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Guest Escape and Uptake in Nonporous Crystals of a Gold(I) Macrocycle

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Abstract: The nonporous gold(I) diphosphine complex $[Au_2(cis\text{-}dppe)_2](NO_3)_2$ [**1**, *cis*-dppe = *cis*-1,2-bis(diphenylphosphino)ethylene] is robust enough to trap guests, but at the same time, it is flexible enough to allow guest release without destruction of its crystal lattice. This nonporous gold(I) compound **1** is also efficient at capturing and releasing carbon dioxide in a controlled manner.

Porous materials, including clays and zeolites, have been used to trap and store gases for decades.[1] The porosity has been regarded as the basis for zeolitic behavior such as gas storage, catalysis, molecular recognition, and size-selective sorption.[2] Thus, it is not astonishing that the engineering of porous crystalline solids has become a highly attractive area of investigation.[3] Other materials, including organic molecular crystals and metal−organic frameworks (MOFs), have been created with larger and larger pores.[3] It was recently demonstrated that seemingly nonporous solid-state structures could behave as porous materials,[4] even though no large, discrete lattice voids linked by passages wide enough to allow molecules to migrate between cavities or open channels are present in these structures. It was concluded that dynamic cooperativity (concerted motion that preserves the integrity of the single crystal) between the structural units may transport a liquid or gaseous guest into the crystal even in the absence of traditional open channels.[4a] This dynamics of the host lattice is a highly synchronized process, and the neighboring molecules cooperate with one another both to relay the guest through the lattice and to maintain the integrity of the crystal.[4a] The small number of materials that are able to absorb and release small molecules despite their seemingly nonporous structures consist of crystals of calixarenes,[4] other cup-shaped molecules,[5] and metal complexes.[6] As part of our studies of gold(I) supramolecules exhibiting unusual structures and properties,[7] we have synthesized a complex that converts between nonporous structures via single-crystalline transformations, facilitating the transport of guest species through its lattice. We have also attempted to postulate a plausible mechanism for guest release and uptake through the lattice by considering the initial and final crystal structures. Furthermore, we show that the crystals trap atmospheric gas molecules despite the absence of large pores in the static solid-state structure.

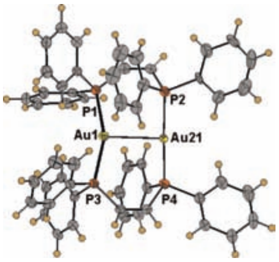

Figure 1. ORTEP view of the $[Au_2(cis\text{-}dppe)_2]^{2+}$ cation with thermal ellipsoids at the 50% probability level. Only the major component of the disordered Au2 (denoted as Au21) is shown. Colors: carbon, gray; hydrogen, dark-brown; phosphorus, orange; gold, yellow.

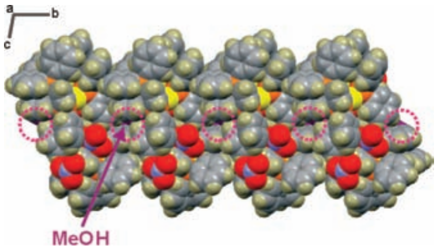

Figure 2. Space-filling projection showing the packing arrangement of $[Au_2(cis\text{-}dppe)_2]^{2+}$ cations and NO_3^- anions in **1**·MeOH. The methanol molecules (purple) are buried inside the phenyl-padded voids, which are marked with dotted magenta circles. Colors: carbon, gray; hydrogen, dark-brown; nitrogen, blue; oxygen, red; phosphorus, orange; gold, yellow.

The complex $[Au_2(cis\text{-}dppe)_2](NO_3)_2$ (**1**) was prepared by reacting $(Me_2S)AuCl$ with *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-dppe) and $AgNO_3$ in a 1:1:1 molar ratio in methanol. Single crystals of $[Au_2(cis\text{-}dppe)_2](NO_3)_2\cdot 0.81MeOH$ (**1**·MeOH) suitable for X-ray diffraction analysis were grown from diffusion of diethyl ether into a methanolic solution of **1**. As shown in Figure 1, the $[Au_2(cis\text{-}dppe)_2]^{2+}$ cation is a 10-membered ring comprising two gold atoms and two bridging *cis*-dppe ligands. One of the gold centers is disordered over two sites [with site occupancies of 0.67(4) and 0.33(4)]. This binuclear $Au_2P_4C_4$ metallacycle shows a short 1,6-transannular Au···Au aurophilic interaction of 2.833(4) Å. Au···Au interactions generally occur perpendicular to the principal axes of the linearly twofold-coordinated Au(I) centers, and their typical lengths range from 2.75 to 3.40 Å.[8] Each gold atom is coordinated by two phosphorus atoms, and the P−Au−P angles range from 156.9(1) to 176.7(1)°.

