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ARTICLE TYPE

Fixation of CO₂ in bi-layered coordination networks of zinc tetra(4-carboxyphenyl)porphyrin with multi-component [Pr₂Na₃(NO₃)(H₂O)₃] connectors

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CO₂ is fixed in a rare $\mu_2\text{-}\eta^2_{\text{O},\text{O}}$ bridging mode by bi-layered coordination networks of ZnTCPP tessellated along the four equatorial directions by [Pr₂Na₃(NO₃)(H₂O)₃]⁸⁺ connecting clusters in a 2:1 ratio (1), but not in the isomorphous free-base porphyrin analogue [(TCPPH₂)₂(Pr₂Na₃(NO₃)(H₂O)₃)_n] (2), revealing the crucial role of the zinc metal in this process.

Photosynthesis and respiration are at equilibrium with one another and play an important role in maintaining the carbon cycle. However, due to different human activities, the amount of CO₂ released into the atmosphere has been rising extensively during the last few decades and has exceeded the amount sequestered in biomass, the oceans, and in other nature sinks. The increased concentration of CO₂ in the atmosphere is directly related to the climate change, and it becomes now a teraton challenge to the scientific community.¹ Thus, there is an urgent need to reduce the accumulation of CO₂ in the atmosphere. For inorganic chemists, it is particularly fascinating to synthesize simple complex(es) by common synthetic procedures which will bind CO₂ or will activate CO₂ for chemical transformations. Chemists have isolated and structurally characterized several synthetic metal complexes having metal-coordinated CO₂ in neutral or in reduced form.^{2,3} In the case of bi-nuclear metal complexes, four binding modes of CO₂ are possible (Figure 1).⁴

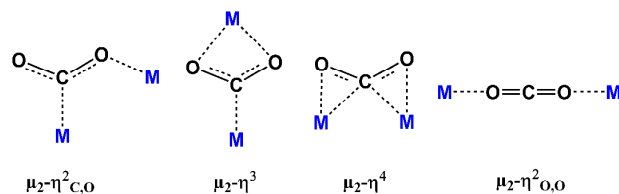
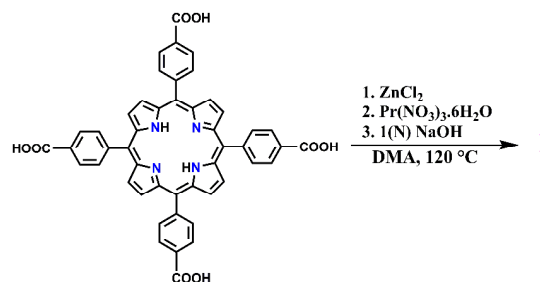


Fig. 1 Possible coordination modes of CO₂ in binuclear metal complexes.

The $\mu_2\text{-}\eta^2_{\text{O},\text{O}}$ coordination mode is generally rare compared to the others. A first complex of this type was reported by Chang et al, using an external CO₂ source.⁵ Later, Phull et al. reinvestigated the complex by theoretical and spectroscopic analysis and concluded that the bridging ligand is actually NCO anion rather than neutral CO₂.⁶ Recently, Fang et al. have reported another complex featuring this type of coordination mode, albeit with an

auxiliary ligand similar to the one which caused the formation of the NCO anion in the first case.^{3d} At this point, the nature of the coordinated ligand in those complexes still remains unclear.⁷

Metal-organic frameworks (MOFs) have attracted an extensive interest in recent years because of their stable architectures and various potential applications including CO₂ capture and storage.⁸ In some cases, the presence of CO₂ molecules inside the MOFs has been confirmed by crystallographic analysis as well.⁹ MOFs can be readily prepared by the self-assembly through extended coordination between metal ions or metal-containing clusters and organic linkers. The use of multiply functionalized rigid and thermally stable tetraarylporphyrins as such linkers has drawn recently particular attention.¹⁰ Thus, extensive application of the tetra(4-carboxyphenyl)porphyrin building block to this end has been widely reported by us as well as by other groups; one of the pioneering and most relevant to the present discussion examples involves a uniquely structured molecular-sieve-type material composed of anionic networks of ZnTCPP [ZnTCPP = 5,10,15,20-tetrakis(4-carboxylatophenyl)porphyrinato-zinc]⁴⁻, templated by Na⁺ ion clusters and cross-linked between the zinc centers by 4,4'-bipyridyl bridges.¹¹ Based on similar crystal-engineering concepts we attempted the synthesis of a series of new ZnTCPP-based coordination polymers capable of trapping CO₂, using both sodium and lanthanoid (Pr, Nd, Sm, Gd and Dy) ions as possible inter-porphyrin connectors. The latter have been shown to be excellent connectors in the formulation of stable MOFs with the TCPP-type linkers.¹²



