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Two Stable Heterometal-MOFs as High-efficiency and Recyclable Catalysts in the CO₂ Coupling Reaction with Aziridines

Xiao-Min Kang, Lin-Hong Yao, Zhuo-Hao Jiao and Bin Zhao*

Abstract: Two stable heterometal-organic frameworks $\{Na[LnCo(DATP)_2(Ac)(H_2O)](NO_3)\cdot DMA \cdot 11H_2O\}_n$ (Ln = Er(1) and Yb(2)) have been harvested with H₂DATP (4'-(3,5-dicarboxyphenyl)-2,2':6',2"'-terpyridine) as organic building block. These two isostructural compounds featuring two-dimensional laver architectures possess outstanding thermal stabilities and excellent chemical stabilities in common organic solvents and different acid/base solutions with pH range changing from 1 to 13. Moreover, compounds 1 and 2 serving as heterogeneous catalysts can efficiently catalyse the CO₂ fixation reaction with various aziridines to result in corresponding oxazolidinones at 70°C. Importantly, the good recyclable performance of 1 is observed in experimental results at least ten times, which are further confirmed by PXRD, TGA and ICP analyses.

Introduction

In recent years, a series of energy and environmental problems have gained utmost attention along with the acceleration of industrialization.^[1] On account of excessive consumption of fossil fuels, a mass of pollutants have been produced, in which waste gas as one of the main contaminants will cause air pollution to threaten the safety of human and nature. Carbon oxide (CO₂), an important greenhouse gas derived from human and industrial actions will be answerable for the climate change, global warming and acid rain.^[2] Meanwhile, CO₂ serving as an attractive C1 source can be extensively used in the synthetic chemistry with many advantages, including nontoxic, abundant, cheap and renewable features.^[3] Hence, meeting the requirements of CO₂ capture and utilization simultaneously is urgent and meaningful. For this purpose, a lot of efforts have been put into the CO₂ coupling reaction with heterocyclic compounds to form multifarious high-valued chemicals, covering oxazolidinones, cyclic carbonates, dimethyl carbonate, formic acid and alkynyl carboxylic acid products, which are acquired from fossil fuel resources currently.^[4] It is worth mentioned that the CO₂ conversion with aziridines into oxazolidinones stimulated tremendous interest on the basis of their efficient reaction capacity, satisfactory atom utilization and ideal reaction products. Oxazolidinones are of the particular importance not only because they can be regarded as the chiral auxiliaries and intermediates in organic synthesis,^[5] but also they can be applied to the pharmaceutical chemistry as antimicrobial pharmaceuticals, like radezolid,^[6] tedizolid^[7] and linezolid.^[8] Previously, different kinds of homogenous catalysts perform good catalytic activities in CO2 cycloaddition reaction with aziridines, such as alkali metal halide, tetraalkylammonium salt

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 E-mail: <u>zhaobin@nankai.edu.cn</u> and α-amino acids. and so forth.^[9] However. the only fly in the ointment is that the homogenous catalysts are hard to be separated and recovered, limiting their practical application to some extent and being contrarv to the sustainable development. Comparably, heterogeneous catalyst with excellent catalytic activity and recyclability plays a crucial part in industrial production.

Metal-organic frameworks (MOFs) composed by metal nodes and organic blockings are sought after by scientific workers on account of their charming architectures,^[10] diverting properties and potential applications.^[11] Importantly, MOFs can be exploited for the CO₂ coupling reactions with terminal alkynes, propargylic alcohols, propargylamines, aziridines and epoxides as high-efficiency and recyclable heterogeneous catalysts.^[12] To the best of our knowledge, no heterometal-MOF as catalyst for CO₂ fixation with aziridines has been reported up to now.

