Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 7105–7110 **7105**
DOI: 10.1021/ic802454w

Catching CO_2 in a Bowl

J. A. Tossell*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742 and The Renewable Energy Institute, George Washington University, Washington, D.C. 20052

Received December 27, 2008

Increased concentrations of CO_2 in the atmosphere contribute to global climate change. Improved methods are needed for removing CO_2 from the flue gas of power plants and/or directly from the atmosphere. A macrocyclic amidourea recently synthesized by Brooks et al., when dissolved in DMSO along with tetrabutyl ammonium fluoride, removes CO_2 from the atmosphere to form a complex in which a CO_3 group is held by a number of O—H-N bonds within the bowl-shaped cavity of the macrocycle. We have calculated the structure, stability, and vibrational spectra of this complex, using density functional techniques and polarized double-ζ basis sets. Both basis set superposition errors and polarizable continuum effects on the complex geometry and stability have been evaluated. The calculated structure is in good agreement with experiment. We predict that this CO_3^{-2} complex (and its HCO_3^- analogue) have larger formation constants by several orders of magnitude than the analogue complex of the amidourea macrocycle with Cl^- (particularly in DMSO solution compared to aqueous solution). Our calculations also indicate that the CO_3^{-2} and HCO_3^- complexes can be distinguished by ^{13}C NMR. The CO_3^{-2} complex also has a distinctive H—N stretch, perturbed by the H-bonding to the CO_3 group. We also calculate the CO_3^{-2} complex to absorb within the visible region, unlike the free macrocycle or typical metal carbonates. Macrocycles of this type may provide a useful route to the absorption of atmospheric CO_2. Our calculations also indicate that changing the solvent from DMSO to water and/or heating the complex will be an efficient way to decompose it to release CO_2.

Introduction

In the search for novel materials that bind CO_2 from power plant flue gases or directly from the atmosphere, advances may occur fortuitously. Recently, slow evaporation from a DMSO solution containing tetrabutyl ammonium fluoride and a complex macrocycle formed from ureas and pyridines yielded a complex with a CO_3 group trapped in the middle of a bowl-shaped cavity.[1] The source of the CO_3 group was apparently CO_2 from the atmosphere of the laboratory. The ready formation of this compound suggests a high stability. Thus, it may be a candidate as a receptor or absorber for atmospheric CO_2.

The overall goal of the experimental work described above was to synthesize new anion receptors, since anion transport is important in many biological systems. The study of anion receptors[2] has become a major field in supramolecular chemistry. However, all previous CO_3^{-2} complexes have been formed through the addition of solid bicarbonates,[2c,2d] rather than through abstraction of CO_2 from ambient air. Although the compounds studied by Brooks et al.[1] may be too difficult to synthesize to be used economically to capture CO_2, principles may emerge from their study which will lead to a deeper understanding of how to design cheaper amide-derived CO_2 receptors. It is also conceivable that living organisms may be developed which are capable of emplacing structurally similar ion receptors within their cell membranes.

To this end we have carried out a number of quantum mechanical studies on the CO_3^{-2} complex described above and on various other complexes related to it, examining structure, stability, and a range of properties which can help in their characterization.

Computational Methods

A good discussion of modern computational chemistry methods (along with an explanation of their "alphabet soup" of acronyms) can be found in a text by Cramer[3] and a review article by Head-Gordon.[4] For the calculation of the gas-phase free energies of the complexes studied we use density functional theory with a B3LYP potential and a CBSB7 basis[5]

*E-mail: tossell@umd.edu.

