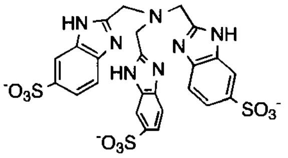
# $CO_2$-Encapsulated Clathrate Hydrate Formed by Sulfonate-Assisting Hydrogen Bonds and Template Contribution from Helper Species of Zinc(II)

Kazuhiko Ichikawa*, Kou Nakata, and M. M. Ibrahim
*Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, Hokkaido 060-0810*

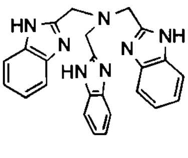
(Received March 29, 2000; CL-000296)

The $CO_2$-encapsulated clathrate hydrate was formed, under a room temperature and atmosphere, by sulfonate-assisting hydrogen bonds among water molecules, where the geometry of the three sulfonate groups in zinc complex with nitrilotris(2-benzimidazolylmethyl-6-sulfonate) **L1**, was controlled by coordination of $Zn^{2+}$.

A number of clathrate hydrates are made of the framework of hydrogen-bonded water molecules, in which the small molecules of $CO_2$, $CH_4$, and Xe are encapsulated into each cavity.[1–4] The cages consist of 12, 14 or 16 hedrons having the several pentagons and hexagons formed by hydrogen-bonded water molecules 2.8 Å apart. On the other hand, the fixation/condensation of $CO_2$ is of current interest from the view of the green house effect and the effective utilization of $CO_2$. It is impossible to prepare the clathrate hydrate of $CO_2$ under a room temperature and atmosphere : it can be existed under higher pressure above 5 atm and at the temperatures lower than 10 °C.[5] The clathrate hydrate of $CO_2$ under the room temperature and atmosphere may be prepared using template technique for the formation of hydrogen bond framework. The concept for the molecular design of template is that (1) the template is soluble in water and has the functional groups of hydrogen atom acceptor to form the hydrogen-bonded framework. (2) The functional groups have the suitable geometry to be able to take part into the three dimensional hydrogen-bonded framework of clathrate hydrate. The sulfonated and water-soluble ligand, **L1**[6] was designed to have three sulfonate groups on each benzene ring. Here, the suitable geometry among the sulfonate groups will be obtained by the complexation of $Zn^{2+}$ with **L1** and expected to assist the three dimensional hydrogen-bonded framework.



**L1**



**L2**

After bubbling of $CO_2$ (ca.30 mL / min) for two hours into aqueous solution at $R$ (= $[Zn^{2+}]_0$ / $[\mathbf{L1}]_0$) = 1.0 , **L1** = 50 mM and pH 7–8.5 the clear solution was changed to gel. The aqueous solutions of **L1** or $Zn^{2+}$ was kept to be clear even though after bubbling $CO_2$. The phase-transition between the gel and clear solution was reversible for bubbling and degassing of $CO_2$. The observed optical microscopic image showed that the gel consists of the flakes with the different sizes of less than 50 µm in length, as shown in Figure 1. The evolved $CO_2$ from the gel at 75 °C was analyzed by gas chromatography: the ratio of zinc complex to $CO_2$ was approximately equal to 1 : 1. Thus, the concentration of $CO_2$ may be controlled by that of zinc complex. For **L1**–Zn 10 mM solution the phase-transition to the gel was not observed.

