Supplementary Material (ESI) for Chemical Communications

Self-assembly hexanuclear metallacontainer hosting halogenated guest species and sustaining structure of 3D coordination framework†

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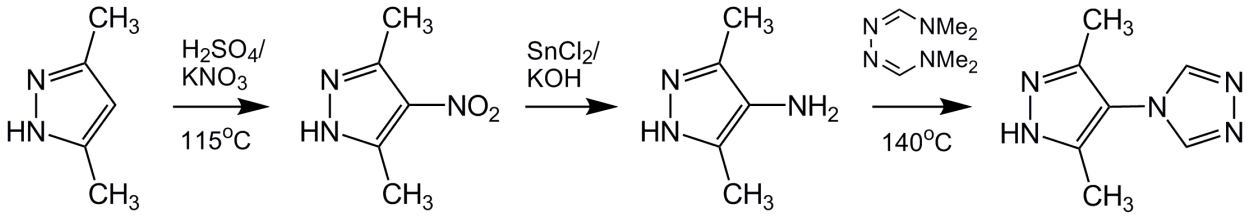
SUPPORTING INFORMATION

CONTENTS

1. Synthesis

1.1. Preparation of the ligand

The organic ligand 4-(3,5-dimethylpyrazol-4-yl)-1,2,4-triazole (H*pztr*) was prepared in a 65% yield by an acid catalized reaction of dimethylformamide azine and 4-amino-3,5-dimethylpyrazole in boiling xylene. The amino compound was obtained in a two-stage synthesis starting with 3,5-dimethylpyrazole:



4-Nitro-3,5-dimethylpyrazole. To a solution of 14.48 g 3,5-dimethylpyrazole in 130 ml conc. H_2SO_4, 26.34 g of solid KNO_3 was added at r.t. with stirring. After dissolution of nitrate, the mixture was stirred at 110-115°C for 8 h, then cooled to r.t., added to 150 g of crushed ice and neutralized with 20% ammonia to pH = 3. The precipitate of the nitropyrazole was filtered, washed with water and dried. Pure product was obtained after a single recrystallization from benzene. The yield was 18.65 g (88%).

4-Amino-3,5-dimethylpyrazole. To a well-stirred suspension of 4-nitro-3,5-dimethylpyrazole (5.07 g, 36 mmol) in a solution of 40.0 g KOH in 100 ml water, solid $SnCl_2 \cdot 2H_2O$ (27.57 g, 122 mmol) was added in three nearly equal portions for 3 h at 90-100°C. The initially developed deep-purple color of the solution dissapears during next 5-6 h at the above temperature. The mixture was cooled to r.t., the solid product was filtered and washed with 3 ml ice-cold water. The yield was 2.60 g (65%). M.p. = 285-290°C. NMR (dmso-d_6, δ): 2.10 (s, 6H, CH_3), 6.10 (s, 2H, NH_2), 12.58 (s, 1H, NH).

4-(3,5-dimethylpyrazol-4-yl)-1,2,4-triazole (H*pztr*). 4-Amino-3,5-dimethylpyrazole (3.33 g, 30 mmol), dimethylformamide azine (4.69 g, 33 mmol) and *p*-toluenesulfonic acid monohydrate (0.24 g, 1.3 mmol) were stirred and refluxed in 25 ml *o*-xylene for 24 h. The reaction proceeds smoothly with evolution of dimethylamine and precipitation of the triazole. After cooling to r.t., the solvent was removed by decantation and the crystalline product was washed with xylene and ethanol. Yield: 3.28 g (67%). M.p. = 259°C. NMR (dmso-d_6, δ): 2.10 (s, 6H, CH_3); 8.48 (s, 2H, CH); 12.60 (s, 1H, NH).

1.2. Synthesis of coordination compounds

A general procedure for the hexanuclear hydroxocopper(II) species was based on heterogeneous reaction of copper(II) chloride, alkali and the ligand in the presence of lipophilic large cations, such as tetraalkylammonium NPr_4^+ and NBu_4^+ or K(18-crown-6)$^+$, in the media of wet dichloromethane (no product formed in a dry CH_2Cl_2). Prior the synthesis the solvent was *saturated with water* by standing overnight under an aqueous layer. Very minor modification of the synthesis was used for preparation of the chloroform adduct **1**, due to instability of the solvent in the presence of alkali. We note that the combination of singly charged centrosymmetric K(18-crown-6)$^+$ cations and singly charged centrosymmetric $[Cl\subset Cu_6(OH)_6(pztr)_6]^-$ anions was essential for the preventing the complicated disorder of the cationic portion (*i.e.* NPr_4^+ or NBu_4^+) in the crystal structre.

