# Inclusion Formation between 1D Coordination Polymer Host and $CS_2$ through Vapor Adsorption

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The formation of $CS_2$ inclusion crystals through vapor adsorption was characterized to show that large $CS_2$ guests are tightly confined in the channel supported on the $\pi$ orbital of the conjugate planes of the channel surface: the manner of guest alignment is strongly influenced by the structures of the guest and channel.

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Many inclusion solids have been reported.[1–3] However, reports of the crystallographic determination of structures containing gas are rare.[4] Structural determination by single-crystal X-ray analysis would greatly advance understanding of the adsorption mechanisms of porous organometallic solids by the use of a highly stable single-crystal host during the gas adsorption process. Recently, we found one kind of single crystal host, $[M(II)_2(bza)_4(pyz)]_n$ (bza and pyz = benzoate and pyrazine, M = Rh(**1**)[5] and Cu[6]), which is suitable for the study of gas-containing structure through gas adsorption.[7,8] Although structural characterization of a gas inclusion crystal for $CO_2$ was achieved, a relatively large guest inclusion structure has not yet been determined that would indicate the influence of guest size on the inclusion structure. A large guest molecule tends to show low vapor pressure; the difficulty in diffusion inside micropores is due to its heavy molecular weight and large intermolecular interaction ability. In this study, we attempted to prepare a $CS_2$ inclusion crystal through vapor adsorption because its weak intermolecular interaction would be advantageous for inclusion formation. It has an abnormally low melting point of −111 °C under atmospheric pressure and a high vapor pressure of 298 Torr at 20 °C.

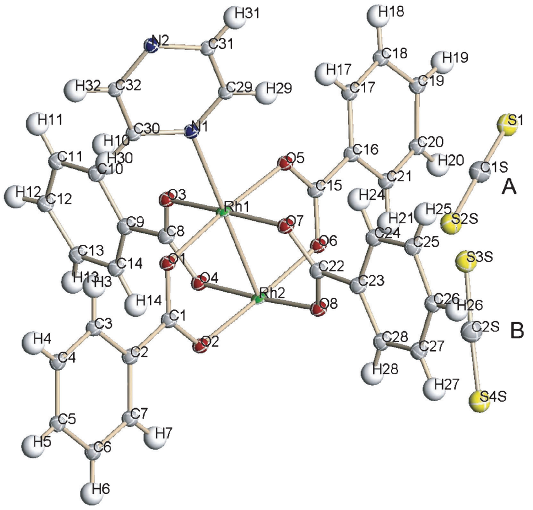

**Figure 1.** Thermal ellipsoid drawing of the chain structure at the 50% probability level with atom labeling scheme of $\mathbf{1}\cdot(CS_2)$. Torsion angles of benzene rings to carboxylate plane (°): O(3)–C(8)–C(9)–C(10), 6.26; O(4)–C(8)–C(9)–C(14), 10.95; O(7)–C(22)–C(23)–C(24), −23.66; O(8)–C(22)–C(23)–C(28), −19.79; O(1)–C(1)–C(2)–C(3), 3.25; O(2)–C(1)–C(2)–C(7), 2.41; O(5)–C(15)–C(16)–C(17), −1.04; O(6)–C(15)–C(16)–C(21), 0.94. (Two disordered $CS_2$ molecules were found in the occupancy ratio with 0.636 (**A**) and 0.364 (**B**))

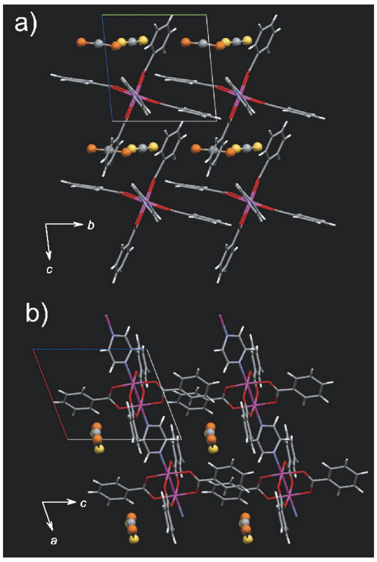

**Figure 2.** Packing views of crystal $\mathbf{1}\cdot(CS_2)$ down the *a* axis (**a**) and *b* axis (**b**). The adsorbed guests are represented using a ball-stick model. Elements are color-coded: rhodium (magenta), carbon (gray), hydrogen (white), nitrogen (blue), oxygen (red), and sulfur (orange or yellow). (Orange and yellow colored sulfur indicate the $CS_2$ with the occupancy of 0.636 (**A**) and 0.364 (**B**), respectively.)