In this contribution, two novel heterometal-MOFs have been harvested bv solvothermal reaction and structurally characterized, formulated as $\{Na[LnCo(DATP)_2(Ac)(H_2O)](NO_3)\cdot DMA\cdot 11H_2O\}_n (Ln = Er (1))$ and Yb (2), $H_2DATP = 4'-(3,5-dicarboxyphenyl)-2,2':6',2'''$ terpyridine). Compound 1 possesses superior resistance to various organic solvents and acid/alkali solutions with pH range changing from 1 to 13. Particularly, with compounds 1 and 2 as catalysts, efficient catalytic performances and ideal targets (oxazolidinones) have been observed in the cycloaddition reactions of CO2 and aziridines with various substituents under different conditions. Moreover, 1 can be recycled at least ten times with negligible change in catalytic activity, which is confirmed by PXRD, TGA and ICP analyses.

Results and Discussion

Description for the Crystal Structure of {Na[ErCo(DATP)₂(Ac)(H₂O)](NO₃)·DMA·11H₂O}_n (1)

Compounds 1 and 2 were harvested by the reaction of mixed solvents DMA/H₂O (3:3), H₂DATP ligand and Ln(NO₃)₃·5H₂O (Ln = Er (1) and Yb (2)) under solvothermal conditions. Singlecrystal diffraction analyses demonstrate that compounds 1 and 2 all crystallize in the monoclinic $P2_1/c$ space group. In view of these two structures are isomorphous, compound 1 as the representative example was introduced in detail for the structural analysis. As described in Figures. 1a and 1b, the asymmetric unit of compound 1 contains one crystallographically distinct Er³⁺, one independent Co2+ and two DATP2- as well as one coordinated Ac⁻, one coordinated water molecule and one free Na⁺, one NO₃⁻, one DMA and eleven water molecules. The presence of NO3⁻ was confirmed by IR spectrum. Each sevencoordinated center Er³⁺ is completed by four carbonyl oxygen atoms (O2, O6, O7, O10) from four different DATP²⁻, one water molecule and two oxygen atoms from one Ac⁻, presenting an irregular decanedron coordination configuration. By contrast, the Co²⁺ occupying the center of octahedron adopts six-coordinated

geometry configuration and is chelated by six nitrogen atoms (N1, N2, N3, N4, N5 and N6) from two H₂DATP ligands. The Er-O and Co-N bond lengths fall into the range of 2.201(4)-2.382(5) Å (average 2.287 Å) and 1.851(5)-1.945(5) Å (average 1.913 Å), respectively. The O-Er-O and N-Co-N bond angles change from 54.48(15)° to 178.15(17)° and 82.4(2)° to 178.5(2)°, respectively (Table S1 in the Supporting Information). These data mentioned above agree well with the reported those previously.^[13] In compound 1, the framework consists of two diverse building blocks [Er(COO)₄(Ac)(H₂O)] and [Co(DATP)₂], which are connected by each other through H2DATP ligands to form a 2D layer architecture (Figure 1c). A distinct structural feature in compound **1** is that it possesses strong π - π stacking interactions between two paralleled benzene rings in neighboring H₂DATP ligands (the distance between ring centroids is about 3.5749 Å, and the dihedral angles range from 0 to 5.547°). The large conjugated π electron system possibly makes a great contribution to the architectural stabilization of framework 1.[14]



Figure 1. a) The asymmetric unit of compound 1. b) The coordination environments of Er^{3+} , Co^{2+} and $DATP^{2-}$. c) View of 2D-layer structure of 1. d) Topological representation of 1. Color codes for atoms: green sphere, Er; pink, Co; red, O; gray, C; blue, N. H atoms and solvent molecules are omitted for clarity.

In order to get a better insight into the complicated framework of **1**, the freely available TOPOS software package was employed.^[15] Then, each [Er(COO)₄(Ac)(H₂O)] unit considered as a 4-connected node links four DATP²⁻, and each Co²⁺ serving as a 2-connected spacer connects two DATP²⁻, and each DATP²⁻ belongs to a 3-connected node coordinates two [Er(COO)₄(Ac)(H₂O)] units and one Co²⁺. In result, the 2D layer structure of **1** can be simplified into a 3,4-connected double-nodal topological network with the Schläfli symbol of {4;6^2}2{4^2;6^2;8^2} (Figure 1d).