Preparation of $[K(18c6)(THF)_2][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 2CH_2Cl_2\cdot 4THF$ (2). A mixture of 18-crown-6 (79.2 mg, 0.3 mmol) and KCl (22.4 mg, 0.3 mmol) was stirred for 1 h in 10 ml of wet dichloromethane. Then solid reagents $CuCl_2\cdot 2H_2O$ (51.0 mg, 0.3 mmol), KOH (33.6 mg, 0.6 mmol) and H*pztr* (49.5 mg, 0.3 mmol) were added to the solution and the stirring was continued for 24 h at rt. The blue color of the CH_2Cl_2 phase was developed during first 3-4 h. The insoluble material was filtered and the product was isolated in the form of deep-blue prisms by slow diffusion of THF vapor to the clear deep-blue filtrate for a period of 3-4 d. The yield was 22%.

Anal. for **2**, $C_{80}H_{130}Cl_5Cu_6KN_{30}O_{18}$. Calc. (%): C, 40.07; H, 5.46; N, 17.52. Found (%): C, 40.56; H, 5.41; N, 17.78.

Preparation of $[K(18c6)(Diox)_2][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 4CHCl_3\cdot 2Diox$ (1). To the dichloromethane solution of the "metallacrown" complex (which is prepared as described above) 10 ml of ether was added. Blue powdery precipitate was filtered off and dried in air. This material was dissolved in 7 ml of chloroform and 10 ml of 1,4-dioxane was layered over the solution. Large deep-blue prisms of the complex grew on the walls of the tube as the solvents interdiffused over a period of 10-12 d. The yield was 20%.

Anal. for **1**, $C_{74}H_{114}Cl_{13}Cu_6KN_{30}O_{20}$. Calc. (%): C, 33.86; H, 4.38; N, 16.01. Found (%): C, 34.09; H, 4.54; N, 16.43.

Preparation of $[Cd\{CdCl_4\subset Cu_6(OH)_6(pztr)_6]\cdot 13EtOH$ (3). This was synthesized using layering technique. In a 20 ml test tube, 4 ml of CH_2Cl_2/EtOH (1:1 v/v) mixture was carefully layered over a solution of 24 mg (0.01 mmol) of complex (**2**) in 6 ml CH_2Cl_2. Then, a solution of 6.8 mg (0.03 mmol) of $CdCl_2\cdot 2.5H_2O$ in 2 ml ethanol was layered over the second layer. Slow interdiffusion of the components for 20-25 d led to crystallization of deep-blues prisms of the product. The yield was 11 mg (45%).

Anal. for **3**, $C_{68}H_{132}Cd_2Cl_4Cu_6N_{30}O_{19}$. Calc. (%): C, 33.70; H, 5.49; N, 17.35. Found (%): C, 33.26; H, 5.27; N, 17.68.

Preparation of $[NPr_4][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 5H_2O$ (4). A mixture of NPr_4Cl (66.3 mg, 0.3 mmol), H*pztr* (49.5 mg, 0.3 mmol), $CuCl_2\cdot 2H_2O$ (51.0 mg, 0.3 mmol) and KOH (33.6 mg, 0.6 mmol) was stirred for 24 h in 10 ml of wet dichloromethane. The blue solution was filtered and large deep-blue prisms of the product were isolated by slow diffusion of THF vapor into the filtrate for 7-8 d. This solvated product is unstable in air and readily loses solvent of crystallization. The crystals were outgased in vacuum at r.t (10^{-3} Torr, 6 h) yielding light-blue powder of (**4**) in 26% yield.

Anal. for **4**, $C_{54}H_{92}ClCu_6N_{31}O_{11}$. Calc. (%): C, 36.68; H, 5.24; N, 24.56. Found (%): C, 36.48; H, 5.12; N, 24.37.

2. Crystal Structure Determination

Diffraction data were collected at 100 K on a Bruker APEXII CCD area-detector diffractometer (φ scans) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scans method). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 package (G.M. Sheldrick, *Acta Cryst.*, 2008, A64, 112.).

$[K(18c6)(Diox)_2][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 4CHCl_3\cdot 2Diox$ (1).

The complex cations $[K(18c6)(Diox)_2]^+$ are situated across a center of inversion. The coordinated dioxane molecule is equally disordered over two positions. The disorder was resolved with restraints in geometry and thermal parameters (DFIX/SIMU). It possible to refine the disordered atoms anisotropically and the hydrogen atoms were at calculated positions.
Two unique solvate dioxane molecules are ordered, both are situated across inversion center.

