The slow magnetic relaxation observed in a mixed carboxylate/hydroxide-bridged compound $[Co_2Na(4\text{-}cpa)_2(\mu_3\text{-}OH)(H_2O)]_\infty$ featuring magnetic Δ-chains†

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Received (in Cambridge, UK) 12th May 2006, Accepted 3rd July 2006
First published as an Advance Article on the web 26th July 2006
DOI: 10.1039/b606765d

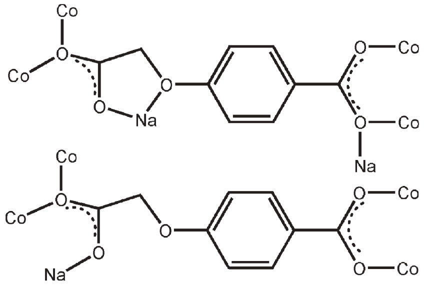
Magnetic Δ-chains in a 3D coordination polymer $[Co_2Na(4\text{-}cpa)_2(\mu_3\text{-}OH)(H_2O)]_\infty$ are well separated by Na^+ ions and organic spacers, and exhibit not only magnetic behaviour of Δ-chain topology but also slow magnetic relaxation.

The fundamental correlation between structures and magnetic properties is a vital motivation in the research of molecular-based magnets.[1,2] Great efforts have been devoted to the generation of structurally unique architectures.[1,3,4] As a section of the Kagomé lattice, the Δ-chain comprising corner-sharing triangles is of particular theoretical interest, because it provides not only the spin frustration but also the properties of a one-dimensional (1D) system. Many theoretical studies have been carried out on the Δ-chain topology.[5] However, only a few genuine 1D Δ-chain structures are known, and the intrachain interaction are very weak.[6] Meanwhile, two compounds built on the Δ-chains based on $M_3(\mu_3\text{-}OH)$ triangles have been reported,[4] but the interchain magnetic interactions make them into magnetic 2D and 3D systems. Therefore, the synthesis of these compounds based on Δ-chains is still a challenge.

In our recent study of magnetic metal–organic frameworks (MOFs) of metal carboxylates,[7] we have used transition metal $M_3(\mu_3\text{-}OH)$ triangles to construct a Kagomé-type compound. Now we report a new 3D Co^{II} MOF $[Co_2Na(4\text{-}cpa)_2(\mu_3\text{-}OH)(H_2O)]_\infty$ (**1**) (4-cpa = 4-carboxylphenoxyacetate)‡, which consists of magnetic Δ-chains based on scalene $Co_3(\mu_3\text{-}OH)$ triangles and exhibits not only intriguing behaviour of Δ-chain topology but also the slow magnetic relaxation.

In the crystal structure§ of **1**, there are three octahedrally coordinated Co^{II} atoms (Co1 at a general position, while Co2 and Co3 are at the inversion centres), two 4-cpa ligands, one μ_3-OH ligand and one μ-aqua ligand, as well as one Na^+ ion in an asymmetric unit. The existence of a μ-aqua ligand is required by the charge balance with the help of the X-ray structure that the Co–O_{aqua} (2.144(2) Å) and Na–O_{aqua} (2.366(2) Å) bond lengths lie in the typical range for the complexes with μ-aqua-bridged Co^{II} and Na^+ ions.[8] Co1 is surrounded by four carboxylate oxygen atoms, a μ_3-OH group and an aqua ligand in a distorted octahedron (Co1–O 2.049(2)–2.144(2) Å; *cis*-O–Co1–O 85.02(5)–96.50(6)°; *trans*-O–Co1–O 171.55(6)–177.66(6)°), and each of Co2 and Co3 is also in a distorted octahedral geometry with four carboxylate oxygen atoms and two μ_3-OH groups (Co2–O 2.013(1)–2.161(1) Å; *cis*-O–Co2–O 82.05(6)–97.95(6)°; *trans*-O–Co2–O 180°; Co3–O 2.064(2)–2.202(2) Å; *cis*-O–Co3–O 83.13(6)–96.87(6)°; *trans*-O–Co3–O 180°). The coordination modes of the 4-cpa ligands are shown in Scheme 1. The μ_3-OH connects three Co^{II} ions into a scalene $Co_3(\mu_3\text{-}OH)$ triangle (Co1···Co2 3.113(1) Å, Co1···Co3 3.054(1) Å, Co2···Co3 4.268(2) Å) in a T-shape fashion (Co1–O–Co2 94.37(6)°, Co1–O–Co3 92.98(6)°, Co2–O–Co3 172.65(9)°), while the Co1···Co2 and Co1···Co3 edges are also bridged by a μ_2:η^2 (Co1–O1b–Co2 93.78(6)°, Co1–O6–Co3 90.90(6)°) and a μ_2:η^1:η^1 carboxylate groups. The $Co_3(\mu_3\text{-}OH)$ triangles are corner-shared *via* Co2 and Co3 to form a zigzag Δ-chain running along the *a*-axis. The adjacent chains are connected to each other by the trigonal-bipyramidally coordinated Na^+ ions through a triple bridge of a μ-aqua ligand, a μ_2:η^2, and a μ_2:η^1:η^1 carboxylate groups, and a single μ_2:η^1:η^1 carboxylate bridge into layers parallel to the *ab* plane, where the shortest interchain Co···Co distance is *ca.* 7.15 Å. The layers are pillared by the organic fragments of the 4-cpa ligands into the final 3D structure in the lattice (Fig. 1).

