Single-Crystal Clathrates

Single-Crystal Adsorbents: A New Observation Field for Light Aggregates**

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Determination of the properties of low-dimensional aggregates using gas clathrate compounds has interested researchers for the past 50 years.[1] The most ideal system for investigating the physicochemical properties of atomic/molecular aggregates would be single-crystal systems due to their extremely high degree of integrity and regularity. Such systems would contribute to a wide range of both pure and applied science; from basic objects to device applications. A single-crystal adsorbent is one of the goals that may be reached through the design of porous solids, and has been the subject of extensive study in recent years for its extended inorganic framework.[2] The ideal system should provide the long-awaited method for studying physicochemical properties of specific aggregate structures produced within the inner surface of the host solid. In fact, all previous observations were only characterized in powdered samples.[1,3] Here, we present a new convenient procedure for the inclusion of a light gas into a single-crystalline state by placing a crystal adsorbent in a gaseous guest atmosphere, which is efficient for ascertaining exact molecular/atomic structures with high resolution for included light aggregates such as oxygen.

We previously reported the empty crystal host of rhodium(II) benzoate pyrazine, $[Rh^{II}_2(bza)_4(pyz)]_n$ (**1**) (Figure 1),[4] which generated a CO_2 inclusion crystal by transition from a closed α phase to an open β phase through the process of smooth physisorption; the CO_2 guests are adsorbed into the generated narrow channels of the β lattice.[5] However, serious difficulties remain for other light-gas guests, such as oxygen, nitrogen, and especially hydrogen or helium due to their weak physisorbing capabilities. It was shown for crystal adsorbent **1** that the α–β phase transition obeys the Clausius–Clapeyron equation in terms of the temperature and pressure of the CO_2 gas. This correlation indicates the possibility that a phase transition could be induced by pressurizing the various gaseous guests (pressure swing), which produces inclusion crystals at low temperature, sufficient to crystallize the included guests (temperature swing). We attempted to construct low-dimensional aggregates inside a single crystal of **1** by the swinging method using oxygen gas; the specific cluster is likely to exhibit quantum effects through the magnetic interaction of unpaired electrons.[6]

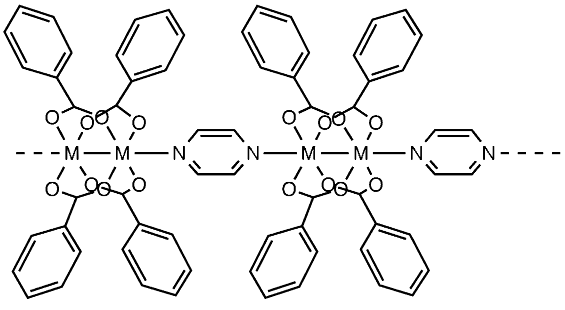

Figure 1. Infinite chain component of **1** ($M = Rh^{II}$).

X-ray diffraction measurements were conducted at temperatures of 298, 90, and 10 K under an oxygen atmosphere, which was prepared by sealing a glass capillary containing a single crystal of **1** and liquid oxygen (2 mm liquid in a 18 mm long capillary) in a liquid nitrogen bath. After the temperature was increased to room temperature, the pressure of the oxygen gas in the capillary was estimated to be ≈9 MPa. Surprisingly, the crystal remained intact and transparent under the conditions of high pressure and low temperature (Figure 2).

Single-crystal X-ray diffraction analysis demonstrated that the crystal of **1** had already undergone a phase transition from an α to a β lattice at room temperature,[7] which has one-dimensional channels (see Figure 3a and b), while X-ray crystallography could not locate the oxygen molecules in the channels, probably due to the thermal motion of the adsorbed oxygen. These results show that a bulk phase transition is

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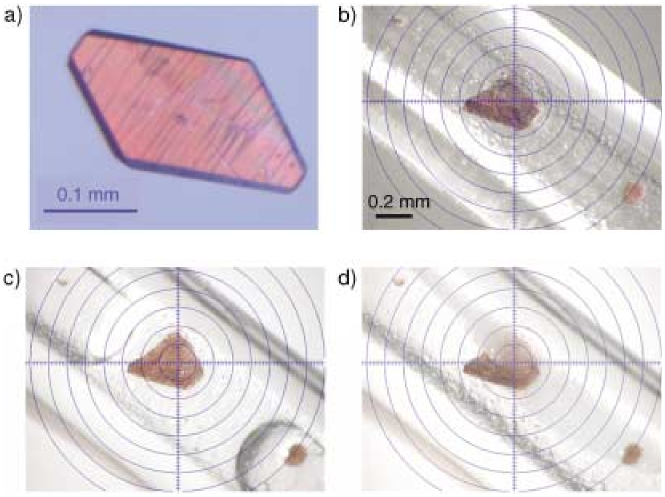

