Self-assembly of a 1D heterotrimetallic Cu(II)-Sr(II)-Na(I) propeller-like chiral coordination polymer with ferromagnetic interactions†

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Self-assembly of metalloligand [CuL]⁻ (H₃L = *N*-5-bromo-salicylaldehydeglycyl-L-tyrosine) with Sr^{2+} and Na^+ results in a 1D μ_2-carboxylate- and H_2O-bridged heterotrimetallic chiral coordination polymer {[Na(CuL)₃Sr(H₂O)₃]·9H₂O}ₙ, which exhibits weak ferromagnetic exchange interactions and optical activity.

Coordination polymers with chiral structure play an important role in molecular recognition processes and biological systems.[1] The study of chiral coordination polymers is a very active interdisciplinary research area with potential applications in asymmetric catalysis, enantioselective synthesis, porous materials, nonlinear optical materials, and magnetic materials.[2] The design and synthesis of chiral polyfunctional materials is a quite challenging topic.[3] Coordination chemistry provides a great variety of chiral mononuclear complexes as suitable metal-containing building blocks or metalloligands for assembling chiral coordination polymers with various topologies and physical properties (optical activity and magnetic property, *etc.*).[4] This building block approach includes the possibility of introducing chiral centers in either metal complexes or ligands to obtain chiral network.[5] Transition metal complexes of chiral dipeptide and its derivatives containing multifunctional coordination groups (carbonyl and carboxylate oxygen) could be good candidates to be used as metalloligands and particularly suitable for constructing extended multi-dimensional heterometallic chiral magnetic supramolecular coordination polymers. Herein, we have designed a novel heterotrimetallic 1D chiral coordination polymer {[Na(CuL)₃Sr-(H₂O)₃]·9H₂O}ₙ(**1**) (H₃L = *N*-5-bromosalicylaldehydeglycyl-L-tyrosine), which is self-assembled by rigid square-planar [CuL]⁻ metalloligand and two types of main group metal ions. To the best of our knowledge, this is the first example of a 1D chiral heterometallic coordination polymer exhibiting ferromagnetic exchange interactions in which three different metal centers such as an alkali metal (sodium), an alkaline earth metal (strontium) and a transition metal atom (copper) coexist.

Glycyl-L-tyrosine (10 mmol), 5-bromosalicylaldehyde (10 mmol) and NaOH (10 mmol) was dissolved and refluxed in MeOH/H₂O (v:v = 1:1), then Cu(OAC)·H₂O (10 mmol) was added to the solution. The resulting mixture was adjusted to pH 9–10 and stirred at 35–40 °C for 2 h. At last SrCl₂·6H₂O (3.5 mmol) was added. The precipitate was recrystallized from aqueous solution. After several days violet crystals suitable for X-ray diffraction were obtained (55% yield).‡

