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Encapsulation of gases in the solid state

Alexander V. Leontiev and Dmitry M. Rudkevich*
Department of Chemistry & Biochemistry, University of Texas at Arlington, TX 76019-0065, USA.
E-mail: rudkevich@uta.edu; Fax: + 817 272 3808; Tel: + 817 272 5245

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A hemicarcerand encapsulates, stores and releases gases in the solid state.

Supramolecular chemistry of industrially and environmentally important gases is rapidly developing, and the synthesis of nanoscale frameworks for their controlled storage, processing and release is of great interest.[1] These porous frameworks involve cross-linked polymers, dendrimers and metal–ligand coordination assemblies.[2] Atwood and co-workers demonstrated that CH_4 and its volatile halogenated derivatives could be reversibly trapped and retained within the lattice voids of van der Waals solids—crystalline calix[4]arene frameworks.[3] Ripmeester further showed that the calixarene cavities in such crystals are also involved in the gas complexation.[4] The notion of cavity-containing solid materials for gas entrapment, storage and release within enclosed spaces is emerging.[3–5] In solution, gases were effectively encapsulated by container-molecules—hemicarcerands[6,7] and self-assembling capsules.[8,1] However, it has been unclear whether such encapsulation occurs in solids. In this communication, we demonstrate that a simple molecular container, a hemicarcerand, reversibly traps, stores and exchanges gases in the solid state at normal temperatures and pressures. Our results expand the scope of encapsulation phenomena, from solution to the gas–solid interphase.

For these studies, we used a traditional molecular container—slightly modified Cram's hemicarcerand **1**[6] (Fig. 1). It possesses two resorcinarene hemispheres, connected by three methylene bridges, and large enough to accommodate a benzene-size guest-molecule. The inner cavity volume is ~110 Å^3. The remaining gap between the two hemispheres allows for reversible encapsulation of DMF, DMA, DMSO, H_2O, MeCN, CH_2Cl_2, CH_2Br_2, THF, and pyridine.[6] Cram showed that CO_2, N_2, O_2, and Xe could also be trapped in $CDCl_3$ solution; the solvent in this case was too bulky to enter the cavity.

Empty hemicarcerand **1** was obtained from hemicarceplex **1**·DMA in boiling mesitylene, followed by chromatography.† Upon routine handling, **1** instantly absorbed N_2 from the atmosphere and/or the laboratory nitrogen line (^1H NMR).

This was the first indication that gas encapsulation might occur without solvent. No visible amount of the **1**·O_2 hemicarceplex was detected. Accordingly, mixture of **1** and **1**·N_2, ~1 : 1, was used in most of the cases. Bubbling CO_2, N_2O and N_2 through $CDCl_3$ or benzene-d_6 solutions of **1** for ~1 h resulted in the corresponding gas complexes. These can be distinguished by NMR spectroscopy (Fig. 2). Hemicarceplexes **1**·CO_2 and **1**·N_2O formed quantitatively. With N_2, only ~50% yield of **1**·N_2 was obtained. This was in

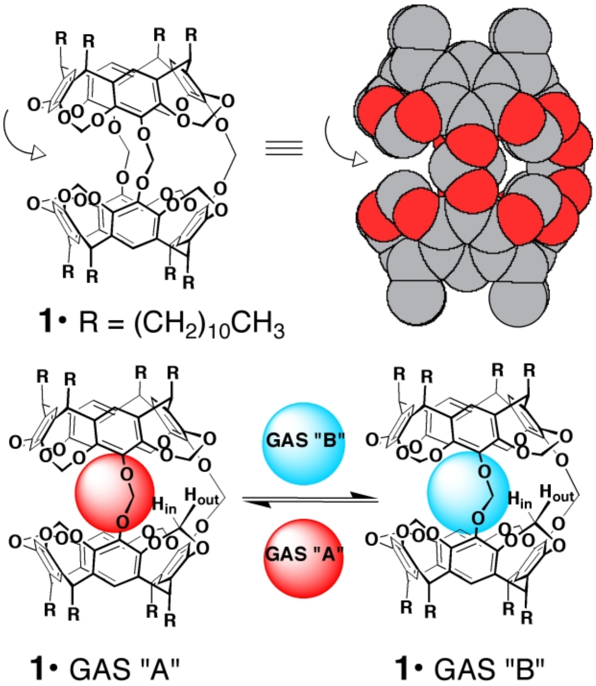

Fig. 1 Gas exchange in hemicarcerand **1** occurs both in solution and in the solid state. The depicted OCH_2O inward-pointed (H_{in}) hydrogens are most sensitive to the gas presence in the cavity. In the MacroModel representation (Version 7.1; MM2), hydrogens and long alkyl chains are omitted.

