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Macrocyclic Influences in CO_2 Uptake and Stabilization

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Supporting Information

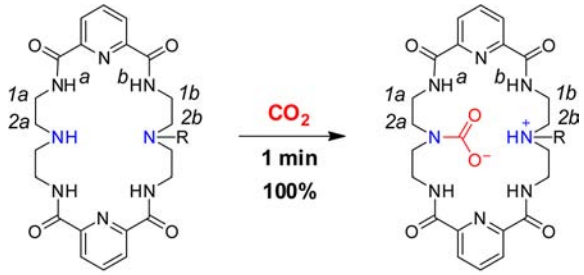
ABSTRACT: Two 24-member diamine-tetraamido macrocycles (R = H and CH_3), readily synthesized in one or two steps, were found to react with CO_2 rapidly and efficiently (100% conversion within 1 min at rt). The resulting carbamate formation was demonstrated by ^1H, ^{13}C NMR, ESI-MS, and X-ray crystallography. The crystal structure clearly showed the carbamate group ($N\text{-}CO_2^-$) formed was tightly bound within the macrocyclic cavity, held by five internal hydrogen bonds, and stabilized by intramolecular carbamate-ammonium salt-bridge formation.

Due to the continuous increase of the concentration of CO_2 in the atmosphere, a major contributing factor to global climate change, CO_2 capture and fixation have become major areas of chemical research. Various CO_2 capture materials and adsorbents including aqueous alkanolamine solutions ("CO_2 scrubbers")[1] and porous solids, such as zeolites, activated carbons, and recently emerged metal–organic frameworks (MOFs),[2] have been studied. Among these, the adsorption of CO_2 scrubber chemistry is based on well-known ammonium carbamate formation reactions in the presence of amines. This chemistry has resulted in a number of functional systems for CO_2 capture and separation, including ionic liquids,[3] organogels,[4] supramolecular polymers,[5,6] and dynamic combinatorial libraries.[7] For example, the late Dmitri Rudkevich utilized ammonium carbamate pairing as a cross-linking agent and constructed elegant supramolecular polymer systems.[5,6]

A key factor in achieving the most efficient adsorption and separation of CO_2 is a better understanding at the molecular level of the factors that influence binding and recovery. Adsorption and fixation can be achieved via direct sequestration of CO_2 within a hollow molecular container and/or enhanced by stabilizing a product resulting from reaction with an amine or hydroxyl group, i.e., carbamate or carbonate/bicarbonate, respectively. Indeed, while metal-bound hydroxide complexes that bind CO_2 are quite prevalent, several groups have shown the direct capture of CO_2 from the atmosphere through encapsulation of carbonate or bicarbonate species via hydrogen bonding[8] or metal coordination[9] within supramolecular or expanded multimetallic host frameworks or assemblies. In terms of carbamate formation and stabilization, however, García-España and co-workers effectively demonstrated carbamate formation in a terpyridinophane-based aza macrocycle, where the carbamate is stabilized through interaction with a bound Cu(II) ion,[10] while Gale's group has shown that alkylcarbamate anions formed upon CO_2 binding can be stabilized by neutral urea-based anion receptors.[11] Leigh's group has reported an interesting binding phenomenon of CO_2 with a similar pincer-like tetraamide macrocycle that does not contain amine groups. However, there is no crystallographic evidence for the mode of binding and no possibility of carbamate formation.[12]

We have also uncovered a rare example of fast and efficient CO_2 uptake via encapsulation-facilitated carbamate formation within amine/amide-based macrocycles **1** and **2** (Scheme 1).

Scheme 1. Rapid Reaction of 1 and 2 with Bubbling CO_2



1 (R = H)
2 (R = CH_3)

1-CO_2
2-CO_2

The bound carbamate appears to fit quite well into the cleft of the folded macrocycle and is held by five hydrogen bonds plus an intramolecular zwitterionic carbamate-ammonium salt-bridge. In addition to the CO_2 reaction, we have also identified synthetic strategies that circumvent the necessity of tedious protection–deprotection steps in the route to both symmetrical and unsymmetrical amide-based macrocycles containing secondary amines. Here we report the results of the CO_2 binding and sequestration studies as well as the new synthetic strategies.