The independent unit of the crystal structure is shown in Fig. 1.§ Compound **1** crystallizes in the chiral trigonal space group *R*3. The chiral imino ligand (H₃L) behaves as a triple negatively charged quadridentate chelate and 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 coordination environment of the copper(II) centers is approximately square-planar. The coordination of Cu and
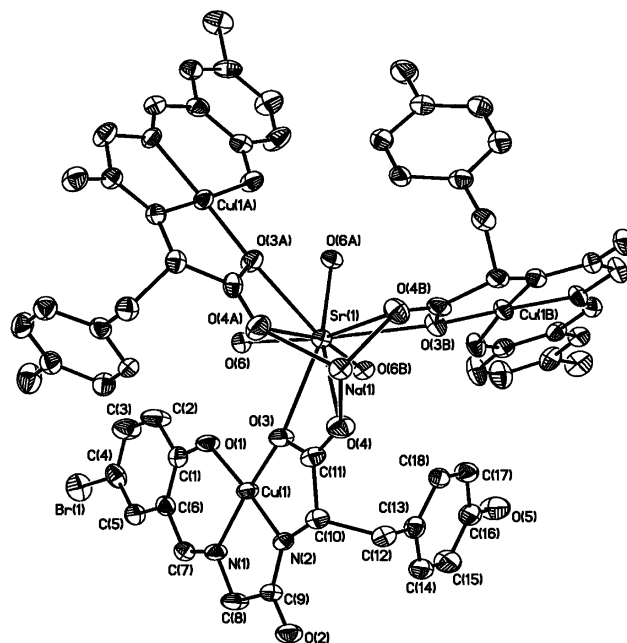
Fig. 1 An ORTEP view of the crystal structure of **1** showing the 30% probability thermal ellipsoid. The lattice water molecules were omitted for clarity. Selected bond distances/Å and angles/°: Cu(1)–O(1) 1.895(6), Cu(1)–O(3) 1.971(6), Cu(1)–N(1) 1.937(7), Cu(1)–N(2) 1.924(6), Sr(1)–O(3) 2.624(6), Sr(1)–O(4) 2.764(6), Sr(1)–O(6) 2.638(5), Na(1)–O(4) 2.376(7), Na(1)–O(6A) 2.483(7); O(1)–Cu(1)–N(2) 174.5(2), Sr(1)–O(3)–Cu(1) 143.9(3), Sr(1)–O(4)–Na(1) 92.6(2), Sr(1)–O6–Na(1B) 93.52(18) (symmetry code: A: 1 − *y*,*x* − *y*,−1 + *z*; B: *x*,*y*,1 + *z*).

L forms a rigid metalloligand [CuL]⁻. Three metalloligands [CuL]⁻ acting as bidentate chelating ligands coordinate to strontium ion through their carboxylate oxygen atoms (O(3), O(4), O(3A), O(4A), O(3B), O(4B)) in three-blade propeller-like arrangement, resulting in a tetranuclear subunit. The three copper ions are arranged at the corners of an equilateral triangle with the Cu···Cu distances of 7.516 Å. The dihedral angle between two "blades" ([CuL]⁻) is 83.0°. Each Cu(II) is connected to the Sr(II) *via* carboxylate oxygen O(3) of the metalloligand [CuL]⁻ with Sr···Cu separations of 4.373 Å. The coordination sphere of the strontium(II) is completed by three aqua ligands (O(6), O(6A), O(6B)). The Sr–O (carboxylic and water oxygen) distances fall with in the range from 2.624(6) to 2.764(6) Å.

The sodium ions connect two adjacent tetranuclear subunits *via* the mixed carboxylate and water bridges in μ_2 mode, leading to a novel 1D chiral propeller-like polymeric chain self-assembly (Fig. 2). The sodium(I) is six-coordinated and linked to three carboxylic oxygen (O(4), O(4A), O(4B)) and three symmetry-related bridging water molecules (O(6C), O(6D), O(6E)).[6] The strontium and sodium ions are arranged alternately at the three-fold axis. The polymeric chain run along the three-fold axis (*c*-axis), and the distance of two adjacent subunits is 7.458 Å.

Each chain is surrounded by six neighboring chains, resulting in a snowflake-like pack (Fig. S1, ESI†). O–H···O hydrogen bonds
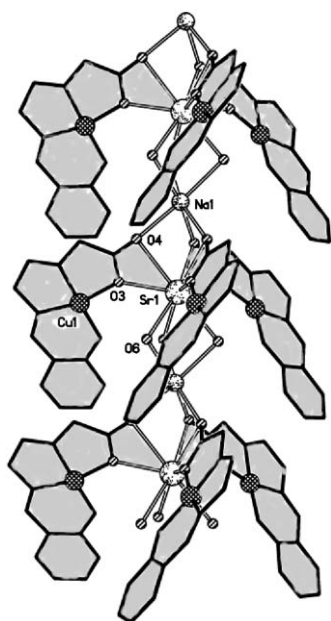
Fig. 2 View of the 1D chiral polymeric chain of **1** along *c*-axis. The tyrosine phenyl rings and lattice water molecules were omitted for clarity.

