Adaptive coordination assemblies based on a flexible tetraazacyclododecane ligand for promoting carbon dioxide fixation†

Shaochuan Li, a Caiping Liu, a Qihui Chen, a,b Feilong Jiang, a Daqiang Yuan, a Qing-Fu Sun d and Maochun Hong d

Coordination hosts based on flexible ligands have received increasing attention due to their inherent adaptive cavities that often show induced-fit guest binding and catalysis like enzymes. Herein, we report the controlled self-assembly of a series of homo/heterometallic coordination hosts \((\text{Me}_4\text{enPd})_n(\text{ML})_m\) \(n = 2/3; M = \text{Zn}(ii)/\text{Co}(ii)/\text{Ni}(ii)/\text{Cu}(ii)/\text{Pd}(ii)/\text{Ag}(ii); \text{Me}_4\text{en}: \text{N}_4\text{N}_4\text{N}_4\text{N}_4\text{-tetramethylmethylenediamine}\) with different shapes (tube/cage) from a flexible tetraazacyclododecane-based pyridinyl ligand (L) and cis-blocking \(\text{Me}_4\text{enPd}(ii)\) units. While the \(\text{Ag}(ii)\)-metalated ligand (AgL) gave rise to the formation of a \((\text{Me}_4\text{enPd})_6(\text{ML})_2\)-type cage, all other \(M(ii)\) ions led to isosstructural \((\text{Me}_4\text{enPd})_6(\text{ML})_3\)-type tubular complexes. Structural transformations between cages and tubes could be realized through transmetalation of the ligand. The buffering effect on the ML panels endows the coordination tubes with remarkable acid–base resistance, which makes the \((\text{Me}_4\text{enPd})_6(\text{ZnL})_3\) host an effective catalyst for the \(\text{CO}_2\) to \(\text{CO}_3^{2–}\) conversion. Control experiments suggested that the integration of multiple active Zn(ii) sites on the tubular host and the perfect geometry match between \(\text{CO}_3^{2–}\) and the cavity synergistically promoted such a conversion. Our results provide an important strategy for the design of adaptive coordination hosts to achieve efficient carbon fixation.

Introduction

Carbon dioxide (\(\text{CO}_2\)) in the atmosphere has been rising due to humans’ reliance on fossil fuels, causing a range of climate problems such as rising temperature and changing sea-levels. To eliminate such problems, it is necessary to develop efficient and economic carbon fixation technologies. In order to transform \(\text{CO}_2\) into valuable compounds, various carbon fixation technologies such as metal-participated chemical conversions, electrocatalysis, and photocatalysis have been developed. Ideally, the carbon fixation process itself should avoid \(\text{CO}_2\) emissions to achieve carbon neutralization. However, it remains a big challenge to develop such carbon fixation processes.

In nature, carbonic anhydrase can convert \(\text{CO}_2\) into \(\text{HCO}_3^{–}\) under mild conditions. Structural analysis shows that carbonic anhydrase contains a flexible cavity that can hold \(\text{CO}_2\) and a coordination unsaturated Zn(ii) ion acting as the active site. Inspired by this, many unusual metal complexes which can be used to fix \(\text{CO}_2\) through binding with carbonate have been reported. Coordination-directed self-assembly has been proven to be an effective approach toward the predictable construction of multicomponent artificial hosts, where enhanced guest reactivity, stabilization of metastable species and unusual reaction pathways have been realized. While atmospheric \(\text{CO}_2\) sequestration by selective binding of carbonate with coordination hosts has already been reported, adaptive coordination hosts that contain multiple active metal sites and can reversibly encapsulate and release the carbonate are still rare.

