Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 8154

Received 1st March 2014,
Accepted 6th March 2014

DOI: 10.1039/c4dt00375f

www.rsc.org/dalton

A two-dimensional homospin Cu(II) ferrimagnet featuring S-shaped hexanuclear secondary building blocks†

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The decomposition of 2-(1-hydroxy-2-methylpropan-2-yl-imino)-1,2-diphenylethanone in the presence of copper acetate promoted the formation of a two-dimensional homospin Cu(II) ferrimagnet featuring S-shaped hexanuclear secondary building blocks and a new pentanodal topology.

Ferrimagnets are drawing increased research interest from both fundamental and device-related perspectives for their permanent magnetization due to the noncancellation of the antiferromagnetic coupled spins.[1] Conventional ferrimagnetic systems are usually achieved by different spin carriers which can be either two kinds of metal ions with different spins[2] or the same metal with different oxidation states,[3] as well as a metal ion with an organic radical[4] or just one organic component bearing two or more kinds of organic radicals with different spin-multiplicities.[5] In contrast, the homometallic homospin ferrimagnetic systems are uncommon and still remain a synthetic challenge for their prerequisites of the particular spatial arrangement and the thus resulting non-compensation of individual spin moments which are difficult to achieve.[6–9] Undertaking the task, a few researchers succeeded in obtaining homospin ferrimagnets. From the magnetic topological point of view, magnetic lattices containing odd-sided polyhedra such as triangles may achieve the non-compensation in antiferromagnetically coupled spin moments, thereby showing ferrimagnetism.[8,10] Based on a consideration of magnetic interaction, the introduction of ferromagnetic interaction and the specific alternation of antiferromagnetic (AF) and ferromagnetic (F) interactions are regarded as one of the important strategies for achieving these systems.[7] In the synthetic strategy, mixed ligands were used to induce different coordination environments and a special topological arrangement for these spin carriers, ensuring the noncancellation of the same kind of spins.[9] In spite of the limited achievement, it is still of great difficulty to tune the reaction conditions to meet the requirements mentioned above for the preparation of the targeted ferrimagnets. Taking the challenge, we managed to explore the synthetic conditions for the formation of the aimed homospin ferrimagnet by a combination of all above-mentioned methods. Carboxylate and alkoxide groups can both mediate magnetic coupling effectively and are both capable of promoting AF and F interactions by adopting appropriate bridging modes and tuning the M–O–M bridging angles, respectively. Furthermore, they are both facile to form a triangular lattice (odd-sided polyhedra) *via* bridging three or more metal ions simultaneously. Thus we managed to use carboxylate and alkoxide ligands to synergistically tune the magnetic topology and magnetic interactions between metal ions with the specific reaction conditions provided by a synergistic decomposition reaction of a Schiff base.

We report here a ferrimagnetic complex $[Cu_3(NH_2C(CH_3)_2CH_2O)(CH_3COO)_5]_n$ (**1**) separated from the reaction of $Cu(CH_3COO)_2$ with a Schiff base of 2-(1-hydroxy-2-methylpropan-2-ylimino)-1,2-diphenylethanone, the formation of which was driven by the decomposition of the Schiff base. There are three crystallographically independent Cu(II) ions, five acetato groups and one 2-amino-2-methyl-1-propanolato ligand in the asymmetric unit of **1** (Fig. 1a). The three Cu(II) ions present square pyramidal geometries completed by five oxygen atoms from five acetato groups for Cu1 and Cu2, and by four oxygen atoms and one nitrogen atom from two acetato groups and two 2-amino-2-methyl-1-propanolato anions for Cu3. Cu1 and Cu2 are connected by four *syn–syn* bridging acetato groups to form a paddle-wheel $[Cu_2(CH_3COO)_4]$ unit with a Cu⋯Cu distance of 2.5992(6) Å. Cu3 and Cu3B are bridged by two 2-amino-2-methyl-1-propanolato anions in chelating-bridging modes to build a $[Cu_2(H_2NC(Me_2)CH_2O)_2]^{2+}$ unit with a Cu⋯Cu distance of 2.9119(9) Å. Two $[Cu_2(CH_3COO)_4]$ units are bridged by one $[Cu_2(H_2NC(Me_2)CH_2O)_2]^{2+}$ unit *via* two acetato O atoms to construct an S-shaped hexanuclear $\{[Cu_2(CH_3COO)_4][Cu_2(H_2NC(Me_2)CH_2O)_2][Cu_2(CH_3COO)_4](CH_3COO)_2\}$ unit.

