Peculiarities of Methane Clathrate Hydrate Formation and Solid-State Deformation, Including Possible Superheating of Water Ice

Laura A. Stern,* Stephen H. Kirby, William B. Durham

Slow, constant-volume heating of water ice plus methane gas mixtures forms methane clathrate hydrate by a progressive reaction that occurs at the nascent ice/liquid water interface. As this reaction proceeds, the rate of melting of metastable water ice may be suppressed to allow short-lived superheating of ice to at least 276 kelvin. Plastic flow properties measured on clathrate test specimens are significantly different from those of water ice; under nonhydrostatic stress, methane clathrate undergoes extensive strain hardening and a process of solid-state disproportionation or exsolution at conditions well within its conventional hydrostatic stability field.

Gas hydrates, also called clathrate hydrates, are nonstoichiometric compounds with structures consisting of a network of $\text{H}_2\text{O}$ molecules hydrogen-bonded together like ice and encaging molecules of small-diameter gases. Common natural gas hydrates may have either of two crystal structures, and methane hydrate, $\text{CH}_4\cdot5.75\text{H}_2\text{O}$ (ideally), is a structure I hydrate constructed from $46\text{H}_2\text{O}$ molecules with eight cavities available for $\text{CH}_4$ gas molecules. In addition to its possible occurrence on the icy moons of the outer solar system at Saturn and beyond (I), methane clathrate occurs on Earth in a variety of geologic settings where $\text{CH}_4$ and $\text{H}_2\text{O}$ are in chemical contact at low temperature (T) and elevated pressure (P), and possibly harbors the largest untapped reservoir of natural gas on Earth (2, 3). Although discovery of extensive clathrate reservoirs in sediments underlying permafrost regions, deep-oceanic environments, and continental margins and shelves has stimulated recent interest in their formation and recoveneability (4), many basic physical properties of methane clathrate are poorly known or unmeasured. We have developed a method for fabricating pure aggregates of methane clathrate in quantities suitable for materials testing and have documented anomalous behavior in the formation, stability, and rheology of this compound at elevated P (5).

Our objective was to synthesize large-volume, low-porosity, cohesive polycrystalline clathrate aggregates with a uniform fine grain size and random crystallographic grain orientation. This technique differed from those of previous studies (6), most of which involved dynamic conditions of rocking, rotation, or continuous agitation of reaction mixtures, resulting in loose or very porous granular aggregates or strongly textured material unsuitable for physical property measurements. We produced our samples by the reaction $\text{CH}_4(g) + 6\text{H}_2\text{O}(s\rightarrow l) \rightarrow \text{CH}_4\cdot6\text{H}_2\text{O}(s)$, by the mixing and subsequent slow, regulated heating of sieved, granular $\text{H}_2\text{O}$ ice and cold, pressurized $\text{CH}_4$ gas in an approximately constant-volume system.

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*To whom correspondence should be addressed.

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**Fig. 1.** Phase diagram for the $\text{CH}_4$-$\text{H}_2\text{O}$ system. Shaded region shows field of methane clathrate stability. At low pressures or high temperatures, clathrate dissociates to $\text{H}_2\text{O}$ plus $\text{CH}_4$ gas. The metastable extension of the $\text{H}_2\text{O}$ melting curve is delineated by the gray curve. Dotted lines trace the sample fabrication reaction path.
reaction vessel (7) (Figs. 1 and 2). The initial CH₄ gas P inside the sample vessel was chosen to fill the porosity between the ice grains at a molar ratio of CH₄ to H₂O (seed ice) in the sample vessel in excess of that required for complete reaction (8, 9).

