-like) deep red needles were initially observed from the hydrothermal reaction of $CoCl_2$ with 2-mnaH_2 and KOH (ratio 1 : 1 : 2), although much better samples were prepared when NaOH was employed as the base.‡ Single crystal X-ray diffraction§ led to the identification of the low symmetry 3-dimensional polymer **1** (in the non-centrosymmetric orthorhombic space group $Pca2_1$, $Z = 4$). The asymmetric unit contains four highly distorted Co^{II} environments. Co1 and Co2 are both within distorted octahedra, Co3 conforms most closely to trigonal bipyramidal coordination geometry, while Co4 is in a square-based pyramid with a single OH_2 ligand (O9) in the apical position (Fig. 1 inset). The most striking detail of the asymmetric unit of **1** is the wide range of coordination modes present between metal ions and the four unique 2-mna ligands. There are a total of six different modes: (a) all ligands form planar 4-membered N,S-donor chelate rings to Co (bite angles in the range 62.4(2)–64.6(2)°); (b) each ligand also forms a near-planar 6-membered S,O-chelate ring, thus leading to *pseudo*-linear bridging *via* RS^-; (c) two carboxylate groups provide *syn,anti*-bridges between metal ions; (d) one carboxylate moiety mediates a distorted *anti,anti*-type bridge; (e) there is a single chelating carboxylate; (f) a single carboxylate-O provides a 1,1′-bridge between metals. Octahedral Co1 and Co2 have 'softer' coordination environments since both are doubly N,S-chelated while each also coordinates to a third thiolate from an adjacent ligand. Single carboxylate-O donor atoms complete their coordination environments. In contrast, the environments around Co3 and Co4 comprise coordination of four O-donors and a single thiolate-S.

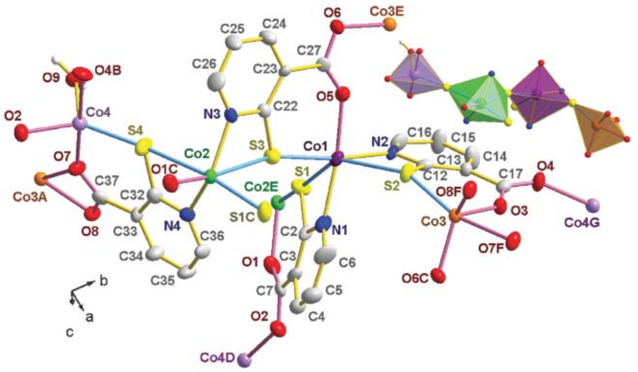

Fig. 1 The extended asymmetric unit of **1**; all unique atoms shown with completed coordination environments. Co–S bonds are shown in blue, Co–O bonds are shown in pink. Inset: polyhedral view of the same four unique Co(II) centers. Selected bond lengths [Å] and angles [°]: Co1–S1 2.652(2), Co1–S2 2.585(2), Co1–S3 2.310(2), Co2–S1C 2.288(2), Co2–S3 2.691(2), Co2–S4 2.739(2), Co3–S2 2.301(2), Co4–S4 2.266(2); S1–Co1–S2 135.62(8), S2–Co1–S3 122.83(8), S1C–Co2–S4 82.35(7), S3–Co2–S4 97.44(8), Co1–S1–Co2E 169.3(1), Co1–S2–Co3 153.4(1), Co1–S3–Co2 158.6(1), Co2–S4–Co4 165.4(1), Co3A–O7–Co4 137.7(2), O7F–Co3–O8F 58.5(2).

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[a] *University Chemical Laboratory, Lensfield Rd, Cambridge, UK CB2 1EW. E-mail: ptw22@cam.ac.uk; Fax: +44 1223 336017*
[b] *Instituto de Ciencia Molecular, Universidad de Valencia. Pol. La Coma s/n, 46980 Paterna, Valencia, Spain*

† Current address: Department of Chemistry, University of California, Berkeley, CA, USA and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, CA, USA.