The dc susceptibility data of a polycrystalline sample of **1** was measured on a Quantum Design MPMS-XL7 SQUID magnetometer. At room temperature, the χT value of **1** is 6.10 cm^{3}mol^{-1}K per Co^{II}_2 unit (Fig. 2), being slightly higher than the spin-only value resulting from the orbital contribution of the octahedral Co^{II} ions.[9] Between 70 and 320 K, **1** obeys the Curie–Weiss law with the C of 7.23 cm^{3}mol^{-1}K and θ of −56 K. The C value corresponds to g = 2.19, being normal for an octahedral Co^{II}, and the large negative value of Weiss constant confirms the dominant exchange to be antiferromagnetic. Meanwhile, the χT value decreases slowly down to 50 K, then abruptly increases up to



Scheme 1 Coordination modes of 4-cpa ligands in **1**.

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† Electronic supplementary information (ESI) available: crystal data (CIF file and additional structural plots), additional magnetic data and XRD patterns. See DOI: 10.1039/b606765d

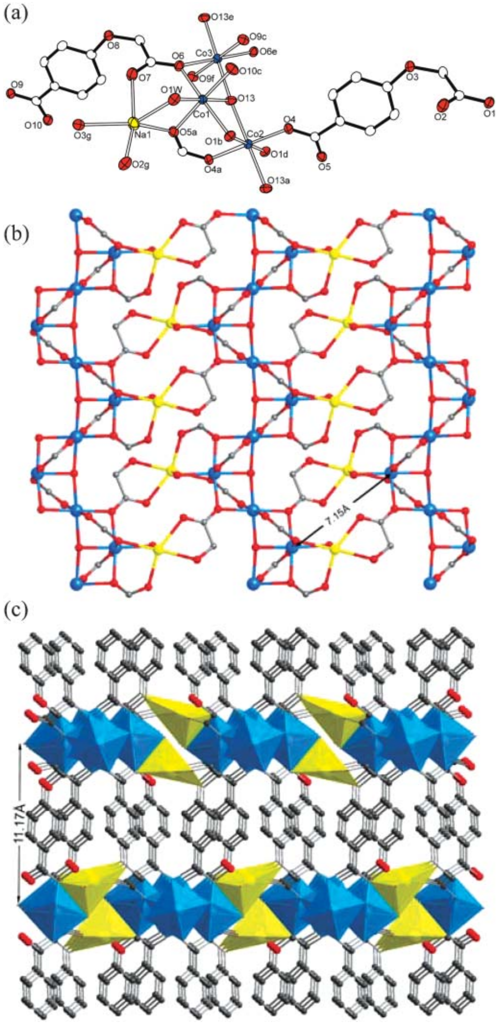

Fig. 1 Perspective views of the Co^{II} coordination environments (a), layer viewed down the *c*-axis (b), and 3D packing viewed along the *a*-axis (c) in **1**. Colour codes: Co blue, Na yellow, C gray, O red. Symmetry operations: (a) $1 - x, 2 - y, -z$; (b) $3/2 - x, -1/2 + y, 1/2 - z$; (c) $1/2 + x, 3/2 - y, 1/2 + z$; (d) $-1/2 + x, 5/2 - y, -1/2 + z$; (e) $-x, 2 - y, -z$; (f) $-1/2 - x, 1/2 + y, -1/2 - z$; (g) $-1/2 + x, 3/2 - y, -1/2 + z$.