CH₄ P increases almost linearly with T up to 271.5 K with a slope governed primarily by the equilibrium thermal expansion of free CH₄ in the reservoir and sample reaction vessel (Fig. 3A). Initial deviation from this linear relation occurred just above the melting T of H₂O ice, 271.5 K at 27.3 MPa, marking the onset of reaction (Fig. 3A, point A) (10). As time proceeds, the rate of P increase slows as the clathrate-forming reaction consumes much of the vapor phase, producing a measurable offset from the initially linear path. The extent of reaction was determined by this deflection of the P-T slope, and complete reaction produced a P drop (ΔP) of 1.8 ± 0.1 MPa (11). The rate of reaction decreased after reaching about 0.5 ΔP, and the final reaction was most readily achieved by continued heating and self-pressurization of the system to 288 K and 29.4 ± 0.2 MPa (Fig. 3A, point E). These peak conditions were attained over an interval of 7 to 8 hours after the sample initially crossed 271.5 K isotherm (Fig. 3A, inset), placing the sample near clathrate dissociation conditions and well above the metastable extension of the H₂O melting curve (Fig. 1). After complete reaction, samples were cooled to 77 K while venting unreacted CH₄. The resulting samples were shown by x-ray diffraction (XRD) measurements to be pure methane clathrate with no more than trace amounts of H₂O ice (<3%) (Fig. 4). That virtually all the H₂O reacted to form clathrate was also consistent with the calculated molar volume reduction of the reaction (11) and with the lack of a measurable P-T anomaly associated with freezing of unreacted liquid H₂O (Fig. 3A, cooling path). Measurements of the mass uptake of CH₄ in fully reacted samples were consistent with complete reaction of the original H₂O to form clathrate of composition near CH₄·6.1H₂O (±0.1H₂O), which is the expected equilibrium stoichiometry for this compound at 25 to 30 MPa CH₄ P (11–13). The resulting samples were translucent, white, cohesive aggregates with uniformly fine, equant grains of 200 to 350 μm. All 15 samples produced under these conditions displayed consistent and reproducible run history curves, CH₄ uptake measurements, XRD patterns, and physical appearances. The fully reacted clathrate samples occupy the same cylindrical volume as the starting seed ice, and samples contain 28 to 30% porosity after full reaction (11). This porosity was easily eliminated by externally pressurizing sealed samples while venting the pore space gas, as discussed below.

Curiously, fabrication histories of fully reacted clathrate samples showed no P-T discontinuities associated with bulk melting of the H₂O ice, even though full reaction to form clathrate required many hours at temperatures well above the H₂O melting curve (14). The positive slope of the P-T curve within a few degrees above 271.5 K showed that there was not immediate and complete melting of the ice as it warmed above its liquidus, and the slope of the curve is steeper than would be predicted if all the melt reacted immediately with methane to form clathrate.

This conclusion was verified by control experiments in which neon (Ne), a nonclathrate-forming gas, was used in place of CH₄ under otherwise identical experimental conditions (15). The results (Fig. 3B) confirmed that rapid and complete melting and refreezing of H₂O ice at its melting point occurred in our apparatus when ice was not in the presence of CH₄, and that the associated P-T melting anomalies are easily detectable. The rapid P drop accompanying ice melting (Fig. 3B) was spread out over about 3.5 K as a result of T gradients in the reaction vessel. The T measured by the sample thermocouple lagged the rising T in the surrounding alcohol bath during the P drop (Fig. 3B, inset), a phenomenon that we attribute to the absorption of heat by the endothermic melting of ice. In comparison, the CH₄ runs displayed no such thermal anomalies between sample and bath, indicating that rapid, extensive melting did not occur (16). A P-T discontinuity accompanied refreezing during the cooling phase of the Ne runs, and no net P offset was recorded after returning to the starting conditions (Fig. 3B). Visual inspection and XRD identification of a quenched sample from a Ne experiment showed that it consisted of a clear cylinder of H₂O ice in the bottom half of the mold. The loosely fitting top disk sank to the base of the mold, also indicating full melting of the seed ice. In contrast, fully reacted methane clathrate samples have uniformly granular textures and no displacement of top disks. The Ne control experiments thus demonstrate that all the indicators of equilibrium ice melting expected in our apparatus were observed when a nonclathrate-forming gas was used in the place of CH₄.
Three partial-reaction experiments were then conducted on samples of CH$_4$ + ice, in which the samples were quenched under pressure at different points along the full reaction curve and subsequently weighed and x-rayed to determine clathrate content as a function of $\Delta P$. (Fig. 3A, squares B, C, and D). The sample quenched at 0.6 $\Delta P$, (C) contained $55 \pm 5\%$ clathrate, and the sample quenched at 0.8 $\Delta P$, (D) contained $78 \pm 5\%$ clathrate. The third sample was taken to 0.4 $\Delta P$, (B) and then slowly cooled to 250 K before quenching. That sample showed a measurable P-T anomaly upon cooling, indicating that some macroscopic melting had occurred. This result was confirmed by XRD and weight measurements, which showed that the 0.4 $\Delta P$, sample contained approximately $28 \pm 5\%$ clathrate, rather than the predicted 40% if no melt were present. These results suggest that during the early stages of reaction up to about 0.5 $\Delta P$, the slow rate of seed ice melting still "outpaces" clathrate formation. After this period, the rate of clathrate formation essentially keeps pace with incipient melting for the remainder of the 8 hours needed for complete reaction under these conditions.