Solvate $CHCl_3$ molecule exhibits typical rotational disorder of chlorine atoms. The unequal partial occupancies (85/15) were established by refinement of thermal parameters and only atoms of the major contribution were refined anisotropically. The uncoordinated triazole group of the organic ligand is also equally disordered over two positions (similarly to the disorder model for complex **3**, see Figure S2). This group was refined anisotropically with set of restraints in geometry (DFIX) and thermal parameters (SIMU).

CH hydrogen atoms were placed in calculated positions and refined within a riding model, with $U_{iso} = 1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl groups). OH hydrogen atoms were located and then fixed with $U_{iso} = 1.5U_{eq}(O)$.

$[K(18c6)(THF)_2][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 2CH_2Cl_2\cdot 4THF$ (2).

Main problem of the refinement was connected with modeling disorder of THF molecules. The coordinated THF molecule of the centrosymmetric $[K(18c6)(THF)_2]^+$ cation

(18c6 ligand itself adopts the most typical nearly D_{3d} conformation) is disordered. This was resolved with two equal contributions from two of the methylene carbon atoms and with restraints in geometry and thermal parameters (DFIX/SIMU) (Figure S1). Atoms of this molecule were left isotropic (U_{iso} = 0.069-0.140 Å^2) and the hydrogen atoms were not added. Also, two of three independent solvate THF molecules are disordered over a center of inversion (no hydrogen atoms added here). One of them was refined isotropically (U_{iso} = 0.063-0.124 Å^2) and with restraints in geometry. In all other cases, non-hydrogen atoms were refined anisotropically and CH hydrogen atoms were placed in calculated positions and refined within a riding model, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. OH hydrogen atoms were located and then fixed with $U_{iso} = 1.5U_{eq}$(O).

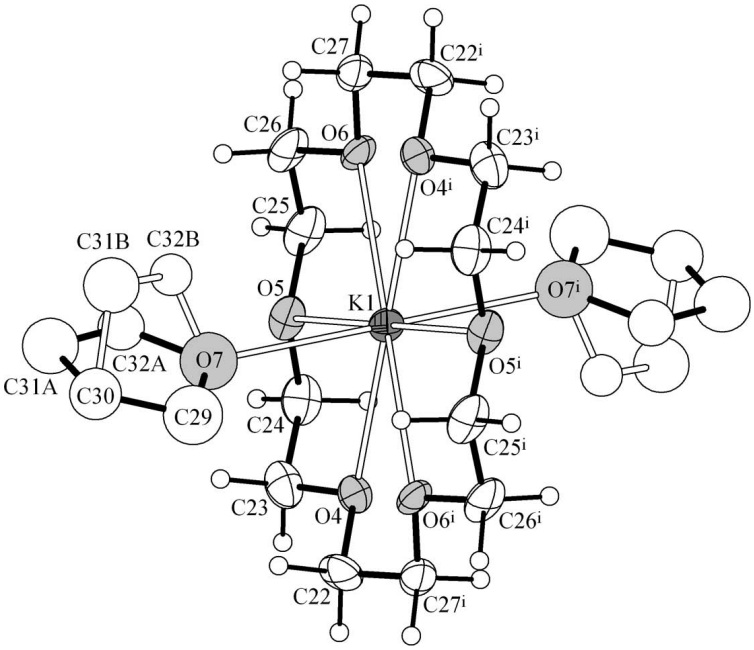


Figure S1. Structure of $[K(18c6)(THF)_2]^+$ cation in **2** showing disordering scheme for THF molecules. Thermal ellipsoids are at 40% probability level, while atoms of THF are isotropic. Bond lengths: K1-O (18c6) 2.746(5)-2.828(5) Å; K1-O (THF) 2 × 2.666(7) Å.

$[Cd\{CdCl_4 \subset Cu_6(OH)_6(pztr)_6]\cdot 13EtOH$ (3).

$[CdCl_4 \subset Cu_6(OH)_6(pztr)_6]^{2-}$ moiety has centrosymmetric structure and is situated over $\bar{3}$ axis. Therefore, only 1/6 of the molecule is independent. Due to the centrosymmetric structure of this host-guest complex, the incorporated $CdCl_4^{2-}$ anion is equally disordered over two positions (one guest anion per two cages). Atoms of tetrachlorocadmate were refined anisotropically without any restraints. Another cage of the "metallacontainer" is populated with ethanol molecule (two other ethanol molecules are located in the framework voids amounting a total solvate composition 13EtOH per single $[CdCl_4 \subset Cu_6(OH)_6(pztr)_6]^{2-}$). This ethanol molecule is disordered by symmetry over three position (3 axis) and considering the 50/50 disorder of the

guests ($CdCl_4^{2-}$/EtOH), atoms of this ethanol were refined with partial contribution factors 1/6. The bond lengths were restrained (±0.01 Å) and hydrogen atoms were not added.