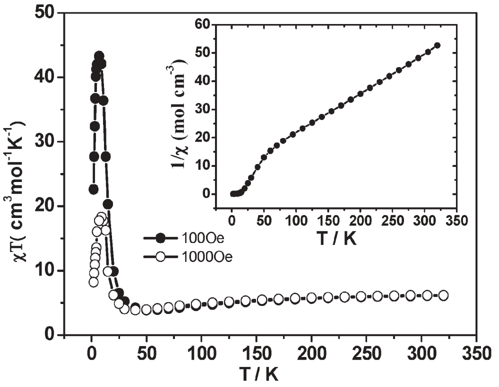

Fig. 2 The temperature-dependent susceptibility of **1** (at 100 Oe and 1000 Oe). Inset: inverse susceptibility $1/\chi$ for **1** at 100 Oe.

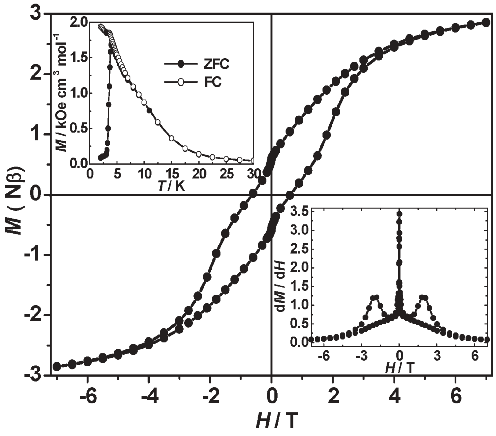

Fig. 3 Hysteresis curve for **1** between ±7 T at 2 K. Insets: FC and ZFC magnetization measured at 300 Oe (upper left), and field-dependence of d*M*/d*H* (lower right).

a maximum before decreasing again. This phenomenon is exactly the behaviour predicted for the Δ-chain and ferrimagnetic-like behaviour,[5] which is also confirmed by the field-cooled (FC) and zero-field-cooled (ZFC) magnetization showing the irreversibility below *ca.* 4.0 K (inset of Fig. 3). Moreover, the χT value is dependent on the applied field at low temperatures, being larger at a small field. For an idealized frustrated arrangement, the three exchange interactions corresponding to the triangle's edges should be equal, and the deviation from equality is likely to lead to suppression of the frustration and variable magnetism of the competitive effections.[4]

A hysteresis loop of **1** is observed clearly at 2 K (Fig. 3), giving a coercive field of *ca.* 6.0 kOe and a remnant magnetization of 0.59 Nβ. The magnetization at 70 kOe is 2.88 Nβ for the formula Co_2 unit, corresponding to 1/2 of that expected for a ferromagnetic arrangement of spins in the Co_2 unit, and suggesting a complicated ground-state spin configuration. The hysteresis loop has an abrupt variation near the zero field, which is clearly characterized by the peaks in the field dependence of d*M*/d*H* (inset of Fig. 3) and is attributable to the magnetic bistability due to a field-induced reorientation of the spins.[4]

In the ac susceptibility data of **1**, the obvious frequency-dependent behaviour is observed (Fig. 4). The relaxation time was obtained from the Arrhénius law $\tau(T) = \tau_0 \exp(-\Delta/k_B T)$, the best set of parameters is $\tau_0 = 2.80 \times 10^{-10}$ s and $\Delta/k_B = 106$ K (Fig. S1†), suggesting a thermally activated mechanism. The value

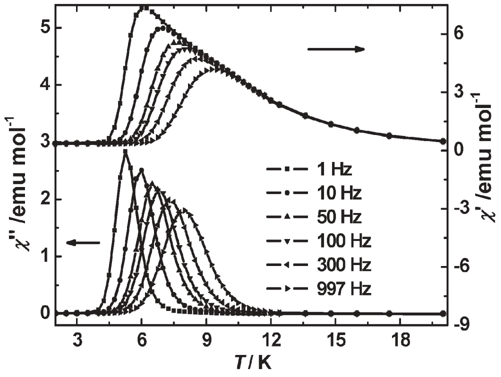

Fig. 4 Temperature dependence of the real χ' and imaginary χ'' parts of the ac susceptibility (H_{dc} = 0 Oe, H_{ac} = 3 Oe) for **1**. The lines are guides.

of τ_0 is close to that expected for the relaxation time of octahedral Co^{II} centres.[10] The shift of peak temperature (T_P) of χ'' was measured by a parameter $\phi = \Delta T_P/[T_P\Delta(\log f)] = 0.15$, being larger than that for a canonical spin glass and closer to a normal value for a superparamagnet.[11] At a fixed temperature of 6 K, χ' and χ'' almost describe a semicircle in the Cole–Cole plot (Fig. S2†), which can be fitted by Debye model with $\alpha = 0.26$, indicating a narrow distribution of relaxation time.[12]

