A novel molecular ladder structure of Cu(II)–Ba(II) coordination polymer exhibiting ferromagnetic coupling

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A novel one-dimensional ladder-like Cu–Ba compound {[Ba(H₂O)₃(CuL)₂]·2H₂O}ₙ (H₃L = Glycylglycine, *N*-[1-(2-hydroxyphenyl)propylidene]), has been synthesized and structurally characterized; it exhibits ferromagnetic interaction.

Self-assembly of coordination polymers from basic building blocks is of considerable interest due to their intriguing diverse architectures and potential applications in catalysis and advanced materials such as magnetic, optic and electronic materials.[1,2,5] The assembly principle is to utilize a building block approach to construct a coordination polymer through covalent and/or intermolecular forces under the support of rigid ligands. Many types of interesting network topologies have been reported recently, including chain,[3] ladder,[4] grid,[5] brick wall,[6] honeycomb,[7] diamondoid,[8] rutile,[9] and α-polonium.[10] Although ladder-like coordination polymers are less well investigated compared with other network topologies, the results obtained from these compounds are surprisingly rich, with both fascinating structural and novel properties such as molecular adsorption[11] and magnetic properties[4] in recent years. As a building block to furnish a coordination polymer, L was considered for the following reasons: a) It could furnish various coordination modes due to the presence of the multifunctional group for coordination to metal. b) Having a rigid structure after coordination with Cu(II), this would allow formation of a multi-dimension framework. c) It has a strong capability of forming hydrogen bonds that play an important role in the assembly of supramolecular compounds. On the other hand, until now, studies on coordination polymers have overwhelmingly focused on the transition metals and studies on main group metals are very rare,[12] whereas heterometallic polynuclear alkaline earth metal–copper compounds have attracted much research attention recently because of their potential applications in copper oxide based superconductors and molecular magnetism.[13] Herein, we describe the synthesis and structure of a novel molecular ladder [Ba(H₂O)₃-(CuL)₂]·2H₂O which exhibits ferromagnetic coupling.

The independent unit of the crystal structure is shown in Fig. 1.† The coordination environment of the copper(II) centers is approximately square-planar. The Schiff-base ligand is deprotonated, thus acting as a triple negatively charged quadridentate ONNO chelate. It coordinated to the copper(II) atom *via* one phenolic oxygen (O(1)), one deprotonated amide nitrogen atom (N(2)), one imino nitrogen atom (N(1)) and one carboxylate oxygen atom (O(3)). The values 1.441 Å for C(10)–N(1) bond, shorter than the usual C–N single bond, and the double bond C(7)–N(1) length of 1.302 Å agree well with the values of Schiff Base type I.[14] The best-fit least-squares plane through the four basal and Cu atoms shows these atoms to be nearly coplanar. The O(1)–Cu(1)–N(2) angle of 178.1° is nearly linear. The phenyl ring [C(1)–C(6)] and the ring of C(1), C(6), C(7), N(1), O(1), Cu(1) chelate ring are almost coplanar with a small dihedral angle of 7.7°. The coordination environment of Cu(2) is similar to that of Cu(1). The coordination of Cu and L forms a rigid structure [CuL]⁻. Barium(II) is 8-coordinated by three water molecules (O(9) to O(11)), three carboxylic oxygen atoms (O(3), O(4), O(4)i; symmetry code i: 1 − x, 2 − y, 1 − z),

and two carbonyl oxygen atoms (O(6), O(2)ii; symmetry code ii: x, 1 + y, z). The Ba–O(water) distances ranging from 2.687 to 2.825 Å are similar to the reported values.[15] The Ba–O (carboxylic and carbonyl oxygen) distances range from 2.670 to 2.839 Å. There are two crystallographically unique [CuL]⁻ anions in the structure. One of the [CuL]⁻ containing O(2) O(3) and O(4) coordinate to barium ions as tridentate unit. The other one [CuL]⁻ coordinate to one barium ion using only one carbonyl oxygen atom O(6) as monodentate unit. The nearest Cu–Cu distance (Cu(1)–Cu(2)) is 3.622 Å. The distances between Cu and the N atom of the nearby [CuL]⁻ are Cu(1)–N(3) 3.226 Å; Cu(2)–N(2) 3.178 Å. The Cu(1), Cu(2), N(2), N(3) are almost coplanar, and the mean deviation from the plane is 0.0065 Å.