IR Studies

IR spectra of compounds **1** and **2** were performed at room temperature and exhibited characteristic bands (Figure S1 in the Supporting Information). The bands centered at v = 1366 and 1370 cm⁻¹ for compounds **1** and **2** respectively are assigned to the presence of NO₃⁻.

PXRD Analyses

The powder X-ray diffraction (PXRD) measurements have been carried out for compounds **1** and **2**. As presented in Figure S2 in the supporting information, good agreement between the experimental patterns and simulated one indicates high purity of **1** and **2**. To further evaluate the solvents stability and pH stability of compound **1**, the crystal samples were soaked in common organic solvents (1,4-dioxane, MeOH, n-BuOH, i-PrOH, CHY, DMF, CH₃CN, CH₂Cl₂, CCl₄ and EtOH) and acid/base solutions with different pH values falling into the range of 1 to 13 for 12 h, respectively. The peaks of treated samples are in consistence with the simulated ones, implying the structural integrity of framework **1** (Figures S3 and S4 in the Supporting Information). Consequently, the experimental results demonstrate that **1** owns outstanding solvent stability and excellent acid/base stability ranging from pH1 to pH13.

TGA Investigations

The thermogravimetric analyses (TGA) were tested in the temperature range from 30 to 700°C under N₂ atmosphere to explore the thermal stability of compounds 1 and 2, as shown in Figure S5 in the Supporting Information. The TGA curves reveal a weight loss of about 20.44% from 25°C to 355°C (calculated 20.72% and 20.63% for compounds 1 and 2, respectively), which is ascribed to the removal of eleven free water molecules, one free DMA molecule and one coordinated water molecule. Then, a continuous weight loss can be observed beyond about 355°C, indicating the collapse of these frameworks. Therefore, both compounds 1 and 2 perform high thermal stabilities above 355°C.

Catalytic Characterization

Given the unsaturated Ln³⁺ Lewis-acid sites in compounds 1 and 2, the catalytic abilities of them have been evaluated in the CO₂ fixation reaction with aziridines. Then, the CO₂ adsorption of compounds 1 and 2 at 298 K have been be tested, as indicated in Figure S6. Taking compound 1 as example, firstly, the cycloaddition reaction of CO₂ and probe substrate 1-ethyl-2phenylaziridine (a) into oxazolidinone has been carried out under 2 MPa for 10 h with 0.1 mmol tetrabutylammonium bromide (TBAB) and 20 mg compound 1 (0.68 mol% based on center metal) serving as additive and catalyst, respectively. As shown in Table 1 (entries 1-4), the catalytic performances for the transformation from 1-ethyl-2-phenylaziridine (a) to 3-ethyl-5phenyloxazolidin-2-one (b) and 3-ethyl-4-phenyloxazolidin-2-one (c) rise first and then fall from 30°C to 90°C. The experimental results demonstrate that both lower and higher temperatures will take the edge off the catalytic efficiency, and quantitative yield (96%) and high selectivity have been observed at 70°C (Table 1, entry 3). Secondly, the influence of other key parameters on catalytic activity of the reaction have been investigated at 70°C, including CO₂ pressure, reaction time as well as the amounts of TBAB and sample 1. Entries 5 and 6 in Table 1 present different catalytic results that the desired products have been gained with yields of 94% and 25% at 1 MPa and 0.1 MPa, respectively. Comparably, 1 MPa was selected as the first-rank CO₂ pressure. Then, shortening the reaction time from 10 h to 5 h, the yield of corresponding product decreases by ten percent (Table 1, entry

7). Then, the catalytic activity shows obvious reduction when 0.05 mmol (16.11 mg) co-catalyst TBAB was used (Table 1, entry 8). With regard to catalyst amount, the yield change of reaction products can be ignored although the sample 1 reaches to 40 mg (Table 1, entry 9). Nevertheless, when 0.1 mmol TBAB was applied alone to the CO₂ transformation at 70°C, only 45% yield for 3-ethyl-5-phenyloxazolidin-2-one has been harvested (Table 1, entry 13), indicating the synergistic effect between cocatalyst TBAB and Er³⁺ Lewis-acid active sites. Consequently, the best reaction conditions should be 70°C under 1 MPa with 0.1 mmol TBAB and 20 mg catalyst for 10 h in solvent-free system. What is particularly noteworthy is that compound 1 features the first heterometal-MOF based catalyst for the CO2 aziridines to result in coupling with corresponding oxazolidinones.