One of two solvate ethanol molecules was refined isotropically. Second EtOH molecule exhibits complicated disorder over several positions, which cannot be satisfactorily resolved. Therefore, in the final refinement, the contribution from this moiety was modeled using Squeeze routine implemented in the PLATON program (A.L. Spek, PLATON, University of Utrecht, The Netherlands, 2001.).

In addition, very high anisotropy for thermal motion of the triazole ring atoms also indicated possible disorder. The refined model in depicted in Figure S2: two contributions of the disorder are related as rotation around N5---N3 axis. Thus N3 and N5 atoms of the ring are orderd, while other three atoms are equally disordered over two positions (C6 and C6A; C7 and C7A; N4 and N4A, N4---N4A 0.74 Å). Soft geometry restraints for geometry of triazole ring were applied (DFIX/FLAT) and the H atoms were added with partial occupancy factors 0.5 (U_{iso} = 1.5U_{eq}(C). Methyl CH hydrogen atoms were placed in calculated positions and refined within a riding model, with U_{iso} = 1.5U_{eq} of the carrier atom.

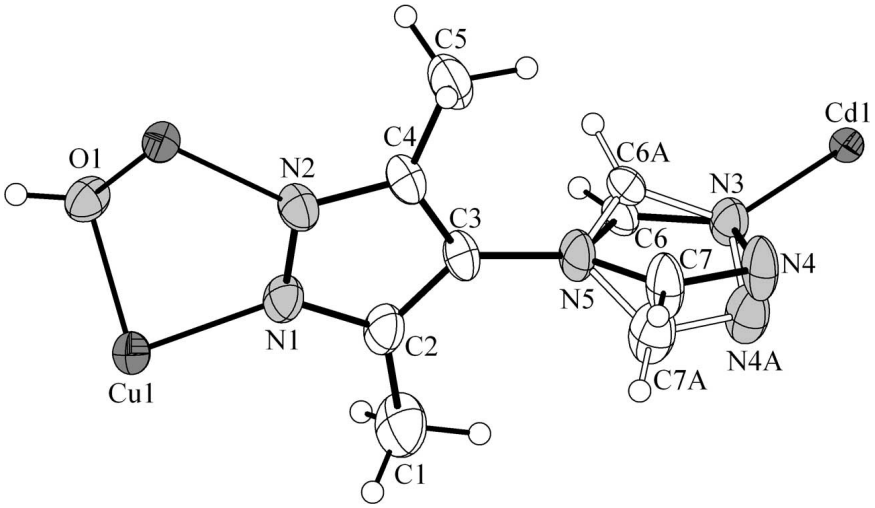


Figure S2. Coordination mode of the organic ligand in heterometallic complex **3** showing disordering scheme (50/50) for the triazole ring. Thermal ellipsoids are at 40% probability level.

3. Theoretical Methods

We have optimized the complexes of the $[Cl\subset Cu_6(OH)_6(pztr)_6]^-$ host (**H**) with $CHCl_3$ (**G1**), CH_2Cl_2 (**G2**), CHF_3 (**G3**) and DMF (**G4**) using DFT calculations. We have used the RI-BP86 functional combined with the def2-TZVP basis set. The RI-BP86 method applied to the study of non-covalent interactions is considerably faster than the BP86 and the interaction energies and equilibrium distances are almost identical for both methods.[1] This level of theory can be qualified as good taking into account the size of the systems studied here. In Figure S3 we show some optimized complexes (C_i symmetry have been imposed in the optimizations of **H·G1**,

H·G2 and **H·G3** complexes). The calculations have been performed using the TURBOMOLE program.[2]

The energetic and geometric characteristics of the complexes are shown in Table 1. From the inspection of the results several interesting point arise. First, the Cu-O, Cu-N and Cu-Cl