Fig. 2 shows the illustration for the assembly of an infinite ladder framework (1-D chain) from [CuL]⁻ unit and node [Ba(H₂O)₃]²⁺. The carboxylic oxygen atom (O(4)) of the tridentate [CuL]⁻unit bridge the adjacent [Ba(H₂O)₃]²⁺(Ba(1), Ba(1)i; symmetry code i: 1 − x, 2 − y, 1 − z) together to form the rungs of the ladder. The nearest Ba–Ba distance is 4.307 Å. The rails of the ladder are made of 7-atoms unit O(2)–C(11)–N(2)–C(12)–C(13)–O(3)–Ba(1) in which carbonyl oxygen (O(2)) of the tridentate [CuL]⁻unit link with [Ba(H₂O)₃]²⁺ along *b* axis (see Fig. 3).

Fig. 4 depicts the temperature dependence of $\chi_m T$ for [Ba(H₂O)₃(CuL)₂]·2H₂O in the range of 1.8–300 K. The value of $\chi_m T$ at 300 K is estimated at 0.526 emu·K·mol⁻¹. As the temperature is decreased from 300 K to 7.3 K, The values of $\chi_m T$ show a gradual increase, indicating a ferromagnetic coupling. After passing though a maximum of 0.673 emu·K·mol⁻¹ at 7.3 K, $\chi_m T$ shows an abrupt decrease, suggesting a weak antiferromagnetic coupling between the ferromagnetic units. Ferromagnetic ordering is demonstrated further by the field dependence of isothermal magnetization performed at 1.8 K (inset of Fig. 4). The magnetization at 1.8 K increases very rapidly in low field, and reaches the saturation value of *ca.*
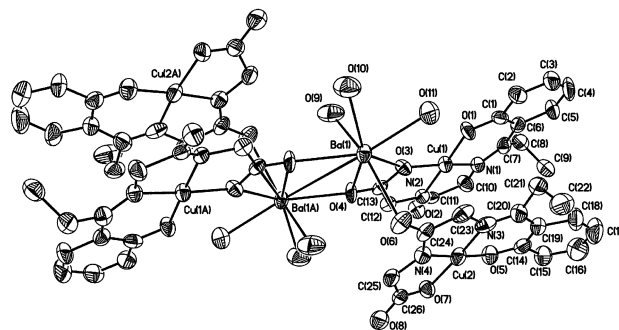

Fig. 1 An ORTEP view of the crystal structure of [Ba(H₂O)₃(CuL)₂] showing the 50% probability thermal ellipsoid. Selected bond distances (Å): Ba(1)–O(4)i 2.670(5), Ba(1)–O(10) 2.687(5), Ba(1)–O(11) 2.728(5), Ba(1)–O(2)ii 2.725(5), Ba(1)–O(6) 2.770(5), Ba(1)–O(9) 2.825(5), Ba(1)–O(4) 2.839(5), Ba(1)–O(3) 2.835(5), Ba(1)–C(13) 3.225(7), Ba(1)–Ba(1)i 4.3070(11), Cu(1)–O(1) 1.853(5), Cu(1)–N(2) 1.875(6), Cu(1)–N(1) 1.907(6), Cu(1)–O(3) 1.974(5), Cu(2)–N(4) 1.869(6), Cu(2)–O(5) 1.860(5), Cu(2)–N(3) 1.939(7), Cu(2)–O(7) 1.960(5). (Symmetry code i: 1 − x, 2 − y, 1 − z; ii: x, 1 + y, z.)

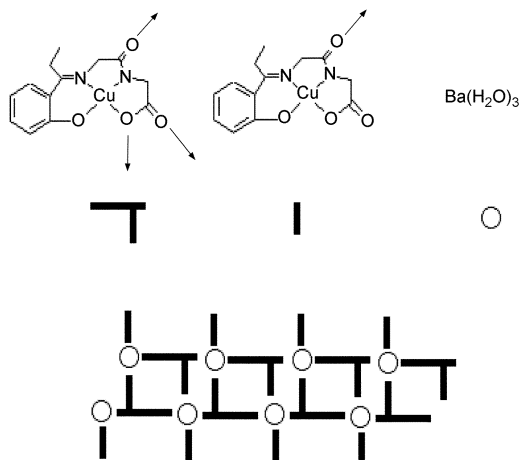**Fig. 2** Scheme of the illustration for the assembly of an infinite ladder framework from the [CuL]⁻ unit and node [Ba(H₂O)₃]²⁺. (The arrows indicate the coordination to the barium.)
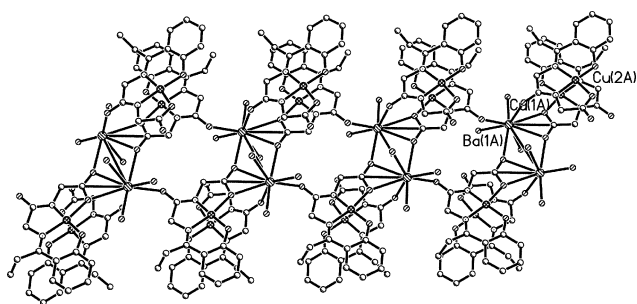

Fig. 3 View of ladder structure of $[Ba(H_2O)_3(CuL)_2]_n$ along *b* axis.