Table 1. Cycloaddition reaction of CO $_2$ with 1-ethyl-2-phenylaziridine under various conditions. $^{a)}$



Entry	Catalyst 1 [mg]	<i>T</i> [°C]	Yield ^{b)} [%]	Conversion ^{c)}	Regio-sel ^{d)}
1	20	30	37	41	91:9
2	20	50	85	87	98:2
3	20	70	96	97	99:1
4	20	90	94	95	99:1
5 ^{e)}	20	70	94	95	99:1
6 ^{f)}	20	70	25	27	91:9
7 ^{g)}	20	70	84	87	96:4
8 ^{h)}	20	70	84	86	98:2
9	40	70	92	93	99:1
10 ⁱ⁾	0	70	31	33	93:7
11 ^{j)}	0	70	34	36	93:7
12 ^{k)}	0	70	36	38	94:6
13	0	70	45	46	98:2

[a] Reaction conditions: 1-ethyl-2-phenylaziridine (294.4 mg, 2.0 mmol), solvent-free, catalyst 1, TBAB (32.2 mg, 0.1 mmol), CO₂ (2.0 MPa), 10 h, 20 mg catalyst 1 loading (based on metal center, about 0.68 mol%); [b] Total yields of **b** and **c** determined by ¹H NMR using 1,3,5-trimethoxybenzene (42.1 mg, 0.025 mmol) as an internal standard; [c] The conversion of products; [d] Molar ratio of **b** to **c**; [e] CO₂ (1.0 MPa); [f] CO₂ (0.1 MPa); [g] t (5 h); [h] TBAB (16.1 mg, 0.05 mmol); [i] TBAB (32.2 mg, 0.1 mmol) and Er(Ac)₃-5H₂O (6.06 mg, 0.014 mmol); [k] TBAB (32.2 mg, 0.1 mmol) and ErCl₃-6H₂O (5.22 mg, 0.014 mmol).

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Previously, some transition metal-based MOFs as catalysts for this catalytic reaction have been reported, like [Cu₃₀], [M₂] (Co, Mn and Ni), [Zn₂₄] and MMPF-10 (M = Zr). For [Cu₃₀], it performs optimal yield of 99% for target product at 100°C under 2 MPa CO₂ pressure with 80 mg catalyst for 12 h.^[16] Adopting the same temperature and CO2 pressure with [Cu30], MMPF-10 has obtained similar yield in 10 h.[17] Additionally, [M2] (Co, Mn and Ni) can catalyze the CO₂ conversion to form oxazolidinones under mild conditions with quantitative yield (86% - 89%): 30°C, 1 MPa, 10 h, 0.1 mmol TBAB and 20 mg catalyst.^[18] Moreover, with 20 mg [Zn₂₄] as catalyst, good activity and excellent yield (99%) have been observed under 2 MPa at 70°C for 12 h.[19] Therefore, on the basis of previous work, the result of highefficiency catalysis will be met at the expense of higher temperature, higher CO₂ pressure, longer time or more catalyst amount. In comparison, compound 1 can catalyze the reaction more easily than [Cu₃₀], [Zn₂₄] and MMPF-10, and possesses more outstanding catalytic capacity than [M₂] (Co, Mn and Ni). Then, the catalytic performance of compound 2 has been assessed by the same strategy, and supreme conditions are identified as 70°C, 2 MPa CO₂, 20 mg catalyst 2 and 0.1 mmol TBAB for 10 h. More rigorous CO₂ pressure for compound 2 than 1 may be attributed to more superior Lewis-acid activity for Er³⁺ than Yb³⁺ (Tables S3 in the Supporting Information).