High-dimensional compounds showing the slow magnetic relaxation, composing ferro- or ferri-magnetic chains are very scarce,[13] and **1** is the first case of Δ-chain topology showing the magnetic relaxation. The magnetic behaviour of **1** is reminiscent of that observed in single-chain magnets (SCM) and frustrated magnets, where the energy barrier originates from the single-ion anisotropy of high-spin Co^{II} in distorted octahedral environment and/or the anisotropic exchange interaction.[10,14,15] Although **1** features Δ-chains, the assignment of the magnetic relaxation to frustration is unreasonable because of the very different exchanges in the scalene triangles. On the other hand, the meaningful values of τ_0 and Δ/k_B of **1** are comparable with the reported SCMs,[14] indicating a single-chain-magnet-like behaviour of **1**. To definitely assign an SCM behaviour for **1**, further investigations such as magnetic anisotropic determinations are needed. Unfortunately, a single crystal big enough for the magnetic measurement could not be grown yet. On the other hand, compared with the known genuine and quasi-Δ-chain structures, we can conclude the magnetically well-seperated Δ-chains are critical for the Δ-chain magnets showing the slow magnetic relaxation. As far as we know, magnetically individual ferro- or ferri-magnetic chains are indispensable for the SCMs. Obviously, the unique structure of 4-cpa plays an important role in the structure and interesting properties of **1**. The ether group of 4-cpa not only avoids the ligand being fully conjugated, but also provides a potential coordination site for Na$^+$ ions. The magnetically inert Na$^+$ ions in **1** divide the layers into individual magnetic Δ-chains, being similar to the diamagnetic ions separating the Kagomé layers in the jarosite AFe$_3$(SO$_4$)$_2$(OH)$_6$ (A = Na$^+$, K$^+$, Rb$^+$, Ag$^+$, Tl$^+$, NH$_4^+$, H$_3$O$^+$, 1/2Pb^{2+} or 1/2Hg^{2+}).[3]

In summary, by the aid of magnetically inert molecular components, well-separated Δ-chains are successfully assembled in the 3D coordination polymer **1**, which shows unusual magnetism and represents the first case of slow magnetic relaxation for the Δ-chain topology. This work demonstrates that crystal engineering can be an effective route in researching magneto-structural correlations of molecule-based materials.

Notes and references

‡ Synthesis of **1**: A mixture of 4-cpaH$_2$ (0.098 g, 0.5 mmol),[16] a solution of NaOH (1 mol L^{-1}, 1.5 ml), and CoCl$_2\cdot$6H$_2$O (0.118 g, 0.5 mmol) in ethanol (7 ml) was sealed in a 15 ml Teflon-lined autoclave and heated at 160 °C for 3 days to give the pink block-like crystals of **1** (yield 81% based on 4-cpa). IR data for **1** ($\tilde{\nu}$, cm^{-1}): 3586(w), 3423(m), 3043(m), 1599(vs), 1546(s), 1401(s), 1258(m), 1213(s), 1062(m), 859(m), 781(m), 712(m), 635(m), 588(m), 473(w). Elemental analysis (%) calcd for **1** (C$_{18}$H$_{15}$Co$_2$NaO$_{12}$): C 38.29, H 2.66%; found: C 38.23, H 2.70%.

§ Crystal data for **1**: C$_{18}$H$_{15}$Co$_2$NaO$_{12}$, M = 564.15, monoclinic, space group $P2_1/n$, a = 8.5377(6), b = 10.0981(7), c = 22.0819(15) Å, β = 99.6730(10)°, V = 1876.7(2) Å^3, Z = 4, D_c = 1.997 g cm^{-3}, final R_1 = 0.0317 for $I \geqslant 2\sigma(I)$, wR_2 = 0.0810 for all data. The intensity data were recorded on a Bruker SMART Apex CCD system with MoKα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.) CCDC 601874. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606765d

Magnetic susceptibility measurements of **1** were performed on a polycrystalline sample fixed with GE7031 varnish on a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369.

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

3 (*a*) B. Moulton, J. Lu, R. Hajndl, S. Hariharan and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2002, **41**, 2821; (*b*) X.-Y. Wang, L. Wang, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2006, **128**, 674; (*c*) D. G. Nocera, B. M. Bartlett, D. Grohol, D. Papoutsakis and M. P. Shores, *Chem.-Eur. J.*, 2004, **10**, 3850; (*d*) D. Grohol, K. Matan, J.-H. Lee, J. W. Lynn, D. G. Nocera and Y. S. Lee, *Nat. Mater.*, 2005, **4**, 323; (*e*) G. Paul, A. Choudhury, E. V. Sampathkumaran and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2002, **41**, 4297; (*f*) C. N. R. Rao, E. V. Sampathkumaran, R. Nagarajan, G. Paul, J. N. Behera and A. Choudhury, *Chem. Mater.*, 2004, **16**, 1441.

