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Solid state gas adsorption studies with discrete palladium(II) $[\text{Pd}_2(\text{L})_4]^{4+}$ cages

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Abstract: The need for effective CO_2 capture systems remains high, and due to their tunability, metallosupramolecular architectures are an attractive option for gas sorption. While the use of extended metal organic frameworks for gas adsorption has been extensively explored, the exploitation of discrete metallocage architectures to bind gases remains in its infancy. Herein we have investigated the solid state gas adsorption properties of a series of $[\text{Pd}_2(\text{L})_4]^{4+}$ lantern shaped coordination cages (L = variants of 2,6-bis(pyridin-3-ylethynyl)pyridine) which had solvent accessible internal cavities suitable for gas binding. The cages showed little interaction with dinitrogen gas but were able to take up CO_2 . The best performing cage reversibly sorbed 1.4 mol CO_2 per mol cage at 298 K, and 2.3 mol CO_2 per mol cage at 258 K (1 bar). The enthalpy of binding was calculated to be 25 – 35 kJ mol⁻¹, across the number of equivalents bound, while DFT calculations on the CO_2 binding in the cage gave ΔE for the cage- CO_2 interaction of 23 – 28 kJ mol⁻¹, across the same range. DFT modelling suggested that the binding mode is a hydrogen bond between the carbonyl oxygen of CO_2 and the internally directed hydrogen atoms of the cage.

Introduction

Metallosupramolecular assemblies, both continuous metal-organic frameworks (MOFs)^[1] and discrete architectures (cages),^[2] display nanoscale cavities which can interact with a variety of guests. The internal void space within MOFs has been exploited to bind drugs^[3] and pollutants^[4] and carry out molecular separations,^[5] and catalysis.^[6] However, due to the high surface areas of MOFs one of the most common applications of these materials is gas adsorption and storage.^[7] This last role is of increasing importance as part of concerted efforts to capture carbon dioxide and lower carbon emissions,^[8] and many MOFs^[9] have been shown to adsorb CO_2 .^[10] In particular, it has been shown that internal functionalisation of MOFs with amine groups^[8b, 10d, 11] can result in highly impressive CO_2 uptake and storage.^[10e, 10f]

The molecular recognition properties of discrete metallosupramolecular assemblies have been extensively

examined in solution and a wide variety of guest molecules have been shown to interact with these metallocage materials. These metallocage systems have been exploited to encapsulate drugs,^[12] environmental pollutants^[13] and reactive species.^[14] Additionally, the nanoscale cavities of metallocages have been used as molecular reaction flasks^[15] and for catalysis.^[16] However, the binding of gases within these discrete systems remains rare. Water soluble iron(II) tetrahedral cage systems have been shown to bind xenon^[17] and sulfur hexafluoride^[18] gas in solution. Recently, metallocages have been shown to bind CO_2 gas. Nitschke and co-workers found that Zn(II) and Cd(II) M_5L_6 trigonal bipyramidal architectures can fix CO_2 from the air and encapsulate the gas as carbonate anions (CO_3^{2-}).^[19] In a similar study, Maverick and coworkers showed that a Cu(I) metallomacrocyclic $[\text{Cu}_2(\text{L})_2]^{n+}$ would react with CO_2 in solution and convert it into oxalate.^[20]

In addition to solution studies of gas binding within metallosupramolecular assemblies there has been increasing interest in the solid-state gas adsorption properties of discrete metallocages. Maverick and coworkers,^[21] have shown that discrete copper(II) containing molecular squares will bind H_2 gas in the solid state, while the groups of Yaghi,^[22] Batten^[23] and Lisowski^[24] have examined the interaction of H_2 , N_2 and CO_2 with discrete metallocages.

As part of our long standing interest^[25] in the molecular recognition properties of metallosupramolecular assemblies we have previously synthesized a family of lantern shaped $[\text{Pd}_2(\text{L})_4]^{4+}$ cages^[2a, 26] which display a central cavity that is lined by four pyridyl units.^[27] These cages and related $[\text{Pd}_2(\text{L})_4]^{4+}$ assemblies^[28] have been shown to interact with a wide variety of guest molecules including organic compounds,^[28-29] inorganic complexes,^[27a, 27b, 30] solvents,^[27a, 27b, 31] and anions.^[27b, 31-32] These systems have been found to interact strongly with guest molecules that feature carbonyl ($\text{C}=\text{O}$) or related functional groups, often within the cavity of the cage, through hydrogen bonding interactions between the oxygen atom of the carbonyl unit and the α -hydrogens (H_c , Scheme 1) of the coordinated pyridyl groups. Additionally, we have shown that fluorine containing anions^[31-32] do not bind in the central cavity of the cages due to repulsive lone pair-lone pair interactions between the anions and the pyridyl units that line the cage cavity. This means that the cavity of the pyridyl lined $[\text{Pd}_2(\text{L})_4]^{4+}$ cages is not normally occupied by anions in solution or the solid state. Thus, it seemed probable that CO_2 might interact strongly and selectively, in the solid state, with our $[\text{Pd}_2(\text{L})_4]^{4+}$ cages via a combination of hydrogen bonding and pyridyl lone pair--- CO_2 interactions similar to those seen in amine functionalised MOFs.

Herein we report an investigation on the gas adsorption properties of a small family of $[\text{Pd}_2(\text{L})_4]^{4+}$ metallocage assemblies.

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The solid-state structures of the cages were examined using single crystal and powder X-ray diffraction studies and thermogravimetric analysis. Then uptake of CO₂ and N₂ gases within the [Pd₂(L)₄]⁴⁺ materials was examined. Additionally, virial modelling, solution phase host-guest chemistry using carbon disulfide as a proxy for CO₂, and DFT calculations have been employed to investigate the mode of binding of CO₂.

Results and Discussion

Synthesis and Characterisation

The ligands **L1** (R = H) and **L2** (R = OCH₂CH₂OCH₂CH₂OCH₃, PEG) were synthesised as previously reported,^[27a, 27b] while **L3** (R = OC₆H₁₃, hexyloxy) was synthesised in 90% yield using analogous methods and characterised by NMR spectroscopies, mass spectrometry, elemental analysis, IR and X-ray crystallography (Supporting Information). The cages **C1**·(BF₄)₄, **C2**·(BF₄)₄ have been reported previously^[27a, 27b] and the new cage **C3**·(BF₄)₄ was synthesised (64% yield) in an analogous fashion by mixing **C3** (2 eq.) with [Pd(CH₃CN)₄](BF₄)₂ (1 eq.) at room temperature (RT) in acetonitrile (Scheme 1, Supporting Information). The cages with hexafluorophosphate counter anions **C1**·(PF₆)₄, **C2**·(PF₆)₄ were synthesised, in reasonable isolated yields (84% and 60%, respectively), by combining the appropriate ligand, [Pd(CH₃CN)₂Cl₂] and AgPF₆, in 2:1:2 ratio in acetonitrile at RT. All cages were synthesised in CH₃CN, a solvent which could be subsequently readily removed at elevated temperature prior to gas adsorption studies. The BF₄⁻ and PF₆⁻ counterions were chosen because we have previously shown that fluorine containing anions remain outside the cage cavity in both the solid state^[27b, 31] and solution,^[32a] while large counterions have also been shown to be excluded from the cavity.^[27a, 32a] Thus the central cavities of the cages should not contain counteranions and any solvent guest molecules, such as acetonitrile and water, that do occupy the cavities should be able to be removed upon warming and evacuation rendering the cavities available for gas adsorption.

The ¹H NMR spectra of the cages exhibited the expected downfield shifts of protons proximal to the coordinating nitrogen atoms upon complexation (for example for **C3**·(BF₄)₄, Δδ(H_c) = 0.91 ppm, Δδ(H_d) = 0.11 ppm, Δδ(H_e) = 0.85 ppm, Figure 1a, Supporting Information). Mass spectrometric analysis confirmed the stoichiometry of the three new complexes, with the spectra all displaying peaks consistent with tetracationic [C]⁴⁺ species resulting from the loss of all four counterions. The experimental and calculated isotope pattern for these ions match well (Supporting Information). Additional support for formation of the desired complexes was obtained from ¹³C NMR and IR spectroscopies and elemental analysis (Supporting Information). ¹⁹F NMR spectroscopy in d₆-DMSO showed that for all cages, the fluorine resonance was unchanged from that of the “free” anion (NaBF₄ δ: 148 ppm, KPF₆ δ: 70 ppm, Supporting Information) indicating that in solution the anion was not interacting with the cage and hence was not encapsulated.

Scheme 1. Synthesis of [Pd₂(L)₄]⁴⁺ cages used in gas adsorption studies. Conditions: (i) Ligand (2 eq.) with either [Pd(CH₃CN)₄](BF₄)₂ (1 eq.) or [Pd(CH₃CN)₂Cl₂] (1 eq.) and AgPF₆ (2 eq.), acetonitrile, RT.