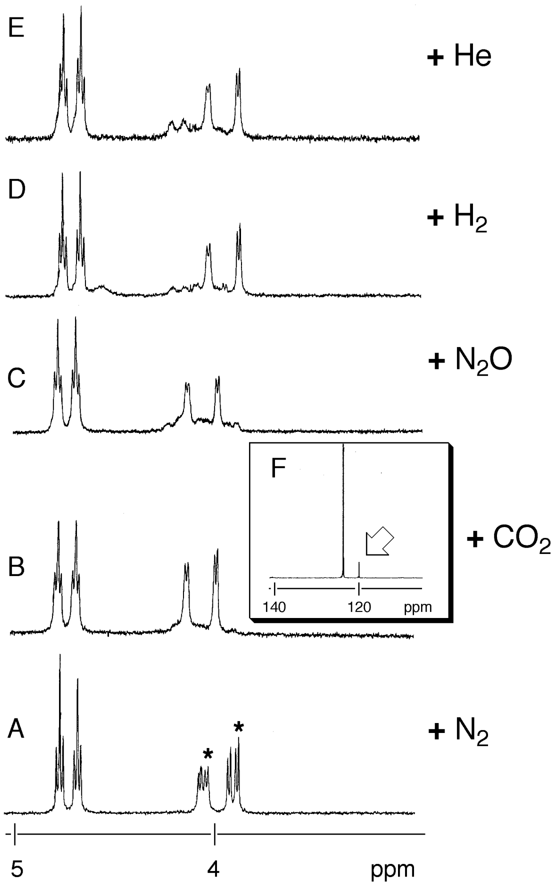

Fig. 2 A–E. Selected ^1H NMR spectra (500 MHz, $CDCl_3$, 295±1 K) of hemicarceplexes **1** with gases: A. N_2. The signals for empty **1** are marked by "*". B. CO_2. C. N_2O. D. H_2. E. He. F. Portion of the ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 295±1 K) of free CO_2 and **1**·CO_2. An arrow marks the latter.

agreement with the Cram data on N_2.[6] In the ^1H NMR analysis, the eight inward-oriented protons of the OCH_2O bridges appeared to be most sensitive to the gas presence in the cavity (Fig. 1). In empty **1**, these protons were situated at 4.02 and 3.89 ppm ($2 \times$ d, $J \sim 7$ Hz), while in $\mathbf{1}\cdot CO_2$ and $\mathbf{1}\cdot N_2O$ they appeared shifted downfield, at 4.13 and 3.99 ppm ($2 \times$ d, $J \sim 7$ Hz) (Fig. 2B,C). In the $\mathbf{1}\cdot N_2$, these doublets were seen at 4.06 and 3.92 ppm (Fig. 2A).

When the $CDCl_3$ solution of **1** was saturated with the ^{13}C-labelled CO_2, two intense CO_2 signals were seen at 124.9 and 121.6 ppm in the ^{13}C NMR spectrum. With the former singlet corresponding to the free gas (blank measurements with $^{13}CO_2$), the latter was assigned to hemicarceplex $\mathbf{1}\cdot CO_2$ (Fig. 2F).

For all three hemicarceplexes with gases, only one set of NMR signals was observed. With the estimated packing coefficients (PC)[9] of ~38 ± 5%, the 1 : 1 stoichiometry was assumed.‡ Low PC values for gases are well accepted in molecular crystallography, and were also observed by Rebek and co-workers for gas co-encapsulation in a self-assembling capsule.[10]

The exchange of CO_2, N_2O and N_2 in and out of the cavity is slow on the NMR time scale, with both free and filled host signals seen separately (at 295±1 K). The decomplexation energy barrier for these processes is therefore >15 kcal mol^{-1}. Accepted in gas separation[11] kinetic diameters for CO_2, N_2O and N_2 are 3.3, 3.3 and 3.6 Å, respectively, and the maximal portal opening in **1** is 4.4 Å (X-ray,[6] MacroModel). Obviously, the portal dimensions, rather than the internal volume, are crucial for the encapsulation.

Gases with smaller kinetic diameters, such as H_2 (2.9 Å) and He (2.6 Å), exhibit fast exchange kinetics. In the ^1H NMR spectra of solutions of **1**, saturated with H_2 and He, only one set of signals was recorded, apparently similar to empty **1** (295±1 K, Fig. 2D,E). Still, the gas encapsulation occurs in these cases. When a 1 : 1 mixture of **1** and $\mathbf{1}\cdot N_2$ was used, the N_2 was totally replaced. The corresponding NMR set for $\mathbf{1}\cdot N_2$ disappeared. Most probably, H_2 and He freely circulate in and out of the cavity, and the PC values suggest that two or even more of these molecules can be accommodated inside.