Figure 2. a) Photograph of a red single crystal of **1** under dry conditions; b–d) the same crystal placed in a thick-walled glass capillary and sealed under oxygen gas (≈ 9 MPa) at 298 K (b), 90 K (c), and 10 K (d). The crystal remained intact under high pressure and low temperature. Oxygen in the capillary was observed in different phases: in the gas phase at 298 K, in liquid–gas equilibrium at 90 K, and in the solid state at 10 K. Liquid oxygen and solid oxygen can be seen in (c) and (d), respectively.

enabled by the pressure swing in a considerably high temperature region for a light gaseous guest.[8] The crystal structure remains essentially unchanged, although the crystal cell parameters change slightly as the temperature decreases. On cooling, the oxygen inclusion crystal was determined to be $\mathbf{1}\cdot3(O_2)$ at 90 K (see Figure 3c).[9] Oxygen gas, which diffuses in the generated channels of the β lattice, crystallizes between 298 K and 90 K and expands the cell volume by 2.4%, which is probably caused by an increase of the adsorbed oxygen in the channel. It should be noted that the observed temperature of crystallization is much higher than the freezing point of 54.4 K for bulk oxygen under atmospheric pressure, while the oxygen outside the crystal was in the liquid phase (Figure 2c). In comparison, for the case with carbon dioxide, the cell parameters of inclusion crystal $\mathbf{1}\cdot3(O_2)$ are significantly different from those of $\mathbf{1}\cdot3(CO_2)$ determined at 93 K (triclinic, $P\bar{1}$, $a = 9.556(3)$, $b = 10.318(4)$, $c = 11.079(5)$ Å, $\alpha = 70.18(3)$, $\beta = 66.12(3)$, $\gamma = 63.02(3)°$, $V = 873.7(6)$ Å^3),[5] in which the cell volume of $\mathbf{1}\cdot3(O_2)$ is 3% less than that of $\mathbf{1}\cdot3(CO_2)$. These observations of the flexibility of the crystal lattice clearly show the adjustable nature of **1** for variable guest structures. In addition, a 1.8% contraction of the inclusion crystal at 10 K[10,11] from that at 90 K is observed, which is primarily due to diminished thermal vibration (see Figure 3d).

At 90 K, the included oxygen molecules are coherently aligned in a linear fashion. The intermolecular distances between molecule centers among the contacted neighbors are 3.55 and 4.24 Å, forming molecular oxygen chains along the one-dimensional channels. The chain structure is most likely regulated by the channel structure (see Figure 3e and g). The parallel oxygen chains are effectively separated by a distance of ≈ 1 nm, which can be regarded as the first example of a single-molecular-chain oxygen crystal within a host lattice. The O–O atomic separations in the oxygen molecules were found to be too short (1.001(14) Å and 0.958(14) Å), which was determined without any constraints. However, a remarkable feature is that the included oxygen structure was easily located without disorder at the considerably high temperature of 90 K, where the thermal motion is effectively suppressed by the cooperative stabilization of the confined guest oxygen and the adjustable host lattice. In fact, even at 50 K, an extremely strongly disordered structure was observed for bulk oxygen in the γ phase.[12] In contrast, the O–O atomic separations in the oxygen molecules became reasonable at 10 K (1.147(17) Å and