(1) Brooks, S. J.; Gale, P. A.; Light, M. E. *Chem. Commun.* **2006**, 4344–4346.
(2) (a) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465–475. (b) Choi, K.; Hamilton, A. D. *Coord. Chem. Rev.* **2003**, *240*, 101–110. (c) Custelcean, R.; Delman, L. H.; Moyer, B. A.; Sessler, J. L.; Cho, W. S.; Gross, D.; Bates, G. W.; Brooks, S. J.; Light, M. E.; Gale, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2537–2542. (d) Caltagirone, C.; Hiscock, J. R.; Hursthouse, M. B.; Light, M. E.; Gale, P. A. *Chem.—Eur. J.* **2008**, *14*, 10236–10243. (e) Brooks, S. J.; Garcia-Garrido, S. E.; Light, M. E.; Cole, P. A; Gale, P. A. *Chem.—Eur. J.* **2007**, *13*, 3320–3329.
(3) Cramer, C, J. *Essentials of Computational Chemistry: Theories and Models*; Wiley: New York, 2002; p 542.
(4) Head-Gordon, M. J. *Phys. Chem.* **1996**, *100*, 13213–13225.
(5) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822–2827.

(essentially a 6-311G(d,p) basis slightly modified to give better convergence to the complete basis set limit). We calculate vibrational spectra at the harmonic level, and the absence of imaginary frequencies confirms that we are at a local minimum. The next step up in accuracy would utilize perturbation theory methods like MP2 to account for electron correlation, but MP2 calculations for such large systems are beyond our present computational capabilities.

To evaluate the hydration free energies of these complexes we use the conductor polarizable continuum method[6] (CPCM), a version of the polarizable continuum method[7] (PCM). There are many different versions of the PCM, but none which give hydration free energies for singly charged anions with average absolute errors of less than about 1−2 kcal/mol versus experiment. Thus, although the hydration term in the reaction free energy is often smaller in magnitude than the gas-phase term, the absolute error in its calculation may well be probably larger. This is undoubtedly the weak link in our calculation of the energetics of complex formation.

We have also calculated NMR shieldings for a number of the species considered, to establish additional criteria for their identification, using the GIAO version of coupled Hartree−Fock perturbation theory.[8] We have utilized 6-31G(d,p) basis sets and the HF method, which should be adequate for calculating shielding trends. Unfortunately, NMR studies on these complexes have not yet been performed.

To evaluate visible-UV absorption spectra we use time dependent density functional theory[9] (TDDFT), typically using a hybrid B3LYP functional and a doubly polarized triple-ζ basis with diffuse functions. This has become the method of choice for calculating electronic spectra of large molecules because of its accuracy and computational efficiency. UV−visible spectra are not yet experimentally available for the compounds discussed.

All calculations are done using GAUSSIAN03,[10] and the structures of complexes are displayed using GaussView.[11]

In evaluating the energetics of complex formation using modest basis sets it is important to consider the effects of basis set superposition error (BSSE) which can be corrected for approximately using the counterpoise method[12] developed by Boys and Bernardi and implemented in GAUSSIAN03.

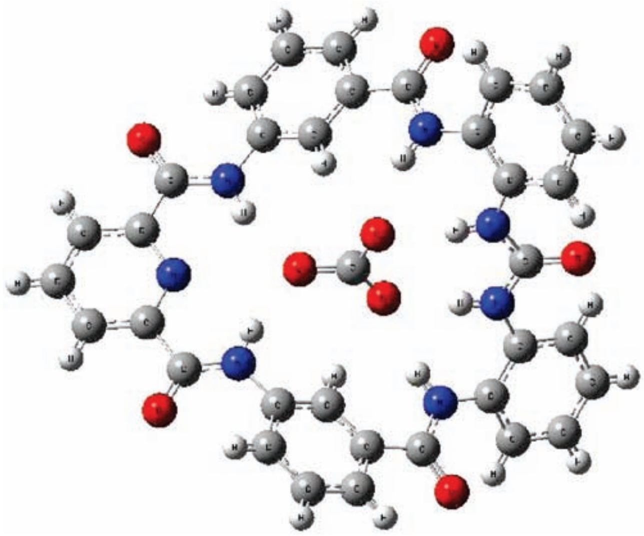

Figure 1. Experimental structure of the CO_3^{-2}---complex (from ref 1).

