From one to three: a serine derivate manipulated homochiral metal-organic framework†

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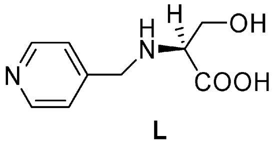
A porous homochiral MOF was constructed from a serine derivate ligand bridged and chelated copper atom subunit, which can expand one chiral center into multitopic homochiral centers to systematically tune the heterogeneous catalytic properties.

In the past decades, the generation of metal-organic frameworks (MOFs) has gained considerable interest because of their variety of topological architectures and diverse fascinating functionalities for potential applications.[1–7] The systematic tunable organic linkers and the various geometrical metal nodes are two key components for the formation of desired functional MOFs. Under suitable reaction conditions, the prescribed architectures of MOFs comprising periodically decorated functionalities can be generated, which might act as promising candidates for special applications.

In our work on the synthesis of functionalized homochiral MOFs, we are particularly interested in the synthesis of coordination solids based on multitopic linkers derived from amino acids because of their biological functional properties and highly selective substrate-binding abilities.[8–10] According to the coordination preferences of transition metal ions, we have modified the serine molecule with a pyridyl unit to generate an effective bridging linker, (*S*)-3-hydroxy-2-(pyridin-4-ylmethylamino)propanoic acid (**L**, Scheme 1). Basically, the additional pyridyl group together with the carboxylate group of **L** can bridge transition metal ions to form extended solid-state materials, while the remaining unit can act as a functional group for special applications. Most important of all, a second homochiral center can be generated when the amino group is coordinated to the metal ion, which is a subsequent induction of the neighboring homochiral carbon center. Furthermore, the metal ion can be chelated by the amino group and the carboxylate group together with two chiral centers, which act as the third chiral center in some cases. Herein we wish to report our recent elaboration on a new 2D homochiral solid $[Cu_2L_2Cl_2]\cdot H_2O$ (**1**), which presents interesting heterogeneous catalytic properties.



L

Scheme 1

The chiral ligand **L** was synthesized according to a literature method,[11] while blue crystals of **1** were formed from a mixture of **L** and $CuCl_2\cdot 2H_2O$ in a mixed solvent of H_2O and EtOH.‡ Compound **1** is not soluble in water and common organic solvents, such as MeOH, EtOH, THF and DMF *etc.* It is very stable in basified solution, but the framework structure can be destroyed by adding strong acidified HCl solution. Single X-ray structural analysis has revealed that **1** crystallizes in the monoclinic $P2_1$ space group.§ There are two copper(II) atoms, two **L** ligands, two chlorides and one water molecule guest in the asymmetric unit (Fig. 1). The Cu atoms comprise two kinds of coordination geometries. Every Cu atom coordinates to one carboxyl group (Cu–O = 1.957(3)–1.973(3) Å), one amino group (Cu–N = 1.981(3)–1.989(3) Å) and one hydroxyl group (Cu–O = 2.392(3)–2.576(3) Å) from one **L** ligand, with one pyridyl group (Cu–N = 2.016(3)–2.023(3) Å) from the neighboring **L** ligand. Additionally, one crystallographically independent copper atom coordinates to one chloride (Cu–Cl = 2.263(1) Å) in square-pyramidal geometry, while another copper atom coordinates to two chlorides (Cu–Cl = 2.263(1)–3.001(1) Å) to generate distorted octahedral geometry. Subsequently, each **L** ligand chelates one copper atom through hydroxyl, carboxyl and amino groups and further bridges a neighboring copper atom *via* the pyridyl group to extend into 1D polymeric chains running along two different orientations. The chains are further coupled by one of the two chlorides to form a thick bilayer framework structure (Fig. 2).

Two striking features of **1** should be noted. In the bilayer framework structure of **1**, the two-directional chains stack on each other in such a way that each Cu(II) center is located *ca.* 4.791 Å below the gaps of the next chain (Fig. 2b and c). Another interesting feature of **1** is that the nitrogen atom of the amino group is induced by the neighboring chiral carbon center to generate the second homochiral center, which is stabilized *via* coordinating to the copper atom. Consequently,

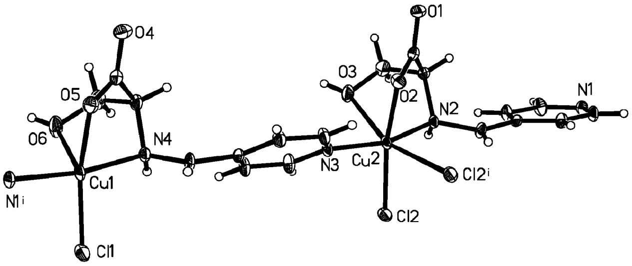


Fig. 1 ORTEP representation of the symmetry expanded local structure for **1** (25% probability ellipsoids).