Gases replace each other in the inner cavity. For example, by flashing hemicarceplex $\mathbf{1}\cdot CO_2$ with N_2 in $CDCl_3$ or benzene-d_6, complex $\mathbf{1}\cdot N_2$ was obtained (together with empty **1**). Upon exposure to the stream of N_2O, this was quantitatively converted into hemicarceplex $\mathbf{1}\cdot N_2O$. Subsequent bubbling H_2 or He replaced N_2O. These transformations were then repeated a number of times, giving reproducible results. Such cycles of exchanges are unprecedented and cannot be easily achieved in conventional encapsulation studies with liquid and solid guests.[12]

Gas entrapment in the solid state was then attempted.

1. Gases were bubbled through $CDCl_3$ solutions of **1** until complete dryness. The corresponding solids were stored for another 0.5 h under the same gas stream and then dissolved in $CDCl_3$ and analysed by ^1H NMR spectroscopy. The respective **1**·Gas complexes were obtained, featuring the same spectra as if prepared in solution (Fig. 2). These solids are indefinitely stable under the respective gas atmosphere. They however lose the gases upon exposure to air. For example, the half-lives of hemicarceplexes $\mathbf{1}\cdot CO_2$ and $\mathbf{1}\cdot N_2O$ are ~30 min (NMR). During this period, a mixture of empty **1** and hemicarceplexes $\mathbf{1}\cdot CO_2$ (or $\mathbf{1}\cdot N_2O$) and $\mathbf{1}\cdot N_2$ can be clearly seen by ^1H NMR spectroscopy. Apparently, N_2 was consumed from the laboratory atmosphere. After 1 h only **1** and $\mathbf{1}\cdot N_2$ were detected.

2. Gases replace each other in the solid state. Upon flashing the powder containing **1** and $\mathbf{1}\cdot N_2$ with CO_2 or N_2O for 1 h, hemicarceplexes $\mathbf{1}\cdot CO_2$ or $\mathbf{1}\cdot N_2O$ were quantitatively obtained. Upon exposure to the stream of H_2, solid hemicarceplex $\mathbf{1}\cdot CO_2$ completely loses CO_2, and the NMR spectrum of thus obtained solid is similar to the spectrum with H_2 reported in solution. Being identical to the exchange in solution, these data somewhat diminish the role of solvent in gas encapsulation.

3. In the control, solid-state and solution experiments with CO_2 and hemicarceplex **1**·Pyrazine, the cavity of which is permanently occupied, no gas-induced NMR changes were detected. This once again emphasizes the role of inner cavities in the described processes and rules out the possibility, that gases are entrapped within the intermolecular voids.

In summary, cavity-containing solids can entrap, store and release gases. Utilizing unique synthetic experiences with molecular containers,[12] the cavity's dimensions and portals can be carefully designed to achieve greater selectivities in gas separation and stabilities in gas storage. Synthesis also opens doors to further modifications for catalytic gas conversion. We are currently testing the scope of gas encapsulation in the solid state and also utilizing molecular containers for storing reactive gases. We are also preparing robust, polymeric cavity-containing materials for gas separation, storage and sensing. Their structure, adsorbent location, sorption capacity and gas transport mechanism will be challenging topics to explore.

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Notes and references

† ^1H and ^{13}C NMR spectra were obtained on a JEOL Eclipse, 500 MHz spectrometer, HRMS MALDI-FTMS spectra were recorded on a IonSpec Ultima FTMS. Empty hemicarcerand **1** was prepared by refluxing hemicarceplex **1**·DMA[6] in mesitylene for 48 h, followed by column chromatography (SiO_2, $CHCl_3$–hexanes, 1 : 1, $R_f = 0.7$). Yield 44%; mp >245 °C (dec); ^1H NMR ($CDCl_3$): δ 7.07 (s, 2 H), 6.74 (s, 4 H), 6.67 (s, 2 H), 6.62 (d, $J = 5.5$ Hz, 2 H), 6.51 (s, 2 H), 6.40 (s, 4 H), 6.24 (d, $J = 7.2$ Hz, 4 H), 6.02 (d, $J = 7.2$ Hz, 4 H), 4.75 (t, $J = 7.7$ Hz, 4 H), 4.67 (t, $J = 7.7$ Hz, 4 H), 4.02 (d, $J = 7.2$ Hz, 2 H), 3.89 (d, $J = 7.2$ Hz, 2 H), 2.15 (m, 16 H), 1.31 (m, 144 H), 0.88 (t, $J = 6.6$ Hz, 24 H); HRMS MALDI-FTMS, *m/z*: 2460.6248. Calc. for $C_{155}H_{224}O_{22}Na$ 2460.6300.

‡ Volumes in Å^3 (Spartan): 14 (H_2), 17 (He), 36 (N_2), 47 (CO_2, N_2O).

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