Sequentially, we further study the catalytic potential of these two compounds in CO₂ cycloaddition reaction with some typical aziridines substituted by different groups under optimized conditions (the synthetic process of aziridines in Scheme S1 in the Supporting Information). Then, the experimental results listed in Table 2 (entries 1-5) reveal that the yields of corresponding oxazolidinones change with the size and types of substituent groups in substrates. For entries 1-3 in Table 2, three aziridines with different substituent groups of ethyl, propyl or butyl at the nitrogen atoms respectively have been utilized to participate in the catalytic reaction. The results indicate that 1ethyl-2-phenylaziridine (Table 2, entry 1) owns better catalytic than 1-propyl-2-phenylaziridine and property 1-butvl-2phenylaziridine (Table 2, entries 2 and 3), giving rise to different yields from 94% to 91% in descending order for them. The higher catalytic efficiency for 1-ethyl-2-phenylaziridine is possibly ascribed to smaller steric hindrance for the ethyl than the propyl and butyl group. Moreover, using 1-ethyl-2-(4-chlorophenyl)aziridine and ethyl-2-p-tolylaziridine as substrates, 3-ethyl-5-(4chlorophenyl)oxazolidin-2-one (86%) and ethvl-5-ptolyloxazolidin-2-one (70%) have been achieved by the CO2 fixation reactions (Table 2, entries 4 and 5). Hence, catalyst 1 can effectively catalyze the coupling reaction of $\ensuremath{\text{CO}}_2$ and multifarious aziridines in solvent-free system under 1 MPa pressure at 70°C. The corresponding by-products of these CO₂ cycloaddition reactions are detected and notified by ¹H NMR analyses (Figure S7).

Next, we also have evaluated the reaction activity of compound **2** in CO_2 cycloaddition with various substituted aziridines under similar conditions to compound **1** except for the reaction pressure (2 MPa). As displayed in Table S4 in the Supporting Information, final yields of corresponding oxazolidinones catalyzed by crystal **2** present the same varying tendency in comparison with those catalyzed by **1**: 3-ethyl-5-phenyloxazolidin-2-one with highest yield of 98% (Table S4 in the Supporting Information, entry 4) and ethyl-5-ptolyloxazolidin-2-one (Table S4 in the Supporting Information, entry 5) with the lowest yield of 70%. Considering the same

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structures of compounds **1** and **2**, we speculate that the otherness of Lewis-acid activity for Er^{3+} and Yb^{3+} may take the responsibility for diverse catalytic abilities of compounds **1** and **2** and different reaction conditions.

Table 2. Synthesis of various oxazolidinones from CO_2 and aziridines with catalyst $1.^{\text{a})}$



[a] Reaction conditions: aziridine (2.0 mmol), solvent-free, 20 mg catalyst 1 loading (based on metal center, about 0.68 mol%), TBAB (32.2 mg, 0.1 mmol), CO₂ (1.0 MPa), 10h; [b] Determined by ¹H NMR using 1,3,5-trimethoxybenzene (42.1 mg, 0.025 mmol) as an internal standard; [c] Molar ratio of N₂ to N₃.

In fact, we all know that the recyclability of heterogeneous catalyst plays an essential part in practical applications. Then, the recycle performance of compound **1** has been explored in the CO₂ cycloaddition reaction. Through centrifugation and filtration strategies, the compound **1** was separated from the residue after reaction. The recycle experiments were repeated ten times, and no significant change in catalytic activity could be observed. The yields of oxazolidinones range from 94% (the first run) to 89% (the tenth run) for compound **1** (Figure 2). As described above, compound **1** features excellent chemical stability in various organic solvents and acid/base solutions with pH range from 1 to 13. After the catalytic cycloaddition reaction of CO₂ with aziridines, compound **1** still remains crystalline state and no significant change in crystal color has been observed.