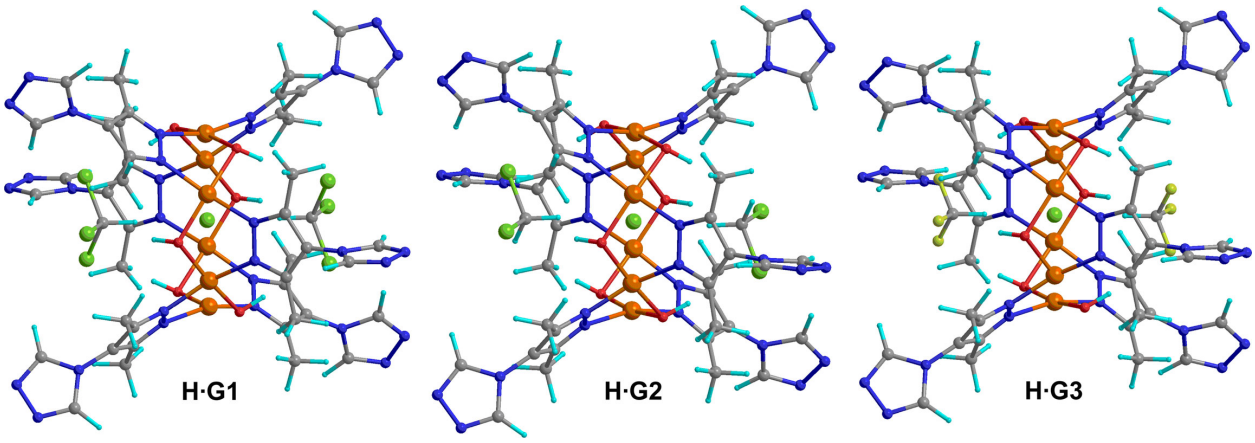


Figure S3. RI-BP86/def2-TZVP optimized complexes with chloroform (**H·G1**), dichloromethane (**H·G2**) and fluoroform (**H·G3**).

distances of the optimized complexes are in reasonable agreement with the experimental values. This result gives reliability to the theoretical level of theory used in the theoretical analysis. Second, the computed noncovalent distances between the different guests and the host are shorter than the experimental ones. This result is not surprising since the equilibrium distances of weak complexes are shorter in the gas phase than in the solid state since additional interactions are present in the solid state. The important point here is that we are able to reproduce the experimental trend in the equilibrium distance, which is shorter in complex **H·G1** than in **H·G2**. Third, the complex **H·G3** presents the shortest equilibrium distance, which indicates that should be the best host of the three considered here. Finally, the latter point is confirmed by examining the interaction energies. The relative interaction energies ($\Delta\Delta E$) indicate that complex guest **G3** should be better absorbed than **G1** and this one better than **G2**.

Table 1. Relative interaction energies of complexes **H·G1-4** in kcal/mol and some relevant distances in Å

Complex	Energy ($\Delta\Delta E$)	d (X···HC)	d (Cu-O)	d (Cu-N)	d (Cu-Cl)
H·G1	-0.29	2.533	1.994-1.999	1.992-1.994	3.092-3.095
H·G2	0.00	2.574	1.997-2.000	1.980-1.983	3.098-3.102
H·G3	-3.07	2.452	2.000-2.001	1.978-1.980	3.098-3.104
H·G4	-4.06	-	1.980-2.003	1.982-1.990	2-957-3.150

An especial mention deserves model complex with dimethylformamide **H·G4**. All our attempts to optimize this complex where the guest is located inside the cavity have been

unsuccessful. The DMF molecules move outside during the optimization reaching to a spatial position where the carbonyl group interacts with the hydrogen atoms of two triazole rings. Here we propose that the DMF displaces the other guests by closing the entrance of the cavity, since it forms two strong hydrogen bonds with the acidic hydrogen atoms of the triazole (see Figure S4). It should be mentioned that the optimization of **H·G4** has been computationally time demanding because no symmetry constrains have been imposed and we have performed several attempts to maintain the DMF inside. Its relative binding energy (see Table 1) is -4.06 kcal/mol indicating that the DMF is able to displace all guests.