1,4,7,10-Tetraazacyclododecane and its derivatives are well-studied macrocyclic ligands to form stable complexes with various metal ions. However, its utilization in coordination-directed self-assembly has been hampered due to its structural flexibility. Herein, we report the synthesis of a series of coordination tubes or cages from a 1,4,7,10-tetraazacyclododecane-\(N_4,N_4,N_4,N_4\)-tetra-p-methylpyridine ligand (L) and cis-blocking \(\text{Me}_4\text{enPd}\) units (Scheme 1). The structure of the final assemblies is found to be sensitive to different metalations on L. Moreover, integration of multiple active Zn(ii) sites on the \((\text{Me}_4\text{enPd})_6(\text{ZnL})_3(\text{NO}_3)_3\) \(\text{Ag}(ii)\) tubular host and perfect \(\text{CO}_3^{2–}\) encapsulation in the cavity promoted its potential utilization in \(\text{CO}_2\) fixation.

*State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China. E-mail: chenqh@fjirsm.ac.cn; qfzhu@fjirsm.ac.cn; hmc@fjirsm.ac.cn
†University of the Chinese Academy of Sciences, Beijing, 100049, China
‡Electronic supplementary information (ESI) available. CCDC 213469, 213472-213476, 213485-213486, 2131470-2131471. For ESI and crystallographic data in CIF or other electronic format see https://doi.org/10.1039/d2sc03093d
Results and discussion

Controlled self-assembly and structural transformations between coordination tubes 1 and 3, and cages 2

The tetraazacyclododecane moiety located at the center of ligand L is prone to being metalated due to the macrocyclic effect. Indeed, treatment of L with Zn(NO₃)₂ led to the quantitative formation of the ZnL metalloligand, as confirmed by ¹H NMR (Fig. 1A and B, S1–S8†) and single crystal X-ray diffraction (SCXRD) studies. In the ¹H NMR spectrum of ZnL, the signal of H₄ is not only down-field shifted but also splits into two peaks, suggesting that metatation of L by Zn(n) rigidified its conformation in solution. In the crystal structure, four pyridine groups on ZnL are in the same plane rather than the randomly distributed form seen on the free L (Fig. 2A and B, S9 and S10†). Reacting Me₄enPd(NO₃)₂ with ZnL in D₂O at 70 °C for 3 h led to formation of one clean complex (1-Zn). ¹H NMR analyses show that both the signals of H₄ and H₆ on 1-Zn shift to the down-field than that on ZnL, due to the coordination of pyridine groups to Pd(n) (Fig. 1C, S11–S13†). Diffusion ordered NMR spectroscopy (DOSY) further indicates the purity and the size (about 2.1 nm) of 1-Zn (Fig. S14†). The X-ray crystal structure of 1-Zn was also obtained, which clearly confirmed its tubular structure \([\text{Me}_4\text{enPd})_6(ZnL)_3]^{18+}\) (Fig. 2C, S15†). Six Pd(n) capping units are located on the six vertices of the triangular prism, while three ZnL ligands define the three faces of the triangular prism, with one NO₃⁻ encapsulated in the tubular cavity. The chelated Zn(n) ion displays a tetragonal pyramid geometry through coordinating with four N atoms from L and one O atom from water. Such coordination mode makes the new-formed metalloligand ZnL adopt the planar conformation, leading to the formation of a tubular structure. The triangular apertures on the tube are about 13.7 Å × 13.7 Å × 13.7 Å. No
Anion effect was observed on the self-assembly of tube 1-Zn, as isostructural tubular complexes were obtained using other Me₄enPd(BF₄)₂, SO₄²⁻, ClO₄⁻, SbF₆⁻ salts (Fig. S16–S20†). One-pot self-assembly starting from I, Zn(NO₃)₂, and Me₄enPd salt also leads to the coordination tube 1-Zn (Fig. S21†).

When other transition metal ions M(n) (M = Co, Ni, Cu) that can adopt similar coordination geometries to Zn(n) ions were used, heterometallic coordination tubes [[Me₄enPd(n)(ML)]₁⁸⁺]²⁻ [M = Co²⁺ (1-Co), Ni²⁺ (1-Ni), Cu²⁺ (1-Cu)] were obtained (Fig. 1D and E, S22–S27†). SCXRD analyses confirm that complexes 1-Ni and 1-Cu are isostructural to tube 1-Zn, except that NO₃⁻ can be found in the cavity of 1-Cu (Fig. 2E and F, S29 and S30†). Although the chelated Co(n) ion in 1-Co displays a distorted octahedral configuration, it has the same coordination form with the ligand L as the Zn(n), so the Co(n) ion also induces the formation of a tubular structure (Fig. 2D, S28†). In short, Zn(n)/Co(n)/Ni(n)/Cu(n) ions can be used as templates to induce the self-assembly of heterometallic tubular tubes (1-M) because they can drive the metallocligand MLs to adopt a planar conformation (Scheme 1A).

