

Chiral Cadmium(II) Metal-Organic Framework from an Achiral Ligand by Spontaneous Resolution: An Efficient Heterogeneous Catalyst for the Strecker Reaction of Ketones

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Supporting Information

ABSTRACT: A thermally stable cadmium-based chiral metal-organic framework (MOF), $\{ [Cd_2(L)(H_2O) -$ (DMF)]·3DMF·2H₂O}_n (1; DMF = N,N-dimethylformamide), has been synthesized from an achiral ligand by spontaneous resolution. The MOF features 1D open channels with a large density of active metal sites and has a 3,6-c binodal net with a rare sit 3,6-conn topology. The metal-bound water and DMF solvents could be easily removed along with the guest molecules in the lattice upon activation to afford the desolvated framework 1'. It exhibits microporous nature, as confirmed by the gas-sorption measurements with carbon dioxide uptake of 43.2 cm³ g⁻¹ at 273 K. The open metal sites in the framework make it an outstanding heterogeneous catalyst in the Strecker reaction for the synthesis of α -aminonitriles in a solventfree state at room temperature with excellent conversion vields.

he fabrication of novel metal—organic frameworks (MOFs) is of current interest in the field of supramolecular chemistry, which originates from their potential applications as functional materials¹⁻⁴ as well as their intriguing molecular topologies.⁵ In particular, the synthesis of chiral MOFs is of immense interest in chemistry such as in enantioselective catalysis⁶ and chiral separation⁷ as well as materials science such as nonlinear optics⁸ and magnetism.⁹

To date, the majority of chiral MOFs and coordination polymers are prepared from enantiopure ligands, which make them homochiral in nature.¹⁰ In contrast, the use of achiral ligands to produce chiral MOFs under spontaneous resolution can be more attractive.¹¹ This is due to the easier synthesis of achiral ligands in comparison to the laborious preparation of chiral molecules. There are relatively few examples of the use of achiral ligands in the self-assembly of chiral MOFs.¹² So far, our understanding of the fabrication of chiral MOFs structured from achiral ligands is very limited and also unpredictable.¹³ Therefore, the development and investigation of new organic struts and their use in the preparation of chiral MOFs are necessary to gain in-depth knowledge of chiral induction in solids.

Among the homochiral MOFs, chiral binaphthyl-based MOFs are well investigated by the group of Lin.¹⁴ Because of the restricted C-C bond rotation, a natural helicity is obtained in these molecules. It has also been observed that V-shaped exobidentate organic molecules can also induce helical networks.¹⁵ This happens because of the natural ability of V-shaped moieties to adopt a twisted geometry in the resulting networks. Similarly, more or less a neglected ligand class is comprised of bis(pyrazole)-¹⁶ and methylenebis(pyrazole)¹⁷-based systems, where the chirality has also been observed, which is ascribed to the restricted rotation of the two C–C-connected pyrazole rings and the V shape of the molecule, respectively.

Herein, we have synthesized a novel V-shaped ligand, L, comprised of a methylenebis(pyrazole) moiety. The introduction of L into coordination frameworks can be of special interest in terms of chiral coordination engineering. From a mechanistic viewpoint, for the ligand L, upon coordination with a metal ion, the rotation freedom of $N-CH_2-N$ bonds of the bis(pyrazole) moiety is restrained and the ligand can be locked in an atropisomerically chiral conformation. Also, the strong and directional bonding interactions could transmit the original chirality from one metal center to another, which can lead to formation of the chiral networks.

In this work, the synthesis of bis[4-(3,5-dicarboxyphenyl)-1H-3,5-dimethylpyrazolyl]methane (Scheme1) was achieved and a

Scheme 1. Schematic Diagram of the V-Shaped Ligand L and Synthetic Procedure for 1



Cd^{II}-ion-based chiral MOF, {[Cd₂(L)(H₂O)(DMF)]·3DMF· $2H_2O_{n}^{1}$ (1; DMF = *N*,*N*-dimethylformamide; see the Supporting Information, SI), has been constructed. Remarkably, 1 has been obtained by spontaneous resolution upon crystallization in the absence of any other chiral source. Also, the MOF presents an unprecedented 3,6-connected binodal sit 3,6-conn topology. Because of the presence of potential Lewis acidic sites in 1, we have explored the heterogeneous catalytic activity for the threecomponent Strecker reaction in a solvent-free state, which is used to prepare α -aminonitriles from a carbonyl, an amine, and a cyano derivative. As reported earlier, ketones gave a very poor yield in this reaction, for which In³⁺-based MOFs have been effectively used as heterogeneous catalysts.¹⁸ A few other reports

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have also shown the Strecker reaction catalyzed by MOFs, 19 but d¹⁰ metal-ion-based MOFs have not been explored until now for catalysis of this reaction.