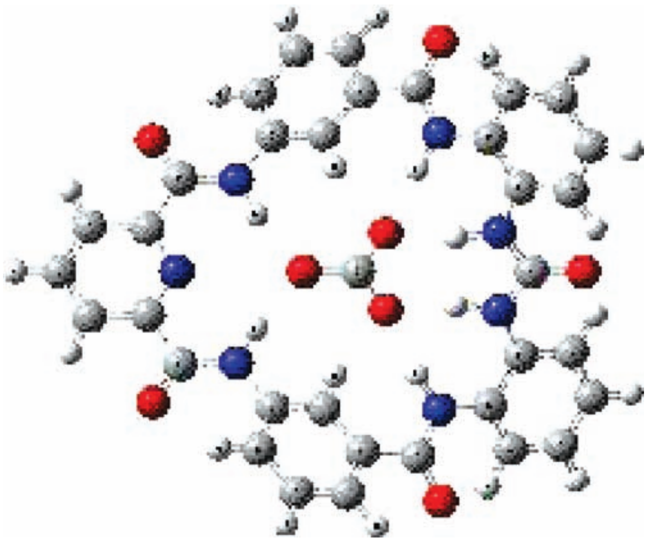

Figure 2. Structure of the CO_3^{-2}---complex calculated at the CBSB7 B3LYP level.

A number of studies on the quantum chemistry of anion receptors have recently appeared.[13−16] Because of the size of the systems involved most have used a semiempirical force field or density functional techniques. The focus has generally been on the geometry of the complex, although complexation energies have sometimes been calculated.

Complexes involving the bicarbonate dimer have also been characterized experimentally.[17] These complexes are also apparently formed by the abstraction of CO_2 from ambient air.

Results and Discussion

The experimental[1] and CBSB7 B3LYP calculated geometries of the $CO_3^{-2}\cdots$complex, shown in Figures 1 and 2, respectively, look very much alike, and the experimental and calculated C−O and O···N distances are very similar, as

(6) Truong, T. N.; Stefanovitch, E. V. *Chem. Phys. Lett.* **1995**, *240*, 253–260.

(7) Tomasi, J. *Theor. Chem. Acc.* **2004**, *112*, 184–203.

(8) Wolinski, K.l; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.

(9) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454–464.

(10) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A. Jr, Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cvossi, M., Scalmani., G. Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M. Li, X., Knox, J. E., Hratchian, J. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dappriach, S., Daniels, A. D., Strain, M. C., Farkas, O.,Nalick,D. K., Rabuck, A. D., Raghavachari, J., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, G., Clifford, S., Cioslowski, J.,Stefanov, B. B.,Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. A., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalex, C., Pople, J. A. *Gaussian 03*, Rev. A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(11) Frisch, A. E.; Dennington, R. D.; Keith, T. A., Nielsen, A. B., Holder, A. J. *GaussView*, Rev. 3.0; Gaussian, Inc.: Pittsburgh, PA, 2003.

(12) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(13) Van Hoorn, W. P.; Jorgensen, W. L. *J. Org. Chem.* **1999**, *64*, 7439–7444.

(14) Wu, Y.-D.; Wang, D.-F.; Sessler, J. L. *J. Org. Chem.* **2001**, *66*, 3739–3746.

(15) Rozas, I.; Kruger, P. E. *J. Chem. Theory Comput.* **2005**, *1*, 1055–1062.

(16) Turner, D. R.; Paterson, M. J.; Steed, J. W. *J. Org. Chem.* **2006**, *71*, 1598–1608.

(17) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Pfeffer, F. M.; Hussey, G. M. *Tetrahedron Lett.* **2003**, *44*, 8909–8913.

Table 1. Calculated C−O, O···H, and O···N (in the O···H(N) Group) Distances (in Å) for CO_3^{-2}, HCO_3^-, and H_2CO_3 Macrocycle Complexes from CBSB7 B3LYP Calculations [a]

X	R(C−O)	R(O--HN) O−H distance	R(O--HN) O−N distance
CO_3^{-2}	1.283, 1.298, 1.298	1.658, 1.658, 1.761, 1.761, 1.841, 1.841	2.70, 2.70, 2.87, 2.87
	1.276, 1.283, 1.289	*1.903, 1.928, 1.874, 1.982, 1.958, 1.990*	*2.73, 2.77, 2.81, 2.84*
HCO_3^-	1.239, 1.249, 1.409	1.827, 1.973, 1.887, 1.960, 2.068, 2.155	2.839, 2.903, 2.938, 2.962, 2.966, 3.131
H_2CO_3	1.211, 1.310, 1.355	2.052, 2.143, 2.202	2.674, 2.950, 3.116

