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# Single-Crystal to Single-Crystal Uptake of Volatile Solids and Associated Chromatic Response in a Porous Metallocycle

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#### **S** Supporting Information

ABSTRACT: Guest molecules have been absorbed into crystals of a metallocyclic host by sublimation of volatile solids at room temperature. The guest exchanges are accompanied by color changes. Since the crystals remain intact, evidence of guest inclusion could be obtained using single-crystal X-ray diffraction. The results are also supported by thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), and ultraviolet-visible spectroscopy (UV-vis).



#### INTRODUCTION

Porous materials such as zeolites and metal-organic frameworks (MOFs) are well-known for their guest uptake properties.<sup>1,2</sup> MOFs have a variety of potential applications due to their versatility, e.g., flexibility, pore size specificity, and our ability to tailor their frameworks.<sup>3-5</sup> Insights into the structure-property relationships of porous materials can lead to better design strategies, which are currently hampered by the unpredictability of crystallization outcomes.<sup>6–8</sup> It is often desirable for materials that respond to a change in external stimuli (heat, pressure, vapors, etc.) to do so without losing their single-crystal nature. Structural elucidation of the host transformation, as well as the host-guest interactions may reveal the key features necessary for targeting specific properties.

Metallocycles<sup>9,10</sup> constitute a promising class of porous materials for the study of structure-property relationships by means of single-crystal X-ray diffraction (SCD) methods. They have relatively simple zero-dimensional structures, and the guest-accessible space is small enough to allow included guests to be located in the host quite easily. We have shown that the guest molecules in metallocycles can be removed to yield the guest-free (apohost) structure and that guest-exchange processes can occur in a single-crystal to single-crystal (SC-SC) manner.<sup>11,12</sup> Studies of the sorption and separation of solvents (in liquid or vapor form) and gaseous molecules are abundant in the literature.<sup>13-16</sup> In contrast, very few studies have been reported that involve the sorption of vapors of solids. Studies that involve structural evidence of the adsorbed guest molecules are even rarer. For example, Lang et al.<sup>17</sup> showed that a mixed ligand MOF was able to effectively separate a solid mixture of naphthalene (na) and anthracene. Kato et al.<sup>18</sup> were able to control the emission color of

luminescent Cu(I) complexes by vapor-induced ligand exchange, and Tarascon et al.<sup>19</sup> showed that incorporation of p-benzoquinone (bq) into a porous material can influence its electrochemical properties. We recently reported the inclusion of naphthalene, p-dichlorobenzene (dcb), and vapors of an organic radical into a metallocyclic host.<sup>20,21</sup> Other reports of solid guest inclusion involved first dissolving the solids and then carrying out guest exchange by placing the insoluble host crystals in the solution. $^{22-24}$  Apart from their use as chemical intermediates, many of these volatile solids form the basis of common products such as moth repellents, tanning agents, odor control and flavourants.<sup>25,26</sup> It is therefore beneficial to study the possible capture and sensing of these molecules by investigating relevant host-guest interactions.

We have previously reported remarkable SC-SC conformational switching<sup>27</sup> of a metallocycle with the formula  $[Cu_2Cl_4L_2] \cdot 2(CH_3)_2CO$ , where L is the ligand 1,4-bis(2methylimidazol-1-ylmethyl)benzene. We also reported the effect of solvent templation on the formation of metallocycles<sup>28</sup> and, more recently, the mechanism of chromatic changes for a series of common solvents as guest molecules.<sup>29</sup> As an extension of this work we now report the incorporation of vapors of the solids pyrazine (py), bq, dcb, and na into a metallocycle by means of single-crystal guest exchange. The formation of the metallocycle  $[Cu_2Cl_4L_2S_2]$  (1), where S is the coordinated dimethyl sulfoxide (DMSO) solvent, is shown in Scheme 1.

Crystals of 1 were immersed in acetonitrile to yield the acetonitrile solvate  $[Cu_2Cl_4L_2]$ ·2CH<sub>3</sub>CN (2) in a SC-SC transformation. Inclusion compounds  $[Cu_2Cl_4L_2] \cdot 2C_4H_4N_2$ 

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# Scheme 1. Formation of $[Cu_2Cl_4L_2S_2]$ (1)<sup>*a*</sup>



 $^{a}$ L = 1,4-bis(2-methylimidozol-1-ylmethyl)benzene and S = DMSO.