Crystals of **1**·MeOH are not porous in the conventional sense, since the MeOH molecules are situated in discrete voids, as shown in Figure 2. The voids are isolated from one another and do not merge to form channels. The solvent molecules are encapsulated in these discrete voids, which are padded with the phenyl functions of the gold(I) macrocycles.

The void volume is 3.9% of the total crystal volume, as estimated using *PLATON*.[9] The methanol molecules are situated along the crystallographic *a* axis, and the voids where the solvent molecules reside are separated by each other by the phenyl functions of the neighboring $[Au_2(cis\text{-}dppe)_2]^{2+}$ cations. It is noteworthy that the single-crystallinity was retained even after removal of the methanol molecules. Crystals of **1** were prepared by heating the crystals of **1**·MeOH at 90 °C under vacuum for ~1 h. The X-ray diffraction analysis of **1** confirmed that no significant change in the structure occurred during this single-crystal-to-single-crystal transformation, except that the space previously filled by solvent molecules became occupied by disordered nitrate anions. The mobility of the nitrogen and oxygen atoms significantly increased in the absence of guest

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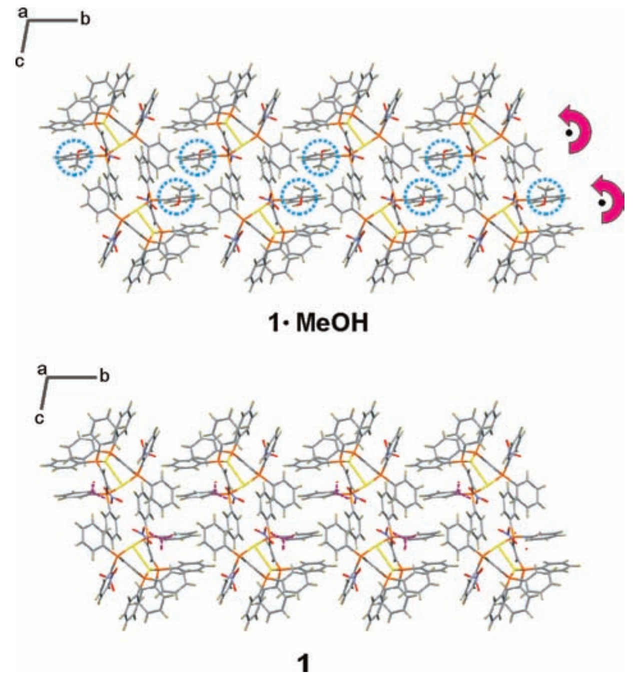

Figure 3. Crystal structures of **1**·MeOH and **1** shown in analogous views depicting the arrangement of [Au_2(*cis*-dppe)$_2$]$^{2+}$ cations and NO_3^- anions. Dotted ice-blue circles show the voids occupied by methanol molecules in **1**·MeOH. The minor disordered nitrate ions in **1** are represented by purple dashed lines. The concerted rotation of the [Au_2(*cis*-dppe)$_2$]$^{2+}$ cations around the crystallographic *a* axis is indicated by magenta arrows. Colors: carbon, gray; hydrogen, dark-brown; nitrogen, blue; oxygen, red; phosphorus, orange; gold, yellow.

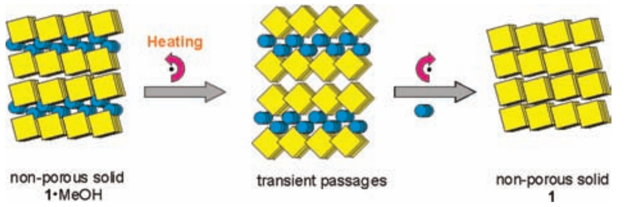

Figure 4. Schematic representation of guest release from a nonporous solid. This mechanism involves concerted rotation of the host molecules to allow guest removal through the as-formed transient passages. Yellow squares represent the gold(I) macrocycles and blue balls the liquid or gaseous guest molecules.