[a] With experimental values in italics for the CO_3^{-2} complex.

shown in Table 1. There is a significant difference between the experimental and calculated dihedral angles involving the peptide bond and the benzene ring adjacent to it, with values of only about 5° in the experimental structure and 20° in the calculated structure. For the CO_3^{-2} moiety there are a total of 6 H-bonding interactions with N−H groups of the macrocycle.

The O---H distances within the O---H-N moieties show more difference between calculation and experiment, but that may be due to the difficulty in characterizing the O---H distance directly using X-ray diffraction. When we optimize the geometry either in the presence of a PCM appropriate for aqueous solution or with the BSSE correction included at each step of the optimization the calculated equilibrium O---H distances change by no more than 0.03 Å, and usually by much less. We do not include in Figures 1 and 2, or subsequent figures, the counterion, tetrabutyl ammonium, which crystallizes along with the complex. Thus, we are making the implicit assumption that the tetrabutyl ammonium ion does not significantly influence the properties of the complexes. Conceivably, the discrepancy in dihedral angle noted above may be an effect of the counterion.

When we protonate the CO_3^{-2} in the complex we see the CO_3 grouping of atoms develop the expected separation between C═O and C−OH distances, as shown in Figures 3 and 4. Both the HCO_3^- and H_2CO_3 complexes are stable local energy minima, with the carbonate species still held inside the bowl-shaped cavity and with H-bonds to the N atoms of the macrocycle. But most of the O···N distances have increased as the H-bonding to the macrocycle is weakened.

We have also calculated the structures and stabilities of Cl^-, Br^-, and NO_3^- complexes. We have calculated the energetics of formation for the macrocyclic complexes, starting from a reference Cl^----complex in solution. That is, we determine the free energy for the process:

$$X + Cl^- \text{---complex} \Rightarrow X\text{---complex} + Cl^-$$

We have done this for both water and DMSO solutions, since DMSO-water was used in the studies of Brooks et al.[1] We have chosen the Cl^----complex as our reference compound since the uncomplexed macrocycle's explicit structure in solution is not well-defined. Should we use the bare macrocycle or one containing a single or multiple waters as the model for this species in solution? Using the Cl^----complex we can avoid this question.

We find that the CO_3^{-2} and the HCO_3^{-1} complexes are both more stable than the Cl^----complex by anywhere from 4 to 17 kcal/mol, as shown in Table 2. Our results support the idea that the CO_3^{-2} complex in DMSO has a very large negative free energy of formation with respect to the Cl^- complex (−16.8 kcal/mol), large enough that it can plausibly

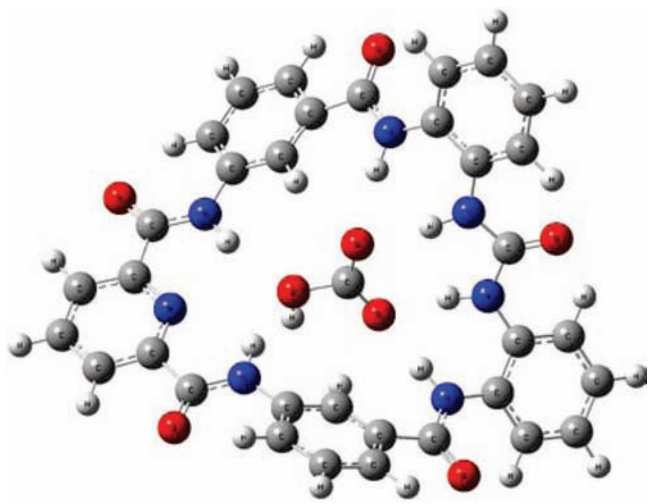

Figure 3. Structure of the HCO_3^----complex calculated at the CBSB7 B3LYP level.