By calculating a hypothetical P-T path for melting of the seed ice in the presence of CH$_4$ gas (17), we show that complete melting of ice, with no clathrate formation, would produce a measurable P reduction equivalent to 0.26 $\Delta P$, (Fig. 3A, gray dotted curve). We then calculated the predicted P deflection of each partial reaction run for clathrate reaction assuming no melting of unreacted ice, compared to that predicted for complete melting of all residual, unreacted ice (Fig. 3A). The deviation of the observed P-T path of the experiments from either the ice-melting curve or the calculated deflections for complete melting of unreacted ice shows that such melting did not occur upon crossing the ice liquidus or up to at least 276 K. Melting may not have been completed until the clathrate reaction was completed near 289 K.

The apparent suppression of the rate of macroscopic ice melting during methane clathrate synthesis raises several questions: Why is complete clathrate reaction achieved only after many hours at temperatures well above the H$_2$O ice melting point, and why is there no evidence for extensive melting of unreacted seed ice during this time? These questions can be partially answered by considering kinetic parameters such as the induction period, during which hydrate formation is negligible and at the end of which the reaction proceeds at appreciable rates. The induction period needed for methane clathrate formation may be related to the intermediate diameter of the CH$_4$ molecule with respect to that needed to stabilize either the clathrate structure I or II cavity size, and the consequent retarded formation of critical nuclei for hydrate growth (2). A second factor influencing reaction kinetics is the chemical communication of CH$_4$ with fresh H$_2$O ice surfaces. For hydrate formation from either solid or liquid H$_2$O, the formation rate greatly diminishes once a surface layer of hydrate has formed. Vigorous shaking or stirring is needed to renew CH$_4$ access to the water or ice surfaces to aid the formation process (18).

Hydrate growth rates under static conditions were measured by Hwang et al. (9), in which methane clathrate was grown on disks of melting ice at constant temperatures. Two stages of hydrate formation were observed: an initial "nucleation" period during which the formation rate increased with time, followed by a "growth" period during which the formation rate decayed with time until no more ice remained on the disks. They showed that growth rates were determined by the rate of supply of the hydrate-forming species to the growth surface, as well as the rate of removal of the exothermic heat of formation from the surface (19). The onset of ice melting along exposed surfaces promoted clathrate formation by providing both a "template" for the formation of hydrates and a heat sink for absorbing the heat of formation during clathrate growth. Our observations generally agree with these interpretations of Hwang et al. (9). We further conclude from sample textures and run records that the

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**Fig. 3. (A) Pressure-temperature (P-T) history of sample fabrication conditions promoting the clathrate-forming reaction CH$_4$ (g) + H$_2$O (ice) $\rightarrow$ CH$_4$·6H$_2$O. Reaction initiates just above the H$_2$O solids but slows substantially after 50%, perhaps as a result of "armoring" effect (see text). Full reaction is achieved by steadily increasing T and is accompanied by a 1.8-MPa pressure reduction ($\Delta P$). Persistence of metastable (superheated) ice is inferred by the lack of a P-T discontinuity in the reaction path upon crossing the ice melting curve at A. In comparison, the predicted P-T path for full melting of all seed ice with no clathrate formation is shown by the gray dotted curve. Partial-reaction experiments (open squares) were quenched after reaching the specific fractions of $\Delta P$ $\rightarrow$ 0 (A), 0.4 (B), 0.6 (C), 0.8 (D), and 1.0 (E)—contained 0, 28, 55, 78, and 100% (±5%) methane clathrate, respectively. Triangles and inverted triangles show the calculated positions associated with no melting and full melting, respectively, of all unreacted ice in each partially reacted sample. That the observed curve does not pass through these positions indicates that whereas some melt accumulates during reaction, complete melting of all unreacted ice is not occurring. (Inset) Temperature-time (T-t) profile shows that 7 to 8 hours are required for full reaction from A to E at these P-T conditions. (B) P-T record of control experiment with Ne gas + H$_2$O ice demonstrates that full melting and refreezing of H$_2$O ice occurs near its solidus when in the presence of nonhydrate-forming gas. (Inset) Detail of T-t History of Ne (g) + H$_2$O ice in the region of ice melting, showing the lag of the sample T (open circles) compared with the bath T (gray trace) associated with the absorption of heat by the endothermic melting of ice (15). No such effect is displayed by the thermal history of the methane clathrate run, also shown (clathrate sample T is black trace, bath T is adjacent gray line).**
superficially hydrate enveloping each seed ice grain not only rate-limits reaction in the grain interiors, but may also effectively "armor" the grain from nucleating melt and consequently suppress the rate of melting of ice grains. Once such a rind of hydrate has encased an ice grain, the most likely process of continued clathrate formation involves solid-state diffusion of CH₄ gas to the ice core (20).