To our surprise, cage complexes 2 were obtained by the in situ self-assembly of L, PdMe₄en(ClO₄)₂ and AgX (X = BF₄⁻, SO₄²⁻), as confirmed by ¹H and DOSY NMR spectra (Fig. 1F, S31–S34 and S36–S39†). The ¹H NMR spectrum of 2(BF₄)⁻ is distinct from that of 1 (Fig. 1C and F). DOSY shows that the size of 2 is about 1.28 nm (Fig. S34 and S39†), much smaller than that of 1. SCXRD confirmed that 2 complexes with different counter ions (either BF₄⁻ or SO₄²⁻) are isostructural coordination cages with the same [(PdMe₄en)₄(AgL)₂]¹²⁺ skeleton (Fig. 2H and I). The crystal structures of 2 show that all the ligands L became the metallated AGL. Both structures are composed of two AGL ligands and four Pd(n) ions with no almost cavity observed (Fig. S35 and S40†). The coordination environments of the Ag(i) centers on the AGL ligands of 2 (BF₄⁻ salt) and 2 (SO₄²⁻ salt) are similar except that one additional axial coordinating H₂O was observed on the former (Fig. 2H and I). The longer Ag–N bond length (2.5 Å on average) compared to that of Zn–N (2.1 Å on average) leads to a slight conical conformation of AGL other than the flat conformation observed for ZnL. This conformational change on AGL leads to the formation of the cage structure. Isostructural cages 2 (NO₃⁻, ClO₄⁻) also could be obtained when AgNO₃ and AgClO₄ were used (Fig. S41†), further confirming that Ag(i) ions can template the self-assembly of coordination cages (2) (Scheme 1B).

It then turns out that the metallation of L was a prerequisite for the successful self-assembly. Trail on direct self-assembly of L with Me₄enPd(NO₃)₂ gave a mixture of products (Fig. S42 and S43†). Interestingly, reacting ligand L with Me₄enPd(ClO₄)₂ led to a new (Me₄enPd)(PdL)₃-type tube complex (3), with the in situ metallation of L with Pd(n). The ¹H NMR spectrum of 3 is clearly different from those of both 1 and 2 (Fig. 1G and S44–S46†). DOSY shows that the size of 3(ClO₄⁻) is about 2.2 nm (Fig. S47†), very close to that of tube 1-Zn. SCXRD finally confirms that 3(ClO₄⁻) is a Pd-chelated triangular coordination tube [[Me₄enPd₃(PdL)₃]ClO₄]₁₈⁺ (Fig. 2G, S48†). The crystal structure of 3(ClO₄⁻) contains two independent tubular molecules. Both of them have a triangular prism structure similar to that of 1-Zn, where six Pd nodes are located on six vertices of the triangular prism and three PdL metalloligands span three faces of the prism. The Pd(n) ions chelated in the PdL ligands adopt the square-planar coordination geometry. Like ZnL, PdL also adopts a planar conformation, so a similar tube complex is formed. A clean tubular complex 3(SbF₆⁻) salt could also be obtained when Me₄enPd(SbF₆)₂ was used (Fig. S49–S52†). However, both Me₄enPd(BF₄)₂ and Me₄enPdSO₄ lead to a mixture of products, demonstrating an obvious anionic effect (Fig. S53†).