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† Electronic supplementary information (ESI) available: Experimental details, and additional tables and figures for **1**. CCDC 976195. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00375f

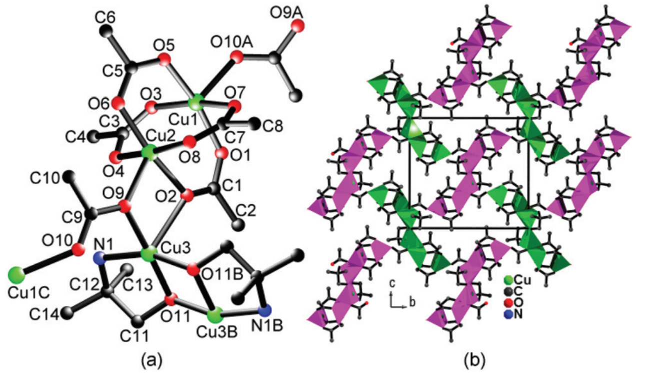

Fig. 1 (a) Molecular structure of **1** with selected atoms labelled. Symmetry codes: (A) −*x* + 2, *y* − 1/2, −*z* + 1/2; (B) −*x* + 2, −*y* + 1, −*z* + 1; (C) −*x* + 2, *y* + 1/2, −*z* + 1/2. (b) Two-dimensional sheet of **1**.

Each hexanuclear unit is further connected to another four ones in a head-to-side style, constructing a two-dimensional sheet. Alternatively, $[Cu_2(CH_3COO)_4]$ units are bridged along the *b*-axis by acetato groups in *anti–anti* bridging modes to form one-dimensional chains, which are further bridged by $[Cu_2(H_2NC(Me_2)CH_2O)_2]^{2+}$ units along the *c*-axis to form the two-dimensional sheet (Fig. 1b and S1†). It shows a new pentanodal 3-connected $(3{\cdot}16^2)(3{\cdot}4{\cdot}5)^2(4{\cdot}16^2)^2$ topology (Fig. S2†). The five acetato groups in the asymmetric unit of **1** present three kinds of bridging modes (Fig. 2a–c). Three carboxylato groups in the $[Cu_2(CH_3COO)_4]$ unit behave as μ_2-bridges (Fig. 2a: *syn–syn*), and the other one in the $[Cu_2(CH_3COO)_4]$ unit adopts a μ_3-bridging mode (Fig. 2b: *syn–syn* : *anti*). The fifth acetato group in **1** acts as a different μ_3-bridging mode (Fig. 2c: *anti–anti* : *syn*). The 2-amino-2-methyl-1-propanolato ligand in **1** behaves also as a μ_2-bridging mode (Fig. 2d: chelating-bridging).

The magnetic behavior of **1** (solid state) observed by a SQUID magnetometer at a DC field of 1000 Oe is shown in Fig. 3a as the temperature dependent χ_M and $\chi_M T$ plot per hexanuclear building unit. Upon cooling, χ_M increases smoothly first, and then increases rapidly below about 22 K reaching a maximum of 0.75 cm^3 mol^{-1} at 2.5 K. Decreasing the temperature, the value of $\chi_M T$ decreases steadily from 1.98 cm^3 K mol^{-1} at 300 K to a round minimum of 0.65 cm^3 K mol^{-1} at about 40 K. As the temperature is lowered further, $\chi_M T$ increases rapidly and reaches a maximum of 4.33 cm^3 K mol^{-1} at 7.9 K, and finally decreases rapidly reaching 1.45 cm^3 K mol^{-1} at 1.96 K. All of these are characteristic of a ferrimagnetic behaviour with dominant antiferromagnetic interactions between the adjacent Cu(II) centers.[11] A further study of $\chi_M T$ *vs.* T in the low temperature range at different fields (Fig. 3b) shows that the maximum in $\chi_M T$ at 7.9 K became less prominent upon increasing the field. This transition at 7.9 K could indicate the onset of long-range magnetic ordering.[12]