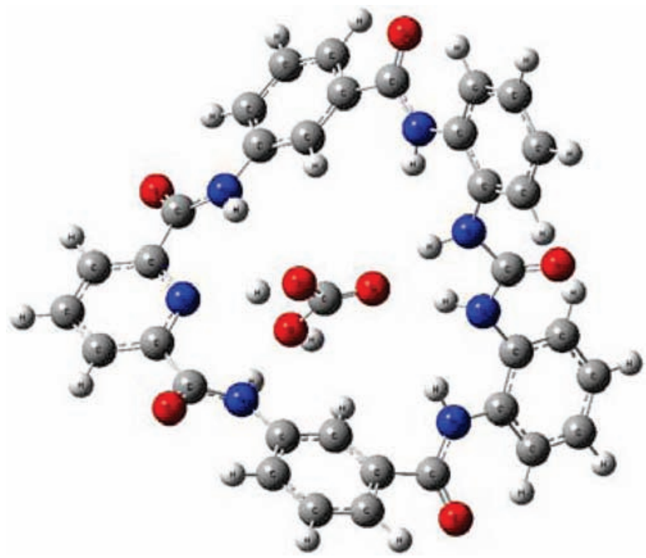

Figure 4. Structure of the H_2CO_3---complex calculated at the CBSB7 B3LYP level.

complex all the CO_3^{-2} derived from dissolution of atmospheric CO_2 in the basic solution produced by hydrolysis of the tetrabutyl ammonium fluoride. From the calculated reaction free energy of −16.8 kcal/mol for the exchange of Cl^- and CO_3^{-2} complexes in DMSO we determine that the stability constant for formation of the CO_3^{-2} complex would be larger by a factor of about 2.0×10^{12} (at 25 °C) than that for Cl^-, projecting a value of 3.8×10^{14} for this stability constant. The largest stability constant measured by Brooks et al.[1] was 1.65×10^4 for $CH_3CO_2^-$ (which was near the upper limit

Table 2. Calculated Energies (in kcal/mol) for Formation of X---Complex from Cl^----Complex in Water or DMSO

X/energy	$\Delta E_{CBSB7\ B3LYP}$	ΔE_{BSSE}	ΔG_{VRT}	ΔG_{CPCM} water	ΔG_{CPCM} DMSO	ΔG water	ΔG DMSO
CO_3^{-2}	−152.7	+46.4	+6.2	+95.4	+83.3	−4.6	−16.8
HCO_3^-	−24.6	+13.3	+8.5	−1.0	−2.5	−3.8	−5.3
H_2CO_3 s-a conformer	+47.2	+4.6	+7.2	−42.8	−37.6	+16.2	+21.4
CO_2	+56.3	−0.7	+0.7	−50.7	−39.3	+5.6	+17.0
Br^-	+3.1	+2.3	+0.4	−4.3	−3.9	+1.5	+1.9
NO_3^-	−10.0	+13.2	+5.6	−7.4	−8.5	+1.2	+0.1

of stability constants that could be determined by their techniques). On the basis of the calculated free energies in Table 2, the calculated stability constant for the HCO_3^----complex is 1.5×10^6, so it is also a very stable complex. Additional calculations of electron correlation effects and vibrational spectra would be needed to determine the free energy for proton dissociation from the HCO_3^----complex, but it may well be stable with respect to the CO_3^{-2}---complex plus a proton in solution. By contrast, a computational attempt to produce a BO_3^{-3} complex of the macrocycle lead to an optimized geometry containing a $B(OH)_3$ group within a set of deprotonated N−H groups.

The H_2CO_3---complex is calculated to be strongly destablilized compared to the Cl^- complex, whether in water or DMSO. Thus, full protonation of the CO_3 group of the complex will lead to decomposition, releasing H_2CO_3 which can further decompose to $H_2O + CO_2$. Likewise the CO_2---complex is calculated to be very much less stable than the Cl^- complex, so that it would not form directly from CO_2 dissolved in the solution. The NO_3^---complex is calculated to be slightly (1.2 kcal/mol) less stable than the Cl^---complex in H_2O and of almost identical stability in DMSO. The Br^- complex is calculated to be less stable than the Cl^- complex by 1.9 kcal/mol in DMSO, equivalent to a factor of 25 difference in their stability constants. The difference observed experimentally[1] is roughly a factor of 19, very similar to the calculated value.