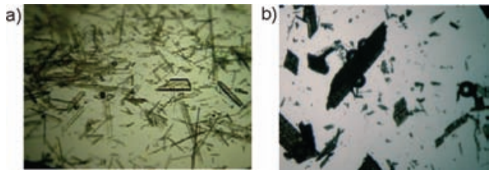

Figure 5. Photographs showing bubbles of air escaping from crystals of **1** in (a) Paratone oil and (b) water. The air bubbles are released as a result of hydratation of **1**, and **1**·H_2O is formed via this novel single-crystal-to-single-crystal transformation.

molecules, as indicated by positional disorder [with site occupancies of 0.555(5) and 0.445(5)] of the nitrate anion. As a result, there are no residual solvent-accessible voids, as was calculated with *PLATON*.[9]

Although the detailed mechanism for removal of methanol is at present unknown, some insight is possible from a comparison of the structures of **1**·MeOH and **1** (Figure 3). Comparison of the unit cell dimensions shows that the crystal volume decreases by 2.2% upon desolvation. In contrast, inhalation and exhalation of sulfur dioxide gas via a breathing mechanism caused a 25% variation in the unit cell volume of a nonporous organoplatinum crystal.[6d] Therefore, a breathing mechanism can be ruled out, and as the crystal lattice of **1**·MeOH is nonporous, the escape of methanol could require a cooperative movement of molecular components in the crystal. Thus, it is apparent that during MeOH release, the hydrophobic voids must open in such a way as to provide a transient channel for solvent removal. We suggest that concerted rotation of the [Au_2(*cis*-dppe)$_2$]$^{2+}$ cations mainly around the crystallographic *a* axis accompanies the process of solvent release, since the overlaid crystal structures of **1**·MeOH and **1** reveal this concerted movement in response to the removal of the MeOH molecules. Therefore, the phenyl functions are drawn apart, providing transient channels for solvent removal along the *a* axis. As a result, the distances between the centroids of the phenyl groups padding the voids are longer in **1** than in **1**·MeOH (for details, see the Supporting Information). Hence, it seems plausible that this nonporous-to-nonporous single-crystal-to-single-crystal transformation could proceed through a mechanism that allows switching between closed (nonporous) structures via a transient open structure (Figure 4). Rotation-related mechanisms involving alkyl-group motions have been proposed for the uptake and release of guest molecules from nonporous crystals.[4e–g,6c] In the case of *p*-*tert*-butylcalix[4]arene crystals, Atwood and co-workers showed that the cooperative rotation of the *tert*-butyl groups assists in the release of entrapped guest molecules.[4e–g]

During the selection of single crystals of **1** in a viscous cryoprotectant (Paratone oil) used for low-temperature X-ray crystallography, we observed that after ~5 min, bubbles of gas emerged from the solid (Figure 5a). In addition, we also noted that numerous bubbles emanate from the crystals in water (Figure 5b). Such regulated gas release from crystalline compounds is an exceptionally unusual phenomenon and has been observed only for nonporous *p*-*tert*-butylcalix[4]arene[4d] and porous barium 1,3,5-benzenetrisulfonate[10] crystals. Fortunately, we were able to determine the crystal structure of the product formed when the crystal of **1** was left in Paratone oil. The single-crystal X-ray diffraction analysis of [Au_2(*cis*-dppe)$_2$](NO_3)$_2$·H_2O (**1**·H_2O) confirmed that water, even in small amounts (<200 ppm) as present in Paratone oil, entered the crystal lattice. In this hydrated **1**·H_2O crystal, the void spaces are occupied by water molecules. FT-IR analysis of the carefully dried crystals formed after treatment of crystals of **1** with water also indicated the presence of water in **1**·H_2O. This novel single-crystal-to-single-crystal transformation from **1** to **1**·H_2O proceeds via progressive substitution of air by water molecules (Figure 5b). Thus, water molecules diffuse through the seemingly nonporous crystal lattice of **1** without disrupting the arrangement of the [Au_2(*cis*-dppe)$_2$]$^{2+}$ macrocycles. To rationalize this, it is presumed that the cooperative rotation of the [Au_2(*cis*-dppe)$_2$]$^{2+}$ cations would allow the guest molecules to diffuse through the as-formed transient channels of the crystal (Figure 4). Nevertheless, the gas release from this nonporous compound upon addition of water is reminiscent of that observed in the case of a porous crystal.[10] Ripmeester and co-workers showed that barium 1,3,5-benzenetrisulfonate crystals are able to entrap and store the external gas atmosphere during dehydration, while upon rehydration, the pores open to release the entrapped gas.[10]

