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Gas–Solid Chemisorption/Adsorption and Mechanochemical Selectivity in Dynamic Nonporous Hybrid Metal Organic Materials

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Supporting Information

ABSTRACT: Gas-solid chemisorption of HCl and adsorption of MeOH/EtOH by nonporous chiral copper(II) coordination complexes **1·MeOH** and **1"·MeOH** occur in a cooperative and dynamic manner to give solvated second sphere adducts **1'· MeOH/EtOH**. The chemisorption process involves dramatic atomic rearrangements in the crystalline state upon cleavage and formation of H-Cl, N-H, Cu-N, and Cu-Cl coordination and covalent bonds from the gas and solid state, respectively. Using mechanochemistry, the chloride-bridged



coordination complex 1"•MeOH is selectively produced by means of a dehydrochlorination reaction, but not in solution in which a mixture of 1•MeOH and 1"•MeOH is obtained. 1"•MeOH also via chemisorption and adsorption can trap HCl and MeOH to give the second sphere adduct 1'•MeOH. The adsorption process is confirmed by forming the second sphere adduct 1'•EtOH by exposing both 1•MeOH and 1"•MeOH to HCl and ethanol. Quantum-mechanical (QM) calculations specific for solid phases give insights into the relative stabilities of the hybrid metal organic materials involved in the mechanochemical reaction producing selectively 1"•MeOH, giving a good agreement with the experimental results.

INTRODUCTION

Functional materials responding in a dynamic way to external stimuli are interesting for applications such as separation, catalysis, sensing, etc. I^{1-5} Usually such research has been focused on permanently porous organic-inorganic materials, referred to as metal organic frameworks (MOFs) or coordination polymers (CPs), that allow the transport and entrapment of molecules within the channels.⁶⁻¹³ An alternative way to prepare metal organic materials having channels where guest molecules can pass through is by means of second sphere coordination interactions,^{14–16} although the process is still challenging when compared to MOFs synthesis.¹⁷ Crystal engineering principles by means of second sphere coordination have been applied in the design and study of hybrid metal organic materials in areas as diverse as separation,¹⁸⁻²⁰ gas adsorption,²¹ light emitting properties,²² and solid-state reactivity.23

Adsorption of molecules from the gas phase in *nonporous* materials is less common because their crystalline structure needs to evolve from closed to open packing undergoing dynamic structural changes upon external stimuli.^{24–27} In this regard, nonporous metal organic materials self-assembled by second sphere coordination showing such dynamic behavior upon external stimuli have gained recent attention. Particularly, the adsorption of HX (where X = Cl or Br) by coordination complexes occurring via *chemisorption* process are one type of

solid-state reaction that received interest in the area of metal organic materials about a decade ago. $^{28-33}$

Reports of such type are necessary to furnish detailed aspects on the structure-function relationship derived from the changes in the coordination geometries upon transformations involving second-to-first coordination spheres and vice versa, along with concerted cleavage and formation of coordination and covalent bonds. Such structural transformations have been demonstrated to have a direct influence on the magnetic properties where the switch from antiferromagnetic to ferromagnetic was induced as a consequence of the changes from a first (coordination polymer) to second sphere (outer sphere adduct) transformation. To the best of our knowledge, so far most of the reported examples of chemisorption of HX deal only with the incorporation of hydrogen chloride/ bromide, but there are no reports of the inclusion of two different molecules by the same material. Examples by Orpen et al.^{29,30} first and later by Brammer et al.³¹⁻³³ focused on experiments in which the nonporous complexes could trap HCl or HBr but without including solvent in a cooperative manner. That is, during the same experiment the nonporous material can adsorb more than one molecular species. Only recently, it has been reported how via single-crystal-to-single-crystal (SC-SC) transformations a nonporous Cu(II) complex included via

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chemisorption HCl and H_2O , but in this case the bond formation is different because it deals always with a second sphere coordination complex changing from $[CuCl_4]^{2-}$ to $[CuCl_3]^-$ and inclusion/release of one H_2O .³⁴ Therefore, research in this topic is needed in order to gain insights into the reactivity of this class of nonporous materials.