The molecular structures of **C1**·(BF₄)₄ and **C2**·(BF₄)₄^[27a, 27b] have been previously determined by single crystal X-ray diffraction and the molecular structures of **C2**·(PF₆)₄ and **C3**·(BF₄)₄ have been determined during this work (Figure 1b, Figure 2, Table 1 and Supporting Information). Disappointingly, we have been unable to generate X-ray quality single crystals of the **C1**·(PF₆)₄ assembly.

The four structures (**C1**·(BF₄)₄, **C2**·(BF₄)₄, **C2**·(PF₆)₄ and **C3**·(BF₄)₄) were all obtained from the vapour diffusion of diethyl ether into acetonitrile solutions of the respective cages, the same solvents used in precipitation and preparation of the powder samples (*vide infra*). All the cages crystallised in the primitive triclinic space group, *P* $\bar{1}$, except for **C1**·(BF₄)₄ which crystallised in the monoclinic spacegroup *C2/m* (Table 1). As expected well defined lantern shaped [Pd₂(L)₄]⁴⁺ cations were present in each crystal. Parts of the PEG chains of **C2**·(PF₆)₄ were disordered and unable to be fully located, but the packing overall was very similar in counterion positioning and core cage

structure to that of **C2**·(**BF**₄)₄ and indeed to **C3**·(**BF**₄)₄ (Supporting Information). All counterions were readily identifiable in each of the structures with the exception of **C1**·(**BF**₄)₄. In the examples where the anions were located they were found external to the cage cavity consistent with the solution ¹⁹F NMR data (Table 1, Figure 2).

Figure 1. a) Partial ¹H NMR stacked spectra (298K, CDCl₃, 400 MHz) of **L3** and **C3**·(**BF**₄)₄. b) depiction of the crystal structure of **C2**·(**PF**₆)₄, and c) **C3**·(**BF**₄)₄. Cationic portions of the structure shown in tube view, counterions in spacefilling view, solvent molecules and hydrogen atoms omitted, and void space^[33] within the cavity shown. Colours: carbon grey, boron salmon, fluorine yellow, nitrogen blue, oxygen red, palladium magenta, phosphorus orange, voids in green.

Table 1. X-ray crystallographic data for cages crystallised from vapour diffusion of diethyl ether into acetonitrile.

Cage	Space group	Counterions	Cavity	Void ^[a] (Å ³)
C1 ·(BF ₄) ₄ ^[b]	<i>C2/m</i>	SQUEEZED ^[c]	SQUEEZED ^[c]	495
C2 ·(BF ₄) ₄	<i>P</i> $\bar{1}$	Both external	4 x (50%) H ₂ O	210
C2 ·(PF ₆) ₄	<i>P</i> $\bar{1}$	Both external	SQUEEZED ^[c]	335
C3 ·(BF ₄) ₄	<i>P</i> $\bar{1}$	Both external	2 x CH ₃ CN	330

[a] Voids calculated in Mercury.^[33] [b] **C1**·(**BF**₄)₄ was also crystallised from vapour diffusion of diethyl ether into DMSO (*Fmm*) with 1 counterion located, externally, and 2 H₂O molecules in the cavity, [c] Denotes the use of the SQUEEZE routine running within PLATON.

Figure 2. Partial X-ray crystal cage structures showing counterion positioning for cages crystallised from vapour diffusion of diethyl ether into acetonitrile: a) **C2**·(**BF**₄)₄, b) **C2**·(**PF**₆)₄, c) **C3**·(**BF**₄)₄, and d) the structure of **C1**·(**BF**₄)₄ obtained from vapour diffusion of diethyl ether into DMSO. Colours: carbon grey, boron salmon, fluorine green, nitrogen blue, oxygen red, palladium magenta, phosphorus orange. Selected distances (Å): a) F---HC_{py} 2.18 – 2.67, F---centroid_{py} 3.05 – 3.25; b) F---HC_{py} 2.29 – 2.53, F---centroid_{py} 3.08 – 3.12; c) F---HC_{py} 2.10 – 2.51; d) F---HC_{py} 2.46.

For **C2**·(**BF**₄)₄ and **C2**·(**PF**₆)₄, one counterion sits between coordinating pyridine rings, and the other sits over the exohedral face of the palladium(II) metal ion with a fluorine orientated towards the cation and hydrogen-bonding to the external pyridyl protons (Figure 2a and b). With **C3**·(**BF**₄)₄ the positioning is similar, but the tetrafluoroborate anion over the palladium(II) metal ion is inverted, with the base of the tetrahedron orientated towards the metal ion (Figure 2c). In the case of **C1**·(**BF**₄)₄, only the cationic portion of the structure was identifiable, we were unable to appropriately model the remainder of electron density and therefore this was accounted for using the SQUEEZE routine within PLATON. The electron count present in voids outside the cage cavity was consistent with the anions not being encapsulated. However, the **C1**·(**BF**₄)₄ cage has also been previously crystallised out of a different solvent system (vapour diffusion of diethyl ether into DMSO), in the orthorhombic space group *Fmm*.^[31] In that example one of the four counterions was identified, sitting again at the exohedral axial site of the palladium(II) ion (and thus also interacting with an adjacent cage in the same manner). Additionally, we have shown both here and previously that in solution the tetrafluoroborate anion is not bound in the cavity.^[32a] Where the cavity contents could be identified, two solvent molecules in each case were

encapsulated: four half occupancy water molecules in **C2**·(**BF**₄)₄ and two acetonitrile molecules in **C3**·(**BF**₄)₄ (Table 1). The acetonitrile molecules adopted a head-to-tail configuration with the nitrile nitrogen atom positioned over the endohedral face of the palladium(II) metal ion and hydrogen bonding to the internally directed cage protons, while a methyl group hydrogen bonds to the central pyridyl nitrogen atom (Supporting Information). The water molecules in **C2**·(**BF**₄)₄ are positioned to interact in a similar fashion with the interior of the cage. Guest-cavity adducts with these tripyridyl [Pd₂(L)₄]⁴⁺ system have consistently displayed similar interactions. For example head-to-tail bound DMF solvent molecules,^[27b, 31] and cisplatin molecules^[27a, 27b, 30c] are each stabilised within the cavity by hydrogen bonding interactions. Similarly, water molecules have been observed to hydrogen bond to the internally directed α -pyridyl hydrogens (H_c, Scheme 1), within the *Fmmm* structure of **C1**·(**BF**₄)₄^[31] and elsewhere.^[32a] Similar endohedral and exohedral solvent interactions have also been seen with acetone^[27a] and in related systems with dimethylsulfoxide and carbonyl-containing compounds.^[28a, 34] Voids calculated for the X-ray structures^[33] showed for the four systems crystallised from acetonitrile, contain a single void per cage, centred in the cavity (Figure 1b and c, Supporting Information). These cavity voids were calculated to be large enough (210 – 495 Å³, Table 1) to accommodate several gas molecules per cage cavity. However, the **C2**·(**BF**₄)₄ and **C3**·(**BF**₄)₄ both displayed lower void space than the **C1** systems. Examination of the X-ray structures suggests that this is due to the substituents (R = OCH₂CH₂OCH₂CH₂OCH₃, PEG and OC₆H₁₃, hexyloxy) packing near the cage cavity of an adjacent cage in the solid state thereby sterically reducing the cage cavity/molecular void space.

Powder X-ray diffraction (PXRD) studies with powdered samples (obtained by vapour diffusion of diethyl ether into acetonitrile solution of the cages) of the cages were carried out. The cages (**C1**·(**BF**₄)₄, **C1**·(**PF**₆)₄, **C2**·(**BF**₄)₄ and **C3**·(**BF**₄)₄) displayed a good fit between the experimental data and that calculated from the available single crystal X-ray structures for **C2**·(**BF**₄)₄ (Figure 3) and **C3**·(**BF**₄)₄ (Supporting Information) indicating that those systems are isolated microcrystalline powders. Interestingly, the fit between the calculated structure for **C1**·(**BF**₄)₄ (anions and solvent removed with the SQUEEZE function) was better for **C1**·(**PF**₆)₄ than **C1**·(**BF**₄)₄. The PXRD data for **C2**·(**PF**₆)₄ suggested that the material was isolated as an amorphous rather than microcrystalline powder (Supporting Information). It is therefore clear that the long-range molecular order (or lack thereof) can vary in some cases between precipitated and crystallized samples (but this does not appear to influence gas adsorption properties, *vide infra*).