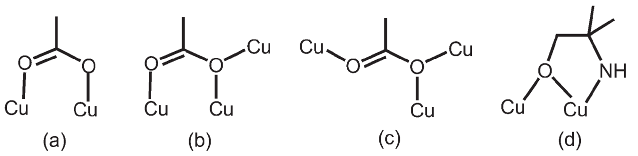

Fig. 2 Bridging modes of acetate and 2-amino-2-methyl-1-propanolato ligands in **1**.

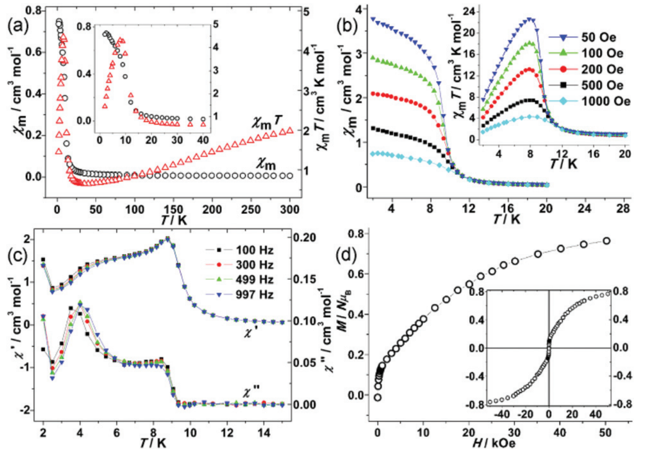

Fig. 3 (a) Plots of χ_M and $\chi_M T$ *vs.* T for **1**. (b) Plots of χ_M and $\chi_M T$ (inset) *vs.* T measured between 2 and 20 K at the indicated applied fields. (c) Temperature-dependent ac magnetic susceptibilities of **1** under different frequencies (100, 300, 499 and 997 Hz) with a zero DC field and an oscillating field of 2.5 Oe. (d) Field dependence of the magnetization below 50.26 kOe for **1**. (Inset: the whole field dependence of the magnetization between −50.26 and 50.26 kOe emphasizing the absence of a hysteresis effect.) Solid lines are guides for the eyes.

To complete the characterization of the magnetic ordering and define more precisely the critical ordering temperature, the real χ' and the imaginary χ'' components of ac susceptibility (Fig. 3c) were measured with a frequency of 100, 300, 499 and 997 Hz and an amplitude of the driving field of 2.5 Oe. It reveals in the real part of the susceptibility a broad and asymmetric peak with a frequency-independent maximum of χ' at 8.8 K and a plateau around 4.4 K showing a tiny frequency dependence. The imaginary part of the ac susceptibility becomes non-zero below 9.3 K, which defines the critical temperature. In comparison to the real χ' components, the imaginary χ'' components present first a shoulder-peak at 8.4 K and then an apparent peak at 4 K which shows some frequency dependency. This indicates the presence of long-range magnetic ordering.[13] The emergence of two peaks on both the real χ' and the imaginary χ'' components of ac susceptibility was also seen in a few heteronuclear ferrimagnetic compounds,[14] but seldom for homonuclear ferrimagnetic compounds. Field-dependent magnetization (M) measurements (0 to 50.26 kOe) at 2.0 K were carried out as presented in Fig. 3d. As the applied field increases, a rapid increase below about 0.5 kOe followed by a much slower increase led to a magnetization of 0.76$N\beta$ at 50.26 kOe, which is much lower than that expected for a total alignment of the moments and suggests a magnetic ordering. No magnetic hysteresis is observed at 2 K for this compound.