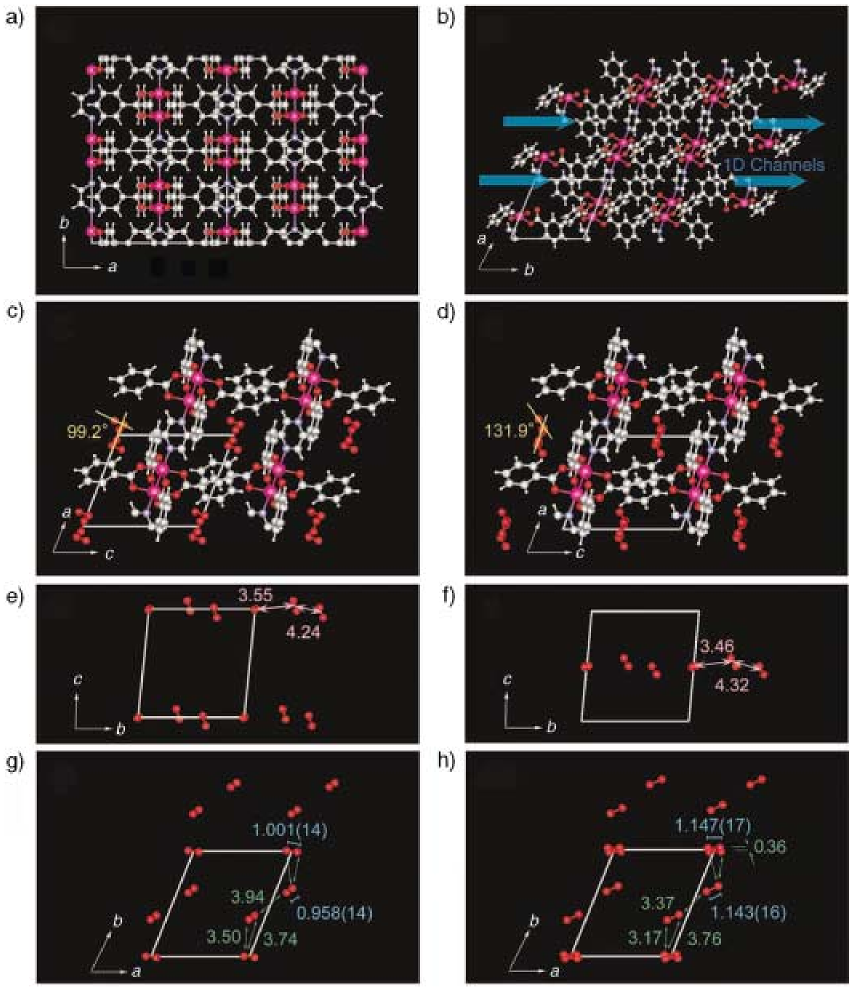

Figure 3. Crystal structure of **1** under various conditions: Pressure-swing transformation from a closed structure without gas (α lattice, *C*2/*m*, reported in ref. [5]) (a) to an open structure (β lattice, $P\bar{1}$) (b) under 9 MPa oxygen pressure at room temperature; views of an oxygen inclusion crystal viewed along the *b* axis at 90 K (c) and 10 K (d); molecular chains of oxygen molecules inside crystal **1** at 90 K (e, g) and 10 K (f, h) with selected distances [Å] and O-O⋯O-O torsion angles [°] (Rh magenta, O red, C and H gray, N blue).

1.143(16) Å). These values represent the first exact bond lengths of molecular oxygen by single-crystal X-ray analysis, while the O–O bond length in α-phase solid oxygen was evaluated to be approximately between 1.15 and 1.22 Å by powder X-ray diffraction analysis at 23 K.[13] The periodic arrangement and configuration of the oxygen atoms in the chain became more crowded at 10 K. The intermolecular distances became short at (3.46 Å) and long (4.32 Å), respectively (see Figure 3 f). The longer separation is accompanied by a short contact between neighboring oxygen atoms at 3.37 Å; the shorter distance is realized by a separation of 0.36(9) Å of the separated oxygen molecules by disorder along the *c* edge (see Figure 3 f and h). The transformation in the oxygen chain indicates that a phase transition occurs in 1D systems of oxygen in regions of low temperature. Thus, a 1D oxygen system will be expected to show its unknown phases with properties of interest because many phases of 3D solid oxygen (bulk), and for 2D (on the surface) have been known to be correlated with specific magnetic properties and conductivity.[14]

The present construction procedure is considered quite effective for light guests, which are difficult to condense, because this method requires a certain gas pressure and can crystallize guests at considerably high temperatures. Furthermore, this procedure has the potential for producing various crystals within the structure of the single-crystal adsorbent, and preferred adsorbates under the control of thermodynamic factors. The derivatives of rhodium(II) benzoate pyrazine replaced with a different metal ion and substituted ligands would produce the first family of specifically designed single-crystal adsorbents. Our investigations[15] and the results for other gas-inclusion crystals will appear elsewhere. The homogeneity, anisotropy, integrity, and transparency of single-crystal adsorbents contributes to the establishment of new techniques for realizing simultaneous measurements for various specific aggregates inside a crystal lattice with new phases. This would be particularly effective for observing specific quantum effects in many low-dimensional systems.