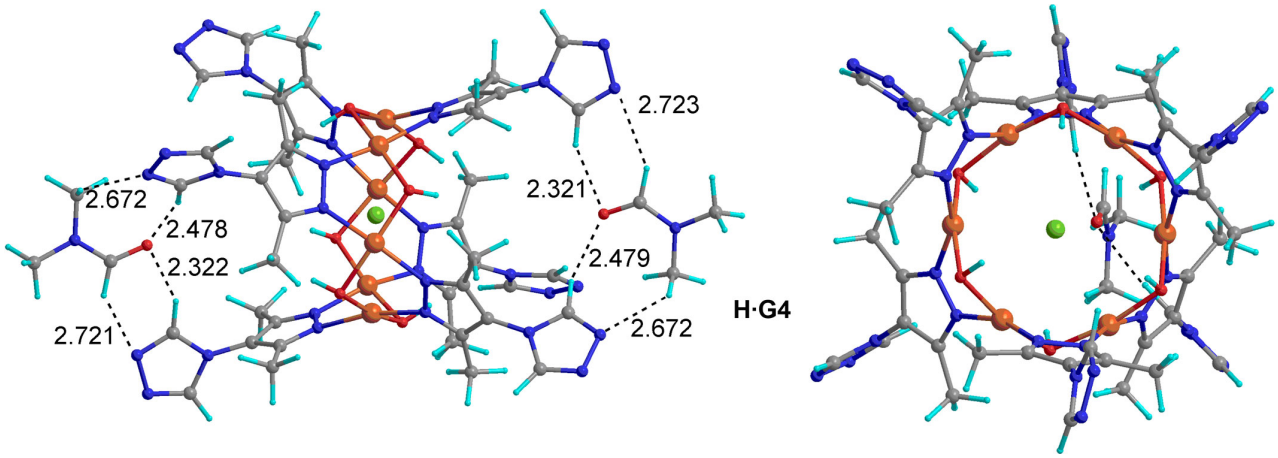


Figure S4. Two views of the RI-BP86/def2-TZVP optimized complex **H·G4**. In the on-top view (right), one DMF molecule has been omitted for clarity.

4. Adsorption studies

Dichlormethane adsorption isotherms were recorded in a magnetic suspension balance (Rubotherm, Germany) equipped with a vapour dosage system that can be operated from ultra high vacuum (0.05 Pa) up to 100 kPa. Three different pressure transducers (MKS, US) were used in a range from vacuum up to 10 Pa, up to 1 kPa and up to 100 kPa with an accuracy of 0.05 %. High pressure adsorption isotherms of carbon dioxide and methane were measured in a magnetic suspension balance (Rubotherm, Germany) operating up to 50 MPa. Highly accurate (0.05 %) pressure sensors (Newport Omega, US) were used to register the pressure of each equilibrium step.

In a typical experiment, a stainless steel sample holder was filled with about 0.1–0.2 g sample of complex **4**. The balance was evacuated for 12 hours at 298 K and 0.05 Pa until constant mass was achieved. For measuring the sorption capacity, the vapour/gas was dosed into the balance chamber to elevated pressures. Equilibrium was achieved, if no further weight increase and pressure change over a time range of approximately 15 min was observed. The temperature was kept constant with an accuracy of ± 0.1 K for each measurement.

Additionally, for each isotherm, a buoyancy correction was used to calculate the surface excess mass from the measured values. A detailed description of this procedure can be found elsewhere[3]. For the determination of the density of carbon dioxide, methane and nitrogen from pressure and temperature, the program *FLUIDCAL* was used[4]. In terms of dichlormethane, the density was calculated by using the Soave-Redlich-Kwong equation of state[5].

In accordance with these preliminary data, the desolvated $[Cl\subset Cu_6(OH)_6(pztr)_6]^-$ salts are able to adsorb dichloromethane from the gas phase. Although the desolvatation led to collapse of the crystal structure and loss of crystallinity, the residual materials preserve certain porosity due to the presence of the significant intramolecular cavities. Additional guest accessible space is provided by the intermolecular voids, which is a common feature for the packings of nearly trigonal molecules. Thus desolvatation of $[NPr_4][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot$Solv (Solv = CH_2Cl_2, H_2O) (10^{-3} Torr, 6 h) yields light-blue powdery material $[NPr_4][Cl\subset Cu_6(OH)_6(pztr)_6]\cdot 5H_2O$ (**4**), which adsorbs 2.66 mmol g^{-1} dichloromethane at 298 K and 0.029 MPa (corresponds to 4 molecules per complex of **3**). As described above, two primary binding sides for dichlormethane molecules per complex exists in terms of one $CH\cdots Cl^-$ and two $OH\cdots Cl^-$ hydrogen bonds for one dichlormethane molecule. From the dichlormethane adsorption isotherm (Figure S5) it can be seen that a saturation regime of up to 4 molecules per complex of **3** could be observed. So, there might be two addional binding sides per complex to bind dichlormethane by excluding condensation effects for subcritical gases, which were typically observed above a relative pressure of 0.3 - 0.4.