Scheme 1 Synthesis of 1.

The zinc containing natural enzyme carbonic anhydrase is known to facilitate the reversible hydration of atmospheric CO₂

to bicarbonate.¹³ Several zinc complexes have been used (also as catalysts) in the fixation of atmospheric CO₂ (as carbonate ion).^{14,15} In this context, we report here on the fascinating polymeric structures of the [Zn(TCPP)₂(CO₂)(Pr₂Na₃(NO₃)(H₂O)₃)_n·solvent MOF (**1**) in which molecules of CO₂ bridge between the zinc centers of parallel zinc-porphyrin species in a rare μ₂-η²_{O,O} coordination mode, and of its "empty" structural analogue [(TCPH₂)₂(Pr₂Na₃(NO₃)(H₂O)₃)_n·solvent synthesized in the absence of the zinc ions (**2**).

In a typical multi component reaction, a mixture of the tetra(carboxyphenyl)porphyrin, ZnCl₂, Pr(NO₃)₃·6H₂O and 1(M) NaOH in dimethyl acetamide (DMA) was heated (Scheme 1), which after cooling resulted in the formation of block shaped crystals of **1**.

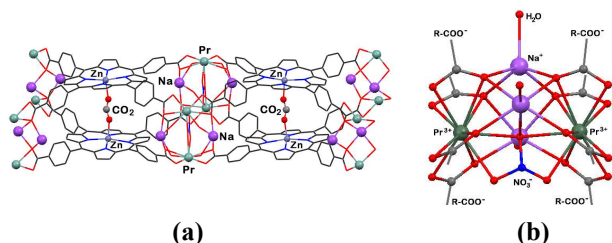


Fig. 2 (a) Segment of the bi-layered coordination polymer in **1** showing the CO₂ bridging between two Zn-ions of adjacent metallo-porphyrins. (b) A closer view of the hetero-metallic connecting cluster.

Single-crystal X-ray analysis of **1** shows that it crystallizes in the monoclinic *C2/m* space group and forms a 2D coordination polymeric network.¹⁶ The network is extended by coordination of the four carboxylate arms of the TCPH to the Pr³⁺ metal ions which in turn are bridged by the NO₃⁻ anion. The inter-porphyrin metal-ion cluster thus formed involves two Pr³⁺, and three Na⁺ ions. The total charge of +9 of this hetero-metallic cluster is counter-balanced by the ligation of eight carboxylate groups of different TCPH moieties and one nitrate ion coming from the Pr(NO₃)₃·6H₂O reactant. The resulting structure (Figure 2) can be best described as composed bi-layered coordination networks of the tetra-anionic zinc-porphyrin linkers and the [Pr₂Na₃(NO₃)(H₂O)₃]⁸⁺ hetero-metallic connectors. Two adjacent five-coordinate zinc centers within the bi-layers are bridged by a CO₂ molecule trapped between them and located on the mirror plane (Figure 2). The observed Zn-O coordination distance is 2.070(5) Å. The C-O distance within CO₂ is 1.131(5) Å (at 110 K), which is about 0.2 Å shorter than the recently reported complex with similar binding mode of neutral CO₂.^{3f}

The bridging CO₂ shows a slightly bent arrangement with O-C-O angle of 155.2(10)°, in good agreement with the observed angle of 158.7(14)° and 166.8(10)° in structures reported earlier.^{3f} Within the connecting clusters every Pr-ion is ten-coordinated to eight O-atoms of four different carboxylate groups and two O-atoms of the nitrate anion (within the corresponding 2.494-2.645(3) Å and 2.485-2.722(3) Å distance ranges), the latter bridging between the two praseodymium ions in the cluster. Two of the nitrate O-atoms connect to the two different metal ions while the third O-atom coordinates to both metals. Every Na-ion is five coordinated to the O-atoms of four carboxylates and one water molecule at 2.222-2.444(4) Å distance range (Figure 2b).