The single crystals of **1** were prepared by the method previously reported.[5] X-ray diffraction measurement was conducted at 90 K in a glass capillary after exposure to $CS_2$ vapor at room temperature. Single crystal X-ray diffraction analysis demonstrated the generation of a crystal $\mathbf{1}\cdot(CS_2)$.[9] The determined crystal cell is similar to the $CO_2$ inclusion crystal 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$^3$).[8] In the refinement of the crystal structure of $\mathbf{1}\cdot(CS_2)$, the final structure was obtained with the space group of $P1$, which provided a plausible structure for accounting for the disordered structure of the included $CS_2$, although the $P\bar{1}$ space group was suggested by PLATON[10] to account for only the symmetry of the host lattice. The included $CS_2$ molecules were found in two positions with the occupancy of 0.636(8) and 0.364(8) for S(1s)–C(1s)–S(2s) (**A**) and S(3s)–C(2s)–S(4s) (**B**), respectively. (Figure 1) This structure strongly indicates that only one $CS_2$ molecule can occupy a channel period because of its large molecular size, (Figures 2 and 3) while that for a $CO_2$ inclusion crystal regularly contains three molecules in a channel period without disorder. Interestingly, the $CS_2$ molecules direct

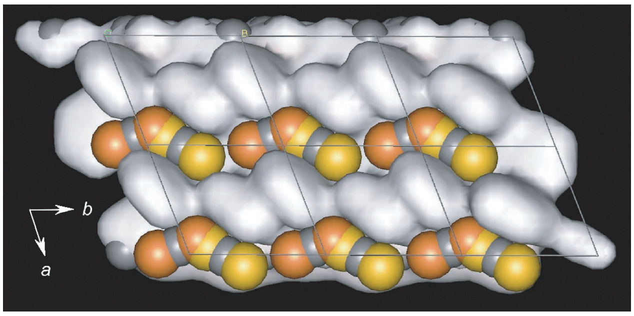

**Figure 3.** Surface view of the channels of **1** with adsorbed $CS_2$ in a space-filling model down the *c* axis. (Orange and yellow colored sulfur indicate the $CS_2$ with the occupancy of 0.636 (**A**) and 0.364 (**B**), respectively.)

their molecular axes along the channel direction, (Figures 2 and 3) while the included $CO_2$ molecules of $\mathbf{1}\cdot3(CO_2)$ were found in parallel for one molecule and perpendicular for two molecules, which were located around the observed **A** and **B** positions of $CS_2$, respectively. The resulting $CS_2$ alignment indicates that the large size of $CS_2$ is compelled into parallel alignment by channel size and geometry. Furthermore, the $P1$ lattice shows that the channel structure is slightly deformed by the steric effect of the included guest $CS_2$. The benzene rings in strong contact with $CS_2$ in position **B** are obviously tilted in 6.29°/10.95° and 19.79°/23.66° against the chain skeleton of the host lattice. (Figure 1) This indicates the regulating nature of the channel surface for the guest structure owing to the adjustable property enhanced by benzene tilting, because benzene tilting of only 9° was observed in the crystal of $\mathbf{1}\cdot3(CO_2)$.[8] The $CS_2$ molecules are captured by the $\pi$-orbital of the conjugate planes of the benzene rings and the C(carboxylate)–C(benzene) planes and secondarily by the H-bond from the benzene rings. (Figure 4)

It seems that the adsorbed $CS_2$, supported by the surrounding conjugated systems, causes a slight deformation of the flexible channel to cooperatively stabilize the inclusion crystal with a large size guest. The distinctly disordered structure strongly indicates the two minimum potential sites for the $CS_2$ guest in the crystal lattice of **1**, and the divided occupancies of the two guest positions are probably correlated with the difference in their potential depth.