The greatly enhanced relative stability of the CO_3^{-2} complex in DMSO compared to water is of course mostly a consequence of the reduced solvation of CO_3^{-2} in DMSO. This result suggests that the stability of the CO_3^{-2}---complex will be enhanced with respect to the Cl^----complex in other solvents of low dielectric constant. Thus, change of solvent from low dielectric constant to higher dielectric constant could be a simple and efficient procedure for destabilizing the CO_3^{-2}---complex and recovering CO_3^{-2} and ultimately CO_2 from it .

We can also estimate the direct effect of T on the reaction substituting CO_3^{-2} for Cl^- in the complex by evaluating the gas-phase ΔG_{VRT} term (the change in zero-point vibrational and thermal contributions to the free energy) as a function of T. Increasing T from 273 to 373 increases ΔG_{VRT} by 5.3 kcal/mol, reducing the relative stability constant by about 4 orders of magnitude. Thus, raising the temperature, a common "stripping" procedure, could also lead to the release of CO_2. Evaluating the temperature effect on the ΔG_{CPCM} term in the free energy will be more complicated since it involves changes in the dielectric constant with T of a mixture of DMSO and water.

We also show a detailed breakdown of the different components of the reaction free energies in Table 2. It is important to note that a number of terms make significant contributions to the total free energy difference in complex formation reactions—the electronic energy, the counterpoise energy (ΔE_{BSSE}), VRT contributions to ΔG, and hydration free energies. In general, the larger the value of the hydration free energy, ΔG_{CPCM}, the less accurate the total aqueous free energy change will be, since this term is obtained from the relatively inaccurate CPCM simulation method. Since the comparison of the stabilities of even the closely related Cl^- and Br^- complex involves significant differences in many of these terms, the excellent agreement of calculation and experiment for the Cl^-, Br^- pair is very gratifying.

Again, we should emphasize that there are two main problems in the calculation of the reaction free energies. The first is the use of the limited basis sets, which we have corrected for approximately using the counterpoise method. The second is the limited accuracy of the CPCM method, particularly for the case of dianions, like CO_3^{-2}. While the accuracy of the CPCM method for monoanions is well established, its accuracy for dianions is still much less certain.

Our calculations of vibrational spectra (done at the 6-31G* B3LYP level to conserve computational resources) also indicate that the N−H stretches perturbed by H-bonding to the O atoms of CO_3^{-2} will be at a substantially lower frequency than in the free macrocycle, giving a distinctive change in the Raman spectrum. The calculated Raman spectrum of this complex is shown in Figure 5. The N−H stretches are found between 2835 and 3269 cm^{-1}, while calculation on the free macrocycle at the same level of theory give N−H stretching frequencies between 3570 and 3600 cm^{-1}.

We have also calculated the ^{13}C and ^1H NMR to establish additional criteria for identifying the $CO_3^{-2}\cdots$complex and related complexes. Our ^{13}C shieldings for the central C atom are shown in Table 3. We present calculated shieldings, shifts compared to the standard $Si(CH_3)_4$ reference along with shielding anisotropies. The calculations indicate that the

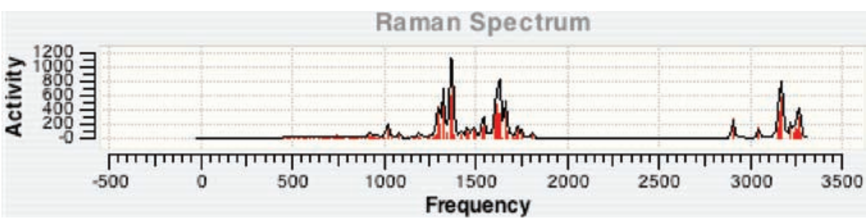

Figure 5. Calculated Raman spectrum for the CO_3^{-2}---complex, using the 6-31G* B3LYP method.