Lower adsorption ability is observed for subcritical CO_2 (1.72 mmol g^{-1} at 3.65 MPa; $P/P_S = 0.55$), while sorption of supercritical molecules such as nitrogen and methane (Figure 2) up to high pressures does not exceed 0.51 and 0.48 mmol/g (10.89 and 4.85 MPa, respectively). Actually the same low value, 0.55 mmol/g at 0.10 MPa, is obtained for the model fluorinated adsorbate refrigerant R404a (44% C_2HF_5, 52% $C_2H_3F_3$, 4% $C_2H_2F_4$). This fact in part could be attributed to a large molecular volume of the fluorinated ethanes, which evidently does not allow situation of the guests inside the metallacontainer cages.

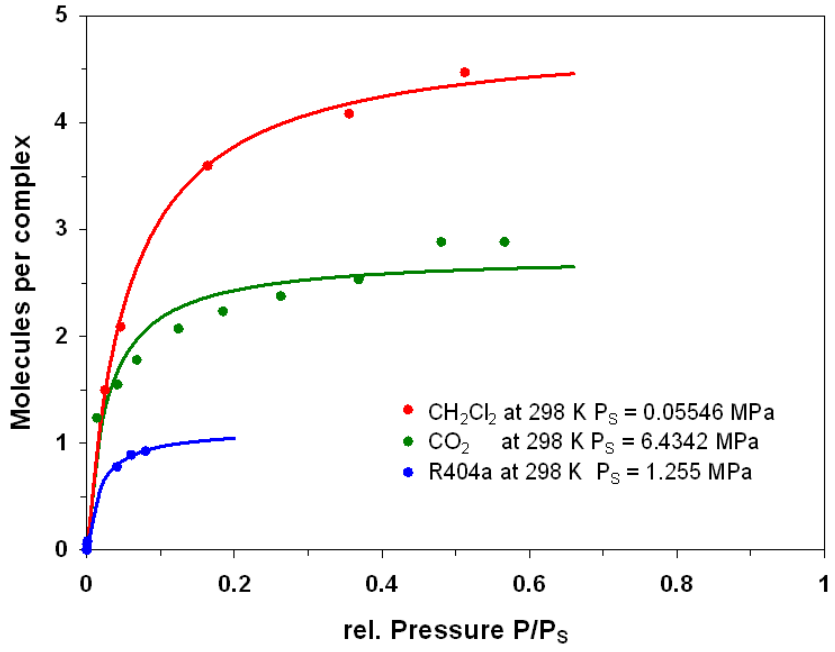


Figure S5. Adsorption isotherm of dichlormethane, carbon dioxide and fluorinated refrigerant R404a at 298 K. Langmuir model was chosen for data fitting.

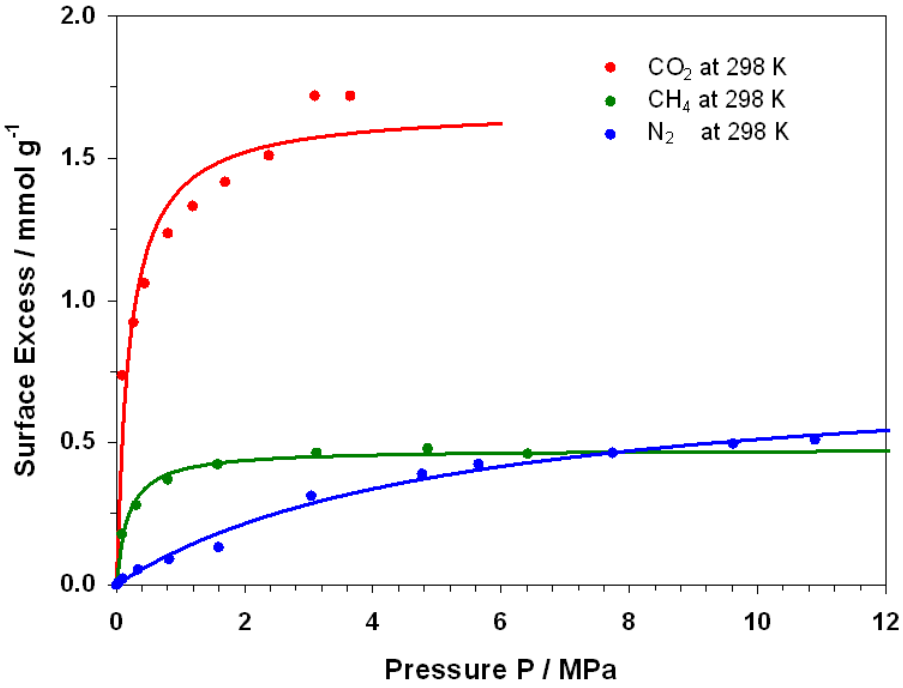


Figure S6. Adsorption isotherm of carbon dioxide, methane and nitrogen at 298 K. Langmuir model was chosen for data fitting.

