A very rare structurally characterized CO2-coordinated metal–organic framework was synthesized by a solvothermal reaction. The CO2 ligand links two open Zn metal centers in a linear and symmetrical μ(O,O') coordination mode with a C–O distance of 1.107(4) Å. The new complex reported here is stable under ambient conditions and may provide a new strategy for CO2 fixation.

Carbon dioxide (CO2), the primary greenhouse gas emitted through human activities, has caused increasing environmental concerns during the past few decades. To now, some effective strategies have been adopted to capture CO2 from gaseous waste. Recently, metal–organic frameworks (MOFs) as a new type of functional materials have attracted intensive attention. A large number of porous MOFs as potential CO2 adsorbents have been reported. These materials exhibit high adsorptive capacities under either low or high pressure due to their extraordinary surface areas, finely tunable pore surface properties, and potential industrial scalability. From a mechanistic point of view, it is extremely important to model the trapped CO2 molecules through single-crystal X-ray diffractions within the frameworks, but this is difficult because most CO2 molecules are disordered in MOFs. Few examples of CO2 molecules trapped in MOFs have been confirmed by crystallographic analysis combined with other complementary methods such as IR spectroscopy and computational studies. Investigation of the manner in which the metal centers coordinate to CO2 molecules will lay a firm foundation to design new MOF materials for the fixation of CO2. So far, a few structurally characterized CO2-containing organometallic compounds have also been verified. Usually, CO2 molecules show four main coordination modes: μ2η2-c,O, μ2η2-c,p, μ2η2-c,p and μ2η2-o,o. Very recently, Nandi and Goldberg reported a zinc porphyrin-based PrNa-MOF in which one CO2 molecule bridges two neighboring Zn(ii) centers in the μ2-η2-o,o coordination mode with an O–C–O angle of 155.2(10)° and a C–O distance of 1.131(5) Å. In this communication, we describe an unprecedented ZnMOF complex in which CO2 molecules are directly fixed by open Zn(n) centers.

The title complex ZnMOF (1) was synthesized by typical solvothermal reactions of Zn(NO3)2·6H2O and a semi-rigid polycarboxylic acid hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane (H6L) in DMF/H2O (6:1 in volume) after heating at 115 °C for 3 days. Its formula was confirmed as [(CH3)2NH2]2[Zn6(OH)(L)2(CO2)]·9DMF·3H2O based on elemental analysis, single-crystal X-ray diffraction, thermogravimetric analysis (TGA) as well as charge balance considerations. The protonated [(CH3)2NH2]+ cations are formed in situ upon heating DMF. Single-crystal X-ray diffraction study revealed that compound 1 crystallizes in an orthorhombic space group Pnma (Table S1, ESI†). Its asymmetric unit contains two crystallographic-independent Zn2+ ions, half ligand L, one μ3-CH3OH anion and a quarter of CO2 molecule (Fig. S1 in ESI†). Other disordered cations and guest molecules are not crystallographically well-defined. As shown in Fig. 1 and Fig. S2a (ESI†), Zn(1) is octahedrally coordinated by six oxygen atoms. Four O atoms in the square plane are from the three carboxylate groups, one vertical O atom is from the CO2 ligand, and the other

![Fig. 1](image-url)
one is from $\mu_3$-OH. The (Zn(1)–O bond lengths are in the range of 2.008(4)–2.139(3) Å. In comparison, Zn(2) is tetrahedrally coordinated by four oxygen atoms, three of which come from three different carboxylate ligands and the last one is from the $\mu_3$-OH ligand shared with Zn(1) (Fig. 1 and Fig. S2a, ESI†). The Zn(2)–O distances vary from 1.943(2) to 1.986(1) Å, which are slightly shorter than those with Zn(1). A Zn(1) ion and two Zn(2) ions are held together by the vertex-sharing $\mu_3$-OH ligand, resulting in a trinuclear Zn$_3$ cluster in the shape of an isosceles triangle. It is interesting that the carbon dioxide molecule (O(1)C(1)O(1)) links two Zn$_3$ clusters in a linear shape of an isosceles triangle. It is interesting that the carbon dioxide molecule (O(1)C(1)O(1)) links two Zn$_3$ clusters in a linear shape of an isosceles triangle.

Free solvent molecules are located in the channels. TOPOS analysis reveals that the whole structure can be simplified as a 4,8-connected $\eta^0$—$\eta^0$—$\eta^1$ network (Fig. S3a, ESI†). In each single net, mesoporous hexagonal channels can be observed approximately 17.8 $\times$ 17.8 Å$^2$ (the length of the b-axis) along the a-axis and 22.3 $\times$ 11.7 Å$^2$ along the b-axis (including van der Waals radii) (Fig. S3b and c, ESI†). From the topological point of view, each independent framework can be reviewed as a $6^6$–$4$-connected uninodal dia net (Fig. S3d–f, ESI†). Then the linearly coordinated CO$_2$ ligand bridged two Zn$^{II}$ SBUs of adjacent independent nets into total 3D frameworks with interconnected channels in a staggered fashion, thus the hexagonal window along the [100] direction is divided into three parts (Fig. 2 and Fig. S4a, ESI†). The coordinated CO$_2$ molecules reside in channel C and link two open Zn sites. A large-size channel of 12.5 $\times$ 10.5 Å$^2$ (type D) can still be observed perpendicular to the ac plane (Fig. 3 and Fig. S4b, ESI†). The channels B and D mentioned above intersect each other, forming two-dimensional intersecting channels in this compound (Fig. S4c, ESI†). Free solvent molecules are located in the channels. TOPOS analysis reveals that the whole structure can be simplified as a 4,8-connected $\eta^0$—$\eta^1$—$\eta^2$ net (Fig. S4d, ESI†) with a solvent-accessible volume of approximately 5715.2 Å$^3$ per unit cell, and a pore volume ratio calculated to be 57.0% using the PLATON program.†