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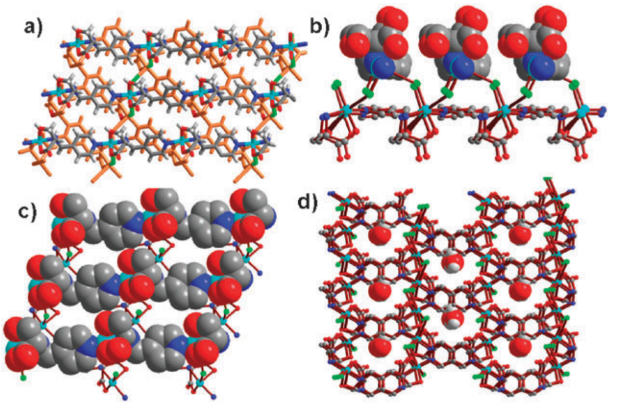
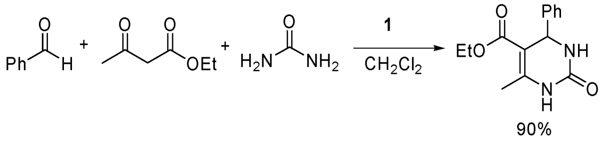


Fig. 2 (a) Perspective view of the lamellar framework of **1** (one orientation chains are highlighted in orange); (b) and (c) side and top views of the geometric relationship between two directional chain frameworks (ball-and-stick and space-filling representations, respectively) within a thick layer; (d) packing diagram of **1** viewed down the *a* axis, showing the cavities that accommodated water molecular guests (space-filling spheres).

the double homochiral center-chelated copper atom is induced into the third homochiral center.

All thick lamellar frameworks are stacked together *via* supermolecular interactions to form a 3D porous framework with 1D chiral channels (5.123 × 2.866 Å^2, van der Waals radii taken into account). The cavities are occupied by water molecule guests, which were confirmed by thermogravimetric analysis (TGA) and PLATON calculations (Fig. 2d).[12] The supermolecular interactions are strong edge…π interactions between the uncoordinated carboxyl group and the pyridyl ring with the shortest O…C distances of 3.056(5) Å, hydrogen bonding between the chloride and the amino group (Cl…N = 3.583(4)–3.683(4) Å), and hydrogen bonding between the hydroxyl group and the uncoordinated carboxyl group (O…O = 2.737(4)–2.742(4) Å). The clathrated water molecular guests contact to the hydroxyl groups of the host framework through relatively weak hydrogen bonding (O…O = 3.053(8) Å), which can be easily removed by heating solid **1** in vacuum. TGA indicates that a weight loss of 3.2% occurred between 20 and 90 °C, corresponding to the loss of solvent molecules (expected 3.0%). There was almost no weight loss up to 191 °C. Above 191 °C, compound **1** began to lose coordinated **L** ligand and to decompose. After a sample of **1** was ground and heated at 110 °C for 5 h, an XRPD of the resultant powder showed a sharp diffraction pattern similar to that of the pristine sample. This result indicates that the neutral chiral porous framework was maintained after the removal of solvent molecules.

The interesting topological framework structure comprising multitopic homochiral centers prompted us to study the heterogeneous catalytic properties of material **1**, as copper(II) compounds are promising catalysts in many important organic transformations, such as cross-coupling reaction, oxidation, Biginelli reaction, Michael addition, *etc.*[13] To evaluate the heterogeneous catalytic properties of **1**, we first probed the Biginelli catalytic reaction of benzaldehyde, urea and ethyl acetoacetate in the presence of solid **1** in CH_2Cl_2 at 40 °C for 12 h to give corresponding dihydropyrimidinone in 90% isolated yield (Scheme 2). Despite the excellent yield reached, however, we failed to observe any enantioenriched isomer from the product. The supernatant from solid **1** was inactive for the reaction, which confirmed the heterogeneous behavior of the catalyst system.

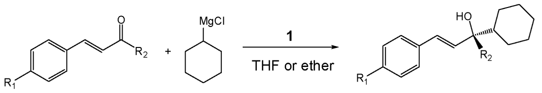


Scheme 2

To further test the heterogeneous catalytic behavior of **1**, addition of Grignard reagent to α,β-unsaturated ketones was used to assess catalytic ability. Solid **1** catalyzed the addition of cyclohexylmagnesium chloride to (*E*)-4-phenylbut-3-en-2-one to afford the 1,2-addition product with excellent conversion (97%) and enantiomeric excess (*ee*) of 65% (Table 1, entry 1). Additional experiments showed that ether solvent media was slightly better than THF, while low reaction temperature can improve the *ee* value but depress the conversion (entries 2–3). Solid **1** also catalyzed 1,2-addition of Grignard reagent to a range of other ketones (aldehyde) to give high conversions with the highest *ee* value up to 99% (entries 5–7). However, the $-NO_2$ substituted substrate only generated the corresponding product with very low conversion (< 10%), which might be a consequence of the weakened electronic density induced by the $-NO_2$ group (entry 8).