Table 3. Calculated ^{13}C NMR Shieldings and Anisotropies (in ppm) for CO_3^{-2}, HCO_3^-, and H_2CO_3 Complexes with Macrocycle, Compared with Some Other CO_3-Like Species and with the $Si(CH_3)_4$ Reference

species	σ^C_{av}	δ^C_{av}	shielding anisotropy
$CO_3^{-2}\cdots$complex	35.2 @calc. geom.	166.7	84.3
	36.6 @exp. geom.	165.3	86.4
HCO_3^---complex	47.6	154.3	75.4
H_2CO_3--complex	50.3	151.6	73.5
CO_2---complex	74.4	127.2	310.6
CO_3^{-2} (g)	28.5	173.4	96.9
HCO_3^-(g)	53.6	148.3	138.9
H_2CO_3 s-a (g)	57.0	144.9	87.8
CO_2(g)	74.2	127.7	313.1
$HCO_3^-\cdots 22H_2O$	41.6	160.3	84.4
$CO_3^{-2}\cdots 22H_2O$	43.0	158.9	77.3
$Si(CH_3)_4$	201.9	0	4.8

Table 4. Calculated ^1H Shieldings for the Three Inequivalent N−H Protons in the Different Complexes[a]

species/N−H groups	top	middle	bottom
free macrocycle	31.8	30.4	27.8
H_2O--complex	27.7	24.8	23.2
Cl^---complex	23.9	24.1	21.6
CO_3^{-2}--complex	17.7	19.5	17.4
NO_3^---complex	23.0	23.7	21.2

[a] Refer to Figure 6 for positions of N−H groups.

CO_3^{-2}---complex will have a distinctively positive ^{13}C shift, compared to other carbonates, such as our $CO_3^{-2}\cdots 22H_2O$ model for carbonate in solution, also included in Table 3. The C becomes more shielded as we protonate the CO_3^{-2} group within the complex, giving us a means for monitoring the protonation state of the carbonate group. The C in the CO_3^{-2}---complex also shows a relatively high shielding anisotropy, consistent with relatively strong bonding within the plane of the CO_3^{-2} group. The shielding of the CO_2 carbon within the complex is essentially identical to that of free gas-phase CO_2, consistent with its weak interaction. By contrast, both HCO_3^- and CO_3^{-2} within the complex are distinctly different in shielding than the free ions or the ions within the water clusters.

The ^1H shieldings for the three inequivalent N−H protons are given in Table 4. Refer to Figure 6 in which these three N−H amide groups at the top, middle, and bottom of the complex are highlighted in light blue. Brooks et al.[1] generally find that the resonances for the protons on the top and bottom N−H groups are most affected by the identity of the ligand group within the cavity. We find that the deshielding of the N−H protons produced by CO_3^{-2} is much larger than that produced by our reference ligand Cl^- or the weakly complexing NO_3^- ligand, and that top, middle, and bottom N−H groups are all deshielded by substantial amounts.

Another important aspect of the electronic structure of the CO_3^{-2} complex is that, on the basis of our TDDFT calculations, its lowest energy absorptions fall in the visible region of the spectrum, at much lower energy than in the free macrocycle, free gas-phase CO_3^{-2} or in carbonate minerals,[18] as shown in Table 5. It is generally found that for anionic species in solution inclusion of PCM hydration gives higher and more accurate absorption energies than for the free ion,[19]

(18) Kondo, S.; Yamashita, H.; Nakamura, K. *J. Phys. Soc. Jpn.* **1973**, *34*, 711–714.
(19) Tossell, J. A. *Geochem. Trans.* **2003**, *4*, 28–33.