Adsorption isotherms for O_2, N_2, H_2, CO, and CO_2 were recorded at 273 K (Figure 6) on freshly prepared crystals of **1**. It appears that under the above conditions, the crystals of **1** were able to discriminate between different gases with respect to both the rate of uptake and the amount absorbed. Thus, CO_2 was absorbed far more rapidly and to a significantly greater extent than O_2, N_2, H_2,

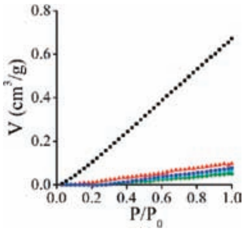

Figure 6. Adsorption isotherms of N_2 (green), CO (ice-blue), H_2 (red), O_2 (blue), and CO_2 (black) on crystals of **1**.

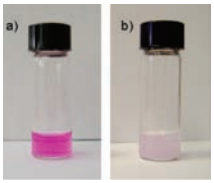

Figure 7. Release of CO_2 from **1** upon addition of water. (a) Dummy probe: Crystals of **1** (without CO_2) were placed in an aqueous NaOH solution (0.1 M) containing 1 drop of phenolphthalein. The fuchsia color of phenolphthalein in this basic solution was persistent. (b) As-prepared (see text) crystals of **1** containing entrapped CO_2 molecules were placed in an aqueous NaOH solution (0.1 M) containing 1 drop of phenolphthalein. The solution immediately changed color from fuchsia to colorless, and intensive sparkling was observed.

or CO. CO_2 was absorbed in amounts below 0.04 mol of gas per mol of **1** at room temperature and 1 atm.

Finally, to show that CO_2 can be trapped, stored, and ultimately released from **1**, a simple experiment was performed. Crystals of **1** were placed into a stainless-steel cylinder, and CO_2 (~6 atm) was introduced into the chamber. This system was opened after 4 h, and the number of CO_2 molecules per formula unit (0.73) was determined on the basis of the elemental analysis data obtained for the bulk product. The crystals were further heated (90 °C) under vacuum (10 mbar) for 1 h to remove the externally adsorbed CO_2. The crystals were then placed into an aqueous NaOH solution (0.1 M) containing 1 drop of phenolphthalein indicator. The solution immediately changed color from fuchsia to colorless as CO_2 reacted with NaOH, and intensive sparkling was also observed (Figure 7). The elemental analysis showed that the nonporous crystals of **1** can store up to 0.67 CO_2 molecule per void, which represents a pore filling of 43.8%. Therefore, this nonporous solid is able to absorb and store CO_2 gas up to 90 °C, although it provides instantaneous gas release when water is added to the system.

In summary, we have shown that the solid formed by $[Au_2(cis\text{-}dppe)_2]^{2+}$ macrocycles and NO_3^- anions can encapsulate various guests in its nonporous crystal lattice. This nonporous compound is robust enough to trap guests, but at the same time, it is flexible enough to allow guest release without destruction of the crystal lattice. Therefore, in accordance with the concept of dynamic cooperativity,[4a] it seems plausible that these single-crystal-to-single-crystal transformations could proceed through a mechanism that allows switching between nonporous structures via a transient open structure. Our results also show that when the MeOH molecules are lost from the $[Au_2(cis\text{-}dppe)_2](NO_3)_2$ complex, the resulting nonporous crystals are able to capture and retain gases such as air and CO_2 even though they do not possess large interstitial cavities. Controlled gas release can then be achieved by the addition of water. Our findings in the field of nonporous materials may provide additional tools for the development of functional crystalline materials with specific properties. Finally, the carbon dioxide capturing, storing, and releasing power of this nonporous gold(I) compound has the potential for flue gas separation, hydrogen purification, and carbon dioxide removal from the air. The extension of gas sorption experiments is currently under investigation.

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Supporting Information Available: Synthetic details; TGA, IR, and GC−MS data; and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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