In recent years, our group has focused on developing mixed functional group amine/amide based macrocycles. Our synthetic strategy has been based on using simple building

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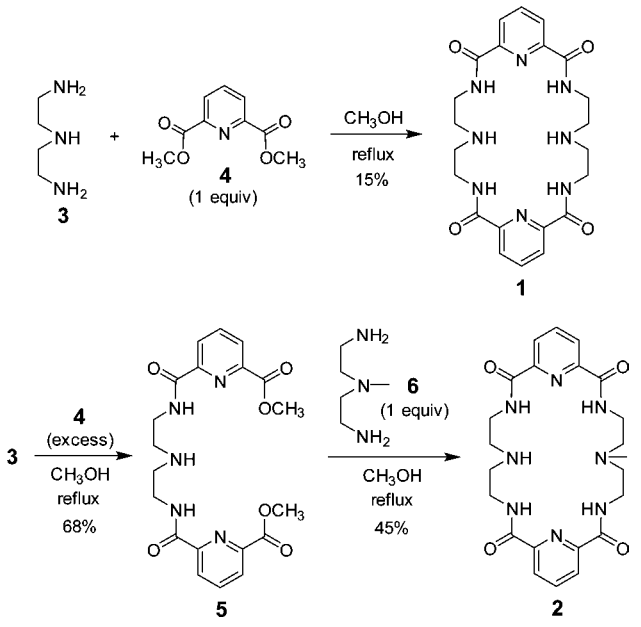
block amine and acyl-containing precursors, which, upon manipulation of reaction conditions, can yield monocyclic, bicyclic, and even tricyclic molecules capable of binding both anions and transition metal ions.[13−19] The 24-membered diamine-tetraamido macrocycle **1** was previously synthesized by five steps starting from diethylenetriamine **3** and 2,6-pyridinedicarbonyl dichloride.[17] This route involved two sequential and tedious protection−deprotection steps using protecting reagents for both the terminal and secondary amines, phthalic anhydride and di-*tert*-butyldicarbonate (Boc_2O), respectively, and gave an overall yield of 10%. Now, by using the less reactive dimethyl 2,6-pyridinedicarboxylate **4** instead of 2,6-pyridinedicarbonyl dichloride, the synthesis can be greatly improved in one step with a 15% yield (Scheme 2).

Scheme 2. Synthesis of the Symmetrical Macrocycle 1 and the Mono-*N*-methyl Substituted Macrocycle 2



The mono-*N*-methyl substituted unsymmetrical macrocycle **2** can also be synthesized in just two steps with a moderate yield by first reacting **3** with an excess of **4** to give acycle fragment **5** and then condensing **5** with *N*,*N*-bis(2-aminoethyl)methylamine **6** (Scheme 2). The successful synthesis is attributed to the presence of the less reactive dimethyl 2,6-pyridinedicarboxylate **4**, which can readily react with the two terminal primary NH_2 sites but is inert to the secondary central amine.

While exploring the solution chemistry of **1**, we observed that when a fresh hot solution of **1** in CH_2Cl_2/CH_3OH was open to the atmosphere, precipitates appeared on the surface of the solution after about 10−20 min. The ESI-MS of the solids showed only two predominant peaks, corresponding to [**1**-CO_2 + Na]$^+$ and [(**1**-CO_2)$_2$ + Na]$^+$, which led us to suspect that **1** was capturing atmospheric CO_2.