As demonstrated in the structural discussion, compound **1** presents a 2D structure constructed from S-shaped hexanuclear units. The noncompensation of the Cu(II) spin carriers and the thus resulting long range magnetic order can be interpreted based on their special arrangement as shown in Fig. 4. Cu1 and Cu2 are linked by four carboxylato groups in *syn–syn*-bridging modes to form a paddle-wheel motif, which favours strong antiferrromagnetic coupling between the two spin carriers.[15] Magneto-structural correlation studies for hydroxide/alkoxide bridged dimers revealed an angular dependence which marks a crossover from antiferromagnetic to ferromagnetic coupling at a Cu–O–Cu bridging angle of about 97.6°.[16,17] However, there exist both cases between Cu2 and Cu3 ions (Cu2–O2–Cu3: 96.28(10)° and Cu2–O9–Cu3: 103.12(10)°). As stated in documents, the antiferromagnetic coupling in this case usually dominates over the ferromagnetic coupling.[17] As a result, Cu2 and Cu3 are presumably antiferromagnetically coupled. Cu3 and Cu3B are double bridged by alcoholic oxygen atoms in an equatorial–equatorial Cu–O–Cu exchange pathway with the Cu3–O11–Cu3B bridging angles of 97.40(11)°, a τ angle of 41.3° and the Cu3–O11 and Cu3–O11B bond lengths of 1.933(2) and 1.943(2) Å, which is facile for ferromagnetic interaction.[18] Cu1 and Cu3 are bridged by one *syn–anti* carboxylato group in an equatorial–apical and nonplanar Cu–O–C–O–Cu exchange pathway mediating a weak ferromagnetic interaction,[19] which also supports the above-mentioned magnetic couplings between Cu1 and Cu2, as well as Cu2 and Cu3. Cu1 in the hexanuclear secondary constructing unit is further linked to Cu2A and Cu3A by one carboxylato group in *anti–anti* : *syn* mode (*anti–anti* mode for nonplanar Cu1–O–C–O–Cu2A *via* an apical–apical exchange pathway and *syn–anti* mode for nonplanar Cu1–O–C–O–Cu3A *via* an apical–equatorial exchange pathway), which facilitates antiferromagnetic and ferromagnetic couplings for Cu1 and Cu2A, and Cu1 and Cu3A, respectively.[19] This kind of magnetic interaction leads to the linkage of the hexanuclear secondary building unit to another four ones, resulting in a 2D magnetic order.

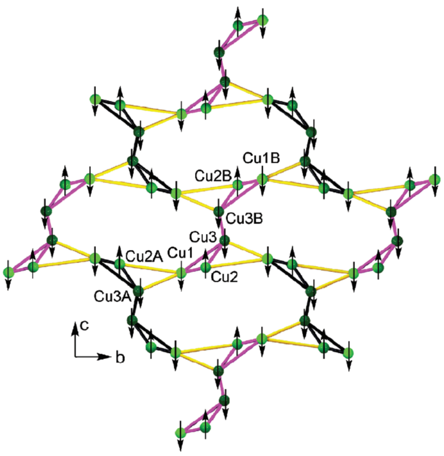

Fig. 4 Schematic illustration of the spin topology in **1** viewed along the *a* direction.

Conclusions

In summary, we demonstrate here a rare homospin Cu(II) ferrimagnet featuring S-shaped hexanuclear secondary building blocks and a new pentanodal 3-connected 2D topology. The decomposition of 2-(1-hydroxy-2-methyl-propan-2-ylimino)-1,2-diphenylethanone made a significant contribution to the formation of the title compound, which provides a strategy for preparing ferrimagnets by tuning the structural parameters *via* the control of specific reaction environments.

Acknowledgements

The authors acknowledge the financial support by the National Natural Foundation of China (grant no. 21261004 and 21271050), Guangxi Natural Science Foundation of China (grant no. 2013GXNSFGA019008 and 2013GXNSFAA019039), and Program for New Century Excellent Talents in University (NCET-10-0095).

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