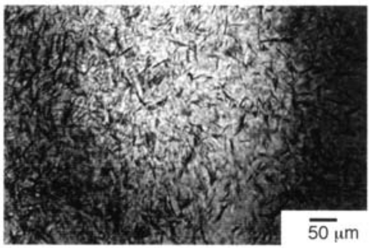


**Figure 1**. Optical microscopic image of gel at $R$ (= $[Zn^{2+}]_0$ / $[\mathbf{L1}]_0$) = 1.0.

The solid $^{13}C$ NMR spectrum of the gel observed using high power decoupling and magic angle spinning technique[7]showed the broad peak around 120 ppm with 7–9 kHz line width (Figure 2 (a)). The broadening is attributed to the fact that the contribution of chemical shift anisotropy was not eliminated enough. The spining rate of more than 9 kHz will give a sharp $^{13}C$ NMR peak: the measurement at more than 2 kHz for the spining rate was impossible because of the gel. At the spining rate of 1 kHz the observed half width demonstrated the increase of half width (10 kHz) compared with 9 kHz at the spining rate of 2 kHz. The line width 5 kHz of the $CO_2$-encapsulated clathrate hydrate was observed by cross-polarization and dipolar decoupling technique.[3] Since the width contains the contribution from chemical shift anisotropy, it corresponds to that of our observation for the gel. After $CO_2$ evolution from the gel, the broad peak was disappeared. Thus, the observed broad $^{13}C$ NMR peak for the gel was assigned to $CO_2$ encapsulated in the cages formed by hydrogen bonded water molecules with the aid of sulfonated zinc complex.

From the view of the $^{13}C$ NMR spectrum for the clear solution obtained after $CO_2$ evolution from the gel (Figure 2(b)), the sharp peaks superimposed on the broad peak were assigned to **L1**–Zn complex. The $^{13}C$ NMR peak at 163 ppm for the clear solution was assigned to be $HCO_3^-$(aq) attributed to the hydration of $CO_2$. The sharp $^{13}C$ NMR chemical shifts for $CO_2$(aq) and $HCO_3^-$(aq) are reported at 126 ppm and 162 ppm, respectively.[8–10]

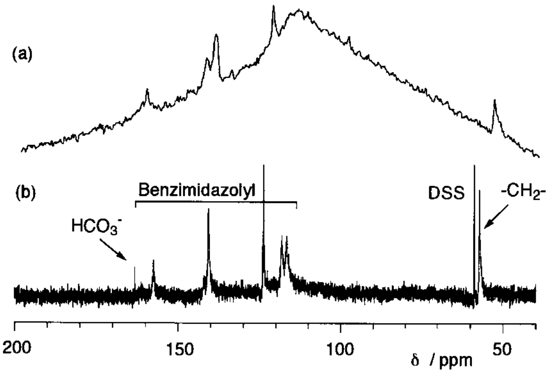


**Figure 2**. Solid state $^{13}C$ NMR spectra of (a) the gel at $R$ = 1.0. (b) $^{13}C$ NMR spectrum of the clear solution obtained after $CO_2$ evolution .

The IR data of $S(=O)_2$–$O^-$ stretching and $CO_2$ bending regions of the gel were shown in Figure 3. From the comparison between the spectra of tris(2-benzimidazolylmethyl)amine **L2** without three sulfonate groups, and $H_3$**L1** (Figures 3 (a) and (b)), a peak at around 1100 $cm^{-1}$ and a separated peak at around 1200 $cm^{-1}$ were assigned to symmetric and asymmetric $S(=O)_2$–$O^-$ stretching modes, respectively[11] Since the $S(=O)_2$–$O^-$ stretching bands of zinc complex with **L1** was identical with that of $H_3$**L1** (Figures 3 (b) and (c)), the sulfonate groups never coordinated to zinc ion. The result of gel (Figure 3(d)) suggests that the two peaks marked by * between 1100–1150 $cm^{-1}$ were appeared as a result of the formation of hydrogen-bonded framework around -$SO_3^-$ group. Consequently, hydrogen-bonded and the free symmetric stretching peaks of $S(=O)_2$–$O^-$ were coexisted in the gel. The observed band at 640 $cm^{-1}$ (Figure 3(d)) was assigned to bending modes since 650 $cm^{-1}$ for encapsulated $CO_2$ were reportd.[2] But the asymmetric stretching mode (around 2340 $cm^{-1}$) was masked by the bands from ligand and solvent.