The ligand L was synthesized in five steps starting from readily available acetylacetone in 47.3% overall yield (Scheme S1). It has been characterized by ¹H and ¹³C NMR and mass spectrometry (Figures S1–S5). The solvothermal reaction of $Cd(NO_3)_2$ with L in DMF/water (H_2O) for 3 days afforded colorless prismatic crystals of 1 (see the SI). Single-crystal X-ray analysis reveals that 1 crystallizes in the chiral space group P1 and has a 3D open structure constructed from Cd–L helical chains [Figure S11; Flack parameter = 0.007(15)]. The solid-state circular dichroism (CD) spectrum confirmed the chirality of the bulk material of 1, which showed a positive Cotton effect (Figure S36). Singlecrystal X-ray structure analysis reveals that the asymmetric unit contains two Cd^{II} ions, one ligand L^{4-} , and one each of the coordinated DMF and H₂O molecules along with three DMF and two H₂O solvent molecules in the lattice. As shown in Figure 1a, the Cd1 center is in a distorted octahedral geometry by



Figure 1. (a) Coordination environment of cadmium(II). (b) Coordination mode of the ligand L^{4-} .

coordinating to two N atoms (N1 and N3) of the chelating bis(pyrazolyl)methane moiety and four O atoms (O1, O2, O3, and O5) of three carboxylate groups of ligand L⁴⁻. One of the –COOH groups is in the chelating mode, while two others are in monodentate and bidentate modes, respectively. The Cd2 center also shows distorted octahedral geometry with ligation from four O atoms (O4, O7, O8, and O9) of three carboxylate groups of L⁴⁻ and two O atoms of axially coordinated DMF and H₂O molecules, respectively. The two metal centers form a dinuclear cluster (Cd…Cd distance, 3.818 Å) via two bridging COOH groups of L⁴⁻. The angle between the two planes of the pyrazole rings in L was 131.53° (Figure 1b). Also, the phenyl rings rotate with angles of 42.42° and 55.80° with respect to the adjoining pyrazole rings. The angle of the N₂C₂₂N₄ moiety of bis(pyrazole) is found to be 111.39°.

The isophthalate moiety of L^{4-} and Cd^{II} dimer center form a 2D zigzag sheet structure perpendicular to the *bc* plane (Figure S12). The sheets were further connected to each other with the help of another ligand L^{4-} , which is linked to the chelating bis(pyrazolyl)methane moiety to form an overall 3D porous structure (Figure S37). The network contains open channels (with an opening of ~11 × 10 Å²) with coordinated H₂O and DMF molecules that point toward the pore wall of the channels. The cavities in the network are filled with DMF and H₂O solvent molecules. The total potential solvent-accessible void volume of 1 was 53.4% (611.9 Å³/1145.5 Å³) when coordinated solvent molecules were also removed to form 1'.

Topologically, each dinuclear metal cluster in 1 connects to six adjacent clusters through half of the ligand L^{4-} , which is acting as a 3-connected node, affording a 3,6-connected framework (Figure S38). The whole network can thus be viewed as a binodal 3,6-c net with stoichiometry (3-c)2(6-c). It has a point

symbol of $\{4.6^2\}_2\{4^2.6^{10}.8^3\}$, which is assigned to a rare topological type, sit 3,6-conn (topos&RCSR.ttd).

Upon analysis of the structure, the metal-ion centers are not stereogenic and not responsible for the chirality induction; it is more closely related to the V-shaped ligand. Here, metal coordination of the chelating bis(pyrazole) moiety has locked the ligand into one conformation. Therefore, rotation is restricted, and with selective and directional coordination with the help of the metal ion, it gives rise to a chiral network. To gain more insight into the cause of the chirality in 1, we have carried out the CD spectra of the ligand alone and the 1:1 $Cd(ClO_4)_2/L$ complex (see the SI) in DMF; it has been found that the free L does not show any signal but the $Cd(ClO_4)_2/L$ complex shows a well-defined CD spectrum, asserting chirality generation in the complex due to the restricted rotation (Figures S8 and S9). The complex has also been characterized by electrospray ionization mass spectrometry, which confirms 1:1 $Cd(ClO_4)_2/L$ complex formation (Figure S10). Moreover, we have carried out the CD spectrum of the mother liquor after MOF filtration (Figure \$35). However, no CD activity has been shown probably because of the fact that the solid MOF after crystallizing out is insoluble in the solvent and any chance of the presence of other enantiomers in the mother liquor is negligible.

TGA and variable-temperature powder X-ray diffraction (VT-PXRD) measurements were carried out to examine the thermal stability of the porous network. TGA of the as-synthesized, methanol-exchanged, and activated samples of 1 was performed (Figures S16 and S17). The thermal stability and phase purity of 1 was also confirmed by VT-PXRD (Figure S14). The experimental PXRD patterns for the as-synthesized compound were in good agreement with the simulated pattern of 1. Further, the VT-PXRD data revealed that the overall framework integrity of 1 is retained up to 210 °C.