Fig. 3 Temperature dependence of $\chi_M T$ values for the polymer. The solid line corresponds to the best-fit curves using the parameters described in the text. The inset shows the magnetization versus the applied magnetic field at 1.8 K.

exist between the chains that originate from the carbonyl oxygen, phenolic oxygen, the coordinated water and uncoordinated water molecules. The chains are stacked *via* hydrogen bonds and the Br···Br interactions in a parallel manner to yield chiral crystals.

Thermogravimetric analysis (TGA) indicates that the violet crystals obtained are stable below 170 °C and three water molecules are coordinated to the metal ions (Fig. S2, ESI†). Circular dichroism (CD) measurements were used to confirm the optically active polymer.[7] The CD spectra of the polymer **1** ground crystals in KBr exhibits negative Cotton effect at $\lambda_{max} = 600$ nm, which is assigned to copper(II) d → d transitions (Fig. S3, ESI†).

Fig. 3 shows the $\chi_M T$ vs. *T* plot of **1** measured on a SQUID magnetometer in the temperature range 2–300 K under 2000 Oe. The room temperature $\chi_M T$ value of 1.230 emuKmol⁻¹ is close to the expected spin-only value of 1.252 emuKmol⁻¹ ($g = 2.11$). The increase of $\chi_M T$ with a decrease in temperature suggests the presence of ferromagnetic interactions between adjacent copper ions. The field dependence of the magnetization (0–70 kOe) measured at 1.8 K shows the saturation of the magnetization (inset of Fig. 3), reaching 3.153 $N\beta$ at 70 kOe for a ferromagnetic trinuclear copper(II) system ($M_S = 3.165\ N\beta$ expected for $g = 2.11$). Such a behavior is characteristic of ferromagnetic exchange interactions, which are expected for the spin coupling between copper(II) ions through the bridging Cu–O–Sr–O–Cu.[8] According to the structural data, the three paramagnetic Cu(II) ions of $S = 1/2$ are equivalent. The magnetic exchange interaction in an equilateral triangle structure may be described by the single interchange parameter *J*. In the case of three Cu(II) ions the corresponding equation has the following form:[9]

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\frac{5e^{3J/kT}+1}{e^{3J/kT}+1} \tag{1}$$

The best-fit parameters were $J/k = 1.43$ K, and $g = 2.11$ with the final agreement factor $R = 1.4 \times 10^{-4}$ [$R = \sum(\chi_M^{obs} - \chi_M^{calc})^2/\sum(\chi_M^{obs})^2$]. Compound **1** represents a new example of the rare phenomenon of ferromagnetic equilateral triangular copper complex.[10]

In conclusion, we have prepared a 1D chiral heterotrimetallic coordination polymer exhibiting weak ferromagnetic exchange interactions in which the chiral metalloligands [CuL]⁻ and aqua ligands link with Sr²⁺ and Na⁺ through μ_2-carboxylate oxygen atoms and μ_2-H₂O. This work presents a simple synthetic pathways for building chiral coordination polymer with potentially new fu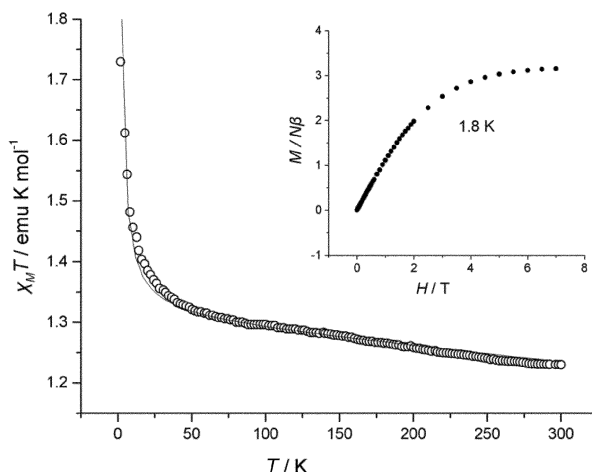nctional properties. Further study on the magneto-optical properties of this chiral coordination polymer and related complexes is in progress.

Notes and references

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