Moreover, the stability of recovered **1** have been further confirmed by PXRD, IR, TGA and ICP analyses. As indicated in Figure S8 in the supporting information, the PXRD experiments after ten catalytic recycling have been carried out. All PXRD peak positions and intensity of recycled **1** agree well with those of as-synthesized **1**, proving the structural integrity and chemical stability of the sample **1**. Simultaneously, the consistency of the IR spectra between sample **1** and the one after ten catalytic recycles indicates its excellent stability (Figure S9). From the TGA cure of recycled **1**, it can be seen that the framework tends to decompose over **350°C**, which provides a fundamental guarantee for catalyst **1** in high temperature environment (Figure S10). Additionally, trace leakage of Er³⁺ ion (0.056%) for the mixture filtrate after ten recycles was detected through ICP test, indicative of the high stability of structure (Table S5).



Figure 2. Recycle experiments for the coupling reaction of CO_2 with 1-ethyl-2phenylaziridine have been conducted for 10 h at 70°C under 1 MPa with 0.1 mmol TBAB and 20 mg catalyst in solvent-free system.

Finally, in order to better make the catalytic mechanism clear, a variety of Erbium sources have been employed to catalyze the CO₂ fixation with aziridines, including Er(Ac)₃, Er(NO₃)₃ and ErCl₃ (0.014 mmol). The low yields of corresponding oxazolidinones were 31%, 34% and 36% respectively, revealing that both free Er3+ and these three inorganic anions have no obvious catalytic effects on the CO2 cycloaddition reaction (Table 1, entries 10-12). In comparison, the yields of oxazolidinones with Er-salts serving as catalyst and TBAB as co-catalyst are inferior to that catalyzed solely by TBAB (45%), which could be due to the interaction between free metal ions with Br ions to hinder the nucleophilic attack. However, when the same amount of catalyst 1 takes the place of Er-salt to catalyze the reaction, the optimum yield (94%) of target product and excellent selectivity have been obtained in terms of other conditions unchanged. Actually, the remarkable enhancement in catalytic efficiency may be attributed to next two factors: (a) The unsaturated seven-coordinated Ln3+ featuring more Lewis-acid sites can effectively activate the substrates and CO₂, which benefits the acceleration of catalytic reaction; (b) The excellent chemical stabilities and high thermostability ensure the structural integrity during catalysis, providing more opportunities for the nucleophilic attack of Br- towards aziridines without the coordination interaction between free Ln3+ and Br- ions.

In consideration of previous reports,^[16-19] the possible mechanism has been presumed for 1/TBAB-catalyzed CO₂ fixation with aziridines into oxazolidinones (Figure S11 in the Supporting Information). For the catalyst 1 as example, firstly, the 2D framework of 1 enriched CO₂ and substrate, and the substrate was activated by unsaturated Erbium Lewis-acid sites binding the N atom from aziridine. Then, the nucleophilic attack of Br on the aziridine gives rise to ring-opening process with two different routes **a** and **b**. Subsequently, carbamate salt has come into being by the reaction of CO₂ and N atom from ring-opened intermediate. Intramolecular ring-closing reaction produces the corresponding oxazolidinone finally. With respect of regioselectivity, N_2 has been gained as the primary product through path **a** with more stable carbamate salt intermediates.

Conclusions

In conclusion, two stable 2D heterometal-MOFs, named as $\{Na[LnCo(DATP)_2(Ac)(H_2O)](NO_3)\cdot DMA\cdot 11H_2O\}_n$ (Ln = Er(1) and Yb(2)), have been prepared through solvothermal synthesis technique and further structurally characterized. TGA and PXRD investigations reveal that they own high thermostability and strong resistance against various organic solvents and acid/base solutions with wide pH range (1 - 13). Importantly, heterogeneous catalysts 1 and 2 can be applied for the CO₂ cycloaddition with ten substituted aziridines to form high-value products. showing excellent catalytic activity and environmentally friendly merit. Particularly, the catalytic activity of recovered 1 can remain uncharged in comparison with original one after ten recycling. To the best of our knowledge, compound 1 belongs to the first heterometal-MOFs based catalyst for the cycloaddition of aziridines and CO2.