Gas adsorption studies

Thermogravimetric analysis (TGA) on powdered sample of the cages indicated that the materials were stable from room temperature up to 140 °C (Supporting Information). The mass loss up to 140 °C was consistent with desolvation (either acetonitrile or water) presumably from the cavities of the cage materials (Supporting Information). Once the sample were

heated past 150 °C decomposition of the cages occurred. Therefore to activate the cage materials for gas adsorption studies, the compounds were desolvated by heating to 100 – 140 °C under vacuum (Supporting Information).

Figure 3. Powder diffraction pattern over the 2 θ range of 5 – 35° for **C2**·(**BF**₄)₄, experimental above in black, calculated below in red.

Preliminary gas adsorption studies were carried out with activated powder samples of the cage materials. CO₂ adsorption studies were carried out at 298 K and 258 K (Table 2, Figure 4, Supporting Information). Type 1 adsorption behaviour was observed with each of the cages, and at both temperatures. The **C1**⁴⁺ cages adsorbed more CO₂ than the other substituted variants (**C2**⁴⁺ and **C3**⁴⁺). The best performing cage was **C1**·(**PF**₆)₄, which at 1 bar adsorbed 1.0 mol CO₂ per mol cage (or, 0.5 mol CO₂ per mol Pd(II)) at 298 K. At 258 K, it sorbed 2.1 mol CO₂ per mol cage (or, 1.05 mol CO₂ per mol Pd(II)). At 258 K and a pressure of 1100 kPa between 4 and 5 mol of CO₂ is adsorbed per mol of **C1**·**PF**₆ or **C1**·**BF**₄ (see Figure 4). Isotherms showing CO₂ adsorption at 298 K indicates that the uptake of CO₂ for each compound drops by ~40% at the higher temperature (see supporting information). These results are similar to what has been observed with other metallocupramolecular cage materials. A discrete metallocupramolecular system reported by Yaghi and coworkers bound 0.8 mol CO₂ per mol Cu(I),^[22b] while the metallomacrocyclic of Lisowski and coworkers encapsulated 1.4 mol per CO₂ per mol Zn(II) (273 K, 1 bar).^[24] Very recently a tube-like metallocupramolecular system from Donnelly and coworkers was found to uptake 0.2 CO₂ per mol Zn(II) ion of the architecture (298 K, 1 bar).^[35]

Table 2. [Pd₂(L)₄]⁴⁺ cages, their respective void spaces,^[33] and CO₂ (298 K and 258 K, 1 bar) and N₂ (77 K, 0.1 bar) gas adsorption.

Cage	Void (Å ³)	CO ₂ adsorption 1 bar (mol/mol)		N ₂ adsorption 1 bar (mol/mol) 77 K
		298 K	258 K	
C1·(BF₄)₄	495	1.4	2.3	0.5
C1·(PF₆)₄	-	1.0	2.1	0.9
C2·(BF₄)₄	210	0.3	1.0	0.1
C2·(PF₆)₄	335	0.7	1.2	1.2
C3·(BF₄)₄	330	0.4	1.1	0.7

As the preliminary gas sorption measurements with the substituted cages **C2·(BF₄)₄** and **C3·(BF₄)₄** indicated they adsorbed lower amounts of CO₂ when compared to the unsubstituted **C1·(BF₄)₄** and **C1·(PF₆)₄**, we did not investigate the properties of the substituted cages further. The higher observed adsorption of CO₂ by the unsubstituted compounds (**C1·(BF₄)₄** and **C1·(PF₆)₄**) could plausibly be explained by two factors: 1) the larger void space present in the solid state structures of the unsubstituted cages (as observed from X-ray crystallography) and 2) weaker hydrogen bonding between the cages and the CO₂ guest molecules. The presence of the electron-donating O-alkyl groups in the cages **C2·(BF₄)₄** and **C3·(BF₄)₄** likely reduced the electropositivity of the palladium(II) ions and the α-pyridyl protons of the coordinated ligands thereby weakening the hydrogen bonding interaction^[30a] between the host cage and the CO₂ guests, thus lowering the affinity for the gas.

Interestingly, CO₂ adsorption did not appear to be dependent upon the retention of the molecular ordering from crystal structures to powdered samples. This suggests that regardless of intermolecular packing, the cavity space remains open and available for gas adsorption.

Figure 4. CO₂ adsorption plots (mol/mol, 258 K) for **C1·(BF₄)₄** (●) and **C1·(PF₆)₄** (■).

In contrast, N₂ adsorption studies (77 K, 1 bar) showed that the cages had little affinity for dinitrogen (Supporting Information). This preference for CO₂ is hardly surprising given the previously discussed attraction between carbonyl-containing compounds and the palladium(II) metal ions and coordinating pyridyl rings of the cages and we set out to examine this further.

CO₂ binding mechanism

The CO₂ adsorption isotherms, at 298 and 258 K, were analysed using the virial method^[36] to determine the enthalpies of adsorption. Energies in the range 25 – 35 kJ mol⁻¹ were observed consistent with interaction between the guest and ligand scaffold of the cages (Supporting Information). In order to investigate whether it was indeed a similar type of interaction with CO₂ as had previously been observed for carbonyl- and nitrile-containing guests, carbon disulphide was used as a proxy in solution-phase ¹H NMR experiments with two of the cages, **C1·(BF₄)₄** and **C2·(BF₄)₄**. Upon introduction of excess CS₂ to a solution of the cages in CD₃CN there was a very slight downfield shift of the peak pertaining to the exohedral proton *ortho* to the coordinating nitrogen for **C1·(BF₄)₄** (H_e) and a larger shift of the same proton for **C2·(BF₄)₄** (Δδ = 0.04 ppm, Supporting Information). There were no appreciable shifts of the resonance of the internally directed proton (H_c). It seemed likely that in the coordinating solvent CD₃CN, which has been shown crystallographically to form a dimer within the cavity (Supporting Information), CS₂ is outcompeted, except where cradled, through addition hydrogen bonding interactions, by the PEG chains on the external face of **C2·(BF₄)₄**.^[37] To test this hypothesis, the experiments were repeated in the less-coordinating solvent CD₃NO₂. Under those conditions downfield shifts of both H_c and H_e were observed for both cages (**C1·(BF₄)₄**: Δδ(H_c) = 0.04 ppm, Δδ(H_e) = 0.04 ppm; **C2·(BF₄)₄**: Δδ(H_c) = 0.03 ppm, Δδ(H_e) = 0.06 ppm, Figure 5). The chemical shifts due to other cage resonances peaks did not move appreciably, indicating that the CS₂ guest interacts primarily with protons *ortho* to the coordinating pyridyl nitrogens.^[38] It should be noted that the size of the chemical shifts were larger for **C1·(BF₄)₄** than for **C2·(BF₄)₄**, in agreement with the solid-state CO₂ adsorption data. This is presumably because the unsubstituted cage is a better hydrogen bond donor when compared to the PEG or O-hexyl substituted systems.

Figure 5. Partial ^1H NMR stacked spectra (298 K, CD_3NO_2 , 400 MHz) for a) $\text{C1}(\text{BF}_4)_4$, b) $\text{CS}_2\text{-C1}(\text{BF}_4)_4$, c) $\text{C2}(\text{BF}_4)_4$ and d) $\text{CS}_2\text{-C2}(\text{BF}_4)_4$.

In order to further probe the nature of CO_2 binding within the cage cavities, DFT calculations (gas phase, B3LYP with the LANL2DZ basis set for palladium atoms and the 6-31G(d) basis set for all other atoms, Supporting Information) were carried out. Energy minimised structures for the CO_2 guest, the empty C1^{4+} cage and host-guest adduct with 1 to 4 bound CO_2 molecules were calculated. The cavity of the C1^{4+} cage was able to accommodate up to four CO_2 molecules, with addition of each CO_2 molecule to the cage being thermodynamically favoured (ΔE for addition of each CO_2 molecule = 23 – 28 kJ mol^{-1} , in good agreement with the virial modelling). The host-guest adduct between five CO_2 molecules and C1^{4+} cage was also modelled. In this case four of the CO_2 molecules occupied the cage cavity and the fifth guest was outside of the cage. Additionally, the binding even for the fifth CO_2 was found to be 11.4 kJ mol^{-1} which is less than half of the values observed for the first four CO_2 molecules.

The calculated structures (Figure 6, Supporting Information) for the systems containing CO_2 with the cage cavity showed the expected hydrogen bonding interactions between the internally directed H_c cage proton and the oxygen atoms of CO_2 . Additionally, there are close contacts between carbon and oxygen atoms on adjacent guest molecules, suggestive of favourable electrostatic interactions between guests. The central carbon atoms of the bound CO_2 guest molecules were found to align with the lone pair of electrons of the pyridyl spacer units of the ligands, suggestive of an additional stabilizing interaction.

