

# Aromatic inclusion within a neutral cavity-containing rectangular grid

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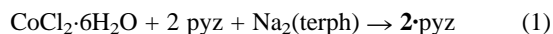
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**Reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with pyrazine and disodium terephthalate in water results in the formation of a neutral cavity-containing rectangular grid,  $[\text{Co}(\text{pyz})(\text{terph})(\text{H}_2\text{O})_2]$ , which includes a tightly bound aromatic as a guest; classification of these frameworks also provides targets for chemical synthesis.**

In a recent report, we demonstrated the one-pot synthesis of a cationic cavity-containing rectangular grid,  $[\text{M}(4,4'\text{-bipy})(\text{pyca})(\text{H}_2\text{O})_2]^+$  **1** [where  $\text{M} = \text{Co}(\text{II})$  or  $\text{Cd}(\text{II})$ ;  $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$ ;  $\text{pyca} = \text{pyridine-4-carboxylate}$ ], which self-assembles in the solid state to form stacked layers.<sup>1</sup> The stacking exhibited by this framework yielded interconnected microchannels which include highly disordered neutral (*i.e.* solvent  $\text{H}_2\text{O}$ ) and charged (*i.e.*  $\text{NO}_3^-$  ions) guest species. In this contribution, we now extend the chemistry of these materials to neutral frameworks and demonstrate, for the first time, the ability of a cavity-containing rectangular grid,  $[\text{Co}(\text{pyz})(\text{terph})(\text{H}_2\text{O})_2]$  **2** (where  $\text{pyz} = \text{pyrazine}$ ,  $\text{terph} = 1,4\text{-benzenedicarboxylate}$ ), to include an aromatic (*i.e.*  $\text{pyz}$ ) as a guest. We also demonstrate that it is possible to classify these and related square grids based on simple charge considerations which we anticipate will aid in the synthesis and sorting of these compounds as new members of each family continue to emerge.

There are, in principle, only four ways in which either a cationic or neutral rectangular grid may be constructed using a  $\text{M}^{2+}$  ion ( $\text{M} = \text{transition metal}$ ) (Table 1).<sup>†</sup> In the first case, both bridging ligands, in terms of charge, must be neutral. In the second case, one bridging ligand must possess a  $-1$  charge. In the third case, both bridging ligands must possess a  $-1$  charge. Finally, in the fourth case, one bridging ligand must possess a  $-2$  charge. In each case, either a square planar or octahedral metal center may be employed for the assembly process. In this study, an example of case 4, which is based upon an octahedral metal center, is presented. Notably, for a square grid, there are only two ways in which such a framework may be constructed. Either the bridging ligand must possess a  $-1$  charge or be neutral. This latter observation is due to the fact that only a single bridging ligand may be used to construct a square grid framework.

When a hot, aqueous solution (5 mL) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (238 mg, 1.0 mmol) was added to a hot, aqueous solution (4 mL) of pyrazine (160 mg, 2.0 mmol) and disodium terephthalate (210 mg, 1.0 mmol) according to eqn (1), crystals of **2**· $\text{pyz}$  suitable for X-ray analysis formed, after cooling, within a period of approximately 1 week (yield 16.2 %, single product). The formulation of **2**· $\text{pyz}$  was confirmed by single-crystal X-ray analysis<sup>‡</sup> and thermogravimetric analysis.



A view depicting the metal ion coordination in **2** is shown in Fig. 1. In a similar way to **1**,<sup>1</sup> the metal center is coordinated to two *trans*  $\mu$ - $\text{pyz}$  ligands, two *trans*  $\mu$ - $\text{terph}$  ions, and two *trans* water molecules that form a slightly distorted octahedral coordination environment. As a result, a cavity-containing rectangular grid has formed. Unlike **1**, however, the anion possesses a  $-2$  charge and the framework is therefore neutral. Notably, the grids lie parallel to the crystallographic *ab* plane