Solid **1** saturated supernatant cannot promote the transformation under otherwise identical conditions. To check whether the basic Grignard reagent can destroy the framework structure, and subsequently utilize the released free ligand or copper ions to catalyze the reaction, we have added α,β-unsaturated ketone into the filtrate from a mixture of Grignard regent and solid **1** in THF under N_2 atmosphere. After 12 h under identical reaction conditions, we cannot detect trace conversion from α,β-unsaturated ketone. All these experiments proved the heterogeneous nature of the

Table 1 Compound **1** catalyzed 1,2-addition of α,β-unsaturated ketones (aldehyde)[a]



Entry	R_1	R_2	Catalyst	Solvent	*Conv.*%	*ee*%[b]
1	H	Me	**1**	THF	97	65
2	H	Me	**1**	Et_2O	98	67
3	H	Me	**1**	THF	48	88[c]
4	H	Me	**L**	THF	84	51
5	H	H	**1**	THF	88	55
6	Me	Me	**1**	THF	93	> 99
7	Cl	Me	**1**	THF	94	97
8	NO_2	Me	**1**	THF	< 10	—

[a] Solid **1** (0.01 mmol), substrate (0.1 mmol) and Grignard reagent (0.12 mmol) were mixed in THF or Et_2O (2 ml) under N_2 at 0 °C, which was warmed to room temperature over 12 h. [b] Conversion% and *ee*% were determined by GC on a *Supelco β-Dex* 120 column. [c] The reaction temperature is −80 °C.

current catalyst system. However, it has been known that copper compounds only promote 1,4-addition of Grignard reagent to α,β-unsaturated ketones.[13] Our results showed the transformation underwent an otherwise catalytic mechanism. To discover which part is responsible for the catalytic process, reference reactions with **L** ligand and $CuCl_2$ were carried out. Free ligand can generate the 1,2-addition product with conversion of 84% and *ee* value of 51%, respectively (Table 1, entry 4), while copper chloride did not work at all. The reference reactions suggest that the transformation is a typically organic functionality promoted process.[14] The improved enantioselectivity for **1** is attributed to the homochiral amino group in solid **1** instead of the achiral center in **L** ligand. Our results demonstrated that the incorporation of suitable synthons in a network can generate a good catalyst. Structural analysis of **1** revealed that the active sites exist mainly on the surface and the small size of the pores avoids the accessibility of substrates to active centers through the channels, which suggest that the catalytic reaction took place on the catalyst surface.

In summary, we have successfully synthesized a new porous homochiral MOF constructed from serine derivate ligand bridged copper atoms. We have observed remarkable asymmetric catalytic activities of the current framework structure for heterogeneous catalysis. This work established a new strategy in the rational expandsion of one chiral center into multitopic chiral centers, which can chelate a metal center as a chiral molecular module for the construction of porous homochiral MOFs to systematically tune heterogeneous catalytic properties.

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Notes and references

‡ **Synthesis of** $[Cu_2L_2Cl_2]\cdot H_2O$ (**1**). Heating a mixture of $CuCl_2\cdot 2H_2O$ (17 mg, 0.1 mmol), **L** (9.8 mg, 0.05 mmol) and NaOH (0.01 mmol) in a mixed solvent of EtOH (3 mL) and H_2O (3 mL) at 50 °C in a capped vial afforded blue crystals of **1** after two days, which were filtered, washed with EtOH, Et_2O and dried at room temperature (Yield: 76% based on **L**). Anal. Cald for $C_{18}H_{22}Cl_2Cu_2N_4O_7$ (%): H, 3.67; C, 35.77; N, 9.27. Found: H, 3.75; C, 35.69; N, 9.16. IR (KBr pellet, ν/cm^{-1}): 1640s, 1625s, 1564w, 1454m, 1429s, 1391s, 1371m, 1350w, 1329m, 1225m, 1106w, 1053s, 1069m, 1035m, 1001m, 929m, 857m, 812m, 796w, 686m, 647w, 569w, 487m.

§ ***Crystal data for*** **1**: $C_{18}H_{22}Cl_2Cu_2N_4O_7$, *M*r = 604.38, monoclinic, space group $P2_1$, a = 10.3787(2) Å, b = 6.6130(1) Å, c = 16.8336(2) Å, β = 103.344(1)°, V = 1124.17(3) Å, Z = 2, T = 293 K, D_c = 1.785 g cm^{-3}, μ = 2.178 mm, $F(000)$ = 612, Flack parameter = 0.017(12), GOF = 0.989, 9767 reflections measured, 4669 unique (R_{int} = 0.0262). The final $R1$ = 0.0371, w$R2$ = 0.0682 for 3721 observed reflections with $I > 2\sigma(I)$ and $R1$ = 0.0541, w$R2$ = 0.0746 for all data with 304 parameters.

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