Conclusions

A series of discrete metallocupramolecular $[\text{Pd}_2(\text{L})_4]^{4+}$ cages were examined as candidates for selective solid-state CO_2 adsorption. The cages are lined by four pyridyl units and single X-ray crystallographic and NMR spectroscopic evidence indicated that the cages did not encapsulate their counterions within the central cavity presumably due to lone pair---lone pair repulsion between the pyridine and fluorine atoms of the anions. This frees the cavities of the cages for guest binding such as gas adsorption.

Figure 6. Cut-away depictions of the DFT calculated structure of $(\text{CO}_2)_2\text{-C1}^{4+}$ in a) tube style with guests in spacefilling mode, and b) as an electrostatic potential map.

TGA analysis suggested that the $[\text{Pd}_2(\text{L})_4]^{4+}$ cages are stable up to 140 $^\circ\text{C}$ and showed that occluded acetonitrile or water molecules could be removed from the cage cavities by heating the material to 100-140 $^\circ\text{C}$ under vacuum. PXRD studies indicated that the majority of the cage material were microcrystalline powders although in one case the isolated cage ($\text{C2}(\text{PF}_6)_4$) was an amorphous material.

Gas adsorption studies with N_2 and CO_2 indicated that the cages had little affinity for N_2 but would take up CO_2 . The unsubstituted C1^{4+} cages adsorbed more CO_2 than the substituted variants. The best performing cage was $\text{C1}(\text{PF}_6)_4$, which at 1 bar adsorbed 1.4 mol CO_2 per mol cage at 298 K, and 2.1 mol CO_2 per mol cage at 258 K. Four CO_2 molecules are likely the limit of what that can be encapsulated within the cavity. Virial modelling indicated enthalpy of binding of 25 – 35 kJ mol^{-1} , across the number of equivalents bound, while DFT calculations

on the CO₂ binding of **C1**⁴⁺ gave ΔE of 23 – 28 kJ mol⁻¹, across the same range. The optimised structures showed the expected interactions between cage and guests: hydrogen bonding between internal cage protons and the carbonyl oxygen of CO₂, with electrostatic interactions between oxygen and carbon atoms of adjacent CO₂ guests. Additionally, the central carbon atom of the bound CO₂ guest molecules were found to align with the lone pair of electrons of the pyridyl spacer units of the ligands, suggestive of a stabilizing interaction. Gas adsorption capacity appeared to be largely unrelated to whether the material was crystalline or amorphous presumably due to the fact that regardless of intermolecular packing, the cavity of the cage remains vacant and available for guest binding. ¹H NMR spectroscopy of the cages in solution with CS₂ as a proxy for CO₂ gave additional evidence that hydrogen bonding to the hydrogen atoms *ortho* to the coordinating pyridyl nitrogen atoms (H_c) was the primary interaction between host and guest. This observation was consistent with the results of the DFT calculation on the host-guest adducts.

This study shows that discrete [Pd₂(L)₄]⁴⁺ cages can be used for solid state CO₂ gas adsorption. While the current systems only display a small cavity for guest binding the cavity is lined with a variety of functional groups that lead to guest selectivity. Thus these small discrete metallocsupramolecular cages could potentially be useful for gas separations. Furthermore, increasing the size of the cages should enable a larger number of guest molecules to be bound within the cavities of these discrete systems and efforts in both these directions are now underway.

Experimental Section

Experimental Details including synthetic processes, characterisation including NMR and MS spectral data, X-ray data (CCDC #: 1541716-1541718), DFT calculation details are available free of charge in the supplementary information.

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Keywords: palladium(II) • carbon dioxide • gas adsorption • host-guest chemistry • metallocages

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- [37] The PEG chains of this cage have been shown to have a similar effect before, creating a preference for exohedral interactions with the mesylate anion which otherwise binds in the cavity, see reference X.
- [38] We initially examined the solution-phase encapsulation of CO₂ by the cages. Dry ice was introduced into CD₃NO₂ solutions of the cages and the interaction monitored by ¹H NMR spectroscopy. No complexation induced shifts were observed, presumably due to the low level of solubility of CO₂ in CD₃NO₂.

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Discrete metallosupramolecular palladium(II) $[\text{Pd}_2(\text{L})_4]^{4+}$ cages are shown to selectively adsorb CO_2 over N_2 . The NMR and DFT studies indicate that the CO_2 guests are bound within the cavity of the cages and interact mainly via hydrogen bonding.

Dan Preston, Keith F. White, James E. M. Lewis, Roan A. S. Vasdev, Brendan F. Abrahams,* James D. Crowley*

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Solid state gas adsorption studies with discrete palladium(II) $[\text{Pd}_2(\text{L})_4]^{4+}$ cages

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Supporting information for this article is given in the document.

Supporting Information

Solid state gas sorption studies with discrete palladium(II) $[\text{Pd}_2(\text{L})_4]^{4+}$ cages

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1 Experimental

1.1 General

All reagents were purchased from commercial sources and used without further purification. The compounds **C1**·(**BF₄**)₄ and **C2**·(**BF₄**)₄,^[1] were generated using the reported procedures. Solvents were laboratory reagent grade with the following exceptions: dry THF, toluene and DCM were obtained by passing the solvents through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Petroleum ether refers to the fraction of petrol boiling in the range 40–60 °C, isopropyl alcohol (IPA), methanol (MeOH), dichloromethane (DCM), ethylenediaminetetraacetate (EDTA), ethynyltrimethylsilane (TMS-acetylene), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) diisopropylamine (*i*Pr₂NH). ¹H and ¹³C NMR spectra were recorded on either a 400 MHz Varian 400 MR or Varian 500 MHz VNMRS spectrometer. Chemical shifts are reported in parts per million and referenced to residual solvent peaks (CDCl₃: ¹H δ 7.26 ppm, ¹³C δ 77.16 ppm; CD₃CN: ¹H δ 1.94, ¹³C δ 1.32, 118.26 ppm, *d*₆-DMSO: ¹H δ 2.50 ppm; ¹³C δ 39.52 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, t = triplet, dt = double triplet, d = doublet, dd = double doublet, s = singlet, br = broad. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra (ESMS) were collected on a Bruker micro-TOF-Q spectrometer. UV-visible absorption spectra were acquired with a Perkin Elmer Lambda-950 spectrophotometer.

1.2 Synthetic scheme for ligand L3

Figure 1.1 Conditions: (i) 1-bromohexane, K₂CO₃, DMF, RT, 90%; (ii) TMS-acetylene, Pd(PPh₃)₂Cl₂, CuI, *i*Pr₂NH, 60 °C, 79%; (iii) Na₂CO₃, MeOH, RT, 95%; (iv) 2,6-dibromopyridine, Pd(PPh₃)₂Cl₂, CuI, *i*Pr₂NH, RT, 90%.

1.3 Synthesis of 1

3-Bromo-5-hydroxypyridine (3.48 g, 20.0 mmol, 1 eq.), 1-bromohexane (2.8 mL, 20 mmol, 1 eq.) and K_2CO_3 (4.15 g, 30.0 mmol, 1.5 eq.) were stirred in DMF (50 mL) at room temperature for 18 h. After diluting with water (250 mL) the reaction was extracted with Et_2O (3 x 200 mL). The combined organic extracts were washed with water (7 x 100 mL) and brine (100 mL) before being dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to give the product as a brown oil. Yield 4.65 g (18.0 mmol, 90%). 1H NMR (400 MHz, $CDCl_3$, 298 K) δ : 8.22 (d, J = 1.9 Hz, 1H, H_a), 8.19 (d, J = 2.6 Hz, 1H, H_b), 7.30 (dd, J = 1.8, 2.6 Hz, 1H, H_c), 3.94 (t, J = 6.5 Hz, 2H, H_d), 1.78-1.71 (m, 2H, H_e), 1.45-1.38 (m, 2H, H_f), 1.32-1.28 (m, 4H, H_g , H_h), 0.89-0.85 (m, 3H, H_i). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ : 155.7, 142.7 (C_a), 136.6 (C_b), 123.8 (C_c), 120.4, 68.8 (C_d), 31.5, 29.0 (C_e), 25.6 (C_f), 22.6, 14.1 (C_i). IR (ATR): ν (cm^{-1}) 3043, 2957, 2930, 2872, 2857, 1574, 1555, 1467, 1447, 1431, 1417, 1391, 1306, 1262, 1219, 1164, 1138, 1007, 879, 857, 695. HR-ESI-MS (DCM/MeOH): m/z = 258.0471 [$M + H$] $^+$ calc. 258.0488. Anal. calc. for $C_{11}H_{16}NOBr$: C, 51.18; H, 6.24; N, 5.43%. Found: C, 51.36; H, 6.11; N, 5.41%.