Scheme 2. Formation of Inclusion Compounds 2-6 by Exposing 1 to Acetonitrile, Pyrazine, *p*-Benzoquinone, *p*-Dichlorobenzene, and Naphthalene, Respectively<sup>*a*</sup>



"Each of the metallocycles is viewed along its crystallographic *a* axis. A photograph of a vial containing crystals is shown for each inclusion compound to show the chromatic response of the metallocycle.

Tab	le	1. Se	lected	Parameters	for Inc	lusion	Compound	s 1-	-6
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structure	guest	host/guest	guest volume (Å <sup>3</sup> )	) <sup>a</sup> N-Cu-N (deg)	Cl–Cu–Cl (deg)	intra Cu…Cu (Å)	conformation	color		
1	dimethyl sulfoxide (DMSO)	1:2	71	164.9(1)	122.30(3)	9.295(1)	UUDD	green		
2	acetonitrile	1:2	49	145.1(3)	125.2(1)	9.955(2)	UDDU	red		
3	pyrazine ( <b>py</b> )	1:2	69	163.0(1)	119.07(3)	9.6793(7)	UUDD	green		
4	p-benzoquinone ( <b>bq</b> )	1:1	96	151.2(1)	126.42(3)	9.8673(8)	UUDD	orange		
5	p-dichlorobenzene (dcb)	1:1	112	148.86(9)	127.32(3)	9.9461(8)	UUDD	orange		
6	naphthalene ( <b>na</b> )	1:1	122	149.8(1)	127.44(3)	9.805(2)	UUDD	brown		
<sup>a</sup> Calculated using a published equation. <sup>30</sup> See Table S1 in the Supporting Information for the sublimation enthalpies of the pure guests in 3										

(3),  $[Cu_2Cl_4L_2] \cdot C_6H_4O_2$  (4),  $[Cu_2Cl_4L_2] \cdot C_6H_4Cl_2$  (5) and  $[Cu_2Cl_4L_2] \cdot C_{10}H_8$  (6) were obtained by exposing 2 to vapors of the respective solids in a second SC–SC transformation. The SCD results are supported by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and ultraviolet–visible

(UV-vis) spectroscopy (see the Supporting Information for details).

# EXPERIMENTAL SECTION

**Crystal Growth and Preparation.** Green crystals of 1 were obtained by layering a solution of  $CuCl_2$  in ethanol (2 mL, 15.2 mg)



Figure 1. (a) and (b) Space-filling projection of a metallocyclic complex in 1 and 2 showing the conformation of the methyl groups (darkened). (c) Perspective view perpendicular to a column of metallocyclic complexes in 1. Host metallocycles are shown as capped stick models and the Cu center and coordinated guest molecules are represented as space filling models. (d) Perspective view perpendicular to a column of metallocyclic complexes in 2. Host molecules are shown as capped stick models and guest molecules are represented as space filling models. The semitransparent orange Connolly surfaces map the guest accessible pockets in 2.

onto a solution of L in DMSO (3 mL, 23.7 mg). Phase purity of the bulk sample was established by PXRD analysis and the crystals are stable to 200 °C, as confirmed by TGA (see the Supporting Information). The mother liquor was decanted and the crystals then washed with ethanol and dried on filter paper. Immersion of the crystals in acetonitrile for several hours yielded the acetonitrile solvate 2 as red crystals. Crystals of 2 were dried briefly on filter paper before being exposed to vapors of the solids **py**, **bq**, **dcb**, or **na** in a closed container at room temperature to yield inclusion compounds 3-6, respectively. The solids were heated mildly (<40 °C) to promote sublimation, and exchanges were complete within 8-24 h, as confirmed by SCD analysis. Scheme 2 shows a summary of the guest exchanges and the chromatic changes associated with each inclusion compound.

The structures of 1 and 2 have already been described,  $^{27,28}$  but the main features are highlighted here for comparison with new inclusion compounds 3–6. Selected crystal parameters are summarized in Table 1.

**Single Crystal X-ray Diffraction.** Data for new crystal structures were recorded on a Bruker Apex II DUO diffractometer and deposited with the Cambridge Structural Database (CCDC entries: 1845303–1845306).

Crystal Data for  $[Cu_2Cl_4L_2] \cdot 2C_4H_4N_2$  (3).  $C_{40}H_{44}N_{12}Cl_4Cu_2$  (M = 961.75 g/mol): monoclinic, space group  $P2_1/c$  (no. 14), a = 8.7204(5) Å, b = 13.1768(8) Å, c = 18.0176(11) Å,  $\beta = 95.2530(10)^\circ$ , V = 2061.7(2) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu$ (Mo K $\alpha$ ) = 1.338 mm<sup>-1</sup>,  $D_c = 1.549$  g/cm<sup>3</sup>, 25 333 reflections measured ( $3.836^\circ \le 2\Theta \le 50.076^\circ$ ), 3646 unique ( $R_{\text{int}} = 0.0632$ ,  $R_{\text{sigma}} = 0.0409$ ) which were used in all calculations. The final  $R_1$  was 0.0352 ( $I > 2\sigma(I)$ ), and  $wR_2$  was 0.0797 (all data). Final GooF = 1.029.