The slope of the P-T path during clathrate synthesis experiments does not change abruptly upon crossing the ice melting curve (Fig. 3A), and there is a period of several tens of minutes during which little clathrate formation or ice melting appears. These results suggest that melting of the ice grains may be inhibited before the growth of a substantial hydrate layer (21). It can be argued that melting should not occur because the only equilibrium phases are methane gas and clathrate (Fig. 1), but over the 8-hour duration of reaction, it is reasonable to assume that equilibrium conditions did not prevail within hydrate-encased grains because of insufficient access of CH₄ to grain interiors. We would expect, therefore, to see evidence of bulk melting as the grain interiors melt before complete reaction. Because we see little or no evidence for either melting or clathrate formation early in the experiment above the ice melting point, we conclude that the armoring effect serves mainly to perpetuate the inhibition of ice melting and its metastable persistence (22).

Although the superheating of ice under clathrate-forming conditions seems implausible, we are unable to find a satisfactory alternative explanation for our observations (23). One possibility is that early-forming clathrate encased and sealed the ice grains and prevented pressure reductions associated with ice melting inside them from communicating with the CH₄ gas occupying the porosity and, in turn, with our gas pressure measurement system. This explanation seems unlikely because the departure of the P-T path from that expected for ice melting is prominent at temperatures just above the onset of reaction (Fig. 3A) and would require that strong clathrate pressure seals form around the ice grains during initial reaction, when the clathrate layer would be thin and presumably weak. Moreover, the hydrate shell would need to have nearly zero thermal conductance because no thermal lag associated with the absorption of heat by endothermic melting was observed during heating above 271.5 K (Fig. 3B, inset). We have not, however, verified the existence of such superheated ice by measuring or experimenting with its physical property characteristics.

The strengths of seven methane clathrate specimens were subsequently measured in constant-strain rate compression tests in a triaxial gas deformation apparatus, with N₂ or He gas as the confining medium (24, 25). The thin, soft jackets of indium in which the samples were grown served to exclude the pressure medium and were later used for examination of deformation microstructures replicated from the outer sample surface. Before deformation, clathrate samples were hydrostatically pressurized and compacted in the apparatus at 170 K (26). One sample (366, Table 1) was quenched after compaction and examined in its undeformed state. Volumetric measurements showed that essentially all porosity was eliminated and that a cylindrical sample shape was maintained with only minor distortion. XRD analysis revealed the presence of a small amount of H₂O ice in the sample, estimated at 7 ± 2 volume %. This ice is likely produced by solid-state disproportionation of clathrate, because increasing P changes clathrate stoichiometry from CH₄·6H₂O to CH₄·5H₂O (12). Such a pressure-induced unmixing process would precipitate the approximate volume fraction of ice detected in the x-ray patterns.

Strength measurements were then performed at conditions ranging from 140 to 200 K, 50 to 100 MPa, and ε = 3.5 × 10⁻⁴ to 3.5 × 10⁻⁶ s⁻¹ (Table 1 and Fig. 5). Test results revealed that methane clathrate has a measurably different steady-state strength than H₂O ice, and that the strength of