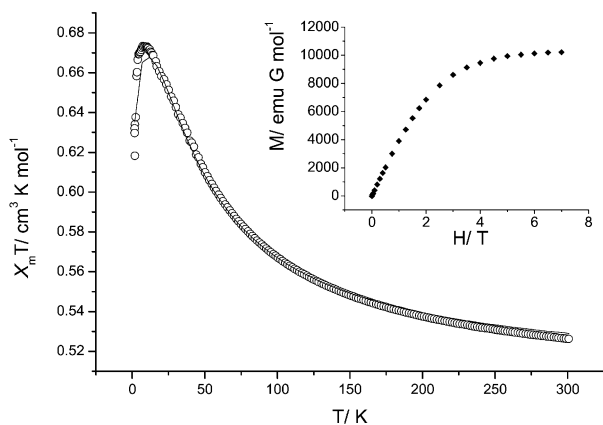**Fig. 4** Temperature dependence of $\chi_m T$ per formula $[Ba(H_2O)_3(CuL)_2]$ for a powder sample. The field dependence of magnetization *M* for $[Ba(H_2O)_3(CuL)_2]$ at 1.8K is given in the inset.

10138 emu·G·mol⁻¹ at 60 kOe. It is reasonable to ascribe the ferromagnetic coupling to the coordination bonds between [CuL]⁻ and Ba²⁺(the dipolar–dipolar interactions may also contribute),[13d,16] and the antiferromagnetic coupling to the interchain interactions. Since the ferromagnetic coupling is much stronger than the antiferromagnetic one, we interpret the magnetic data in terms of the ferromagnetic dimer model with a weak interdimer antiferromagnetic interaction, using:

$$\chi_m = \frac{4C}{T\{3 + \exp(-2J / k_B T)\} - 2zJ' / k_B} \tag{1}$$

Where *C* corresponds to the Curie constant, k_B is the Boltzmann constant, *J* is the ferromagnetic intradimer coupling constant, *J'* expresses the antiferromagnetic interdimer coupling constant, and *z* is the number of the nearest neighbors. The derivation of eqn (1) is described elsewhere.[17] The best fit

parameters were $C = 0.542$ emu K mol⁻¹, $J/k_B = 14.3$ K, and $zJ'/k_B = -0.586$ K with a final agreement factor $R = 2.0 \times 10^{-6}$ [$R = \Sigma(\chi_m^{obs} - \chi_m^{calc})^2/\Sigma(\chi_m^{obs})^2$].

In conclusion, we have prepared a ladder coordination polymer in which the rigid [CuL]⁻ anion link with [Ba(H₂O)₃]²⁺ forming rails and rungs of the ladder. The magnetic data were interpreted in terms of a ferromagnetic dimer with a weak interdimer antiferromagnetic interaction. This work reveals that H₃L is a useful building block of ferromagnetic coordination compounds.

Notes and references

† Glycylglycine (10 mmol), 2-hydroxypropiophenone(10 mmol) and LiOH (20 mmol) were dissolved and refluxed in MeOH/H₂O(v : v = 1 : 1) CuCl₂·2H₂O(10mmol) was then added to the solution and the resulting solution was adjusted to the pH = 9–11. At last BaCl₂·2H₂O(5 mmol) was added. The precipitate was recrystallized from DMF solution. After two months violet crystals suitable for X-ray diffraction were obtained. Elemental analysis (C, H, N) satisfied the formula: C₂₆H₃₆O₁₃N₄Cu₂Ba.

Crystallographic data of [Ba(H₂O)₃(CuL)₂]·2H₂O are: C₂₆H₃₆O₁₃N₄-Cu₂Ba, Fw = 877.01, triclinic, *P*1̄, a = 8.2483(13), b = 9.7341(16), c = 20.871(3) Å, α = 77.325(3) β = 81.574(3) γ = 81.341(3)°, V = 1605.0(4) Å³, Z = 2, D_calc = 1.815 g cm⁻³, T = 293 K, R = 0.0548 [I > 2σ(I)], and 5563 independent reflections. CCDC reference number 217031. See http://www.rsc.org/suppdata/cc/b3/b308474d/ for crystallographic data in .cif or other electronic format.

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