The presence of CO₂ in this compound is confirmed by infrared spectroscopic analysis. The spectrum of the crystalline sample of **1** exhibits a strong band at 2339 cm⁻¹ for the asymmetric stretching vibration of CO₂ (Figure 3). The observed stretching frequency is somewhat higher than the 2169 cm⁻¹ and 2165 cm⁻¹ of the other structures in which two O atoms of CO₂ are linked between Mo^{VI} and Co^{II} from two neighboring polyoxoanions.^{3f} However, this value is quite comparable with the ν_{asym} = 2348 cm⁻¹ of free CO₂.^{3a} This is not surprising considering that the C=O bond distance (1.131(5) Å) observed in **1** is comparable with that in the free CO₂ (C=O = 1.16 Å)¹⁷ and is among the shortest distances ever observed in the CO₂ coordinated metal complexes irrespective of whether the CO₂ is present in a neutral or reduced form.^{2,3}

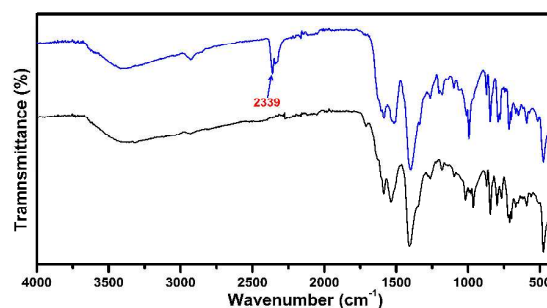


Fig. 3 Comparison of IR spectra of **1** (top) and **2** (bottom). The band at 2339 cm⁻¹ indicative of the presence of CO₂ in **1**, is missing in the spectrum of **2**.

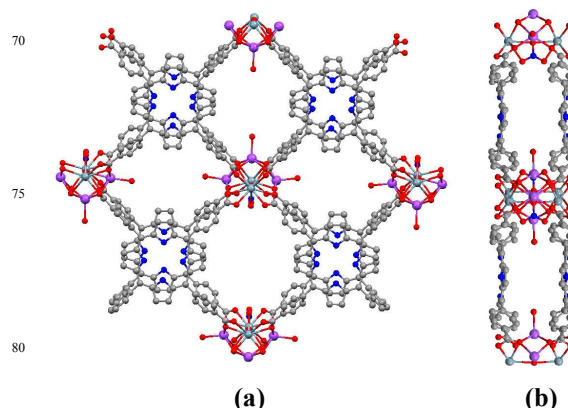


Fig. 4 Face-on (a) and edge-on (b) view of the bi-layered coordination network in **2** with the free-base porphyrin linkers. The composition and structure of the inter-porphyrin connecting synthons are similar to those in **1**, as shown in Figure 2b. The Pr-O distance range of the ten-coordinate Pr ions is within 2.498-2.703(4) Å. The Na-O distances of the five-coordinate Na ions are within 2.269-2.439(5) Å.

When the reaction shown in Scheme 1 was carried out in similar conditions but in the absence of ZnCl₂, the corresponding product **2** was found nearly isomorphous with **1**, crystallizing also in the monoclinic *C2/m* space group with similar cell parameters.¹⁶ The coordination polymer now formed consists of free-base porphyrin linkers and lacks the zinc binding sites responsible for the fixation of CO₂ in structure **1**. Thus, as expected, CO₂ couldn't be trapped in the crystals of compound **2**.

Still the connectivity features of the polymeric network and the overall crystal structure in **2** are very similar to that of **1** (Figure 4). The infrared spectrum of the solid sample of **2** doesn't show any band at $\sim 2300\text{ cm}^{-1}$ in comparison to **1**, while the remaining

finger print region of the two materials shows a remarkable similarity (Figure 3).

