Inorganic Chemistry

An Amine Functionalized Metal–Organic Framework as an Effective Catalyst for Conversion of CO₂ and Biginelli Reactions

Ashish Verma, Dinesh De, Kapil Tomar, and Parimal K. Bharadwaj*®

Department of Chemistry, IIT Kanpur, Kanpur-208016, India

Supporting Information

ABSTRACT: A highly porous and thermally stable anionic Zn(II)-framework, $\{[(CH_3)_2NH_2^+]_2[Zn_3((\mu_3-O))(L)_2(H_2O)] \cdot 4DMF \cdot 2H_2O\}_n$ (1), having exposed metal sites and pendant amine groups has been synthesized adopting the solvothermal technique. This anionic 3D framework showed two-fold interpenetration with 45.1% void volume. It has a 3,6-c binodal net with rare sit 3,6-conn topology. The metal bound aqua ligand could be easily removed along with the guest molecules in the lattice upon activation to afford the desolvated framework 1'. This produced exposed metal sites that, along with the pendant amine groups incorporated in the ligand, generated a coordination space in the framework to make it an outstanding heterogeneous catalyst for the chemical fixation of CO_2 with various epoxides under atmospheric pressure and in the three-component Biginelli reaction with different aldehydes, ethyl acetoacetate, and urea to afford dihydropyrimidinones.



INTRODUCTION

Due to the increasing dependence on fossil fuels to meet our energy needs during the last few decades, the release of the greenhouse gas CO₂ has increased exponentially.¹⁻³ Climate change due to excessive CO₂ emission from the anthropogenic and industrial activity is a serious environmental problem. This is causing random weather patterns as we already witnessed in recent years. Therefore, the CO_2 emissions need to be urgently reduced to avoid climate change. Carbon capture and storage (CCS) is one of the strategies to reduce carbon emissions.² However, this process is high energy demanding. Capture and conversion of CO₂ to fuel and fine chemicals is one of the best ways to tackle the challenges of environment and energy together.⁵ This process simultaneously reduces the atmospheric CO₂ emissions and provides an alternative, renewable feedstock for the chemicals industry. In this respect, conversion of CO₂ into cyclic carbonates through the cycloaddition of CO2 with epoxides is a useful and 100% atom economic reaction.⁶ Traditionally, this reaction involved highly toxic and corrosive phosgene.⁷ There have been reports regarding the use of metal organic frameworks (MOFs) as heterogeneous catalysts in the conversion of CO₂ to cyclic carbonates to overcome the problems associated with homogeneous catalysts which includes the problem in separation of products and recycling of the catalyst.⁸⁻¹¹ Also, heterogeneous catalysts like metal oxides,¹² porous organic polymers,¹³ and zeolites¹⁴ have been developed, but most of them need high temperature to activate the reaction. Therefore, conversion to cyclic carbonates near atmospheric pressure is very much in demand presently.¹⁵ Additionally, MOFs with decorated pore surfaces are also found to be suitable as heterogeneous catalysts in several other

organic transformations¹⁶ apart from applications in adsorption,¹⁷ separation,^{18,19} and sensing.²⁰

Thus, in order to address the aforementioned issue of utilization of CO_2 through transformation into industrially important chemicals using heterogeneous catalysis, multifunctional MOF materials are needed which can catalyze more than one reaction at a time. Keeping all of these in mind, we designed and synthesized a bent tricarboxylate based linker (H₃L; Scheme 1) where an amino group has been incorporated. The amino group is not expected to bind a metal ion but can decorate the coordination space, making it useful for selective gas adsorption and catalysis.²¹ As expected, the linker readily formed solvothermally, a porous and highly stable Zn(II) based anionic framework, $\{[(CH_3)_2NH_2^+]_2[Zn_3-((\mu_3-O))(L)_2(H_2O)]\cdot4DMF\cdot2H_2O\}_n$ (1; Scheme 1). The





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accessible Lewis basic $-NH_2$ functionalized channels and the presence of Lewis acidic sites (unsaturated metal centers) in 1' (desolvated framework) make this framework interesting for potential application as heterogeneous catalyst. The framework 1' shows high efficiency in the cycloaddition of CO_2 to various epoxides under relatively mild conditions. Besides, 1' is found to be an excellent heterogeneous catalyst in the three-component Biginelli condensation reaction involving urea, ethyl acetoacetate, and an aromatic aldehyde to afford dihydropyrimidinones. These dihydropyrimidinones are useful compounds in the pharmaceutical industry such as potassium channel antagonist, antibacterial activity, in mitotic kinesin inhibition, antihypertensive agents, and so on.^{22–26}

EXPERIMENTAL SECTION

Materials and Measurements. The metal salt and other reagentgrade chemicals were procured from Sigma-Aldrich and used as received. All solvents were procured from S. D. Fine Chemicals, India. These solvents were purified following standard methods prior to use. The details of spectroscopic techniques are provided in the Supporting Information.