With the structure of hetero/homometallic coordination tubes 1 and 3, and cages 2 determined, we then wondered whether controllable structural transformation between cages and tubes can be achieved through transmetalation on the ML. Indeed, the addition of Zn(n) ions to the Ag-chelated cage 2 triggered its complete transformation into Zn-chelated tube 1-Zn (Fig. S54–S56†). Due to the much stronger coordination ability of Zn(n) than Ag(i) with L, it is difficult for Ag(i) ions to drive the back transformation. Even with a large excess of Ag(i) ions, only a partial transformation from tube 1-Zn to cage 2 was observed (Fig. S57–S59†). Similarly, cage 2 can be completely transformed into tube 3 by the addition of Pd(n) salts, where use of Pd(SbF₆)₂ can greatly promote this transformation (Fig. S60–S62†), while back transformation from tube 3 to cage 2 is successful by the addition of AgBF₄ or AgNO₃, but not for AgSbF₆ (Fig. S63–S65†). We infer that SbF₆⁻ may have a stronger interaction with tube 3 than cage 2, so it can promote the conversion of cage 2 to tube 3 but hamper the back transformation. In brief, controllable transformations between cages and tubes can be realized via transmetalation on the ligands with a certain degree of anion effects (Scheme 1D–G).

Fine-tuned shapes and cavities on the tubular complexes

It’s worth noting that the utilization of the flexible tetraazacyclododecane-based ligand not only facilitates the incorporation of various metal ions on the coordination tubes, but also provides a good opportunity to fine-tune the volumes of their central cavities. Based on the crystal data, deformations of geometry on L depending on its metallation with different metal ions are clearly observed, leading to gradual volume changes from 316 (1-Ni) to 409 [3(ClO₄⁻)]Å³ (Fig. 3B). For the isostructural heterometallic tubes 1-Zn/Ni/Cu, their central metals share the same coordination environment, and the volumes of the tubes are found to be proportional to the M–N bond lengths on MLs (N-Ni < N-Cu < N-Zn). We infer that shorter coordination bonds make the MLs panels more convex, while such conformational changes do not cause significant changes to the triangular opening (Fig. 3A). 1-Co and 3(ClO₄⁻) with quite different coordination environments on MLs bear much larger volumes than the above three tubes, with the largest volume of 409 Å³ measured for tube 3(ClO₄⁻), which is ca. 1.3 times that for 1-Ni. We infer that the volume increases in these two tubes are due to their less curved ML panels.

Acid–base resistance of coordination tubes

Stability of the coordination assemblies is an important prerequisite for their applications.²¹,²² Impressively, ¹H-NMR for
tubular 1-Zn in aqueous solutions confirmed that it maintained its structural integrity under both strongly acidic (pH = 1) and basic conditions (pH = 12) but would decompose in stronger acidic (pH = 0) or basic (pH = 13) solutions (Fig. S66†). Tubes 1-Co and 1-Ni also remain stable at pH 12, but their acid resistance is poorer than that of 1-Zn (Fig. S67 and S68†). For comparison, a simple coordination complex (Me4enPd) Py2(NO3)2 (Py = pyridine) was synthesized. 1H-NMR tests indicate that it can only remain intact in a smaller pH range (pH 3–11; Fig. S69†), suggesting that multi-component cooperativity on the tube enhances its structural stability. The buffering effect of ML, i.e., accepting H+ on the N atoms of tetraazacyclododecane and OH− on the metal centers via axial coordination, should also contribute to the observed acid–base resistance of the tube complexes. While many acid or base resistant coordination hosts have been reported, few of them are stable toward both acidic and basic conditions. Coordination hosts built from inert coordination bonds, such as Pt–N, and Zr–O bonds, tend to show enhanced stability.107,108 Compared with the strategy of using stronger coordination bonds, here we improve the acid–base stability of the host by creating a local buffer environment, which provides a useful strategy for the construction of stable coordination hosts.