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**Table 1.** Mechanical test conditions and results. Pₐ, confining pressure with N₂ or He gas medium; εₛ, total strain; σₛ, yield strength; and σₛₚ, steady-state strength.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Step</th>
<th>T (K)</th>
<th>Pₐ (MPa)</th>
<th>εₛ (s⁻¹)</th>
<th>εₛ</th>
<th>σₛ (MPa)</th>
<th>σₛₚ (MPa)</th>
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<td>160</td>
<td>59</td>
<td>3.5 × 10⁻⁴</td>
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<td>59</td>
<td>3.5 × 10⁻⁶</td>
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<td>60</td>
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<td>160</td>
<td>59</td>
<td>3.5 × 10⁻⁴</td>
<td>0.160</td>
<td>100</td>
<td>-</td>
<td>Brittle failure; ~25% ice post-deformation*</td>
</tr>
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<td>50</td>
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<td>71</td>
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<td>Failure, multiple events</td>
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<td>50</td>
<td>3.5 × 10⁻⁴</td>
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<td>-</td>
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<td>168</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Pressurization and compaction only; 5 to 10% H₂O ice after compaction</td>
</tr>
<tr>
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<td>185</td>
<td>100</td>
<td>3.5 × 10⁻⁵</td>
<td>0.138</td>
<td>-</td>
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<td>100</td>
<td>3.5 × 10⁻⁴</td>
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<td>96</td>
<td>90</td>
<td>~30% H₂O ice post-deformation</td>
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<td>168</td>
<td>100</td>
<td>3.5 × 10⁻⁵</td>
<td>0.185</td>
<td>-</td>
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<td>Strain hardening; 25% ice</td>
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<td>-</td>
<td>100</td>
<td>Identical run as 368 with gas collection; system emplaced; no evolved CH₄ gas‡</td>
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<tr>
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<td>0.230</td>
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<td>80</td>
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*All samples were analyzed pre- and post-deformation by powder XRD. †Samples 367, 368, 369, and 370 all underwent identical pressurization and compaction as 366 before testing. ‡Runs 369 and 370 had a gas collection system attached throughout testing to detect evolved CH₄ gas. |
clathrate appears to be less T-sensitive than ice (Fig. 5A). Moreover, the characteristics of transient deformation were markedly different (Fig. 5B). Whereas \( H_2O \) ice typically exhibits a strength maximum before leveling off to steady flow stress, usually within the first 5 to 10% of strain, methane clathrate exhibits monotonic strain hardening drawn out over the first 15% or more of strain.

Comparison of pre- and postdeformation XRD analyses shows that the samples underwent further structural changes while deforming within the clathrate stability field. XRD peak intensities of the deformed samples suggest that 25 ± 10 volume % ice precipitated during deformation, compared with <3% ice in the X-ray patterns of as-grown clathrate (Fig. 4) and 7% ice in the pressurized-only sample. It is possible, however, that heterogeneous ice precipitation or deformation-enhanced textural and grain size changes in the precipitated ice increased the apparent ice peak intensities (27). No peaks were observed in postdeformation X-ray patterns to indicate growth of any other phase besides ice and structure I methane clathrate. After first detecting this apparent solid-state disproportionation of the clathrate, we attached a gas collection system to the vent line for two of the runs to observe and collect possible \( CH_4 \) gas evolving during deformation. The only gas that vented, however, was that squeezed from the pores during initial pressurization before deformation. No gas evolved from the system during any portion of deformation testing or subsequent unloading. Although collapse of the clathrate structure could occur if as-molded material were strongly nonstoichiometric and hence contained significant gas molecule vacancies, this is unlikely because we measured full uptake of \( CH_4 \) gas into the as-molded material. We therefore conclude that at the deformation conditions of this study, methane clathrate apparently undergoes a form of stress-enhanced exsolution or precipitation within its nominal P-T field of thermodynamic stability.

Over the time scales of our experiments, the \( CH_4\cdot H_2O \) system exhibits several peculiar features, including the metastability of ice + \( CH_4 \) mixtures both below and above the \( H_2O \) ice liquidus line and the prominent solid-state precipitation of ice from deformed polycrystalline methane clathrate within the nominal stability field of the clathrate. Although the time scales of clathrate growth and ice precipitation probably differ from those of other clathrate environments, the peculiarities we observed may have relevance to the growth and stability of methane clathrate in terrestrial permafrost and marine sediments and in the outer solar system. We describe here a simple method for growing dense, polycrystalline methane clathrate suitable for material testing, a development that should aid subsequent investigations of its growth and physical properties.