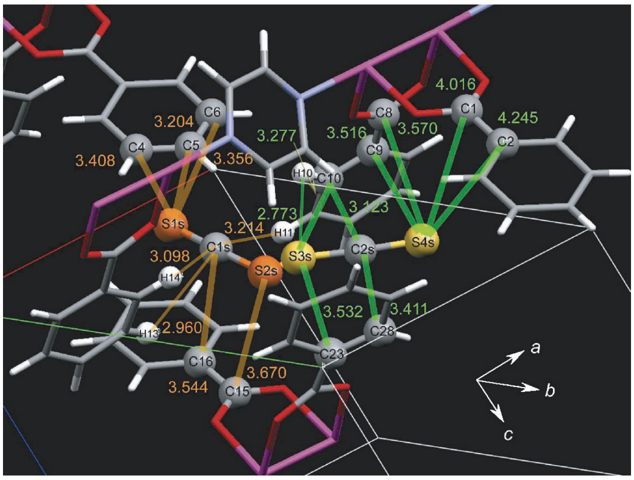

**Figure 4.** Environments of adsorbed $CS_2$ in the channels of **1** with short contact distances (Å) (orange lines for **A** and green lines for **B**).

Considering the tightly confined structure of the $CS_2$ inclusion crystal, the mechanism of inclusion formation is quite interesting. The determined static structure strongly indicates the difficulty encountered by diffusion of the $CS_2$ guests inside the channels. This suggests the necessity for considering the dynamic effect of the transferring guest rather than the static structure. Moreover, the inclusion crystal could not be formed by soaking in $CS_2$ liquid, which definitely shows the importance of the guest phase for inclusion formation and the necessity of a gaseous guest in the adsorption process of **1**.[11]

In conclusion, the effect of guest size was clearly evident in inclusion formation. The included $CS_2$ guests are supported by the $\pi$-orbital of the conjugated planes consisting of the channel surface as well as the adjustable deformation of the channel structure. Single crystal X-ray measurements for gas inclusion crystals can directly provide the necessary information for understanding the adsorbing method and the processes for the various guests.

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9 Single crystal X-ray diffraction data for all structures was measured on a Bruker SMART APEX CCD area (graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) with a nitrogen flow temperature controller. A well-formed single crystal **1** was sealed inside a 0.5-mm diameter glass capillary after exposure to $CS_2$ vapor at room temperature. The capillary was mounted and then carefully cooled in a cold nitrogen stream to 90 K. Crystal data for $\mathbf{1}\cdot(CS_2)$: $C_{33}H_{24}N_2O_8Rh_2S_2$, red plate, $0.18 \times 0.18 \times 0.08$ mm$^3$, 846.48 gmol$^{-1}$, triclinic, $P1$, $a = 9.5439(18)$, $b = 10.3152(19)$, $c = 10.548(2)$ Å, $\alpha = 74.866(4)°$, $\beta = 64.828(4)°$, $\gamma = 64.634(4)°$, $V = 845.3(3)$ Å$^3$, $Z = 1$, $D_{calcd} = 1.663$ Mgm$^{-3}$, $T = 90$ K; 4958 ($R_{int} = 0.0329$) unique reflections (6150 total measured). The structure was refined to $R1 = 0.0929(0.1200)$, $wR_2 = 0.2334(0.2738)$ for 3778 reflections with $I > 2\sigma(I)$) (for all data), goodness-of-fit on $F^2 = 1.115$, largest diff. peak (hole) = 4.744 [0.53 Å from Rh(2)] (−4.394 [0.51 Å from Rh(1)]) e Å$^{-3}$. Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares calculations on $F^2$ (SHELXL97). CCDC 225954.

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11 The crystal structure with soaking in $CS_2$ liquid for a week revealed a $C2/c$ crystal without any guests, which is the same crystal determined at 93 K under gas cut-off condition in Ref. 8.