Experimental Section

All single-crystal X-ray analyses were performed on a Bruker Smart APEX CCD area diffractometer with a helium-flow temperature controller (Japan Thermal Eng. TC-10 KCP) using graphite-monochromated $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed at calculated positions and refined using a riding model. CCDC-220620–220624 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[7] Crystal data for **1** at 298 K in ≈ 9 MPa of oxygen gas: 770.35 g mol^{-1}, triclinic, $P\bar{1}$, $a = 9.474(8)$, $b = 10.222(13)$, $c = 10.715(13)$ Å, $\alpha = 72.09(2)$, $\beta = 64.933(13)$, $\gamma = 62.737(14)^\circ$, $V = 827.2(16)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.546$ Mg m^{-3}, $R_1 = 0.0994$ (0.2202), $wR_2 = 0.2248$ (0.2726) for 770 reflections with $I > 2\sigma(I)$ (for 1721 reflections (2908 total measured)), GOF (F^2) = 0.957, largest diff. peak (hole) = 1.193(−2.763) e Å^{-3}.

[8] The α–β phase transition was not observed for **1** when wrapped up in silicon grease (under gas cut-off conditions) under an oxygen pressure of ≈ 10 MPa. This shows that gas adsorption causes the crystal-phase transition. Crystal data for **1** at 298 K (10 MPa): 770.35 g mol^{-1}, monoclinic, $C2/m$, $a = 18.12(3)$, $b = 9.552(13)$, $c = 12.352(18)$ Å, $\beta = 128.52(2)^\circ$, $V = 1672(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.530$ Mg m^{-3}, $R_1 = 0.0859$ (0.1377), $wR_2 = 0.2152$ (0.2404) for 569 reflections with $I > 2\sigma(I)$ (for 944 reflections (2707 total measured)), GOF (F^2) = 1.073, largest diff. peak (hole) = 1.152(−1.246) e Å^{-3}.

[9] Crystal data for $\mathbf{1}\cdot 3(\mathrm{O_2})$ at 90 K: 866.36 g mol^{-1}, triclinic, $P\bar{1}$, $a = 9.573(3)$, $b = 10.381(3)$, $c = 10.597(3)$ Å, $\alpha = 74.165(5)$, $\beta = 64.346(6)$, $\gamma = 63.723(6)^\circ$, $V = 846.9(4)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.699$ Mg m^{-3}, $R_1 = 0.0560$ (0.0982), $wR_2 = 0.1045$ (0.1182) for 2629 reflections with $I > 2\sigma(I)$ (for 4182 reflections (6175 total measured)), GOF (F^2) = 0.936, largest diff. peak (hole) = 2.160(−1.614) e Å^{-3}.

[10] Crystal data for $\mathbf{1}\cdot 3(\mathrm{O_2})$ at 10 K: 866.36 g mol^{-1}, triclinic, $P\bar{1}$, $a = 9.571(3)$, $b = 10.288(3)$, $c = 10.531(3)$ Å, $\alpha = 74.379(6)$, $\beta = 64.127(5)$, $\gamma = 63.558(5)^\circ$, $V = 831.8(4)$ Å^3, $Z = 1$, $\rho_{\mathrm{calcd}} = 1.730$ Mg m^{-3}, $R_1 = 0.0682$ (0.1114), $wR_2 = 0.1503$ (0.1775) for 2735 reflections with $I > 2\sigma(I)$ (for 4063 reflections (5802 total measured)), GOF (F^2) = 0.986, largest diff. peak (hole) = 3.451(−1.905) e Å^{-3}.

[11] The crystal structure of **1** at 10 K in an inert oil (under gas cut-off conditions) was regarded as the same structure as that of **1** at 93 K (γ phase) in an inert oil reported in ref [5]. Crystal data for **1** in an inert oil at 10 K: 770.35 g mol^{-1}, monoclinic, $C2/c$, $a = 17.384(4)$, $b = 9.5754(19)$, $c = 19.522(4)$ Å, $\beta = 98.561(8)^\circ$, $V = 3213.4(12)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.592$ Mg m^{-3}, $R_1 = 0.0625$ (0.1036), $wR_2 = 0.1210$ (0.1441) for 2852 reflections with $I > 2\sigma(I)$ (for 4049 reflections (11742 total measured)), GOF (F^2) = 1.093, largest diff. peak (hole) = 1.109(−1.542) e Å^{-3}.

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