4 (*a*) S. O. H. Gutschke, D. J. Price, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed.*, 2001, **40**, 1920; (*b*) D. Cave, J.-M. Gascon, A. D. Bond, S. J. Teat and P. T. Wood, *Chem. Commun.*, 2002, 1050; (*c*) S. M. Humphrey and P. T. Wood, *J. Am. Chem. Soc.*, 2004, **126**, 13236.

5 (*a*) J. J. Borrás-Almenar, E. Coronado, C. J. Gómez-Garcia, R. Georges and C. Muñoz-Roca, *Chem. Phys. Lett.*, 1991, **186**, 410; (*b*) J. J. Borrás-Almenar, E. Coronado, J. C. Gallart, R. Georges and C. J. Gómez-Garcia, *J. Magn. Magn. Mater.*, 1992, **104–107**, 835; (*c*) T. Nakamura and K. Kubo, *Phys. Rev., B*, 1996, **53**, 6393; (*d*) H. Otsuka, *Phys. Rev., B*, 1995, **51**, 305.

6 (*a*) C. Ruiz-Pérez, M Hernández-Molina, P. Lorenzo-Luis, F. Lloret, J. Cano and M. Julve, *Inorg. Chem.*, 2000, **39**, 3845; (*b*) H. Kikuchi, Y. Fujii, M. Chiba, S. Mitsudo and T. Idehara, *Polyhedron*, 2005, **24**, 2835.

7 (*a*) M.-H. Zeng, W.-X. Zhang, X.-Z. Sun and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2005, **44**, 3079; (*b*) Y.-Z. Zheng, M.-L. Tong, W.-X. Zhang and X.-M. Chen, *Chem. Commun.*, 2006, 165.

8 (*a*) L. Pan, B. S. Finkel, X.-L. Huang and J. Li, *Chem. Commun.*, 2001, 105; (*b*) P. Yan, S. Gao, L.-M. Zheng, Z.-M. Wang and X.-Q. Xin, *Chem. Commun.*, 2003, 1076; (*c*) D. J. Price, A. K. Powell and P. T. Wood, *J. Chem. Soc., Dalton Trans.*, 2000, 3566.

9 (*a*) M. Kurmoo, *Chem. Mater.*, 1999, **11**, 3370; (*b*) H. Kumagai, M. Akita-Tanaka, K. Inoue and M. Kurmoo, *J. Mater. Chem.*, 2001, **11**, 2146; (*c*) A. Rujiwatra, C. J. Kepert, J. B. Claridge, M. J. Rosseinsky, H. Kumagai and M. Kurmoo, *J. Am. Chem. Soc.*, 2001, **123**, 10584; (*d*) M. Kurmoo, H. Kumagai, S. M. Hughes and C. J. Kepert, *Inorg. Chem.*, 2003, **42**, 6709.

10 (*a*) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem., Int. Ed.*, 2001, **40**, 1760; (*b*) T.-F. Liu, D. Fu, S. Gao, Y.-Z. Zhang, H.-L. Sun, G. Su and Y.-J. Liu, *J. Am. Chem. Soc.*, 2003, **125**, 13976.

11 (*a*) A. H. Morrish, *The Physical Principles of Magnetism*, Wiley, New York, 1966; (*b*) J. A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor & Francis, London, 1993.

12 K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341.

13 X.-J. Li, X.-Y. Wang, S. Gao and R. Cao, *Inorg. Chem.*, 2006, **45**, 1508.

14 (*a*) R. Clérac, H. Miyasaka, M. Yamashita and C. Coulon, *J. Am. Chem. Soc.*, 2002, **124**, 12837; (*b*) R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve, M. Verdagurer, Y. Draomzee, D. Gatteschi and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2003, **42**, 1483; (*c*) S. Wang, J.-L. Zuo, S. Gao, H.-C. Zhou, Y.-Z. Zhang and X.-Z. You, *J. Am. Chem. Soc.*, 2004, **126**, 8900.

15 (*a*) E.-C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezma-Gairaud and G. Christou, *J. Appl. Phys.*, 2002, **91**, 7382; (*b*) H. Oshio and M. Nakano, *Chem.-Eur. J.*, 2005, **11**, 5178; (*c*) A. Caneschi, D. Gatteschi, N. Lalioti, R. Sessoli, L. Sorace, V. Tangoulis and A. Vindigni, *Chem.-Eur. J.*, 2002, **8**, 286.

16 C. F. Koelsch, *J. Am. Chem. Soc.*, 1931, **53**, 304.