**Table 1** Summary of rectangular grids

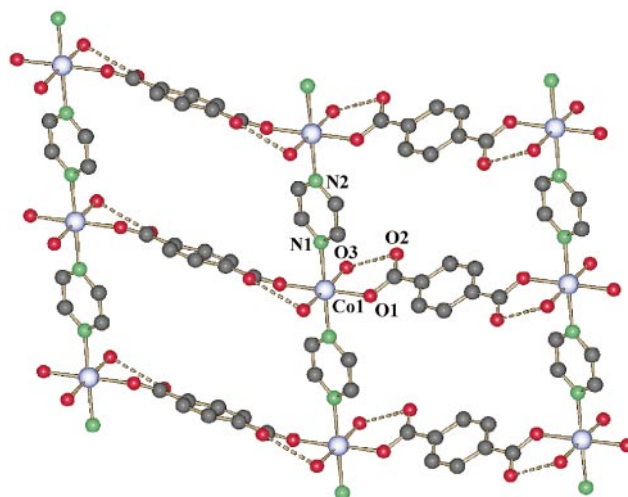
Case	Metal <sup>a</sup>	Ligand I	Ligand II	Ref.
1	$\text{M}^{2+}$	Neutral	Neutral	2
2	$\text{M}^{2+}$	$-1$	Neutral	1
3	$\text{M}^{2+}$	$-1$	$-1$	—
4	$\text{M}^{2+}$	$-2$	Neutral	3, this study

<sup>a</sup> Square planar or octahedral transition metal center.

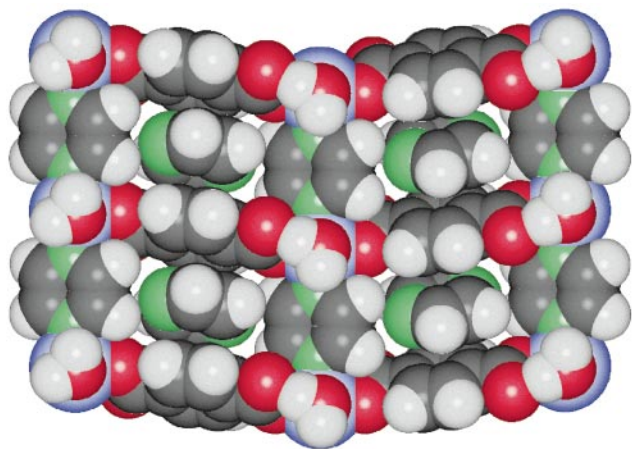
and exhibit intragrid  $\text{M} \cdots \text{M}$  separations of  $7.2 \times 11.3 \text{ \AA}$  across each  $\text{pyz}$  ligand and  $\text{terph}$  ion, respectively. In a similar way to **1**, the anion participates in two  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds with two coordinated water molecules [ $\text{O} \cdots \text{O} 2.683(2) \text{ \AA}$ ] such that the carboxylate moieties of the ligand lie approximately orthogonal to the  $\text{MN}_2\text{O}_2$  plane.

As shown in Fig. 2, the bridging ligands of **2** have generated a cavity with dimensions suitable to accommodate a molecule of  $\text{pyz}$ . The included guest, which, in contrast to **1**,<sup>1</sup> is well ordered, participates in  $\pi$ - $\pi$  interactions (centroid $\cdots$ centroid  $3.34 \text{ \AA}$ ) and  $\text{C} \cdots \text{H} \cdots \text{N}$  hydrogen bonds ( $\text{C} \cdots \text{N} 3.34 \text{ \AA}$ ) with the anion and bridging  $\text{pyz}$  ligand, respectively. Although aromatic guest inclusion has been demonstrated in discrete<sup>7,8</sup> and infinite square assemblies,<sup>9,10</sup> these observations illustrate, for the first time, the ability of a rectangular framework to host an aromatic guest.