CO2 fixation promoted by coordination tubes

Considering that the coordination tube 1-Zn contains three Zn active sites and is tolerable toward basic solutions, we then studied its applications in carbonic anhydrase mimicking. The CO2 dissolution experiment indicates that CO2 has better solubility in DMSO/H2O (1 : 2 v/v) mixed solvent than pure water (Fig. S70†). So, a DMSO-d6/D2O mixed solvent containing 1-Zn (5 mM) and NaOH (0.01 M) was used for the CO2 capture reaction. When CO2 gas was continuously injected into this solution at room temperature for 3 h, a signal at 160 ppm assignable to CO3− was clearly observed in 13CNMR (Fig. 4B(c) and (d)), whereas no CO3− was observed without adding 1-Zn, or with 1-Co, 1-Ni as the catalysts (Fig. 4B(a) and (b), S71†). A control experiment with a mononuclear ZnL1(NO3)2 (L1 = 1,4,7,10-tetraazacyclododecane) complex as the catalyst, which contains a similar Zn(a) active site, also showed no CO2 conversion (Fig. S72–S74†). Taking together all these experiments, it is clear that both the existence of the Zn metal sites

© 2022 The Author(s). Published by the Royal Society of Chemistry

Fig. 3 (A) The average lengths of triangular apertures on different tubular structures. (B) The volumes of cavities on tubes 1-Ni (316 Å3), 1-Cu (329 Å3), 1-Zn (361 Å3), 1-Zn-CO32− (377 Å3), 1-Co (389 Å3), and 3(ClO4−) (409 Å3).

Fig. 4 (A) The 1-Zn tube assisted CO2 to CO32− conversion. (B) The 13C NMR spectra of CO2 (a), the blank experiment (b), 1-Zn (c) and 1-Zn promoted CO2 to CO32− transformation (d), after removing CO32− with Ca2+ (e), and reuse of tube 1-Zn (f). (C) The IR spectra of tube 1-Zn before and after CO2 fixation. (D) The crystal structure of 1-Zn-CO32−.
and the formation of the tubular cavity are indispensable to facilitate the CO\textsubscript{2} to CO\textsubscript{3}\textsuperscript{2−} conversion.

Further studies indicate that adding more NaOH and prolonging the reaction time cannot enhance the yield of CO\textsubscript{3}\textsuperscript{2−} in solution (Fig. S75†). The IR spectra of 1-Zn after the reaction show a new absorption peak at 1350 cm\textsuperscript{-1}, which is obviously red-shifted compared with that in Na\textsubscript{2}CO\textsubscript{3} (∼1440 cm\textsuperscript{-1}) (Fig. 4C, S76†). The crystal of the 1-Zn-CO\textsubscript{3}\textsuperscript{2−} host–guest complex was obtained through slowly diffusing THF vapor into the reaction system. SCXRD confirmed that one CO\textsubscript{3}\textsuperscript{2−} is tightly captured inside the tube cavity. Encapsulation of CO\textsubscript{3}\textsuperscript{2−} also causes induced-fit cavity deformations, with the size of the triangular window changing to 13.1 Å × 13.6 Å × 14.0 Å and the volume increasing to 377 Å\textsuperscript{3} compared to that of 1-Zn (Fig. 3B, S77†). Multiple hydrogen bonds and the existence of strong electrostatic interactions lead to a strong host–guest interaction between CO\textsubscript{3}\textsuperscript{2−} and the 1-Zn host (Fig. 4D). We speculate that the formed 1-Zn-CO\textsubscript{3}\textsuperscript{2−} host–guest complex is inactive and hinders the turnover of further CO\textsubscript{2} conversion. Considering that Ca(n) ions can react with CO\textsubscript{3}\textsuperscript{2−} to produce water-insoluble CaCO\textsubscript{3} (Ksp = 2.80 × 10\textsuperscript{-8}), they have been used to grab the CO\textsubscript{3}\textsuperscript{2−} encapsulated inside cavity. Further experiments showed that after removal of CO\textsubscript{3}\textsuperscript{2−} encapsulated by the cavity, the tube 1-Zn can be regenerated and reused (Fig. 4B(e) and (f)). Although many coordination hosts that can fix CO\textsubscript{2} by binding with carbonate have been reported,\textsuperscript{95-102} the newly formed strong metal–oxygen interactions make these hosts unable to be reused. Thus, tube 1-Zn represents a rare coordination host that can catalyze CO\textsubscript{2} conversion like carbonic anhydrase. In short, efficient and mild CO\textsubscript{2} conversion like the carbonic anhydrase is cheaper and can tolerate harsh conditions.