REFERENCES AND NOTES


4. Because hydrates concentrate \( CH_4 \) by a factor of 165 with respect to 

\[ \begin{align*}
\text{Fig. 5. (A) Variation of strength with temperature for methane clathrate, showing measurably different strength than } H_2O \text{ ice. } H_2O \text{ ice flow law relations are from } (25). \text{ Clathrate data points with arrows indicate faulting behavior. (B) Stress-strain curves of deformed methane clathrate (run } 368) \text{ showing systematic strain hardening, compared with the sharp yielding, strain softening, and steady-state flow of } \text{“standard” polycrystalline } H_2O \text{ ice.}
\end{align*} \]
The reaction of metal complexes with dioxygen \( \text{O}_2 \) generally proceeds in 1:1, 2:1, or 4:1 (metal:O\(_2\)) stoichiometry. A discrete, structurally characterized 3:1 product is presented. This mixed-valence trinuclear copper cluster, which contains copper in the highly oxidized trivalent oxidation state, exhibits \( \text{O}_2 \) bond scission and intriguing structural, spectroscopic, and redox properties. The relevance of this synthetic complex to \( \text{O}_2 \) at the trinuclear active sites of multicopper oxidases is discussed.

The copper-mediated activation of \( \text{O}_2 \) plays a vital role in biological and synthetic oxidative catalysis (1–4). Recent investigations of \( \text{O}_2 \) reduction with Cu(I) complexes have shown that Cu is remarkably versatile regarding both the degree of reduction and the coordination mode of the reduced \( \text{O}_2 \) species. Reductions to superoxide (2, 5), peroxide (2, 3, 6, 7), and water (2) involving one, two, and four electrons \( (e^-) \), respectively, have been documented, in which each Cu(I) supplies one electron. The variety of Cu sites found in natural enzymes that bind or activate \( \text{O}_2 \) reflects this versatility. The Cu enzymes responsible for the \( 4e^- \) reduction of \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \)—laccase, ceruloplasmin, and ascorbate oxidase—each contain a trinuclear Cu active site (8–12) with an additional mononuclear “blue” Cu site 12 A distant (9). The known binuclear Cu proteins hemocyanin and tyrosinase (3, 6) bind \( \text{O}_2 \) through \( 2e^- \) reduction to \( \text{O}_2^{-2} \), but the fully reduced trinuclear site is the minimal structural subunit required for biological \( \text{O}_2 \) bond cleavage and reduction to \( \text{H}_2\text{O}_2 \) (8, 13).

A self-assembly approach to the synthesis of a bi- or trinuclear Cu-O\(_2\) cluster from monomeric Cu(I) complexes and \( \text{O}_2 \) assumes facile assembly and thermodynamic stability of the resulting product under the reaction conditions. Accordingly, the use of simple ligands is an appropriate strategy. A number of monomeric 1:1 Cu(I)N-peralkylated-diamine complexes were examined by manometry for 3:1 CuO\(_2\) reactivity. Structural and spectroscopic studies of the oxidation of one such Cu(I) complex (1) demonstrate the formation of a trinuclear intermediate (2) in the Cu(I)-mediated reduction of \( \text{O}_2 \) whose 3:1 stoichiometry is unprecedented not only in the case of Cu but among all discrete metal-O\(_2\) reactions (Scheme 1, \( \text{Me} = \text{methyl} \)). Its structural, spectroscopic, and redox properties indicate that, in the process of \( \text{O}_2 \) bond cleavage, the three Cu(I) sites in 2 are oxidized by a total of four electrons, forming a mixed-valence cluster with bridging oxide ligands that stabilize one of the Cu sites in its normally inaccessible state, then advanced just sufficiently to tightly compress the sample in order to compact it with minimal plastic deformation. Six of the samples were compacted by means of an internal vent line to eliminate the pore-space gas, and two of the samples were compacted without the venting capability. The two nonvented samples (281 and 282; Table 1) showed equally large fractions of ice in their post-deformation x-ray patterns as the vented samples.

27. Indium jacket replicates of deformed sample surfaces showed evidence of heterogeneous ice precipitation. Areas with evolved ice appear on jackets of all deformed samples as discrete patches with noticeably finer grain size than the surrounding clathrate.

28. We thank B. Kamb, J. Kargel, K. Kvenvolden, and W. McKeegan for critically reviewing the manuscript and for helpful discussions. This work was supported under NASA order W-18,927 and was performed in part under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405ENG-48.

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A Trinuclear Intermediate in the Copper-Mediated Reduction of O\(_2\):
Four Electrons from Three Copper

Adam P. Cole, David E. Root, Pulakesh Mukherjee, Edward J. Solomon, T. D. P. Stack*