Figure 1.2 Partial 1H NMR spectrum ($CDCl_3$, 298 K, 400 MHz) of 1.

Figure 1.3 Partial ^{13}C NMR spectrum ($CDCl_3$, 298 K, 400 MHz) of 1.

1.4 Synthesis of 2

A round bottom flask (RBF) was charged with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.08 g, 0.1 mmol, 0.05 eq.) and CuI (0.04 g, 0.2 mmol, 0.1 eq.) and purged with N_2 . A solution of **1** (0.59 g, 2.3 mmol, 1 eq.) in $i\text{-Pr}_2\text{NH}$ (10 mL) was added via syringe, followed by ethynyltrimethylsilane (0.64 mL, 4.6 mmol, 2 eq.). The reaction mixture was stirred at 60 °C for 24 h. 0.1 M EDTA/ $\text{NH}_4\text{OH}(\text{aq})$ (10 mL) was added and stirred for 30 minutes. Water (80 mL) was added and the aqueous phase extracted with DCM (4 x 50 mL). The combined organic phases were dried (MgSO_4), filtered and the solvent removed *in vacuo*. After purification by column chromatography on silica, eluting with DCM, the product was obtained as a light brown oil that eventually solidified. Yield 0.50 g (1.8 mmol, 79%). ^1H NMR (400 MHz, CDCl_3 , 298 K) δ : 8.25 (d, J = 1.6 Hz, 1H, H_a), 8.20 (d, J = 2.9 Hz, 1H, H_b), 7.20 (dd, J = 1.6, 2.9 Hz, 1H, H_c), 3.95 (t, J = 6.5 Hz, 2H, H_d), 1.79-1.72 (m, 2H, H_e), 1.46-1.39 (m, 2H, H_f), 1.33-1.29 (m, 4H, H_g , H_h), 0.88 (t, J = 7.0 Hz, 3H, H_i), 0.24 (s, 9H, H_j). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ : 154.6, 144.8 (C_a), 138.2 (C_b), 123.1 (C_c), 120.4, 101.6, 97.9, 68.5 (C_d), 31.6, 29.1 (C_e), 25.7 (C_f), 22.7, 14.1 (C_i), -0.1 (C_j). IR (ATR): ν (cm^{-1}) 3049, 3031, 2947, 2929, 2870, 2157, 1592, 1577, 1553, 1423, 1395, 1293, 1248, 1183, 1151, 1056, 1031, 833. HR-ESI-MS (DCM/MeOH): m/z = 276.1758 [$\text{M} + \text{H}$] $^+$ calc. 276.1778; 298.1571 [$\text{M} + \text{Na}$] $^+$ calc. 298.1598. Anal. calc. for $\text{C}_{16}\text{H}_{25}\text{NOSi}$: C, 69.76; H, 9.15; N, 5.08%. Found: C, 69.91; H, 9.27; N, 5.08%.

Figure 1.4 Partial ^1H NMR spectrum (CDCl_3 , 298 K, 400 MHz) of **2**. Figure 1.5 Partial ^{13}C NMR spectrum (CDCl_3 , 298 K, 400 MHz) of **2**.

1.5 Synthesis of **3**

To a stirring solution of **2** (1.58 g, 5.74 mmol, 1 eq.) in MeOH (30 mL) was added Na₂CO₃ (0.67 g, 6.3 mmol, 1.1 eq.). After stirring vigorously at RT for 60 minutes the reaction was filtered through cotton wool and the solvent removed *in vacuo*. After purification by flash column chromatography on silica (1:1 petroleum ether/DCM) the product was obtained as a light brown oil. Yield 1.15 g (5.68 mmol, 95%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ : 8.28 (s, 1H, H_a), 8.24 (s, 1H, H_b), 7.21 (s, 1H, H_c), 3.95 (t, J = 6.5 Hz, 2H, H_d), 3.17 (s, 1H, H_i), 1.79-1.72 (m, 2H, H_e), 1.46-1.38 (m, 2H, H_f), 1.32-1.28 (m, 4H, H_g, H_h), 0.88 (t, J = 7.0 Hz, 3H, H_i). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ : 154.6, 144.8 (C_a), 138.4 (C_b), 123.5 (C_c), 119.4, 80.4, 80.3, 68.6 (C_d), 31.6, 29.1 (C_e), 25.6 (C_f), 22.6, 14.1 (C_i). IR (ATR): ν (cm⁻¹) 3302, 3047, 3030, 2928, 2872, 2858, 2154, 1579, 1556, 1422, 1394, 1318, 1287, 1249, 1169, 1150, 1057, 1030, 014, 839, 759, 702, 648. HR-ESI-MS (DCM/MeOH): m/z = 204.1376 [M + H]⁺ calc. 204.1383. Anal. calc. for C₁₃H₁₇NO·0.4H₂O: C, 74.18; H, 8.52; N, 6.65%. Found: C, 74.06; H, 8.20; N, 6.49%.

Figure 1.6 Partial ¹H NMR spectrum (CDCl₃, 298 K, 400 MHz) of **3**.

Figure 1.7 Partial ¹³C NMR spectrum (CDCl₃, 298 K, 400 MHz) of **3**.

1.6 Synthesis of L3

A RBF was charged with 2,6-dibromopyridine (0.14 g, 0.57 mmol, 1 eq.), **1a** (0.29 g, 1.4 mmol, 2.5 eq.), Pd(PPh₃)₂Cl₂ (0.02 g, 0.03 mmol, 0.05 eq.) and CuI (0.01 g, 0.06 mmol, 0.1 eq.) and purged with N₂. *i*Pr₂NH (10 mL) was added via syringe and the reaction stirred at RT for 36 h. 0.1 M EDTA/NH₄OH(aq) (50 mL) was subsequently added and the resulting mixture stirred for 2 h. The mixture was extracted with DCM (3 x 50 mL), dried (MgSO₄), filtered and the solvent removed *in vacuo*. After purification by column chromatography on silica (acetone/DCM gradient 1:9 to 1:4) the product was obtained as a crystalline yellow powder. Yield 0.25 g (0.51 mmol, 90%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ: 8.41 (d, J = 1.7 Hz, 2H, H_c), 8.30 (d, J = 2.8 Hz, 2H, H_e), 7.75 (dd, J = 7.4, 8.2 Hz, 1H, H_a), 7.53 (d, J = 7.8 Hz, 2H, H_b), 7.42 (dd, J = 1.7, 2.9 Hz, 2H, H_d), 4.02 (t, J = 6.6 Hz, 2H, H_f), 1.85-1.78 (m, 2H, H_g), 1.51-1.43 (m, 2H, H_h), 1.37-1.33 (m, 4H, H_i, H_j), 0.92 (t, J = 7.0 Hz, 3H, H_k). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ: 154.7, 144.8 (C_c), 143.5, 139.1 (C_e), 136.9 (C_a), 126.8 (C_b), 123.2 (C_d), 119.4, 90.8, 86.5, 68.7 (C_f), 31.6, 29.1 (C_g), 25.7 (C_h), 22.7, 14.2 (C_k). IR (ATR): ν (cm⁻¹) 3044, 2961, 2916, 2854, 2207, 1578, 1553, 1461, 1439, 1421, 1398, 1328, 1310, 1248, 1221, 1168, 1058, 1027, 1013, 955, 974. HR-ESI-MS (DCM): m/z = 482.2824 [M + H]⁺ calc. 482.2802. Anal. calc. for C₃₁H₃₅N₃O₂: C, 77.31; H, 7.32; N, 8.72%. Found: C, 77.21; H, 7.28; N, 8.58%.

Figure 1.8 Partial ¹H NMR spectrum (CDCl₃, 298 K, 400 MHz) of L3. Figure 1.9 Partial ¹³C NMR spectrum (CDCl₃, 298 K, 400 MHz) of L3.