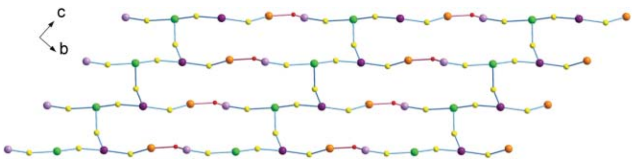

Fig. 2 The magnetic sheet of single atom O- and S-bridged sublattices comprised of 'double comb' CoS zigzag chains (green, purple metals) found in **1**.

The extended lattice of **1** is complex and most easily described by firstly considering its CoS and CoO sublattices (Fig. 2), since the single atom bridges (particularly thiolate) are expected to mediate the strongest magnetic exchange interactions. All four ligands in the asymmetric unit provide nearly linear M–S–M bridges (in the range 153.4(1)–169.3(1)°), which are expected to induce strong antiferromagnetic exchange interactions.[8] Parallel CoS chains run along the crystallographic *c* axis and contain all four metal centers (Co4–S–Co2–S–Co1–S–Co3). These are cross-linked by perpendicular interactions at Co1 and Co2, giving rise to a 'double comb' motif consisting of a zigzag spine of $(\text{–S1–Co1–S3–Co2–})_\infty$ with (–S2–Co3) and (–S4–Co4) 'teeth' on either side. The next strongest magnetic exchange interactions in **1** will be provided by single atom-O bridges (O7) which generate a 'brick wall' motif of $Co_{10}S_8O_2$ rings. These layers are joined together by Co–OCO–Co bridges to form a 3-dimensional superexchange lattice. The Co–O lattice is also based on a double comb type topology where chains of carboxylate-bridged metals (Co1–Co3–Co4–Co3) are linked into zigzags at Co3 centers, while (–OCO–Co2) 'teeth' terminate from Co4 equivalents. The 3-dimensional packing of **1** is very dense: there is little symmetry to the extended lattice and when viewed parallel to *a* (Fig. 3a) and *b* (Fig. 3b), its close-packed nature becomes evident; the material is essentially a 3-dimensional metal–organic 'block'. When viewed parallel to *c*, the linkage of adjacent magnetic sheets (projecting into the page) by carboxylate bridges can be seen (Fig. 3c).

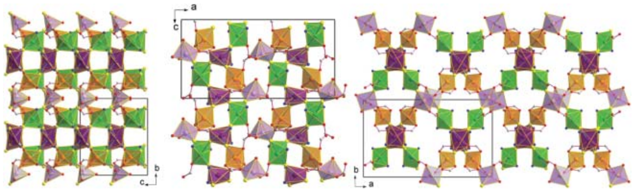

Fig. 3 (Left) Polyhedral view of **1** viewed along *a*. All aromatic carbon atoms have been omitted for clarity. (Center) Projection along *b*. (Right) Linking of 2-dimensional single atom-bridged sheets of Co^{II} into a 3-dimensional lattice by carboxylate bridges.

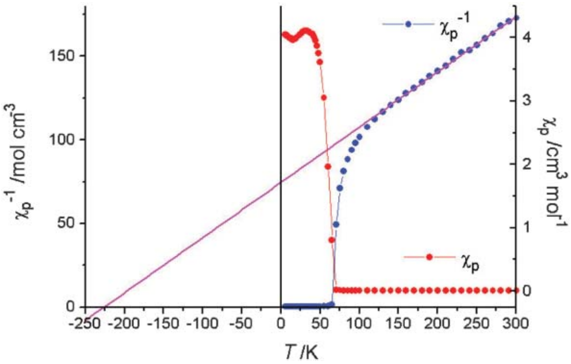

Fig. 4 Graphs of susceptibility (red) and inverse susceptibility (blue) for compound **1** along with a fit to the Curie–Weiss law.