In the as-synthesized material, the coordinated DMF and H₂O as well as guest solvent molecules can readily be removed at hightemperature and vacuum conditions to obtain the activated compound 1'. It also exhibits open pores of $\sim 11 \times 10$ Å², which are readily accessible and present a surface lined with two open Cd^{II} sites with chiral pores. Site I has a coordinated DMF solvent molecule, while site II has a coordinated H₂O molecule (Figure \$39). The porosity of 1 was examined on an activated sample by the gas-sorption measurements. Activation was carried out by placing the methanol-exchanged sample under vacuum at 120 °C for 12 h. The gas-sorption measurements indicate that it can adsorb appreciable amounts of carbon dioxide (CO₂) but a negligible amount of N₂ at 77 K (Figure S33). The CO₂ adsorption measurement at 273 K and 1 atm revealed a type I isotherm with a saturated CO_2 uptake of 43.2 cm³ g⁻¹, which is characteristic of a microsporous material corresponding to a Brunauer-Emmett-Teller surface area of 382 m² g⁻¹ (Figure S40). Furthermore, at 298 K, the maximum uptake of CO_2 is 26 $\text{cm}^3 \text{g}^{-1}$ at 1 atm. The isosteric heat (Q_{st}) of CO₂ was also calculated from the isotherms at 273 and 298 K. The initial Q_{st} value was found to be 32.69 kJ mol⁻¹, which implies a high binding affinity of the framework toward CO_2 (Figure S34).

The microporous nature and coordinatively unsaturated open metal sites, which are well positioned to interact with guest molecules that enter the framework pores, suggested that 1' should function as an active heterogeneous catalyst for Lewis acid promoted reactions.

After reviewing the literature, we found that the Strecker reaction, especially for ketones, has not been investigated by d¹⁰ metal-ion-based MOFs as catalysts. Therefore, catalytic activity

of 1' was undertaken for the three-component Strecker reaction in a solvent-free state. This reaction provides a most direct and viable method for the synthesis of α -aminonitriles, which are versatile building blocks for the synthesis of α -amino acids and their derivatives.²⁰

To check the feasibility of 1' for the three component Strecker reaction, we began with the simplest aldehyde, benzaldehyde and trimethylsilyl cyanide (TMSCN), and aniline as substrates. For the reaction, catalytic amount of 1' was placed in a Schlenk tube followed by addition of three reactants. The reaction was performed in a solvent free state at room temperature under N₂ atmosphere. The increment of the reaction was monitored by TLC analysis. Formation of the desired products, α -amino nitriles, was confirmed by the ¹H NMR spectra (Figures S19–S29). The results of the reaction are summarized in Table 1. To

Table 1. Results Obtained for the Strecker Reaction Catalyzed by $1'^a$



^{*a*}Reaction conditions: ketone (0.1 mmol), amine (0.1 mmol), TMSCN (0.12 mmol), and catalyst 1' (10 wt %) at 25 °C for 4 h. ^{*b*}Isolated yields after silica gel chromatography.

our delight, benzaldehyde showed very good conversion yields (99%) which further inspired us to check the more reluctant substrate, different ketones, for the reaction. The results of the catalytic activity of 1' (Table 1) reveal that both electronwithdrawing as well as electron donating groups attached to ketone molecules gave good yields. We have also checked the enantiomeric excess (ee) of the products but unfortunately, no ee was observed. The probable reason can be the bulky phenyl groups in the two substrates which possibly are not able to penetrate inside the channels of the MOF and as a result cannot induce asymmetric catalysis. The catalyst was separated by filtration, washed with chloroform and methanol, followed by drying under vacuum at 100 °C for 5 h to regenerate the active catalyst 1'. The integrity of the framework was maintained even after four cycles of the reaction, as confirmed by the PXRD of the recovered catalyst (Figure S18). Also, it can be reused up to three cycles with slight loss (11%) in its catalytic activity (Figure S30).

The heterogeneous nature of 1' was evaluated by performing the leaching test (Figure S31). After the beginning of reaction for 1 h, the solid 1' was separated from the reaction mixture and the mother liquor was transferred to an empty Schlenk flask. The reaction progress was not observed after 4 h which proves that the catalyst 1' is necessary to perform the reaction.

To better understand the relationship between the structure and reactivity, we proposed a mechanism for the reaction catalyzed by 1 (Figure S32). The MOF 1 possesses an openframework structure having Lewis acidic sites that can activate the imine intermediate (electrophile) and therefore lead to inherently high surface reactivity per unit area. Besides this, 1' possesses an accessible O atom of one monodentate coordinated -COOH group, which imparts basic character (Lewis basicity) to the framework and can help in driving the reaction by activating the TMSCN (nucleophile).

In summary, we report herein one chiral Cd^{II} MOF with a Vshaped bis(pyrazole)-based achiral ligand by spontaneous resolution. The MOF represents a rare sit 3,6-conn topology. The activated framework is thermally stable and contains open Lewis acid sites. The microporous nature of 1 was proven by the gas-sorption experiment. The framework is able to catalyze the three-component Strecker reaction in solvent-free conditions at room temperature. To the best of our knowledge, it is the first Cd^{II} -based MOF that can catalyze the Strecker reaction of ketones in high conversion yields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01915.

Experimental details, characterization procedures, crystallographic data with refinement details, selected bond lengths and angles, TGA, and PXRD patterns (PDF)

Accession Codes

CCDC 1562129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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