In both crystals (**1** and **2**) the bi-layered coordination networks are stacked one on top of the other. The intermolecular organization (solvent excluded) shows channel-voids of van der Waals width of $\sim 7.0\text{ \AA}$ that propagate through the bilayers (Figure 5), indicating that these solids may be potential reagents for absorption/storage studies of other gas and liquid guest materials as well. In **1** and **2** the interstitial voids within and between the bi-layered polymeric assemblies are accommodated by disordered molecules of the H_2O and DMA crystallization solvent that couldn't be modelled from the diffraction data.

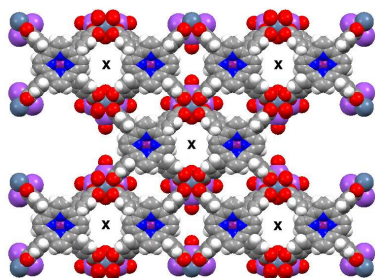


Fig. 5 The space-filling packing diagram of **1** (view along c -axis) showing the wide intra-lattice channel voids (denoted by "X"). Na-coordinated water molecules (their H-atoms are not shown) protrude into the other channels.

In conclusion, we have isolated a 2D bilayered MOF with ZnTCPP linkers and multi-component inter-porphyrin connectors, with neutral molecules of CO_2 coordinated to the zinc centers within the bilayers in a rare $\mu_2\text{-}\eta^2_{\text{O},\text{O}}$ mode. No CO_2 is observed in similarly structured MOF formulated with the free-base TCPPH₂ ligands, indicating that zinc is essential for fixation of CO_2 in this type of materials. Remarkably similar fixation of CO_2 within bilayered MOFs of ZnTCPP has been observed also using other lanthanoid ions (Nd, Sm, Gd, Dy) in the reaction shown in Scheme 1, while no fixation occurred in the polymeric product of a similar process involving free-base TCPPH₂ and Dy ions. The corresponding materials have been isolated and their structures (**3-7**, see ESI) confirmed by single-crystal X-ray diffraction, providing further support of the above findings. Comparative evaluations of their structural, gas absorption, luminescence and topological features are under way and will be published elsewhere. These results demonstrate a uniquely elegant application of MOF materials (among the few known to date)^{8-10,18} in binding CO_2 . In the presented examples the CO_2 is attached to specific sites in the structure, one molecule of CO_2 per two porphyrin units, which represents a rather low loading capacity (in **1** nearly $0.5\text{ mmol CO}_2/\text{gram sorbent}$, $\sim 2\text{ wt\%}$). Correspondingly, these materials may not be suitable for practical applications in comparison to other more effective sorbents for atmospheric CO_2 capture.^{8-10,18}

At the end a question remains as to whether the CO_2 captured in compounds **1** and **3-6** came from the atmosphere or was