Crystal Data for  $[Cu_2Cl_4L_2] \cdot C_6H_4O_2$  (4).  $C_{38}H_{40}N_8O_2Cl_4Cu_2$  (M = 909.66 g/mol): monoclinic, space group  $P2_1/c$  (no. 14), a = 8.3863(8) Å, b = 13.1957(13) Å, c = 18.5052(18) Å,  $\beta = 95.0990(10)^\circ$ , V = 2039.7(3) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu$ (Mo K $\alpha$ ) = 1.349 mm<sup>-1</sup>,  $D_c = 1.481$  g/cm<sup>3</sup>, 30 747 reflections measured (3.796°  $\leq 2\Theta \leq 50.132^\circ$ ), 3603 unique ( $R_{\text{int}} = 0.0623$ ,  $R_{\text{sigma}} = 0.0329$ ) which were used in all calculations. The final  $R_1$  was 0.0324 ( $I > 2\sigma(I)$ ), and  $wR_2$  was 0.0709 (all data). Final GooF = 1.090.

Crystal Data for  $[Cu_2Cl_4L_2]\cdot C_6H_4Cl_2$  (5).  $C_{38}H_{40}N_8Cl_6Cu_2$  (M = 948.56 g/mol): monoclinic, space group  $P2_1/c$  (no. 14), a = 8.6547(9) Å, b = 13.1570(14) Å, c = 17.9749(19) Å,  $\beta = 95.1190(10)^\circ$ , V = 2038.6(4) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu$ (Mo K $\alpha$ ) = 1.476 mm<sup>-1</sup>,  $D_c = 1.545$  g/cm<sup>3</sup>, 31.393 reflections measured ( $3.842^\circ \le 2\Theta \le 56.626^\circ$ ), 5068 unique ( $R_{int} = 0.0511$ ,  $R_{sigma} =$ 

0.0359) which were used in all calculations. The final  $R_1$  was 0.0392 ( $I > 2\sigma(I)$ ), and  $wR_2$  was 0.0865 (all data). Final GooF = 1.090.

Crystal Data for  $[Cu_2Cl_4L_2] \cdot C_{10}H_8$  (6).  $C_{42}H_{44}N_8Cl_4Cu_2$  (M = 929.73 g/mol): monoclinic, space group  $P2_1/c$  (no. 14), a = 8.6638(18) Å, b = 13.099(3) Å, c = 17.966(4) Å,  $\beta = 95.190(4)^\circ$ , V = 2030.6(7) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu$ (Mo K $\alpha$ ) = 1.353 mm<sup>-1</sup>,  $D_c = 1.521$  g/cm<sup>3</sup>, 14 151 reflections measured ( $3.854^\circ \le 2\Theta \le 56.704^\circ$ ), 5031 unique ( $R_{int} = 0.0630$ ,  $R_{sigma} = 0.0780$ ) which were used in all calculations. The final  $R_1$  was 0.0453 ( $I > 2\sigma(I)$ ), and  $wR_2$  was 0.1100 (all data). Final GooF = 0.996.

**Thermogravimetric Analysis.** After complete exchange, as inferred from the color change, thermal analysis of the crystals indicated a mass loss that corresponds with the guest identity and occupancy as observed in the single-crystal structures, with the exception of compounds 4 and 6 (Supporting Information, section 4). The weight loss for compound 4 is consistent with slightly more than half of the expected guest molecules and infrared spectroscopy revealed that crystals heated at 120 °C still contained **bq** (Supporting Information, section 6). Intermolecular interactions are discussed in the "Results and Discussion" section; however, we note that the incomplete removal of the guest is not likely due to a weak hydrogen bond alone. Further investigation is needed to explain the incomplete removal of the guest in 4. Guest removal from 6 coincides with decomposition of the host.

**Powder X-ray Diffraction.** PXRD results indicate that the bulk samples are phase pure and that the single crystal selected for SCD was representative of the bulk sample (Supporting Information, section 5).

**Fourier Transform Infrared Spectroscopy.** Characteristic vibrational bands at the expected wavenumbers confirms the presence of the guest molecules in the channels of the host (Supporting Information, section 6).