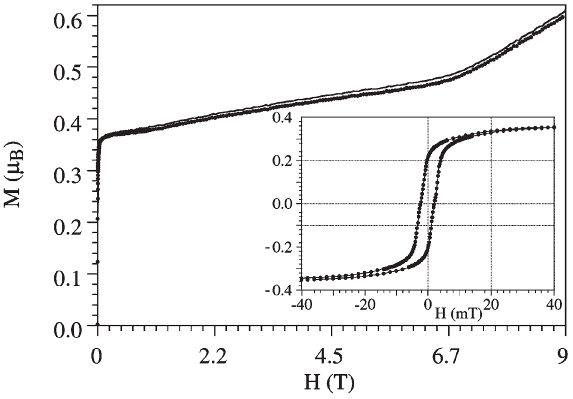

Fig. 5 Isothermal magnetization at 5 K of **1**. Inset shows the hysteresis cycle and the rapid saturation in the low field region.

The magnetic behavior of **1** has been studied using DC and AC SQUID magnetometry on polycrystalline samples. The DC data follow the Curie–Weiss law very well between 125 and 300 K giving $C = 3.02(3)$ cm^3 K mol^{-1} (per Co(II) ion) and $\theta = -225(4)$ K (Fig. 4). The Curie constant, *C*, is larger than expected for an $S = 3/2$ ion if only the spin contribution is considered. This is due to the presence of a significant orbital contribution, typical in Co(II) ions. In fact, the *C* value is in the range observed for Co(II) ions (2.7–3.4 cm^3 K mol^{-1}).[11] The Weiss temperature, θ, indicates that the dominant exchange interaction is strongly antiferromagnetic. The thermal variation of the DC susceptibility (χ_m) (Fig. 4) shows a sharp increase below *ca.* 67 K before reaching a maximum at 40 K followed by a local minimum at 15 K before increasing gently again as *T* decreases. The large Weiss constant and high T_C confirm that the better energy match between metal and sulfur orbitals can lead to strengthened superexchange, as described above. Measurement of χ_m in a range of applied fields shows that this abrupt increase is less pronounced with increasing magnetic fields due to saturation effects. This is more clearly shown in the isothermal magnetization at low temperature which shows a sharp increase to reach a saturation value of *ca.* 0.35 B.M. at magnetic fields above *ca.* 10 mT. For higher fields, the magnetization shows a smooth and linear increase with a change in slope at *ca.* 7 T (Fig. 5). Furthermore, the isothermal magnetization shows a hysteresis cycle with a coercive field of *ca.* 2.5 mT (inset in Fig. 5). These three facts: the abrupt increase of χ_m below *ca.* 67 K, the fast saturation of the magnetization and the presence of a hysteresis cycle, suggest the presence of a long range ordering in **1** with a T_C around 67 K. Since the coupling is strongly antiferromagnetic and the saturation value of the magnetisation is well below the expected one for a parallel alignment of the spins of four Co(II) ions (*ca.* 15 B.M. assuming $g = 2.5$, as deduced from the *C* value), we can conclude that **1** exhibits a weak ferromagnetism due to spin canting that prevents the complete cancellation of the spins of the Co(II) ions. By comparison of the isothermal magnetisation data with the ideal value of M_{sat} for ferromagnetic alignment, we estimate the canting angle to be 2.5°. This spin canting is favored by the single ion anisotropy of the Co(II) ions and by the four

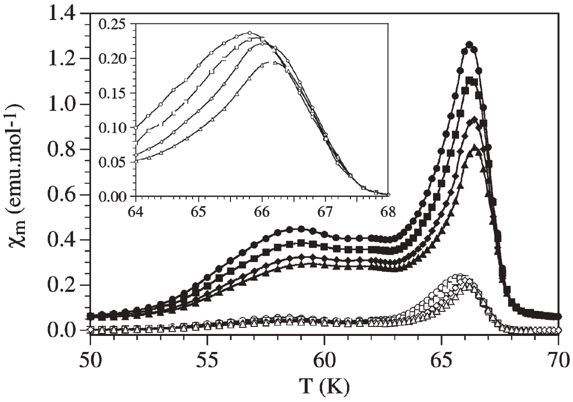

Fig. 6 Frequency dependence of the AC susceptibility of **1** at 1, 10, 110 and 332 Hz (circles, squares, rhombuses and triangles, respectively). χ' filled symbols, χ'' empty symbols. Inset shows the frequency dependence of the χ'' peak at *ca.* 66 K.