1.7 Synthesis of $\mathbf{C1} \cdot (\text{PF}_6)_4$

A combination of $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$ (38 mg, 0.15 mmol) and AgPF_6 (74 mg, 0.29 mmol) in CH_3CN (2 mL) was stirred in the absence of light for 1 h prior to filtration through Celite and addition to a suspension of **L1** (75 mg, 0.27 mmol) in CH_3CN (5 mL), and stirring for one hour. After centrifugation (4,000 RPM, 10 minutes), the supernatant was removed and added to diethyl ether, resulting in precipitation of the product as an off-white powder (107 mg, 0.56 mmol, 84%). ^1H NMR (400 MHz, solvent, 298 K) δ : 9.54 (s, 2H, H_f), 9.37 (d, $J = 5.3$ Hz, 2H, H_c), 8.34 (d, $J = 8.0$ Hz, 2H, H_d), 8.00 (t, $J = 7.7$ Hz, 1H, H_a), 7.85 (dd, $J = 6.1, 7.9$ Hz, 2H, H_e), 7.80 (d, $J = 7.8$ Hz, 2H, H_b). ^{13}C NMR (100 MHz, d_6 -DMSO, 298 K) δ : 153.0 (C_c), 151.0 (C_f), 143.5 (C_d), 141.8, 138.3 (C_a), 128.6 (C_b), 127.3 (C_e), 121.5, 93.3, 83.6. IR (ATR): ν (cm^{-1}) 1981, 1560, 1447, 1300, 1140, 837. HR-ESI-MS (DMSO/ CH_3CN): $m/z = 334.5581$ [**C1**] $^{4+}$ calc. 334.5473; 457.7327 [**C1** + Cl] $^{3+}$ calc. 457.7194; 563.5308 [**C1** - **L1** + 2Cl] $^{2+}$ calc. 563.5155. Anal. calc. for $[\text{Pd}_2(\text{C}_{24}\text{H}_{11}\text{N}_3)_4](\text{PF}_6)_4 \cdot 6\text{H}_2\text{O}$: C, 45.05; H, 2.79; N, 8.30%. Found: C, 44.82; H, 2.57; N, 8.17%.

Figure 1.10 Partial ^1H NMR spectrum (d_6 -DMSO, 298 K, 400 MHz) of $\mathbf{C1} \cdot (\text{PF}_6)_4$. Figure 1.11 Partial ^{13}C NMR spectrum (d_6 -DMSO, 298 K, 100 MHz) of $\mathbf{C1} \cdot (\text{PF}_6)_4$.

Figure 1.12 Partial stacked ^1H NMR spectra (CD_3CN , 298 K, 400 MHz) for a) **L1** and b) **C1**·(PF_6)₄.

Figure 1.13 Partial mass spectrum ($\text{DMSO}/\text{CH}_3\text{CN}$) of **C1**·(PF_6)₄.

1.8 Synthesis of $\text{C2} \cdot (\text{PF}_6)_4$

[Pd(CH₃CN)₂Cl₂] (21 mg, 0.080 mmol) and AgPF₆ (40 mg, 0.16 mmol) were combined in CH₃CN (0.75 mL) and the mixture was stirred in the absence of light for one hour. The suspension was filtered through Celite and resulting solution was added to a stirred solution of **L2** (75 mg, 0.15 mmol) in CH₃CN (0.75 mL). After 15 minutes, the solution was centrifuged (13,000 RPM, 10 minutes), the supernatant was removed and added to diethyl ether, resulting in precipitation of the product as an off-white powder (90 mg, 0.02 mmol, 60%). ¹H NMR (400 MHz, CD₃CN, 298 K) δ: 8.95 (s, 2H, H_c), 8.86 (d, J = 2.4 Hz, 2H, H_e), 7.90 (t, J = 7.8 Hz, 1H, H_a), 7.79 (s, 2H, H_d), 7.69 (d, J = 7.9 Hz, 2H, H_b), 4.34 – 4.31 (m, 4H, H_f), 3.87 – 3.85 (m, 4H, H_g), 3.66 – 3.63 (m, 4H, H_h), 3.50 – 3.48 (m, 4H, H_i), 3.29 (s, 6H, H_j). ¹³C NMR (100 MHz, CD₃CN, 298 K) δ: 157.0, 145.2 (C_c), 142.3, 139.1 (C_e), 137.8 (C_a), 128.6, 128.5, 122.9, 93.3, 82.4, 71.5 (C_h), 70.3 (C_i), 69.6 (C_f), 68.8 (C_g), 57.9 (C_j). IR (ATR): ν (cm⁻¹) 3079, 2893, 1991, 1583, 1437, 1246, 1052, 835. HR-ESI-MS (DMSO/CH₃CN): m/z = 570.6905 [**C2**]⁴⁺ calc. 570.6737; 700.2502 [**C2** + **L2** + H]⁴⁺ calc. 700.2313; 772.9053 [**C2** + H + Cl]³⁺ calc. 772.8905. Anal. calc. for x: C, ; H, ; N, %. Found: C, ; H, ; N, %.

Figure 1.14 Partial ¹H NMR spectrum (CD₃CN, 298 K, 400 MHz) of **C2**·(PF₆)₄. Figure 1.15 Partial ¹³C NMR spectrum (CD₃CN, 298 K, 100 MHz) of **C2**·(PF₆)₄.

Figure 1.16 Partial stacked ^1H NMR spectra (CD_3CN , 298 K, 400 MHz) for a) **L2** and b) **C2·(PF₆)₄**.

Figure 1.17 Partial mass spectrum ($\text{DMSO}/\text{CH}_3\text{CN}$) of **C2·(PF₆)₄**.

1.9 Synthesis of $\text{C3} \cdot (\text{BF}_4)_4$

To a stirring suspension of **L3** (96 mg, 0.2 mmol, 2 eq.) in CH_3CN (3 mL) was added dropwise a solution of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (44 mg, 0.1 mmol, 1 eq.) in CH_3CN (2 mL) and stirred for 1 h. The product was precipitated as tan crystals by vapour diffusion of Et_2O . Yield 79 mg (0.03 mmol, 64%). ^1H NMR (500 MHz, CD_3CN , 298 K) δ : 8.91 (d, $J = 1.5$ Hz, 8H, H_c), 8.83 (d, $J = 2.7$ Hz, 8H, H_e), 7.87 (dd, $J = 7.5, 8.2$ Hz, 4H, H_a), 7.71 (dd, $J = 1.5, 2.7$ Hz, 8H, H_d), 7.66 (d, $J = 7.8$ Hz, 8H, H_b), 4.16 (t, $J = 6.6$ Hz, 8H, H_f), 1.83-1.77 (m, 8H, H_g), 1.50-1.44 (m, 8H, H_h), 1.38-1.34 (m, 16H, H_i, H_j), 0.92 (t, $J = 7.1$ Hz, 12H, H_k). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ : 158.0, 145.9 (C_c), 143.4, 139.8 (C_e), 138.8 (C_a), 129.5 (C_d), 129.4 (C_b), 123.8, 94.2, 83.5, 71.1 (C_f), 32.1, 29.4 (C_g), 26.1 (C_h), 23.3, 14.3 (C_k). IR (ATR): ν (cm^{-1}) 3086, 2956, 2931, 2856, 1586, 1557, 1468, 1444, 1337, 1319, 1267, 1247, 1229, 1165, 1145, 1100, 1028, 878, 815. HR-ESI-MS (CH_3CN): $m/z = 534.7220$ [**C3**] $^{4+}$ calc. 534.7254; 741.9653 [**C3** + BF_4] $^{3+}$ calc. 741.9687; 750.6261 [**C3** + H + Br + CH_3OH] $^{3+}$ calc. 750.6181; 1135.4394 [**C3** + BF_4 + CHOO] $^{2+}$ calc. 1135.4521; 1156.4483 [**C3** + 2BF_4] $^{2+}$ calc. 1156.4551; 1169.4421 [**C3** + BF_4 + Br + CH_3OH + H] $^{2+}$ calc. 1169.4292; 1182.4331 [**C3** + Br + CH_3CN + H_2O] $^{2+}$ calc. 1182.4307. Anal. calc. for $[\text{Pd}_2(\text{C}_{31}\text{H}_{35}\text{N}_3\text{O}_2)_4](\text{BF}_4)_4 \cdot 10\text{H}_2\text{O}$: C, 55.85; H, 6.05; N, 6.30%. Found: C, 55.76; H, 5.91; N, 6.39%.

Figure 1.18 Partial ^1H NMR spectrum (CDCl_3 , 298 K, 400 MHz) of $\text{C3} \cdot (\text{BF}_4)_4$.

Figure 1.19 Partial ¹³C NMR spectrum (CD₃CN, 298 K, 400 MHz) of **C3·(BF₄)₄**.

Figure 1.20 Partial mass spectrum (DMSO/CH₃CN) of **C3·(BF₄)₄**.

1.10 ^{19}F NMR data

Figure 1.21 Partial stacked ^{19}F NMR spectra (d_6 -DMSO, 298 K, 376 MHz) of a) NaBF_4 , b) $\text{C1}\cdot(\text{BF}_4)_4$, c) $\text{C2}\cdot(\text{BF}_4)_4$, d) $\text{C3}\cdot(\text{BF}_4)_4$, e) KPF_6 , f) $\text{C1}\cdot(\text{PF}_6)_4$, g) $\text{C2}\cdot(\text{PF}_6)_4$.