**Ultraviolet–Visible Spectra.** UV–vis results confirmed experimentally the characteristic colors of the samples resulting from the different identities of the guest molecules (Supporting Information, section 7).

# RESULTS AND DISCUSSION

Compound 1 crystallizes in the monoclinic space group  $P2_1/c$ . Two Cu centers, each coordinated by two chloride ions, are shared by two C-shaped molecules of L to form a neutral cyclic complex. The aperture of the metallocyclic complex is occupied by coordinated DMSO guest molecules such that the coordination geometry around each metal center is



Figure 2. Perspective view perpendicular to the channel in 3 (a), 4 (b), 5 (c), and 6 (d). Host molecules are shown as capped stick models and guest molecules are shown in a space filling representation. The semitransparent orange Connolly surface maps the solvent accessible volume inside the channel.

approximately trigonal bipyramidal. These complexes stack in columns, each surrounded by six neighboring columns and held in place by  $\pi-\pi$  interactions between neighboring complexes of adjacent columns (Scheme S1).

While guest removal and exchange occurs with relative ease for metallocycles with volatile, weakly interacting guest molecules, it is reasonable to expect removal or exchange of coordinated DMSO to be more challenging. Indeed, exposure of 1 to solid vapors of **py**, **bq**, **dcb**, and **na** had no effect on the crystals, even after several days. Crystals of 1 remain intact up to 150 °C under dynamic vacuum before starting to decompose.

Surprisingly, the coordination bond can be cleaved by immersing the crystals in acetonitrile to yield **2**. A gradual change in color from green to red indicates the progress of guest exchange, the completion of which was ultimately confirmed by SCD and TGA (see the Supporting Information). The crystal structure of **2** is the same as that published previously.<sup>27</sup>

One of the features of the metallocycle is the ability of the methyl groups to rotate around the Cu–N bond. We will therefore use the same convention as before<sup>27</sup> to describe the conformational changes, i.e., by referring to the methyl groups as pointing up (U) or down (D). With reference to the projections in Figure 1, starting at the top left and proceeding clockwise, the methyl groups of 1 are in the UUDD conformation.

During the transformation from 1 to 2 the conformation switches to UDDU. Although the space group and crystal system remain unchanged the unit cell dimensions change notably, with the largest change being evident in the  $\beta$  angle (from 95.486(3)° in 1 to 91.596(4)° in 2). In 2, the host/ guest ratio is 1:2, with pairs of antiparallel acetonitrile molecules centered within the pocket formed by each metallocycle. The Cu coordination geometry becomes distorted tetrahedral and no significant interactions between the host and the guest molecules are discernible.

The crystals resulting from the vapor exchanges share some structural features. For example the methyl groups of the host all assume UUDD alignment, and the pockets initially present in 2 merge to form 1D channels in 3-6 (Figure 2).

As in 2, the **py** molecules occupy the host in a host/guest ratio of 1:2, while the larger guest molecules in 4-6 result in host/guest ratios of 1:1. Despite the presence of aromatic moieties in the hosts and the guests, most of the close contacts observed in 3-6 are beyond the accepted range for  $\pi-\pi$  stacking interactions. Close inspection of the geometries and interactions in the different inclusion compounds testifies to the flexibility of the host in accommodating different guest molecules.

The py molecules in 3 are present as slightly offset parallel pairs in each metallocycle. The separation distance between the centroids of the aromatic guests is 4.6024(3) Å (Figure S16a). Other close contacts of 4.5434(3) and 4.5886(3) Å