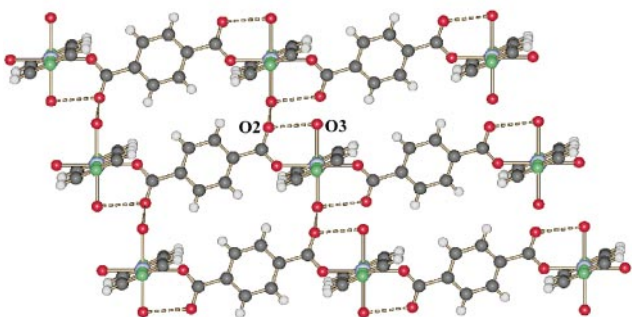
A view depicting the extended structure of **2** is shown in Fig. 3. As in **1**<sup>1</sup> and  $\text{Cu}(4,4'\text{-bipy})(\text{pyz})(\text{H}_2\text{O})_2(\text{PF}_6)_2$  **3**,<sup>2</sup> the grids self-assemble in the solid state such that they form stacked layers. Notably, the grids of **2** interact by way of  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds [ $\text{O} \cdots \text{O} 2.808(3) \text{ \AA}$ ], which involve coordinated water molecules and carboxylate moieties of the  $\text{terph}$  ion, such that adjacent layers lie offset. This, in turn, generates guest-



**Fig. 1** A view of **2** depicting the coordination environment around the  $\text{Co}(\text{II})$  metal centres. Selected interatomic distances ( $\text{\AA}$ ):  $\text{Co}(1) \cdots \text{O}(1)$  2.059(2),  $\text{Co}(1) \cdots \text{O}(3)$  2.121(2),  $\text{Co}(1) \cdots \text{N}(1)$  2.190(3),  $\text{Co}(1) \cdots \text{N}(2)$  2.163(3),  $\text{O}(2) \cdots \text{O}(3)$  2.683(2). All bond distances are within expected ranges. The guest has been omitted for clarity.



**Fig. 2** A space-filling model of 2-pyz. The guest is held within the cavity by a combination of  $\pi$ - $\pi$  interactions and C-H...N hydrogen bonds.



**Fig. 3** A view depicting the O-H...O hydrogen bonds [O(2)...O(3) 2.808(3) Å] which occur between the stacked layers of 2.

filled microchannels which run in an oblique direction with respect to the layers. Interestingly, thermal analysis of 2-pyz reveals that, in contrast to 1, the guest is tightly bound within the lattice. The TGA trace displays a rapid weight loss of 20.0% (calculated 19.1%), from 107 to 252 °C, which corresponds to one molecule of pyz. § The resulting material, [Co(pyz)(terph)(H<sub>2</sub>O)<sub>2</sub>], then slowly decomposes with loss of pyz and the terph ion to yield the metal oxide.

The results reported herein illustrate the utility of using the process of self-assembly for the construction of *multi*-component host-guest architecture. By selecting appropriately functionalized components, we have shown that it is possible to extend the chemistry of rectangular grids involving bridging pyridines/diazines and carboxylate moieties to neutral frameworks. Considering the relatively small number of cavity-containing rectangular frameworks which have been synthe-

sized to date (Table 1), it is also now possible to target certain grids, for chemical synthesis, which have not yet been constructed (*e.g.* case 3), in which case members of each family may display similar properties. We are also currently exploring further inclusion properties of 2, with a view to determine whether other aromatic guest molecules can be isolated within the framework.

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## Notes and references

† To place our results in the context of those obtained to date, we limit our discussion to M<sup>2+</sup> ions (M = transition metal) and exclude anionic frameworks.

‡ *Crystal data* for 2-pyz: monoclinic, space group *C2/c*,  $a = 11.415(1)$ ,  $b = 7.161(1)$ ,  $c = 20.585(2)$ ,  $\beta = 96.189(2)$ ,  $U = 1682.8(3)$  Å<sup>3</sup>,  $D_c = 1.66$  g cm<sup>-3</sup>, Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å) for  $Z = 4$ . Least-squares refinement based on 1496 reflections with  $I_{net} > 2.0\sigma(I_{net})$  (out of 1835 unique reflections) led to a final value of  $R = 0.039$ . Aromatic hydrogen atoms were placed by modeling the moieties as rigid groups with idealized geometry, maximizing the sum of the electron density at the calculated hydrogen positions. Structure solution was accomplished with the aid of SHELXS-86<sup>4</sup> and refinement was conducted using SHELXL93<sup>5</sup> locally implemented on a Pentium-based IBM compatible computer. CCDC 182/1084.

§ For comparison, 1 exhibits an initial weight loss at 25 °C. Similar square-based systems have been shown to exhibit initial guest weight losses below 70 °C.<sup>10-12</sup>

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