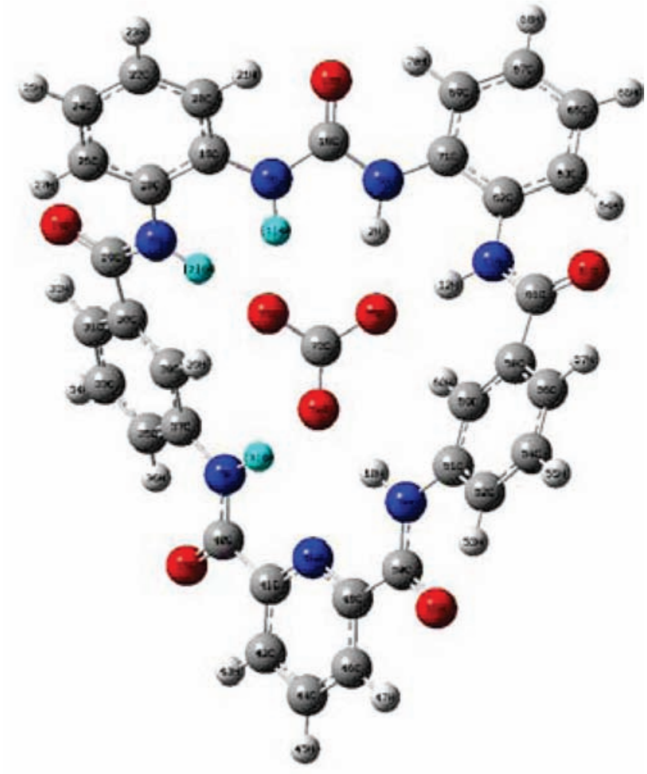

Figure 6. CO_3^{-2}---complex, with H atoms of the three inequivalent N−H groups marked in light blue.

Table 5. Calculated UV-Visible Energies (in eV) for the CO_3^{-2} Complex in Gas-Phase and PCM, for the Macrocycle Alone, and for Gas-Phase CO_3^{-2}, Using the TD B3LYP Method with a 6-31G(d,p) Basis, with Experimental Value for Calcite

species	ΔE
CO_3^{-2}---complex (g)	0.53, 0.64, 1.50
CO_3^{-2}---complex in PCM	1.79, 1.94, 2.46
HCO_3^-----complex (g)	2.79, 2.83, 3.19
HCO_3^----complex in PCM	3.54, 3.57, 3.87
H_2CO_3---complex (g)	2.63, 2.90, 2.92
H_2CO_3---complex in PCM	3.47, 3.70, 3.72
free macrocycle (g)	3.35, 3.50, 3.68
CO_3^{-2} (g)	6.10, 7.77, 7.77
Calcite exp.	7−9

but even within the PCM the CO_3^{-2}---complex still has its absorptions in the visible. This indicates that the electronic environment of the CO_3 group in this complex is much different than it is in typical carbonate minerals. On the other hand for the HCO_3^- and H_2CO_3 complexes the absorptions move into the near UV. Thus, we should be able to determine the protonation states of such complexes from their visible color.

Summary

We have established that modestly demanding DFT methods can yield a good description of the structure and energetics of the CO_3^{-2} macrocycle complex. The energetics of formation of the complex are favorable for both CO_3^{-2} and HCO_3^-. Both the ^{13}C NMR and the Raman spectra of the CO_3^{-2}---complex have distinctive features, showing a strongly deshielded C and significantly reduced N−H stretching frequencies.

The CO_3^{-2} complex considered in this work may provide a means for capturing CO_2 from the air. The simplest approach would be to dissolve the atmospheric CO_2 in a solution of the amidourea macrocycle and a tetraalkyl ammonium fluoride in a solvent of low dielectric constant and to then recover the CO_2 from the CO_3^{-2}---complex by changing to a more polar solvent and/or by heating the complex.

Our preliminary computational results also indicate the CO_3^{-2} will form a complex with a local energy minimum even when the N−H containing groups do not form a macrocycle, but are simply individual molecules. Thus complicated synthesis of a macrocycle may not be needed to form stable carbonate complexes.

The scientific basis supporting a procedure for capturing CO_2 from power plant effluent through creation of solid polymeric H_2CO_3 has been discussed in a previous paper.[20] The process discussed here is a complementary one, which may be most useful for removing CO_2 from ambient air.

Acknowledgment. This work was supported by DOE Grant DE-FG02-94ER14467. Prof. J. Davis (UMCP) brought this complex to the attention of J.A.T. and provided valuable comments on the work.

(20) Tossell, J. A. *Inorg. Chem.* **2006**, *45*, 5961–5970.