different coordination environments shown by the four Co(II) ions and is consistent with the crystallisation of **1** in a non-centrosymmetric space group.

In order to determine the critical temperature precisely, AC magnetic measurements were performed (Fig. 6). We observe a sharp increase below *ca.* 68 K and a sharp maximum in the real part of the susceptibility, χ_m' at 66.2–66.4 K with a broad shoulder at *ca.* 58.9–59.4 K. This signal is accompanied by an out-of-phase signal, χ_m'' that becomes non-zero below a temperature of 68.0 K, which defines T_C, with a sharp maximum at 65.8–66.2 K and a shoulder at 58.3–58.6 K. This behavior confirms the presence of long range order at T_C = 68 K.

Interestingly, the χ_m'' maximum at *ca.* 66 K varies slightly with the frequency (0.4 K in the frequency range 1–332 Hz, inset in Fig. 6). This frequency dependence is too small to be attributed to superparamagnetic behavior of the weak ferromagnet nor to a movement of the domain walls. In fact, the activation energy calculated from an Arrhenius analysis gives a value of 4 × 10^4 K, which is 400 times higher than the typical values of domain wall movements[12] even allowing for the fact that in **1** we should expect a high activation energy as a result of single ion effects and the strong coupling encountered. A plausible explanation may be a spin glass-like behavior since **1** presents simultaneous ferro- (from the spin canting) and antiferromagnetic (from the many –S–, –O– and –OCO– bridges) exchange couplings and may present some degree of frustration in the very complex magnetic lattice. Finally, the needed randomness in the magnetic lattice may arise from crystal defects and/or from the presence of up to four different coordination environments in the Co(II) ions.[13] The same features were observed when measurements were performed on a Nujol-restrained sample. This confirms that this behavior is actually intrinsic for this compound, and not sample dependent.

In conclusion, we have shown that hydrothermal synthesis is an effective way of preventing disulfide formation in reactions intended to produce metal thiolates. We confirm that hydrothermal synthesis is also a good method for preparing intricate coordination networks. Most importantly, this work shows that the incorporation of thiolate bridges is indeed a route to magnetic networks with higher ordering temperatures.

Notes and references

‡ *Synthesis of 1.* To a stirred solution of 2-mercaptonicotinic acid (1.0 mmol) and NaOH (1.0 M, 1.9 cm^3) in H_2O (3.1 cm^3) was added a solution of $CoCl_2$ (1.0 mmol) in H_2O (5 cm^3) to give an opaque purple slurry (ratio = 1 : 1 :1.9). The mixture was heated for 15 h at 210 °C and cooled slowly (0.10 °C min^{-1}) to yield fine deep red crystals in high purity (yield 153 mg, 71%). Anal. found: C, 32.7; H, 1.6; N, 6.2. $C_{24}H_{14}Co_4N_4O_9S_4$ requires: C, 33.3; H, 1.6; N, 6.5%. λ_{max} (powder/nm): 565(0.69), 527(0.69), 425(0.89). ν_{max} (KBr/cm^{-1}): 3422 m, 3067 w, 1583 s, 1566 m, 1534 m, 1500 w, 1448 m, 1396 s, 1370 m, 1243 m, 1155 m, 1134 m, 1093 m, 1062 w, 1007 w, 962 w, 879 m, 763 m, 727 w, 668 m.