Here we report how two nonporous coordination complexes can incorporate two different molecules via chemisorption and adsorption in a cooperative manner. Chemisorption of HCl and adsorption of MeOH and EtOH occur within nonporous coordination complexes to produce solvated second sphere adducts. Knowing that HCl can be inserted into Cu-N coordination bonds upon bond cleavage and bond formation,^{29,31} we have used Cu complexes suitable for hydrochlorination reactions according to the size matching distance among cations and anions and the labile nature of copper(II) centers. The coordination complex $L[CuCl_2]$ ·MeOH (1. MeOH) containing the enantiomeric (R,R)-N,N'-dibenzyl-1,2-diaminocyclohexane (L) ligand has been studied. When 1-MeOH is exposed to vapors of HCl in MeOH the chiral second sphere adduct [2HL]²⁺[CuCl₄]²⁻·MeOH (1'·MeOH) is formed after concerted dramatic structural changes. Interestingly, in a selective manner, the dehydrochlorination reaction of 1'•MeOH via liquid assisted grinding (LAG) in the presence of KOH yields a different chloride-bridged coordination complex product L[CuCl₂]₂·MeOH (1"·MeOH), also chiral, that traps simultaneously HCl and MeOH giving 1'. MeOH (Scheme 1). However, in this case the chemisorption

Scheme 1. Chemical Structure of L and Synthesis of Coordination Complex 1·MeOH^a



^{*a*}Gas-solid transformation of **1**·MeOH into second sphere adduct **1**′· MeOH, its mechanochemical transformation into **1**″·MeOH and reversibility to give **1**′·MeOH upon HCl and MeOH inclusion.

occurs involving a large number of Cu–N coordination bonds that are cleaved, when compared with 1'•MeOH, due to the nature of the bridging halide bonds in 1"•MeOH. The chemisorption and adsorption processes also occur with EtOH instead of MeOH in both 1•MeOH and 1"•MeOH, thus confirming the adsorption process. Density functional theory (DFT) calculations specific for crystalline solid phases were used to estimate the relative stabilities of the compound structures obtained in the mechanochemical LAG reaction, showing good agreement with experimental results.

RESULTS AND DISCUSSION

The chiral coordination complex **1·MeOH** was prepared by dissolving 0.029 g (0.10 mmol) L and 0.017 g (0.10 mmol) CuCl₂·2H₂O in 4 mL of methanol and left to crystallize over a week. Blue single crystals suitable for single crystal X-ray diffraction (SC-XRD) were obtained. X-ray crystallographic analysis demonstrates that the blue crystals correspond to a solvated Cu complex crystallizing in the tetragonal system in the chiral space group $P4_32_12$.³⁵ The copper metal is chelated to the two N atoms of L forming a five member ring (Figure 1b). The included MeOH molecule is pinned by two hydrogen



Figure 1. (a) Crystal structure of 1·MeOH without MeOH molecules showing the open nature although being nonporous. (b) View of the chelated five member ring with the circled area displaying one of the coordination bonds that is broken when exposed to HCl gas. (c) Ex situ PXRD patterns of 1·MeOH (bottom), the product of 1·MeOH after being exposed to HCl (middle) and experimental from single crystals of 1'·MeOH (top).

bond interactions: one as hydrogen bond acceptor via N–H··· O $(d_{\text{N1}\cdots\text{O1}}: 2.951(3) \text{ Å})$ interaction, and the other by an O– H···Cl $(d_{\text{O1}\cdots\text{Cl1}}: 3.165(2) \text{ Å})$ hydrogen bond donor to one of the chloride ligands in the copper metal center. The hydrogen bond interactions expand along the *c*-axis (Figure S1).

The inclusion of methanol in **1·MeOH** is important because it accounts for the ca. 20% of the total unit cell volume in the form voids (Figure 1).³⁶ This can be explained by the enantiomeric nature of the coordination complex, which implies that a nonefficient packing of molecules, hence lower stability in non-centrosymmetric space groups, is preferred over centrosymmetric space groups, and that could facilitate its dynamic behavior and inclusion of HCl and MeOH especially for large and flexible molecules such as **L**.