X-ray Structural Studies. A suitable single crystal of 1 was mounted on a Bruker SMART II diffractometer equipped with a graphite monochromator and Mo-K α (λ = 0.71073 Å, 140 K) radiation. Data collection was performed using φ and ω scans. The structure was solved using direct method, followed by full matrix leastsquares refinements against F^2 (all data HKLF 4 format) using the SHELXL 2014/7²⁷ program package. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction were applied. Non-hydrogen atoms were refined with hydrogen atoms placed geometrically and refined using the riding model. The solvent molecules in 1 are highly disordered. Therefore, the PLATON-SQUEEZE²⁸ program was used to remove those peaks. The solvent molecules were calculated on the basis of combined study of TGA, elemental analysis, and removed electron counts which are included in the molecular formula. The crystal and refinement data are collected in Table 1, while selected bond distances and angles are given in Table S1 (Supporting Information (SI)).

Synthesis of Ligand. The ligand (H_3L) was synthesized in several steps, details of which are given in the SI.

{[(CH_3)₂ NH_2^+]₂[$Zn_3((\mu_3-O))(L)_2(H_2O)$]·4 $DMF\cdot2H_2O$ }_n (1). A mixture of H₃L (20 mg, 0.05 mmol) and Zn(NO₃)₂·6H₂O (30 mg, 0.10 mmol) in DMF (2.0 mL), H₂O (0.5 mL), and EtOH (0.5 mL) was heated at 90 °C under autogenous pressure in a Teflon-lined stainless steel autoclave for 72 h, followed by cooling to room temperature at a rate of 10 °C/h to afford 1 as light yellow block-shaped crystals in 64% yield. The crystals were repeatedly washed with water, followed by acetone, and air-dried. Anal. Calcd for C₅₈H₇₄N₈O₂₀Zn₃: C, 49.78; H, 5.33; N, 8.01%. Found: C, 49.12; H, 5.08; N, 7.82%. IR (cm⁻¹): 3445 (broad), 3392 (s), 2926 (m), 1656 (s), 1610 (s), 1547 (s), 1385 (s), 1308 (m), 1180 (w), 1105 (w), 1016 (w), 872 (w), 788 (m), 734 (w), 677 (w), 485 (w).

RESULTS AND DISCUSSION

Single crystal X-ray studies showed that 1 is an amine group decorated anionic MOF. It was formulated as $\{[(CH_3)_2-NH_2^+]_2[Zn_3((\mu_3-O))(L)_2(H_2O)]\cdot 4DMF\cdot 2H_2O\}_n$ based on the elemental analysis, TGA, IR spectra, and SXRD. 1 crystallized in a monoclinic space group $P2_1/c$ (Table 1). The asymmetric unit contains, three Zn(II) ions, two ligand moieties, one μ_3 -O anion, one coordinated water, and disordered solvent molecules along with two dimethylammonium $((CH_3)_2NH_2^+)$ (dma) cations. Unfortunately, the dma cations, which are generated

Table 1. X-ray Crystallographic Data and Refinement Parameters for 1

	1
formula	$C_{42}H_{26}N_2O_{14}Zn_3$
$M_{\rm w} ~({\rm g}~{\rm mol}^{-1})$	978.82
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	13.6154(10)
b (Å)	22.7304(17)
c (Å)	19.5742(14)
α (deg)	90.00
β (deg)	97.496(2)
γ (deg)	90.00
V (Å ³)	6006.1(8)
Z	4
$ ho_{ m calcd}~(m g~ m cm^{-3})$	1.082
$\mu(MoK\alpha) \ (mm^{-1})$	1.237
F(000)	1976
collected reflns	11 165
independent reflns	7628
goodness-of-fit (GOF) on F^2	1.048
R1, wR2 $(I > 2\sigma I)^{a}$	0.0674, 0.1546
R1, wR2 (all data) ^a	0.1046, 0.1717
CCDC number	1546167
R1 = $\sum_{v(F_o)^2 \mid 1/2} F_o - F_c / \sum F_o $ and wR2	$= \sum w(F_o ^2 - F_c ^2) / \sum $