In order to confirm the CO$_2$ molecule was indeed fixed successfully in the ZnMOF (1), several verifiable methods are adopted. Firstly, four randomly selected crystals were used for single-crystal X-ray diffraction analyses on different CCD diffractometers, and the experimental details are depicted in the ESI,† as shown in Tables S1 and S2. All results display that a linear coordinated CO$_2$ ligand appears obviously in position and strongly binds two metal sites. Secondly, to gain more insight into the CO$_2$ bonded in the ZnMOF (1), IR spectroscopy was used as a complementary method to study the interaction of carbon dioxide with the metal site and provides further evidence for the existence of CO$_2$ in 1. As depicted in Fig. S5 (ESI†), an absorption band at 2456 cm$^{-1}$ can be assigned to the stretching vibration of the C-O bond from the bridging CO$_2$ ligand. In comparison to free linear carbon dioxide (v$\text{sym}$ = 2348 cm$^{-1}$), the value is at a higher frequency, but consistent with experimentally observed shorter bond length in other materials reported to date.†

Thirdly, the solid sample (80 mg) of complex 1 was placed in a 1.5 mL centrifugal tube with 1 mL of H$_2$O, then concentrated H$_2$SO$_4$ (40 µL) was added and sealed. Some small bubbles could be observed immediately, due to the destruction of the framework of 1 by H$_2$SO$_4$ thereby releasing the coordinated CO$_2$ molecules. After 5 h, the small bubbles were gathered into a big bubble. In order to observe the phenomenon more clearly, a similar experiment was done in glass vials (5 mL), then capped and kept still, as shown in Fig. S6 (ESI†). As a comparison, concentrated H$_2$SO$_4$ with the same volume was added into a pure DMF solution as well as the DMF solution with Zn$^{2+}$ salt, respectively, but no change was observed. Then the
or even refix CO2 molecules, which is more interesting to us, so that generation of CO2 from DMF can be examined using GC analysis.

As shown in Fig. 4, the results indicate that the CO2 molecules in air are almost negligible, the released CO2 molecules from compound 1 are very clear and the peak matches well with the one from pure CO2 gas. The results discussed above strongly demonstrate that the CO2 ligand is connected to the framework of ZnMOF (1).

Another important question also needs to be resolved about the source of the CO2 molecule in ZnMOF (1). The most likely scenario is the in situ decomposition of solvent DMF during the solvothermal synthesis under acidic conditions, which is a very common process and has also been verified by this work (Fig. S7, ESI†) and others by mass spectrometry (MS) analysis.5,14 To demonstrate the generation of CO2 from DMF, several solutions containing pure DMF (1 mL), the DMF solution with Zn2+, as well as the DMF solution with H4L and Zn2+ for ZnMOF (1), have been prepared and heated at 80 °C for 48 h, then the upper gas was used for GC measurements and for detecting the variation of CO2 gas. It is noteworthy that CO2 gas was indeed detected from DMF (Fig. S7, ESI†).

Thermogravimetric-mass spectrometry (TG-MS) analysis (Fig. 5) was also performed by heating the crystals of compound 1 under a N2 atmosphere from room temperature to 800 °C. For comparison, analysis with pure H4L was also carried out under the same experimental settings. The initial release of CO2 molecules begins even at a relatively low temperature of 70 °C. Then the first CO2 peak was observed at 115 °C, which may have originated from the coordinated CO2 molecules and partial decomposition of DMF molecules located in the channel of ZnMOF (1). The second stage of CO2 release was found in the temperature range of 350 to 550 °C, corresponding to the decomposition of carboxylate ligands. These results are in accordance with those of TGA analyses. A further test was performed to investigate whether the ZnMOF (1) can release or even refix CO2 molecules, which is more interesting to us, so that its thermal stability can be examined by PXRD measurements after heat treatment at 120 °C first. It is a pity that a significantly different pattern compared to the simulated one was obtained, implying that the original structure has changed, even collapsed.

In conclusion, we report a very rare structurally ascertained example of the CO2-bound metal–organic framework. The successful synthesis of compound 1 provides a definitive pattern to understand CO2 fixation and may give a promising route to capture CO2 in MOFs. In addition, the linearly bridging pattern of the CO2 ligand displays an important structure model for CO2 coordination chemistry.

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Notes and references