A possible cavity-assisted CO\textsubscript{2} conversion process was proposed as follows (Fig. S78†): (1) Zn(n) ions in tube 1-Zn are coordination unsaturated, which can coordinate with OH\textsuperscript{−} to form Zn–OH units under basic conditions; (2) The Zn–OH group attacks the CO\textsubscript{2} in solution to form HCO\textsubscript{3}\textsuperscript{−}, which is the rate-determining step of the conversion of CO\textsubscript{2}. Compared to the OH\textsuperscript{−} coordinated to harder Co(n) and Ni(n), the enhanced nucleophilicity of Zn–OH makes it more efficient to attack CO\textsubscript{2}; (3) HCO\textsubscript{3}\textsuperscript{−} deprotonates into CO\textsubscript{3}\textsuperscript{2−} due to the pK\textsubscript{a}-shifting effect inside the cavity of the highly charged cationic host.\textsuperscript{109} In fact, DFT calculations show that the CO\textsubscript{3}\textsuperscript{2−} in 1-Zn host–guest complexation energy was as high as −1349 kJ mol\textsuperscript{-1}; (4) the CO\textsubscript{3}\textsuperscript{2−} sequestration by Ca(n) achieves the recycle of the catalyst and facilitates the reaction turnover.

Conclusions

A series of homo/heterometallic coordination assemblies have been synthesized from a tetraazacyclododecane-based ligand. Both self-assembly and structural transformations of coordination tubes/cages can be controlled in a cooperative manner using metal templates and auxiliary anions. The tubular complexes show adaptive cavities depending on the metallation of the ligand and the anions. The Zn-containing heteroleptic tubular complex not only shows impressive acid–base stability but also can catalyze the CO\textsubscript{2} to CO\textsubscript{3}\textsuperscript{2−} conversion, standing for a rare example of an efficient and recyclable carbonic anhydrase-mimicking supramolecular system. Mechanistic studies confirm that the integration of multiple active metal sites and an open CO\textsubscript{3}\textsuperscript{2−}-binding pocket is important for the CO\textsubscript{2} fixation. This work not only offers a new ligand candidate for the self-assembly of multi-variant coordination hosts, but also provides an important principle for the design of supramolecular catalysts toward CO\textsubscript{2} fixation.

Data availability

All experimental and computational data associated with this work are available in the ESL.†

Author contributions

S. Li and C. Liu performed the experiments. F. Jiang and D. Yuan helped with data analysis. Q. Chen, Q.-F. Sun, and M. Hong designed the project. All authors were involved in the preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2021YFA1500400, 2018YFA0704500, and 2017YFA0206800), the Key Research Program of Frontier Science CAS (QYZDY-SSW-SLH025), and the National Natural Science Foundation of China (21871265, 21731006, and 21825107).

Notes and references

1 C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. Mac Dowell, J. C. Minx, P. Smith and C. K. Williams, Nature, 2019, 575, 87–97.
2 G. Mezei, Chem, 2019, 5, 499–501.
3 L. Liang, C. Liu, F. Jiang, Q. Chen, H. Xue, H.-L. Jiang, J. Qian, D. Yuan and M. Hong, Nat. Commun., 2017, 8, 1233.
4 L. Jiao, X. Zhu, Y. Zhang, W. Yang, S. Zhou, A. Li, C. Xie, H.-L. Jiang, J. Am. Chem. Soc., 2021, 143, 19417–19424.
5 L. L. Ling, W. Yang, P. Yan, M. Wang and H. L. Jiang, Angew. Chem., Int. Ed., 2022, 61, e202116396.
6 T. Ouyang, H.-J. Wang, H.-H. Huang, J.-W. Wang, S. Guo, W.-J. Liu, D.-C. Zhong and T.-B. Lu, Angew. Chem., Int. Ed., 2018, 57, 16480–16485.
7 K. K. Kannan, B. Notstrand, K. Fridborg, S. Lövgren, A. Ohslosson and M. Petef, Proc. Natl. Acad. Sci. USA, 1975, 72, 51–55.
8 P. Woolley, Nature, 1975, 258, 677–682.