from the decomposition of the solvent DMF,²⁹ could not be located in the electron density map due to the severely disordered nature within the large cavity. The charge of three Zn²⁺ ions is balanced from six carboxylate groups of L³⁻, and the charge of μ_3 -O²⁻ is balanced by two ((CH₃)₂NH₂⁺) cations. Zn1 and Zn2 are four coordinated from four O atoms of three COO⁻ groups and one oxo anion (μ_3 -O) in a distorted tetrahedral geometry, while Zn3 is coordinated from six O atoms from four COO⁻ groups, one oxo anion, and one coordinated water molecule in an octahedral geometry. These Zn(II) ions link together to give an unusual Zn₃O SBU (Figure 1a) which is quite different from the Cr₃O(COO)₆ SBU found in MIL-101.³⁰

Framework 1 has a 6-c Zn₃O SBU, in which two Zn(II) ions are in tetrahedral geometry while one Zn ion is in octahedral geometry (Figure 1b). This type of unusual Zn₃O SBU is rare in the literature and was previously observed in one Zn-MOF reported by Qian et al.³¹ The framework in 1 is composed of trinuclear Zn₃O(COO)₆ SBUs which are bridged by six tricarboxylate ligands L^{3-} to form an overall 3D structure (Figure 2).

The framework contains considerable open 1D channels along the *a*-axis (Figure 3) of dimensions 11.695 × 9.618 Å² diagonally with a solvent accessible volume of 45.1% (2709/ 6006 Å³) as calculated by PLATON.

The topological analysis of 1 using TOPOS³² revealed that the Zn₃O SBUs can be viewed as six connected nodes and the L^{3-} ligands as three connected nodes. Therefore, 1 can be envisioned as a very rare, 3,6-c binodal net with stoichiometry (3-c)2(6-c) with sit 3,6-conn (topos&RCSR.ttd) topology (Figure 4). The point symbol for the net is $\{4.6^2\}_2\{4^2.6^{10}.8^3\}$. To the best of our knowledge, MOFs with sit 3,6-conn topology remain relatively rare, although (3,6)-connected rutile, pyrite, ant, anh, and qom nets have been observed.³³⁻³⁹

u



(b) Figure 1. (a) $Zn_3O(COO)_6$ SBU and (b) coordination modes of L^{3-}



Figure 2. 3D view of 1 showing the single network.



Figure 3. A view of **1** showing the two-fold interpenetration and open channels along *a*-axis.

Overall, the framework structure is anionic with $((CH_3)_2NH_2^+)$ cations as well as DMF and water molecules residing in the channels as determined by TGA, IR spectra, and elemental analysis (Figures S6 and S7 in the SI). In the IR spectrum, strong peaks at 1385 and 1610 cm⁻¹ suggest coordinated carboxylate groups, whereas the peak due to DMF appeared at 1656 cm⁻¹. The presence of $((CH_3)_2NH_2^+)$



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Figure 4. Topological representation of 1 showing the 3,6-c binodal net.

cations could be confirmed by peaks at 3350–3500 cm⁻¹ (N-H stretching), 1050–1200 cm⁻¹ (C-N stretching), and 872 cm⁻¹ (N-H bending). The framework possesses both active metal sites as well as free basic $-NH_2$ groups open up inside the pore walls. The temperature dependent PXRD analysis showed that the as-synthesized MOF is stable up to at least 210 °C (Figure 5).



Figure 5. Variable-temperature powder X-ray diffraction of 1.

The TGA curve for 1 reveals a weight loss of 24.8% (calculated 25.2%) between 30 and 230 °C corresponding to the loss of four DMF and three water molecules (two free and one coordinated). Thereafter, a small weight loss (2% from 220 to 380 °C) prior to decomposition was observed corresponding to the loss of two $((CH_3)_2NH_2^+)$ cations.⁴⁰ The TGA curve of the MeOH exchanged sample showed that all DMF molecules could be replaced by MeOH. From 30 to 108 °C, a sharp weight loss of 16.8% corresponds to loss of all exchanged MeOH and coordinated water molecules, after which a welldefined plateau is observed up to 386 °C, beyond which a sharp weight loss depicts the framework decomposition (Figure S8 in the SI). Furthermore, the methanol molecules can easily be removed from the pores by heating 1 at 100 °C for 12 h under vacuum to obtain a desolvated 1'. Compared to the PXRD pattern of as-synthesized 1, peak positions after methanol exchange and activated 1 have no obvious change (Figure S9 in the SI), indicating the stability of the host framework after removal of coordinated and guest molecules. Inspired by the

rather high thermal stability, the MOF was tested for its catalytic activities.