§ *Crystal data.* $C_{24}H_{14}Co_4N_4O_9S_4$, M = 866.35, orthorhombic, a = 20.8760(6), b = 12.3647(2), c = 10.9125(2) Å, V = 2816.79(11) $Å^3$, T = 180(2) K, space group $Pca2_1$, Z = 4, μ(Mo-Kα) = 2.673 mm^{-1}, 15465 reflections measured, 4610 unique (R_{int} = 0.0688). Final values $R1$ = 0.0598 and w$R2$ = 0.0932 (all data). CCDC 287016. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600347h

1 For recent reviews, see: (*a*) C. Janiak, *Dalton Trans.*, 2003, **14**, 2781; (*b*) E. Coronado, A. Forment-Aliaga, J. R. Galan-Mascaros, C. Gimenez-Saiz, C. J. Gomez-Garcia, E. Martinez-Ferrero, A. Nuez and F. M. Romero, *Solid State Sci.*, 2003, **5**, 917; (*c*) D. Maspoch, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; (*d*) L. Ouahab, *Coord. Chem. Rev.*, 1998, **178–180**, 1501; (*e*) C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1434.

2 See for example: H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Férey and A. K. Cheetham, *J. Am. Chem. Soc.*, 2003, **125**, 1309; A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjørgen and K. P. Lillerud, *J. Am. Chem. Soc.*, 2005, **127**, 6361; S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2005, **127**, 6506; S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2082.

3 Q. Ye, Y. H. Li, Y. M. Song, X. F. Huang, R. G. Xiong and Z. Xue, *Inorg. Chem.*, 2005, **44**, 3618.

4 See for example: E. Coronado, M. Clemente-Leon, J. R. Galan-Mascaros, C. Gimenez-Saiz, C. J. Gomez-Garcia and E. Martinez-Ferrero, *J. Chem. Soc., Dalton Trans.*, 2000, **21**, 3955; G. Zu, Z. M. Wang, Z. He, Z. Lu, C. S. Liao and C. H. Yan, *Inorg. Chem.*, 2002, **41**, 6802; R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141.

5 S. Hermes, M. K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2005, **44**, 6237.

6 H. Ohno, *Science*, 2001, **291**, 840; J. J. Attema, G. A. de Wijs, G. R. Blake and R. A. de Groot, *J. Am. Chem. Soc.*, 2005, **127**, 16325; S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science*, 2001, **294**, 1488.

7 L. A. Gerrard and P. T. Wood, *Chem. Commun.*, 2000, 2107; S. M. Humphrey and P. T. Wood, *J. Am. Chem. Soc.*, 2004, **126**, 13236; S. O. H. Gutschke, A. M. Z. Slawin and P. T. Wood, *J. Chem. Soc., Chem. Commun.*, 1995, 2197.

8 S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701.

9 O. Kahn, *Molecular Magnetism*, Wiley-VCH, Weinheim, 1993.

10 S. M. Humphrey, R. A. Mole, M. McPartlin, E. J. L. McInnes and P. T. Wood, *Inorg. Chem.*, 2005, **44**, 5981; S. M. Humphrey, R. A. Mole, J. M. Rawson and P. T. Wood, *Dalton Trans.*, 2004, 1670; D. Cave, J.-M. Gascon, A. D. Bond, S. J. Teat and P. T. Wood, *Chem. Commun.*, 2002, 1050.

11 R. March, W. Clegg, R. A. Coxall, L. Cucurull-Sánchez, L. Lezama, T. Rojo and P. González-Duarte, *Inorg. Chim. Acta*, 2003, **353**, 129.

12 F. Bellouard, M. Clemente-Leon, E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, F. Romero and K. R. Dunbar, *Eur. J. Inorg. Chem.*, 2002, 1603; E. Coronado, C. J. Gómez-García, A. Nuez, F. M. Romero, E. Rusanov and H. Stoeckli-Evans, *Inorg. Chem.*, 2002, **41**, 4615.

13 J. A. Mydosh, *Spin glasses: an experimental introduction*, Taylor and Francis, London, 1993.