2 Single Crystal X-ray Data

2.1 L3

Concentration of a chloroform solution of **L3** gave colourless needle crystals of **L3**. X-ray data were collected at 100 K on an Agilent Technologies Supernova system using Cu K α radiation with exposures over 1.0°, and data were treated using CrysAlisPro^[2] software. The structure was solved using SIR-97^[3] and weighted full-matrix refinement on F^2 was carried out using SHELXL-97^[4] running within the WinGX^[5] package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were placed in calculated positions and refined using a riding model. The structure was solved in the orthorhombic space group *Pccn* and refined to an R_1 value of 4.1%. Present in the asymmetric unit is **L3** (Figure 2.1).

Figure 2.1 Ellipsoid Mercury representation of the asymmetric unit of **L3**. Ellipsoids shown at 50% probability level.

2.2 C2·(PF₆)₄

Vapour diffusion of diethyl ether into an acetonitrile solution of **C2·(PF₆)₄** gave colourless crystals of **C2·(PF₆)₄**. X-ray data were collected at 100 K on an Agilent Technologies Supernova system using Cu K α radiation with exposures over 1.0°, and data were treated using CrysAlisPro^[2] software. The structure was solved using SIR-97^[3] and weighted full-matrix refinement on F^2 was carried out using SHELXL-97^[4] running within the WinGX^[5] package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were placed in calculated positions and refined using a riding model. The structure was solved in the triclinic space group *P1* and refined to an R_1 value of 10.4%. Present in the asymmetric unit is half of a **C2**⁴⁺ cation, and two PF₆[−] anions (Figure 2.2).

Figure 2.2 Ellipsoid Mercury representation of the asymmetric unit of **C2·(PF₆)₄**. Ellipsoids shown at 50% probability level.

The PEG chains on the structure were disordered, and required modelling using the PART, DFIX and ISOR commands. Additionally, parts of them had to be left isotropic, and two terminal methyl groups could not be located. Nonetheless, the core structure of the cage was well defined, and was a close fit for the previously obtained (and superior in terms of data quality) structure of **C2·(BF₄)₄**, in that the unit cell dimensions and superimposed structures were very similar (Figure 2.3).

Figure 2.3 Superimposed crystal structures of **C2·(BF₄)₄** (green, blue) and **C2·(PF₆)₄** (orange, violet). The two crystallographically independent counterions are shown once apiece. Hydrogen atoms and solvent molecules omitted for clarity.

There was diffuse electron density within the cavity that could not be appropriately modelled, and the SQUEEZE routine running within PLATON was employed to solve this problem, with the void electron count consistent with the presence of two acetonitrile solvent molecules (Table 2.1, compare with the structure for **C3·(BF₄)₄**).

Table 2.1 SQUEEZE details for **C2·(PF₆)₄**.

Platon squeeze void average x	0.500
Platon squeeze void average y	1.000
Platon squeeze void average z	0.000
Platon squeeze void volume	480
Platon squeeze void electron count	87
Platon squeeze void content	There are 43.5 electrons to be accounted for per cage (87/Z), which we assign to two CH ₃ CN solvent molecules (4 x 22 electrons) for 88 total electrons.

2.3 **C3·(BF₄)₄·2CH₃CN·4H₂O**

Vapour diffusion of diethyl ether into an acetonitrile solution of **C3·(BF₄)₄** gave colourless crystals of **C3·(BF₄)₄·2CH₃CN·4H₂O**. X-ray data were collected at 100 K on an Agilent Technologies Supernova system using Cu K α radiation with exposures over 1.0°, and data were treated using CrysAlisPro^[2] software. The structure was solved using SIR-97^[3] and weighted full-matrix refinement on F^2 was carried out using SHELXL-97^[4] running within the WinGX^[5] package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were placed in calculated positions and refined using a riding model. The structure was solved in the triclinic space group $P\bar{1}$ and refined to

an R_1 value of 14.2%. Present in the asymmetric unit is half of a C3^{4+} cation, two BF_4^- anions, one acetonitrile solvent molecule encapsulated in the cationic cavity, and two water molecules (20% and 25% occupancy each).

Atoms C70 and C82 were disordered and modelled with the ISOR command. Both tetrafluoroborate anions were disordered. The PART command was used to resolve this in both cases. The first BF_4^- had three fluorides (F2, F3, F4) parted with 70% occupancy in the major site and 30% in the minor. The second had a boron and two fluorides parted with equal (50%) occupancy over both sites, with additional disorder in one case modelled with the SIMU command (B22 F21 F22 F25 F26). The two water molecules were given occupancy of 25% and 20%. Lastly, the end of one of the hexyl chains (C1, C2, C3 and associated hydrogens) was disordered over two sites, again modelled with the PART command with equal occupancy of 50% over both sites.

Figure 2.4 Ellipsoid Mercury representation of the asymmetric unit of $\text{C3} \cdot (\text{BF}_4)_4 \cdot 2\text{CH}_3\text{CN} \cdot 4\text{H}_2\text{O}$. Ellipsoids shown at 50% probability level.

2.4 Crystallographic data

Identification code	L3		C2·(PF ₆) ₄	
Empirical formula	C ₃₁ H ₃₅ N ₃ O ₂		C ₅₈ H ₆₂ F ₁₂ N ₆ O ₁₂ P ₂ Pd	
Formula weight	481.62		1431.47	
Temperature	100.5(10) K		100.01(10)K	
Wavelength	1.54184 Å		0.71073 Å	
Crystal system	Orthorhombic		Triclinic	
Space group	<i>Pccn</i>		<i>P</i> $\bar{1}$	
Unit cell dimensions	a = 11.12790(10) Å	α = 90°.	a = 14.9660(10) Å	α = 115.672(4)°.
	b = 19.4631(2) Å	β = 90°.	b = 16.6190(10) Å	β = 94.848(3)°.
	c = 12.32520(10) Å	γ = 90°.	c = 17.3940(10) Å	γ = 112.518(4)°.
Volume	2669.43(4) Å ³		3435.1(4) Å ³	
Z	4		2	
Density (calculated)	1.198 Mg/m ³		1.384 Mg/m ³	
Absorption coefficient	0.590 mm ⁻¹		0.408 mm ⁻¹	
F(000)	1032		1464	
Crystal size	0.3193 x 0.1326 x 0.0795 mm ³		0.3207 x 0.1591 x 0.1328 mm ³	
Theta range for data collection	4.544 to 73.505°.		1.538 to 26.423°.	
Index ranges	-13<=h<=13, -24<=k<=23, -14<=l<=15		-18<=h<=18, -20<=k<=20, -21<=l<=21	
Reflections collected	23664		49274	
Independent reflections	2669 [R(int) = 0.0353]		13771 [R(int) = 0.0606]	
Completeness	99.90% to theta = 67.684°		100.00% to theta = 25.242°	
Absorption correction	Gaussian		Gaussian	
Max. and min. transmission	1.00000 and 0.85088		1.00000 and 0.65061	
Refinement method	Full-matrix least-squares on F2		Full-matrix least-squares on F2	
Data / restraints / parameters	2669 / 0 / 165		13771 / 13 / 855	
Goodness-of-fit on F2	1.37		1.381	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1465		R1 = 0.1038, wR2 = 0.3109	
R indices (all data)	R1 = 0.0431, wR2 = 0.1500		R1 = 0.1126, wR2 = 0.3234	
Largest diff. peak and hole	0.236 and -0.203 e.Å ⁻³		3.422 and -1.388 e.Å ⁻³	

Identification code	C3·(BF₄)₄·2CH₃CN·4H₂O	
Empirical formula	C ₁₂₈ H _{147.80} B ₄ F ₁₆ N ₁₄ O _{8.90} Pd ₂	
Formula weight	2584.84	
Temperature	100(2) K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 15.077(5) Å	α = 113.683(5)°.
	b = 16.532(5) Å	β = 96.121(5)°.
	c = 17.434(5) Å	γ = 114.752(5)°.
Volume	3410.9(18) Å ³	
Z	1	
Density (calculated)	1.258 Mg/m ³	
Absorption coefficient	2.793 mm ⁻¹	
F(000)	1341	
Crystal size	0.28 x 0.13 x 0.07 mm ³	
Theta range for data collection	3.20 to 77.03°.	
Index ranges	-17<=h<=19, -20<=k<=20, -21<=l<=21	
Reflections collected	36605	
Independent reflections	14032 [R(int) = 0.0794]	
Completeness	97.30% to theta = 77.03°	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8285 and 0.5085	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14032 / 36 / 853	
Goodness-of-fit on F ²	1.878	
Final R indices [I>2sigma(I)]	R ₁ = 0.1416, wR ₂ = 0.3230	
R indices (all data)	R ₁ = 0.1668, wR ₂ = 0.3366	
Largest diff. peak and hole	5.996 and -1.476 e.Å ⁻³	

2.5 Solvent-cage host-guest interactions

Figure 2.5 Selected interactions for a) $\text{C2} \cdot (\text{BF}_4)_4$, distances: and b) $\text{N}_{\text{py}} \cdots \text{HO}$ 1.982 Å, $\text{OH} \cdots \text{O}$ 2.016 Å, $\text{O} \cdots \text{HC}$ 2.495 Å, $\text{F} \cdots \text{HC}$ 2.665 Å, 2.179 Å, $\text{F} \cdots \text{Pd}$ 3.088(5) Å; $\text{C3} \cdot (\text{BF}_4)_4$, distances: $\text{Pd} \cdots \text{N}_{\text{CH}_3\text{CN}}$ 3.44(1) Å, $\text{N}_{\text{py}} \cdots \text{HC}$ 2.71, $\text{N}_{\text{CH}_3\text{CN}} \cdots \text{HC}$ 2.52.