Gas Adsorption Studies. The porous and robust nature of 1 and the presence of both $-NH_2$ group and potential open metal sites in the channels prompted us to study the gas adsorption studies. Activation of 1 was achieved by keeping the crystals in anhydrous methanol for 5 days, followed by heating at 100 °C under high vacuum for 12 h, to produce guest free 1'. The N₂ gas sorption measurement at 77 K (Figure 6) revealed



Figure 6. N_2 sorption isotherm of 1' at 77K.

the type I isotherm, suggesting the microporous nature of 1'. The BET surface area was estimated as 318 m² g⁻¹. We next explored CO₂ adsorption in 1' at 273 and 298 K up to a relative pressure $P/P_0 = 1$ (Figure 7). The maximum CO₂ uptake



Figure 7. CO_2 sorption isotherm of 1' at 273 and 298 K.

capacity at 273 K was found to be 67.6 cm³ g⁻¹, whereas the uptake value at 298 K was 32.0 cm³ g⁻¹. The CO₂ uptake capacity is substantial and can be attributed to favorable interactions between CO₂ molecules and $-NH_2$ groups of 1'. The isosteric heat of adsorption, Q_{st} (Figure S10 in the SI) afforded a value of 37 kJ mol⁻¹.

Cycloaddition of CO₂ to Various Epoxides. The presence of open metal sites in 1' is important for CO₂ fixation as revealed by the research done which shows that CO₂ molecules occupy a position near unsaturated metal centers (UMCs) at low pressure.^{41,42} Therefore, we have investigated the heterogeneous catalytic activity of 1' toward cycloaddition of CO₂ with various epoxides to form cyclic carbonates. To accomplish this solvent-free synthesis, styrene oxide (3 mL, 1 equiv), 1' (10 wt %), and tetrabutylammonium bromide (TBAB) as co-catalyst (42 mg, 0.005 equiv) were introduced into a 100 mL stainless steel high-pressure reactor

(Table 2). The temperature of the reactor was increased and maintained as desired, and the reactor was pressurized with

Table 2. Results Obtained for the Cycloaddition Reaction of CO_2 with Various Epoxides^{*a*}

	<mark>8</mark> +	$\frac{1'(10 \text{ wt }\%)}{1}$, TBAB				0-K	
	R	$T_2 = T_2$	Р	R	\mathcal{L}^{0}		
Entry	Epoxide	Product	t (h)	T	Р	%	
				(°C)	(bar)	Yield⁰	
1			6	100	20	99	
2			6	100	10	95	
3			12	100	1	96	
4			12	50	1	92	
5	ci 🔨	ci 🔨	12	50	1	94	
6	C ^o A		12	50	1	87	
7	Å	<mark>بگر</mark>	6	50	10	98	

"Reaction conditions: epoxides (25 mmol, 1 equiv), 1' (10 wt %), TBAB (40 mg, 0.005 equiv). No solvent was added. ^bConversion was evaluated from the ¹H NMR spectra.

 CO_2 (99.999%) in the pressure range from 10 to 20 bar. The reaction mixture was kept stirred at 250 rpm under the above conditions for a period of 6 h. After the completion of the reaction, the reactor was quickly cooled down in a cold water bath, and then pressure was released slowly. A 10 mL portion of CH_2Cl_2 was then added, and the whole mixture was filtered to remove the catalyst from the product. The used catalyst was dried at 100 °C for 5 h under vacuum to regenerate the active catalyst 1'. The yields of the product were determined by ¹H NMR, while GC-MS showed the formation of desired product (Figure S11 in the SI). The maximum conversion was 99% (Table 2, entry 1), which was significantly high.