Upon bubbling CO_2 into solutions of **1** or **2**, the macrocycles were completely converted to the CO_2 adducts **1**-CO_2 and **2**-CO_2 within 1 min, respectively (Scheme 1). As shown in Figure 1a, the ^{1}H NMR of **1** in DMSO-d_6 showed one simple set of amide N*H* and ethyl $CH_2{}^1CH_2{}^2$ signals corresponding to the symmetrical structure. The middle secondary amine N*H* signal was not observed probably due to peak broadening. Upon bubbling CO_2 into the solution of **1** for 1 min, the ^{1}H NMR

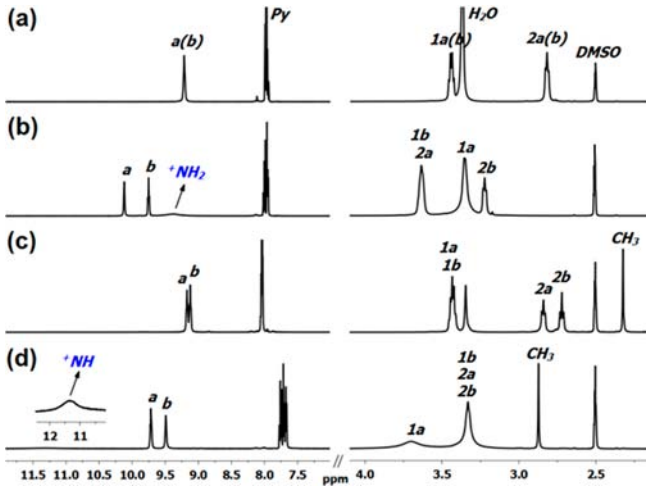


Figure 1. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) of (a) **1** and (b) after bubbling CO_2 for 1 min (**1**-CO_2), (c) **2** and (d) after bubbling CO_2 for 1 min (**2**-CO_2). See Scheme 1 for H atom assignments.

dramatically changed (Figure 1b). No signals corresponding to **1** remained, indicating complete conversion to the carbamate complex. The assignment of the new signals that emerged was accomplished with the aid of 2D COSY and HSQC NMR experiments (see Supporting Information). The spectrum suggested the formation of an unsymmetrical product with two downfield-shifted amide N*H* signals (*a* and *b*), two sets of $CH_2{}^1CH_2{}^2$ signals (*1a*, *2a* and *1b*, *2b*), and one broad $NH_2{}^+$ signal. These results pointed to the formation of the carbamate product, in which one of the two secondary amine NH groups attacked CO_2 to form the carbamate, N−$CO_2{}^-$. The other amine becomes protonated from released H^+, thus serving to balance the charge, resulting in a zwitterionic product. Such an intramolecular dual-cooperative process could be the reason for the fast and efficient transformation. The mono-*N*-methyl substituted macrocycle **2** underwent a similar transformation after bubbling CO_2. As shown in Figure 1c and d, the two sets of amide N*H* and ethyl $CH_2{}^1CH_2{}^2$ signals of **2** also shift and one broad NH^+ signal was also observed.

Carbamate formation was also confirmed by ^{13}C NMR and mass spectral measurements. As in the proton NMR the very simple spectrum due to the symmetrical ring system in **1** became more complex upon carbamate formation (Figure 2a and b). The signals for **2**-CO_2 also shifted. For both complexes a new signal at 165 ppm appeared, assigned to the carbamate N−$CO_2{}^-$ carbon (Figure 2c and d). As noted earlier, ESI-MS showed only two predominant peaks for each of the carbamate complexes, corresponding to a monomeric adduct and a dimeric pair, [**1**-CO_2 + Na]$^+$ and [(**1**-CO_2)$_2$ + Na]$^+$, and [**2**-CO_2 + Na]$^+$ and [(**2**-CO_2)$_2$ + Na]$^+$ (see Supporting Information). While we have no crystallographic confirmation, one could envision such dimeric pairs to result from the formation of interlocked dimers held together by two carbamates within the neighboring cavities via intermolecular amide N−H···O−C hydrogen bonds.