Experimental Section

Materials

All the chemicals including metal salts, organic ligand and solvents utilized in this work for crystals preparation were purchased without further purification. Erbium nitrate pentahydrate ($Er(NO_3)_3 \cdot 5H_2O$, 99 wt%) and Ytterbium nitrate pentahydrate ($Yb(NO_3)_3 \cdot 5H_2O$, 99 wt%) were provided by Energy Chemical (China). H₂DATP ligand (97 wt%) and DMA solvent were achieved from Jinan heng chemical and Concord (China), respectively.

Synthesis of Compound 1

Er(NO₃)₃·5H₂O (0.0090 g, 0.02 mmol) and 4'-(3,5dicarboxyphenyl)-2,2':6',2"'-terpyridine (0.0099 g, 0.025 mmol) were dissolved in a DMA/H₂O mixture with solvent ratio of 1:1 (3 mL : 3mL). Addition of 100 µL HNO3 was employed to regulate the pH value of the solution. Then the resulting mixture was sealed in a 7 mL capped vial, and was heated at 100 °C for 3 days under autogenous pressure. The solvothermal reaction was cooled slowly down to room temperature at 2 °C/h. Orange block crystals of compound 1 were prepared (89% yield based on $Er(NO_3)_3 \cdot 5H_2O).$ Element analysis (%) calcd for $NaC_{52}H_{62}CoErN_8O_{26}\!\!:$ C, 42.65; N, 7.65; H, 4.24. Found: C, 42.49; N, 7.51; H, 4.31 (Table S6 in the Supporting Information).

Synthesis of compound 2

The synthesis of compound **2** is similar to that of **1**, except that $Er(NO_3)_{3}\cdot 5H_2O$ takes the place of $Yb(NO_3)_{3}\cdot 5H_2O$ (0.0112g, 0.025 mmol). Coupling the H₂DATP ligand and $Yb(NO_3)_{3}\cdot 5H_2O$ in mixed solvents (DMA/H₂O) in 7 mL capped vial under same hydrothermal conditions afforded orange block single crystals (88% yield based on $Yb(NO_3)_{3}\cdot 5H_2O$). Elemental analysis (%) for **2** (NaC₅₂H₆₂CON₈O₂₆Yb), Calcd: C 42.48, H 4.22, N 7.62. Found: C 42.35, H 4.33, N 7.48 (Table S6 in the Supporting Information).

General Methods and Characterization

The Fourier transform infrared (FT-IR) spectra were measured by a Bruker Tensor 27 spectrophotometer as KBr pellets in the range at 400 - 4000 cm⁻¹. The element analyses (EA) data for C, N and H were collected on Perkin-Elmer elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-2500 diffractometer by using Cu K α radiation (λ = 1.54056 Å) with a scan speed of 5° min⁻¹ and 2 θ region from 3° to 60°. The thermogravimetric analyses (TGA) were performed by a Netzsch TG 209 TG-DTA analyzer with test temperature from 25°C to 700°C under nitrogen atmosphere. The ¹H NMR spectra of the catalytic products were monitored through a Bruker 300 spectrometer and 1,3,5-trimethoxybenzene was served as internal reference with chemical shifts in ppm. The leakage contents of metal ions (Eu³⁺ and Yb³⁺) after catalytic recycling in filter liquor were characterized by ICP-9000(N+M) spectrometric analyses.

General procedure for the CO₂ coupling with aziridines to form oxazolidinones was described as following: taking compound **1** as example, first step, 2 mmol the corresponding aziridines, 0.1 mmol tetrabutylammonium bromide (TBAB) (32.2 mg), and 20 mg **1** (0.014 mmol) (corresponding to 0.68 mol% metal center) were slowly introduced into stainless-stale reaction vessel (25 mL). Then CO₂ (2 MPa) was introduced into the vessel by using carbon dioxide gas-holder and the resulting reaction mixture was stirred at different temperatures, respectively. After 10 h, when the reaction was cooled down to room temperature, 0.025 mmol 1,3,5-trimethoxybenzene (42.1 mg) as an internal standard and 5 mL CH₂Cl₂ were added into the reaction products. The mixture was stirred 5 min and the desired product was applied to ¹H NMR after distillation under reduced pressure.