generated in situ under the solvothermal conditions. The DMA that was used as solubilising and crystallization solvent may hydrolyze in such conditions to yield acetic acid and dimethyl amine in equilibrium with acetate anion and dimethylammonium cation. The acetic acid can further decompose to generate CO_2 , but this process requires very harsh condition ($500\text{-}900^\circ\text{C}$).¹⁹ Moreover, the yield of **1** was considerably reduced (from 6% to 2-3%) when the sonication of the solution (after addition of 1N NaOH) was done with properly capped vial suggesting exposure of the solution to air is needed for formation of **1** (this applies to compounds **3-6** as well). In addition, when a "blank" reaction was carried out in the presence of only the free-base porphyrin and 1N NaOH (i.e. in absence of both $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and ZnCl_2) in similar conditions, the resulting 3D MOF (**8**) contained an acetate ion (generated in situ in the reaction medium) incorporated into the supramolecular network to account for charge balance (see ESI). In view of the above it is plausible that the trapped CO_2 in **1** and **3-6** is of atmospheric origin.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: X-ray crystallographic details in CIF format. CCDC 1014715-1014720 (**1-6**) and 1021602-1021603 (**7-8**). See DOI: 10.1039/b000000x/
[‡] *Synthesis of 1*: 7.9 mg (0.01 mmol) of TCPPH₂, 2 mg (0.15 mmol) ZnCl_2 and 17.4 mg $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.04 mmol) were taken in a screw capped glass sample vial (4 mL) containing 2.5 mL DMA. The solution was then heated at 120°C for 12 hours in a bath-reactor. Next, 0.5 mL 1(N) NaOH solution was added to it and sonicated for 2 minutes (without the vial cap) to partially dissolve the formed precipitate. The entire solution was then heated at 120°C for additional 24 hours. Block shaped purple crystals of **1** were obtained on cooling to room temperature. Crystals were separated by filtration and washed with DMA, dried in air. Yield: 6 %. Elem. anal. Calcd (found) for $\text{C}_{97}\text{H}_{54}\text{N}_9\text{O}_{25}\text{Na}_3\text{Zn}_2\text{Pr}_2$: C, 52.31 (53.12); H, 2.44 (2.86); N, 5.66 (5.74). FT-IR (cm^{-1}): 2339 (s, ν_{CO_2} asymmetric) 1582, 1516, 1397, 1180, 993, 872, 845, 791, 714, 591, 476.
Synthesis of 2: 7.9 mg (0.01 mmol) of TCPPH₂ and 17.4 mg $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.04 mmol) were taken in a screw capped glass sample vial (4 mL) containing 2.5 mL DMA. The solution was then heated at 120°C for 3 hours in a bath-reactor. Next, 0.5 mL 1(N) NaOH solution was added to it and sonicated for 2 minutes (without the vial cap) to partially dissolve the formed precipitate. The entire solution was then heated at 120°C for additional 24 hours. Block shaped purple crystals of **2** were obtained on cooling to room temperature. Crystals were separated by filtration and washed with DMA, dried in air. Yield: 11 %. Elem. anal. Calcd (found) for $\text{C}_{96}\text{H}_{58}\text{N}_9\text{O}_{23}\text{Na}_3\text{Pr}_2$: C, 56.07 (56.62); H, 2.84 (2.89); N, 6.13 (6.24). FT-IR (cm^{-1}): 1586, 1536, 1407, 1187, 995, 963, 871, 845, 797, 711, 592, 476.

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- 16 *Crystal Data of 1*, [C₉₇H₄₈N₉Na₃O₂₅Pr₂Zn₂]_n·solvent, formula weight 2221.01 (solvent excluded), monoclinic, space group C2/m, $a = 32.9263(6)$, $b = 35.2939(7)$, $c = 11.3229(2)$ Å, $\beta = 109.952(1)^\circ$, $V = 12368.5(4)$ Å³, $Z = 4$, $T = 110(2)$ K, $D_{\text{calc}} = 1.193$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 1.23$ mm⁻¹, 42799 collected data and 11129 unique reflections ($\theta_{\text{max}} = 25.06^\circ$), $R_{\text{int}} = 0.044$. The final $R1 = 0.056$ for 7692 observations with $F_o > 4\sigma(F_o)$, $R1 = 0.076$ ($wR2 = 0.176$) for all unique data, $|\Delta\rho| \leq 2.26$ e/Å³. CCDC 1014715. *Crystal Data of 2*, [C₉₆H₅₃N₉Na₃O₂₃Pr₂]_n·solvent, formula weight 2051.26 (solvent excluded), monoclinic, space group C2/m, $a = 33.0534(12)$, $b = 35.2658(13)$, $c = 11.3000(6)$ Å, $\beta = 109.685(3)^\circ$, $V = 12402.1(9)$ Å³, $Z = 4$, $T = 110(2)$ K, $D_{\text{calc}} = 1.099$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.84$ mm⁻¹, 43564 collected data and 11614 unique reflections ($\theta_{\text{max}} = 25.42^\circ$), $R_{\text{int}} = 0.052$. The final $R1 = 0.069$ for 6502 observations with $F_o > 4\sigma(F_o)$, $R1 = 0.106$ ($wR2 = 0.195$) for all unique data, $|\Delta\rho| \leq 2.08$ e/Å³. CCDC 1014716.
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