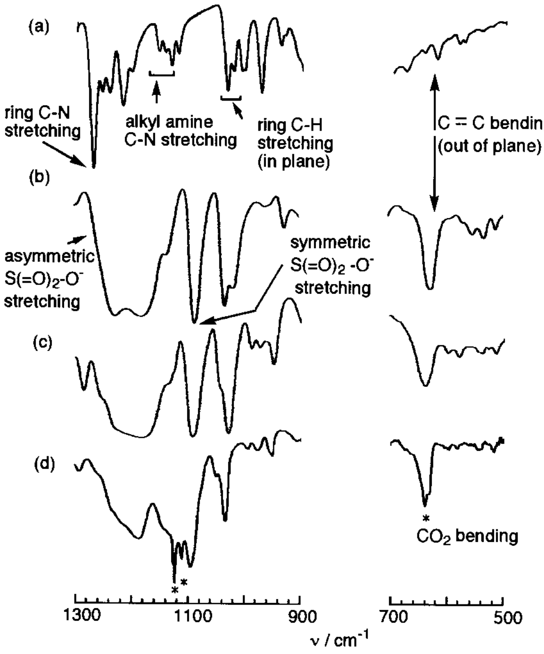


**Figure 3.** IR.spectra of $S(=O)_2$-$O^-$ stretching and $CO_2$ bending regions. (a) **L2**, (b) $H_3$**L1**, (c) zinc complex with **L1**, (d) the gel prepared at $R = 1.0$.

Since the cage formation was facilitated by sulfonate groups in zinc complex with **L1**, the $CO_2$ molecules were encapsulated into each cage which was made of water molecules as well as sulfonate groups by their hydrogen bonds. The reason why the clathrate hydrate of $CO_2$ was produced under the room temperature and atmosphere is as follows ; the $Zn^{2+}$, which is the helper species having the function of the template effect, has fixed the reasonable geometry among three sulfonate groups of each benzimidazolyl in **L1** to produce the hydrogen-bonded framework. The conformation among three zinc-bound benzimidazolyl moieties was given by the molecular structure of **L2**–zinc complex,[8,9,12] which was characterized by X-ray crystallography.[13] This zinc-directing conformation may controll the geometry among three sulfonate groups in each benzimidazolyl moiety. Since the intramolecular O···O distance 2.4–2.6 Å[14] of sulfonate group is similar to OH···O distance of hydrogen-bond between water molecules in water, some edges of hydrogen-bonding cages of water molecules can be replaced by O atoms of each sulfonate group as acceptor of hydrogen atoms of $H_2O$: the IR peaks associated with * at around 1120 $cm^{-1}$ (Figure 3(d)) showed the evidence for hydrogen-bonded -$SO_3^-$ groups in the framework of the clathrate hydrate of $CO_2$. Thus, $Zn^{2+}$ was a helper species to keep suitable geometry among the three -$SO_3^-$ and the zinc complex with **L1** played a role of the template for the formation of cages by hydrogen-bonds at room temperature and atmosphere. The sulfonate groups assisted the growth of hydrogen-bonded framework of water molecule cages at starting point.

The recovery of encapsulated $CO_2$ from the gel was much more efficient than the case of saturated solution of $CO_2$(aq) and $HCO_3^-$(aq) . Because it is impossible to become less than the saturated concentration. The sulfonate-assisting clathrate hydrate of $CO_2$ may be applied to the effective recovery of $CO_2$ from the view of both environmental earth and utilization.