The structure of **2**-CO_2 was unambiguously determined by X-ray crystallographic analysis. Suitable crystals were grown by slow evaporation of a solution of **2** in CH_3OH after bubbling CO_2. Some crystals also slowly deposit from the air−solution interface upon exposure to air over a longer period in the absence of bubbled CO_2. As shown in Figure 3, the macrocycle adopts a folded conformation with the two pyridine rings

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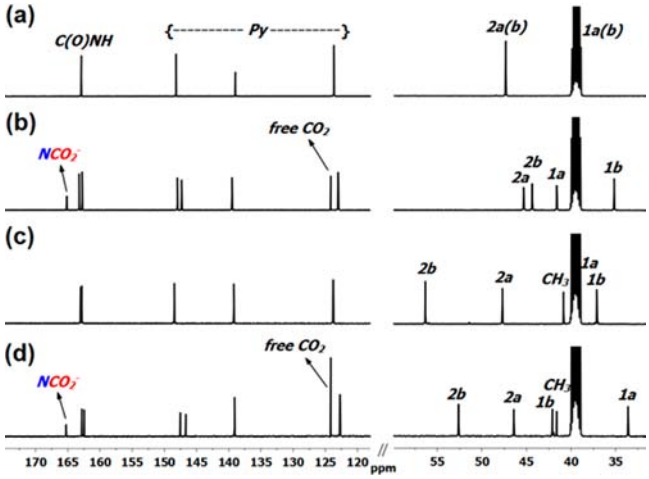

Figure 2. ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) of (a) **1** and (b) after bubbling CO_2 for 1 min (**1**-CO_2), (c) **2** and (d) after bubbling CO_2 for 1 min (**2**-CO_2). See Scheme 1 for C atom assignments.

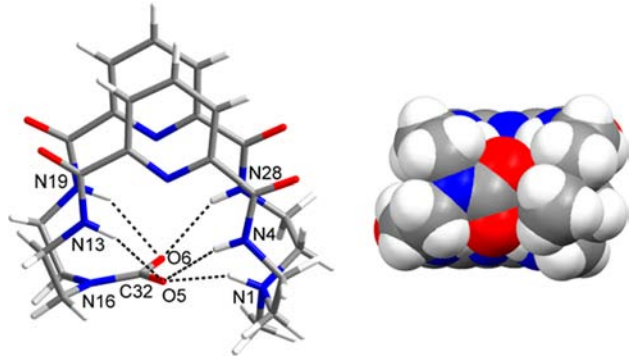

Figure 3. Crystal structure of **2**-CO_2: (a) perspective view showing hydrogen bonding and (b) space filling view.

separated by 3.657 Å (centroid to centroid distance). This folded conformation appears to be characteristic for 24-membered diamine-tetraamido pyridine-based macrocycle units as indicated in our previously reported cases, for both supramolecular and transition metal complexes.[15,17,18] As noted above, the carbamate fits snuggly in the macrocyclic cavity, held via hydrogen bonding and electrostatic interactions. One short hydrogen bond exists between the anionic carbamate group and positive ammonium group (N1−H···O5 distance = 2.745 Å) resulting in an intramolecular salt-bridge. All four amide groups also form hydrogen bonds with the carbamate group, including three moderate and one weak interaction (N−H···O distances = 2.919, 2.957, 2.993, and 3.192 Å).

Since facile and efficient release of stored CO_2 is also of vital interest, the ease with which the condensation reaction was reversed was also examined. As might be expected due to the strong hydrogen bonding and electrostatic hold of the bound carbamate, the reverse reaction was not facile. However, heating at 100 °C, accompanied by bubbling Ar for 1 h in DMSO-d_6, resulted in complete conversion back to **1** (Figure 4). Upon bubbling CO_2 again for 1 min, carbamate formation again readily occurs. This back and forth conversion cycle can be carried out multiple times without any apparent ligand decomposition. The conversion of **2**-CO_2 back to **2** occurred more rapidly under the same conditions and was complete in 10 min (see Supporting Information).