2.6 Void figures

Voids calculated in Mercury, probe radius 2 Å, grid spacing 0.7 Å.^[6]

a)

b)

Figure 2.6 Voids of a) $\text{C1} \cdot (\text{BF}_4)_4$ and b) $\text{C2} \cdot (\text{BF}_4)_4$. Cationic portions of the structure shown in tube view, counterions in spacefilling view, solvent molecules and hydrogen atoms omitted, and void space within the cavity shown. Colours: carbon grey, boron salmon, fluoride yellow, nitrogen blue, oxygen red, palladium magenta, voids in green.

3 Powder X-ray Data

Data were collected on a PANalytical X'Pert PRO MPD Diffractometer, with a copper anode (K- α 1: 1.5406 Å, K- α 2: 1.54443 Å), with tube current 30 mA and tube tension 40 kV. The collection range was 3.00209 to 34.99409 °2 θ , with 0.004 °2 θ steps and 10.075 s collection time per step. Calculated powder diffraction patterns were obtained in Mercury.^[7]

Figure 3.1 Powder diffraction pattern over the 2 θ range of 5 – 35° for a) $C1 \cdot (BF_4)_4$, b) $C1 \cdot (PF_6)_4$, c) $C2 \cdot (PF_6)_4$, and d) $C2 \cdot (BF_4)_4$, experimental above in black, calculated below in red.

4 Thermogravimetric analyses

Thermogravimetric analyses were conducted on a METTLERTGA/SDTA851 apparatus. Samples are held at a temperature of 25 °C for a period of 5 minutes and subsequently heated to 450 °C. During the measurements a flow of N₂ (2 mL/min) is passed over the sample.

Figure 4.1 TGA plot for C1·(BF₄)₄

Figure 4.2 TGA plot for C1·(PF₆)₄

Figure 4.3 TGA plot for $C2 \cdot (BF_4)_4$

Table 4.1 Desolvation data obtained from TGA analysis of selected cages.

CAGE	M_w cage (g mol ⁻¹)	% Desolvation by mass	M_w solvent (g mol ⁻¹)	Estimated solvent content
$C1 \cdot (BF_4)_4$	1685.32	4.82	81.25	2 x CH ₃ CN = 82.10 g mol ⁻¹
$C1 \cdot (PF_6)_4$	1917.17	3.77	72.26	4 x H ₂ O = 72.04 g mol ⁻¹
$C2 \cdot (BF_4)_4$	2630.38	3.58	94.28	5 x H ₂ O = 90.05 g mol ⁻¹

5 Gas Sorption Data

5.1 Gas sorption experimental procedures

The following relates to gas sorption studies undertaken. Prior to gas sorption measurements each sample was heated under dynamic vacuum over-night. The following temperatures employed for evacuation of each sample were selected on the basis of thermogravimetric analysis.

C1·(BF₄)₄ was heated at 140 °C, the heated solid had resultant mass: 0.0977 g.

C1·(PF₆)₄ was heated at 120 °C, the heated solid had resultant mass: 0.0886 g.

C2·(BF₄)₄ was heated at 140 °C, the heated solid had resultant mass: 0.0944 g.

C2·(PF₆)₄ was heated at 100 °C, the heated solid had resultant mass: 0.0684 g

C3·(BF₄)₄ was heated at 120 °C, the heated solid had resultant mass: 0.0742 g

For each material, the same sample was employed for each measurement, between gas sorption measurements the sample was heated at their respective evacuation temperatures under dynamic vacuum for at least one hour. Gas sorption data were measured using a Sieverts-type BELsorp-HP automatic gas sorption apparatus (BEL Japan Inc.). 99.999% purity CO₂, N₂, He (employed as an inert gas) and H₂ were used for sorption studies.

Non-ideal gas behaviour of each gas at each measurement and reference temperature was corrected for. Source data were obtained from the NIST fluid properties website.^[8] For isotherm measurements ranging from 258 – 298 K, sample compartment temperatures were controlled by a Julabo F25-ME chiller/heater that re-circulated fluid at +/- 0.1 °C through a capped, jacketed stainless steel flask housed within a polystyrene box. A calibrated external Pt 100 temperature probe monitored the flask temperature. Cryogenic temperatures were maintained with a BEL liquid N₂ level controller. Prior to gas sorption measurements, samples were held at the measurement temperature for a minimum of one hour to allow full thermal equilibrium to be attained before data collection. Isotheric CO₂ sorption enthalpies were calculated using a least-squares fitting of a virial-type thermal adsorption equation that modelled ln(P) as a function of the amount of surface excess of gas sorbed at 258 and 273 K.^[8] Optimised virial coefficients and R² values relating to CO₂ fitting are given in Table S1.

Table S1: Optimised virial coefficients for modelling excess CO₂ for all compounds

Compound	C1·(BF ₄) ₄	C1·(PF ₆) ₄	C2·(BF ₄) ₄	C2·(PF ₆) ₄	C3·(BF ₄) ₄
a0	-4282.79	-3952.59	-3447.18	-3315.22	-3385.24
a1	425.2792	851.3729	140.0801	276.9231	1006.981
a2	287.7401	-15.9779	353.7253	261.1885	-428.624
a3	127.8789	-264.768	133.1694	96.39319	-497.778
a4	-212.28	119.0537	-220.275	-241.757	529.9288
a5	49.76074	-14.6625	88.68767	49.84861	-130.759
b	17.16719	17.12289	18.34494	17.70425	17.35919
R²	0.9994453	0.9989638	0.9975228	0.9942465	0.9919644

5.2 CO₂ sorption

Figure 5.1 CO₂ sorption for C1·(BF₄)₄.

Figure 5.2 CO₂ sorption for C1·(PF₆)₄. Figure 5.3 CO₂ sorption for C2·(BF₄)₄.

Figure 5.4 CO₂ sorption for $\text{C2} \cdot (\text{PF}_6)_4$. Figure 5.5 CO₂ sorption for $\text{C3} \cdot (\text{BF}_4)_4$.

5.3 N₂ Sorption

Figure 5.6 N₂ sorption for C1·(BF₄)₄ (77 K).

5.4 Enthalpies of CO₂ adsorption

Figure 5.7 Enthalpies of adsorption for $\text{C1} \cdot (\text{BF}_4)_4$ (■), $\text{C1} \cdot (\text{PF}_6)_4$ (●), $\text{C2} \cdot (\text{BF}_4)_4$ (▼), $\text{C2} \cdot (\text{PF}_6)_4$ (▲), and $\text{C3} \cdot (\text{BF}_4)_4$ (◆).

6 CS₂ Binding

Figure 6.1 Partial ^1H NMR stacked spectra (298 K, CD_3CN , 400 MHz) for a) $\text{C1} \cdot (\text{BF}_4)_4$, b) CS_2 and $\text{C1} \cdot (\text{BF}_4)_4$, c) $\text{C2} \cdot (\text{BF}_4)_4$ and d) CS_2 and $\text{C2} \cdot (\text{BF}_4)_4$.

7 Computations

Geometry optimizations were performed using density functional theory (DFT), using the B3LYP functional calculated *in vacuo*. A LanL2DZ basis set including an effective core potential was used to represent palladium(II) and a 6-31G(d) basis set used on all remaining atoms. The Cartesian coordinates of the cationic cage structure were obtained from X-ray crystallographic data (as previously reported).^[9] The coordinates of the cage structure were frozen and the guests allowed to optimise their geometries and positions freely. All calculations were performed using Gaussian09.^[10] Molecular models available as xyz files. Up to four CO₂ molecules could be accommodated within the cavity. The fifth CO₂ molecule optimised in an exterior position. The relative energies of successive interaction of CO₂ molecules with **C1**⁴⁺ were calculated using the difference between the products-reactants systems of the following chemical equation:

Figure 7.1 Depictions of the calculated structures of $[(\text{CO}_2)_{(n+1)}\text{C1}]^{4+}$ with the respective energies for each adduct.

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