**References and Notes**

1 D. W. Davidson, in "Water, A Comprehensive Treatise," F. Franks Ed., Plenum Press, New York (1973).
2 F. Fleyfel and J. P. Devlin, *J. Phys. Chem.* **92**, 631 (1988).
3 J. A. Ripmeester, C. I. Rattcliffe, *Energy Fuels*, **12**, 197 (1998).
4 E. D. Sloan, Jr., "Clathrate hydrates of natural gases," Marcel Dekker, New York (1998).
5 W. J. North, V. R. Blackwell, and J. J. Morgan, *Environ. Sci. Technol.*, **32**, 676 (1998).
6 Sodium 3-nitro-4-aminobenzenesulfonate was reduced to 3,4-diaminobenzenesulfonate hydrochloride by $SnCl_2$ at 70 °C. The mixture of 3,4-diaminobenzenesulfonate hydrochloride and nitrilotriacetic acid was refluxed in 4 M HCl for 4 days and the precipitate of $H_3$**L1** was filtered. The precipitate was dissolved by addition of NaOH solution and decolorlized by charcoal. Anal. Calcd for $H_3L1.4H_2O$: C, 40.05; H, 4.05; N, 13.62; S, 13.37%. Found: C, 40.34; H, 3.82; N, 13.57; S, 13.24%. $^1H$ NMR for Na salt ($D_2O$): δ 4.14 (s 6H $CH_2$), 7.47 (d 3H $C_6H_3$), 7.73 (d 3H $C_6H_3$), 8.13 (s 3H $C_6H_3$). $^{13}C$ NMR for Na salt ($D_2O$): δ 55.28 ($CH_2$) and 115.22, 117.12, 123.95, 137.67, 139.32, 141.23, 155.92 (7 carbon atoms of benzimidazole ring). The synthesis of the ligand $H_3$**L1** was carried out using water as solvent and no organic solvent from the concept of green chemistry (P. T. Anastas, J. C. Warner, "Green Chemistry," Oxford University Press, Oxford (1998)).
7 Solid $^{13}C$ NMR spectra for gel were measured with reference to $CH_2$ of glycine on a Bruker MSL 400 spectrometer at 24 °C.
8 K. Nakata, M. K. Uddin, K. Ogawa, and K. Ichikawa, *Chem. Lett.*, **1997**, 991.
9 K. Ichikawa, K. Nakata, M. M. Ibrahim, and S. Kawabata, *Advances in Chemical Conversions for Mitigating Carbon Dioxide Studies in Surface Science and Catalysis*, **114**, 309 (1998).
10 E. T. Strom and D. E. Woessner, *J. Am. Chem. Soc.*, **103**, 1255 (1981).
11 K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York (1986).
12 Anal. Calcd for [**L2**Zn($OH_2$)]·[**L2**ZnCl]·$(ClO_4)_3$·$4H_2O$ $CH_3COCH_3$: C, 42.91; H, 4.09; N, 13.74; Cl, 9.93%. Found: C, 42.74; H, 4.06; N, 13.78; Cl, 10.03%.
13 The compound [**L2**Zn($OH_2$)]·[**L2**ZnCl]$(ClO_4)_3$.$12H_2O$ was crystallized from acetone–$H_2O$ (v/v 20:1) solution containing [**L2**Zn($OH_2$)]$(ClO_4)_2$ and [**L2**ZnCl]$ClO_4$. The zinc ion was coordinated by three benzimidazolyl groups and its apical position was occupied by $H_2O$ or $Cl^-$ with an equal probability. Crystal Data: $M$ = 756.86, 0.30 × 0.20 × 0.20 mm. hexagonal, space group $P6_3/m$, $a$ = 14.552(6), $c$ = 21.815(4) Å, $U$ = 40001 Å$^3$, $Z$ = 4, $Dc$ = 1.256 g $cm^{-3}$, F(000) = 1564.00, m(MoKα) = 8.05 $cm^{-1}$. Data were collected on Rigaku RAXIS IV imaging plate diffractometer using graphite monochromated Mo Kα radiation at 23 ± 1 °C. 2148 reflection. 1509 observed [$I > 3\sigma I$]. The structure was solved by direct method[15] and expanded using Fourier techniques to $R$ = 0.061. $R$w = 0.082. rmax, min = 0.55, –0.43 eÅ$^3$. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.
14 A. F. Wells, "Structual Inorganic Chemistry," 4th ed. Clarendon Press, Oxford (1975).
15 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, AGuagliardi, and G. Polidori, *J. Appl. Cryst.*, **27**, 435 (1994).