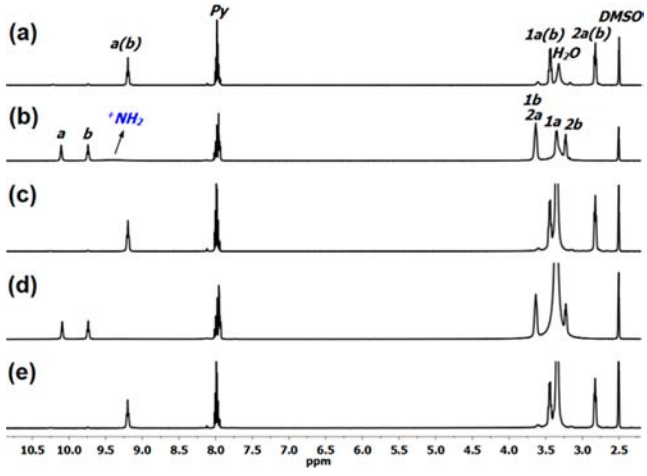

Figure 4. ^1H NMR (400 MHz, DMSO-d_6, 298 K) showing reversible transformations between **1** and **1**-CO_2. (a) **1**, (b) bubbling CO_2 for 1 min, (c) heating at 100 °C with Ar bubbling for 1 h, (d) bubbling CO_2 for 1 min, (e) heating at 100 °C with Ar bubbling for 1 h. See Scheme 1 for H atom assignments.

As part of the exploration of factors affecting the reversibility of CO_2 binding, we examined carbamate formation with two of the macrocyclic precursors, **3** and **5** (Scheme 2). The diethylenetriamine contains only amine sites, while **5** possesses the two amide groups. While both **3** and **5** rapidly form the carbamate when CO_2 is bubbled through the solutions, the reaction with **5** only goes to 85% completion (see Supporting Information). Furthermore, as anticipated the resulting carbamates are not as stable and can be easily converted back to the initial free amine forms by just bubbling Ar for a short time at room temperature (Table 1). Thus, it would appear that

Table 1. Experimental Conditions Required for Complete Release of CO_2 from the Carbamate Solutions in DMSO-d_6[a]

carbamates	experimental conditions
1-CO_2	heating at 100 °C with Ar bubbling for 1 h
2-CO_2	heating at 100 °C with Ar bubbling for 10 min
3-CO_2	bubbling Ar for 15 min
5-CO_2	bubbling Ar for 5 min

[a]As tested by ^1H NMR. The solutions of the CO_2 adducts were obtained by bubbling CO_2 through solutions of the ligand (20 mM) for 1 min.

CO_2 binding and the subsequent stability of the resulting product are facilitated by the "macrocyclic effect" for **1** and **2**, both of which contain a greater number of potential binding sites in close proximity compared to **3** and **5**. We are currently continuing to explore the influence of structural factors on the kinetics of this reversibility.

In conclusion, two 24-member diamine-tetraamido macrocycles **1** and **2** were efficiently synthesized by one-step and two-step routes, respectively. The more streamlined routes result in increased yields and the need for fewer chemicals and are certainly less time-consuming, all prerequisites for potential future scale-up. Additionally, both macrocycles showed fast and efficient CO_2 uptake via carbamate formation (100% conversion within 1 min at rt). While the rapid uptake of CO_2 by amine-containing systems is common and often readily reversible, the resulting two macrocyclic complexes are apparently stabilized by a "macrocyclic effect" that includes

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multiple well-placed hydrogen bonds and an electrostatic zwitterionic interaction. The downside is that the reverse process for CO_2 release requires heating at a relatively high temperature of 100 °C. The reduced time needed for this reaction in **2**-CO_2, however, suggests that it may be possible to control the kinetics of CO_2 release by careful manipulation of the macrocyclic framework. We are currently exploring the chemistry of these and related macrocyclic and acyclic systems for future applications in CO_2 capture, storage, and release.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. Synthetic details, ^{1}H and ^{13}C NMR spectra of new compounds, 2D COSY and HSQC NMR spectra, ESI-MS and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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