exist between the py guest and the imidazole moieties of the host (Figure S16b). The change in color of the crystals from red to green can be attributed to the formation of a sterically hindered coordination bond (2.494(3) Å) between one nitrogen atom of each py guest to a Cu center. In 4, each guest molecule is situated midway between two metallocycles (Figure S17). In a face-on view of the guest, bq molecules are sandwiched between imidazole moieties of two neighboring host molecules with a face-to-face separation distance of 3.8293(4) Å between the host and guest aromatic moieties. The phenyl moieties of the host hold the guest in place with edge-to-face  $\pi - \pi$  interaction distances of 4.8210(5) Å between the host and the guest. Weak C-H…O hydrogen bonds (C…O distance of 3.68(4) Å) are observed between the oxygen atoms of bq and the methyl groups of the host molecules on either side of the guest. The asymmetric unit of 5 contains half a guest molecule, which is disordered over two positions (Figure \$18). The major component of the disordered guest molecule has an occupancy of approximately 70% per host formula unit and is centered within each metallocycle. The occupancy of the minor component is approximately 30% per host formula unit and, similar to the guest in 4, each minor dcb molecule is situated midway between two host molecules (see the Supporting Information). Edge-to-face  $\pi - \pi$  interactions exist between the phenyl moieties of the host and the major component of the guest, with a centroid-to-centroid distance of 4.9067(5) Å. Similar to 4, the minor component of the guest is sandwiched between imidazole moieties of its neighboring host molecules with a separation distance of 3.7639(4) Å and a separation distance of 4.7086(5) Å between the guest and phenyl moieties of the host on either side. Type I<sup>31</sup> halogen… halogen contacts are observed between guest molecules, with Cl…Cl distances of 3.792(2) Å for the major position and 3.24(2) Å for the minor position, which are within the accepted range of close contacts for this type of interaction.<sup>32</sup> The guest molecules in 6 are centered in each cyclic unit. Unlike the guest molecules in structures 3-5, na contains no heteroatoms, and the na molecules are orientated to maximize the close contacts between aromatic moieties in the inclusion compound. When considering one of the phenyl moieties of naphthalene, three close contacts with the host metallocycle are observed. Face-to-face contacts between this moiety and the two nearest imidazole moieties of the host have centroid separation distances of 4.3311(10) and 4.8285(11) Å, while an edge-to-face  $\pi - \pi$  interaction with the phenyl moiety of the host shows a centroid-to-centroid separation distance of 4.7850(11) Å. By symmetry, the same contacts reside between the second phenyl moiety of the guest and the remaining aromatic moieties of the host.

The crystal parameters presented in Tables 1 and S3 show the geometrical and conformational changes that the metallocycle undergoes as a result of including different guest molecules. Some of the changes are quite subtle while other changes are quite dramatic. For example, the inter- and intramolecular Cu...Cu distances do not differ by much between structures. In contrast, conformational switching of the methyl group positions from UUDD in 1 to UDDU in 2 and back to UUDD in 3-6 is particularly remarkable because it does not result in loss of crystal singularity.

During the transformation from 1 to 2, the color of the crystals changes from green to red, and this can easily be rationalized as being due to the changes in the coordination sphere around the metal center. The N-Cu-N angles

decrease by approximately  $19^{\circ}$ , while an increase of approximately  $3^{\circ}$  is observed in the Cl–Cu–Cl angles. A strong interaction with the coordination sphere, as observed in the transformation from **2** to **3**, results in an increase in N– Cu–N angles by approximately  $18^{\circ}$  and a decrease in Cl–Cu– Cl angles of  $6^{\circ}$ . This is accompanied by a change in color from red to green. Even subtle changes in the coordination geometry during the transformation from **2** to **4**, **5**, or **6** result in color changes from red to orange or brown.

The number of inclusion compounds presented here is not sufficient to effectively identify trends and draw conclusions about the role of intermolecular interactions in determining the position of the guest in the host framework. As noted previously,<sup>33</sup> the host–guest structure is likely influenced by a combination of factors, including inter- and intramolecular interactions, shape-fit considerations,<sup>34</sup> and cooperative move-ment<sup>35</sup> between the host and the guest. It is envisioned that a library of structural evidence of guest inclusion may provide insight into the structure–property relationships of such materials, which may in turn elucidate trends to be exploited in rational design.

#### CONCLUSIONS

We have investigated the capture of volatile solids in a metallocyclic host by means of exchanging guest molecules in a SC-SC manner. We have provided structural evidence for the inclusion of py, bq, dcb, and na into crystals of a flexible metallocycle (enforcing the formation of guest-accessible channels from previously isolated pockets). Guest molecules with different sizes, shapes, and functional groups occupy different positions in the host framework, which changes the geometry of the coordination sphere. This gives rise to the different colors for the different systems; such chromatic responses to guests can potentially be exploited for use as sensors and indicators.<sup>36</sup> We emphasize that a strongly coordinated guest should not deter exploration of the potential porosity of a material. It has already been demonstrated that coordination bonds can be cleaved in this manner either for exchange or complete removal of ligands.<sup>37</sup> The latter can yield open metal sites<sup>38</sup> that may potentially be exploited for catalysis, sensing or sorption. Further studies are currently under way to investigate the potential separation and sensing properties of the metallocycle reported here.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02028.

Synthetic procedures, TGA, PXRD, FT-IR, UV-vis and additional experimental details (PDF)

#### Accession Codes

CCDC 1845303–1845306 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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