5. Cartesian Coordinates

H·G1

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Cu -1.8665  0.8507  2.3235
Cu -0.1331  2.9633  0.8708
Cu  1.7313  2.1154 -1.4518
O -3.0507 -0.6326  1.6945
```

```
H -3.3112 -0.3766  0.7831
O -0.4809  2.2410  2.7021
H  0.3283  1.7352  2.9339
O  0.2255  3.3691 -1.0530
H -0.5445  2.9983 -1.5362
N -2.8676  2.2826  1.3651
N -2.1060  3.2111  0.7256
N -7.1237  5.9409  0.1063
N -7.2082  5.1564 -1.0290
N -5.4152  4.5142  0.1236
N  1.8161  3.2569  1.1688
N  2.6350  2.8849  0.1484
N  6.5774  5.7286  3.2191
N  6.7792  4.4785  3.7744
N  5.0123  4.3590  2.4258
N  1.1413  1.7316 -3.3160
N  1.1988  0.4273 -3.6978
C -5.2757  1.8238  1.8899
H -5.6301  2.3055  2.8261
H -4.9164  0.8075  2.1418
H -6.1521  1.7407  1.2164
C -4.1745  2.6154  1.2551
C -4.2406  3.8136  0.5058
C -2.9061  4.1616  0.1900
C -2.3802  5.3555 -0.5450
H -1.3406  5.1698 -0.8777
H -2.3773  6.2588  0.1018
H -3.0066  5.5911 -1.4287
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H -5.6962  5.9586  1.7285
C -6.1900  4.3175 -1.0046
H -5.9492  3.5531 -1.7535
C  1.9388  4.4158  3.3878
H  0.9313  3.9853  3.5482
H  1.8330  5.5196  3.3214
H  2.5701  4.2028  4.2734
C  2.5454  3.8513  2.1408
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C  3.9095  3.2318  0.4405
C  5.0538  3.0040 -0.4980
H  4.7767  2.2485 -1.2578
H  5.9562  2.6566  0.0438
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H  5.7068  2.6158  3.5273
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H -0.0026 -1.0553 -6.4307
N  0.1401  1.9897 -6.7713
C  0.9008  2.3978 -7.8499
H  1.9931  2.4875 -7.8008
C -1.1523  2.0160 -7.2610
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O -0.2255 -3.3691  1.0530
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N  2.8676 -2.2826 -1.3651
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N  7.1237 -5.9409 -0.1063
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N -1.8161 -3.2569 -1.1688
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H  4.9164 -0.8075 -2.1418
H  6.1521 -1.7407 -1.2164
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C  4.2406 -3.8136 -0.5058
C  2.9061 -4.1616 -0.1900
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H  2.3773 -6.2588 -0.1018
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H -5.0928 -6.4499 -1.8241
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H -5.7068 -2.6158 -3.5273
C -0.6441 -3.9854  4.2937
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H -1.5405 -4.4819  4.7230
H -0.5470 -4.3078  3.2391
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Cl -2.6173  2.2594 -2.9443
Cl -2.5026 -0.5649 -3.7648
Cl -4.2662  0.2551 -1.5561
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H  1.8778 -0.3824  1.6566
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Cl  0.0000  0.0000  0.0000
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H·G2

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H  1.7274  1.1511  2.6611
O -1.1502 -2.0226  2.6756
H -1.9731 -1.7348  2.2324
O  1.1196 -3.3452 -0.3226
H  1.9462 -2.8303 -0.2325
N -1.7300  2.0161  2.8779
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N -6.0810  2.8912  6.4919
N -6.8407  2.4408  5.4187
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N  1.4986 -2.6124  2.5013
N  6.3741 -3.6656  5.3018
N  5.5224 -4.2140  6.2530
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H -2.4239  4.4291  2.1160
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C -2.8095  0.6440  4.2399
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H -2.9153 -0.4293  6.1017
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H·G3

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H  0.3177  1.7544  2.9325
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H -0.5386  3.0265 -1.5509
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N  1.7956  3.2555  1.1612
N  2.6219  2.8816  0.1387
N  6.4661  5.9833  3.0272
N  6.7030  4.7815  3.6833
N  4.9537  4.5082  2.3437
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Cl  0.0000  0.0000  0.0000
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H·G4

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```

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