Single-Crystal Structure Determination

Suitable crystals **1** and **2** were picked for single-crystal X-ray diffraction analyses under a cooled N₂ atmosphere. All crystallographic measurements were carried out by a Super Nova Single Crystal Diffractometer configured with a graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å). The ω - φ scan technique was employed, and the crystal data was corrected for Lorentz-polarization effects. Then, the structures of compound **1** and **2** were solved by directed methods and refined by using full-matrix least squares on F^2 with SHELXS and SHELXL programs.^[20] In terms of non-hydrogen atoms, they were refined

by utilizing anisotropic parameters while all the hydrogen atoms were placed in calculated positions and refined employing a riding model. In consideration of seriously disordered solvent molecules in compounds **1** and **2**, the PLATON/SQUEEZE have been used to remove them.^[21] The final formulas and structures of **1** and **2** have been confirmed by the element analysis and TGA analysis (Table S6 and Figure S5 in the Supporting Information). Detailed crystal data and structure refinement for compounds **1** and **2** are given in Table 3. Selected bond distances and angles are listed in Table S1 in the Supporting Information. The CCDC numbers of **1** and **2** are 1907482 and 1907484, respectively, and the files contain the supplementary crystallographic data for this paper.

Table 3. Crystal data and structure refinements for compounds 1 and 2.

	1	2	
formula	NaC52H62CoErN8O26	NaC52H62CoN8O26Yb	
Fw	1463.08	1469.04	
<i>T</i> /K	120.00(10)	120.00(10)	
Cryst. Syst.	monoclinic	monoclinic	
Space group	P21/c	P21/c	
a/Å	10.0421(2)	10.0081(3)	
b/Å	29.0407(7)	29.0640(9)	
c/Å	19.0694(8) 19.0006(11)		
<i>α</i> /°	90	90	
β/°	94.100(2)	93.713(4)	
γ/°	90	90	
Volume/Å ³	5547.0(3)	5515.2(4)	
Ζ	4	4	
$ ho_{calc}g/cm^3$	1.406	1.399	
µ/mm ⁻¹	1.868	2.051	
<i>F</i> (000)	2976.0	2984.0	
2θ range for data collection/°	6.006 to 50.02	5.858 to 50.016	
Reflections collected	25544	24445	
Rint	0.0597	0.0488	
Goodness-of-fit on <i>F</i> ²	1.036	1.147	
Final <i>R</i> indexes	$R_1 = 0.0515,$	$R_1 = 0.0650,$	
[l>=2σ (l)]	<i>wR</i> ₂ = 0.1115	$wR_2 = 0.1399$	
Final R indxes	$R_1 = 0.0729,$ $R_1 = 0.0735,$		
[all data]	$wR_2 = 0.1193$ $wR_2 = 0.1437$		
$\Delta ho_{max/min}$	1.586/-1.076	2.108/-1.906	

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Conflict of interest

The authors declare no conflict of interest.

Keywords: heterometal-organic frameworks • heterogeneous catalysis • CO₂ fixation • oxazolidinones • cyclicity

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Two stable heterometal-MOFs $\{Na[LnCo(DATP)_2(Ac)(H_2O)](NO_3)\cdot DMA\cdot 11H_2O\}_n$ (Ln = Er(1) and Yb(2)) have been harvested and structurally characterized, presenting excellent catalytic performances and cyclicity in the CO₂ fixation with aziridines into high-valued oxazolidinones



Xiao-Min Kang, Lin-Hong Yao, Zhuo-Hao Jiao and Bin Zhao^{*[a]}

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Title Two Stable Heterometal-MOFs as High-efficiency and Recyclable Catalysts in the CO₂ Coupling Reaction with Aziridines