As we were searching for mild conditions, the conversion of CO₂ was also performed at the atmospheric pressure. At atmospheric pressure, all the reactants were taken in a two-neck round-bottom flask and CO₂ was bubbled through the reaction mixture under heating condition (Table 2, entries 3 and 4). Interestingly, the conversions in this case are found to be 96% and 92%. Using this catalyst system, other epoxides could also be converted to corresponding cyclic carbonates with excellent yields (Table 2, entries 5-7). The characterization of the desired carbonates was confirmed by the ¹H NMR spectra (Figures S13-S16 in the SI). The catalyst could be reused without showing any significant loss in catalytic activity and the framework integrity (Figures S17 and S18 in the SI). Catalyst was found to be purely heterogeneous and showed no leaching of Zn(II) ions according to the hot filtration test (Figure S19 in the SI).

Catalytic Activities of 1' in the Biginelli Reaction. The excellent stability of 1' against heat, the presence of open Zn(II) coordination sites, $-NH_2$ groups decorated channels, and optimized pores fulfill the essential prerequisites of the framework to act as a heterogeneous catalyst. Frameworks built with Zn(II) ions have been proven to catalyze many organic reactions such as Mukaiyama aldol reactions, oxidation of thioethers, transesterification reactions, and so on.^{43–47} Here, we have explored the heterogeneous catalytic activity of 1' in three-component Biginelli coupling reactions involving ethyl acetoacetate, urea, and aromatic aldehydes to give dihydropyrimidinones (Table 3), which show a wide scope of important pharmacological properties.

Table 3. Results Obtained for the Biginelli Reactions of Aromatic Aldehydes with Ethyl Acetoacetate and Urea^{*a*}

R [●] H +	• • • • • • • • • • • • • • • • • • •	H ₂ N NH ₂	Catalyst (10 wt %)			
Entry	Substrate	Time(h)	% Yield ^b			
Linuy			With 1'	Without 1 ′		
1	С	2	93	15		
2	O ₂ N H	2	80	8		
3	H ₃ C	2	81	18		
4	Meo	2	84	13		
5	F H	2	90	10		
6	CI H	2	91	11		
7		2	15	6		
8		2	11	5		

"Reaction conditions: Aldehyde (1.0 mmol), ethyl acetoacetate (2.0 mmol), and urea (1.5 mmol) were reacted at 60 $^{\circ}$ C in the presence of 1' (10 wt %) under a N₂ atmosphere. ^bYields of the isolated product.

In general, a mixture of 1.0 mmol of aldehyde, 2.0 mmol of ethyl acetoacetate, and 1.5 mmol of urea was reacted at 60 °C in the presence of 1' (10 wt %) under a nitrogen atmosphere and solvent-free conditions. The increment of the reaction was monitored by TLC analysis. The catalyst was separated by filtration and washed with CH_2Cl_2 and methanol, followed by drying under vacuum at 100 °C for 5 h, to regenerate the active catalyst. The integrity of the framework was maintained even after three cycles of the reaction, as confirmed by the PXRD of the recovered catalyst (Figures S20 and S21 in the SI). Formation of the desired product, dihydropyrimidinone was confirmed by the ¹H NMR and ¹³C NMR data (Figures S22–

S33 in the SI). The results of the catalytic activity of 1' (Table 3) revealed that aromatic aldehydes having electron-withdrawing or electron-donating groups gave good yield. In the case of bulky aldehydes, the reaction rate is sluggish and the yields are much less (Table 3, entries 7 and 8). This observation shows that bulky substrates do not fit inside the framework cavity. The proposed mechanism of the catalysis reactions is similar to the mechanism proposed by Sweet.⁴⁸ The nature of the catalyst is purely heterogeneous and showed no leaching of Zn(II) ions according to the hot filtration test (Figure S34 in the SI).

CONCLUSIONS

In this study, a new amine group decorated anionic Zn(II)framework, **1**, has been synthesized and characterized by X-ray crystallography. It possesses a rare **sit 3,6-conn** topology and exhibits high catalytic activity for the conversion of CO_2 to cyclic carbonate under mild conditions. Additionally, it shows an excellent heterogeneous catalytic activity in the Biginelli reactions with an aldehyde, ethyl acetoacetate, and urea to afford dihydropyrimidinones. In each case, after easy separation, the framework **1** can be recycled without any noticeable decrease in activity at least up to three times.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01286.

Materials and methods, scheme, IR, TGA, PXRD, ESI-MS, NMR data, and additional figures (PDF)

Accession Codes

CCDC 1546167 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.

AUTHOR INFORMATION

Corresponding Author

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*E-mail: pkb@iitk.ac.in.
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ORCID 💿

Parimal K. Bharadwaj: 0000-0003-3347-8791

Notes

The authors declare no competing financial interest.

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