The coordination geometry in **1·MeOH** suggests that the uptake of HCl gas could occur by a *chemisorption* process and form a second sphere adduct following Cu–N coordination bond cleavage and formation of N–H and Cu–Cl bonds in the

presence of MeOH. Therefore, the dynamic behavior of 1• MeOH has been monitored by its ability to uptake HCl from the gas phase by exposing microcrystalline powders of 1• MeOH to vapors of HCl in MeOH. After 12 h a clear color change from blue to yellow is observed, suggesting a modification of the coordination sphere in the Cu metal. This is corroborated by the ex situ PXRD pattern which shows a completely different diffraction pattern against the experimental one (Figure 1c).

Upon recrystallization of the yellow powders, SC-XRD crystallography reveals that the product corresponds to the second sphere adduct $[2HL]^{2+}$ $[CuCl_4]^{2-}$ ·MeOH (1'·MeOH) including also MeOH. It crystallizes in the orthorhombic system in the $P2_12_12_1$ space group, and the simulated PXRD pattern shows a rather good match with the experimental powder diffraction pattern (Figure 1c). Thus, Cu–N coordination bond cleavage and new N–H and Cu–Cl bond formation occurred upon HCl *chemisorption* following a rupture of the covalent bond from the H–Cl incoming gaseous molecules.

In 1'·MeOH there is one distorted $[CuCl_4]^{2-}$ anion and one diprotonated $[2HL]^{2+}$ cation in the asymmetric unit containing also MeOH. Each L ligand is linked with two neighboring $[CuCl_4]^{2-}$ through five hydrogen bonds (Figure 2a), in which



Figure 2. (a) Crystal structure of $1' \cdot \text{MeOH}$ showing the charge assisted hydrogen bonding interactions among $[2HL^{2+}]$ and $[CuCl_4]^{2-}$ (dashed lines) with MeOH involved on it. (b) Packing of $1' \cdot \text{MeOH}$ viewed along the *a*-axis. Color code: carbon: orange; nitrogen: blue; chloride: green; copper: brown; hydrogen: white.

MeOH is incorporated forming a linear chain along the *a*-axis. Methanol is accommodated between the double protonated $[2HL]^{2+}$ cation and $[CuCl_4]^{2-}$ anion through two N–H···O hydrogen bonds in which MeOH acts as acceptor of hydrogen bonds (iv and (v) with distances ($d_{N1\cdotsO1S}$: 2.874(7) Å and ($d_{N2\cdotsO1S}$: 2.770(6) Å); and one O–H···Cl interaction among methanol and $[CuCl_4]^{2-}$, where MeOH acts as hydrogen bond donor ($d_{O1S\cdotsCl4}$: 3.267(6) Å) (ii) as shown in Figure 2.

In our previous work regarding dehydrochlorination reactions by mechanochemical means, we reported the *quasi*-chelating motif^{37,38} in large and flexible ligands. In the *quasi*-chelating motif, the dianion and dication are directly hydrogen bonded via strong charge assisted hydrogen bonds due to a good size match among both ions. It is known that the proximity of H and Cl atoms in the hydrogen bonding motif in the second sphere adduct is crucial for the development of the dehydrochlorination reaction.³⁹ We note that the -N-C-C-N- separation distance in $[2HL]^{2+}$ is 2.978(3) Å and fits the Cl separation distance in the $[CuCl_4]^{2-}$ dianion, to allow a 1:1 charge assisted hydrogen bond interaction. However, in the present case such *quasi*-chelating motif is slightly different to the previously reported because there is an interfering methanol molecule in the *quasi*-chelating hydrogen bond interaction.

The presence of solvent guest molecules involved in the hydrogen bonding has been recently studied upon dehydrochlorination reactions, showing that the good size match between cations and anions affects the chelation.⁴⁰ In some cases, the role of the noncoordinated solvent can drive the restoration of certain hydrogen bonding architectures (i.e., most likely acting as a templating molecule) even through intermediate amorphous phases in a sort of memory effect.⁴ However, not many examples of such specific ionic interaction (1'•MeOH) involving also solvent molecules in chemisorption/ adsorption processes have been reported so far. We note an example in which MeOH is displaced from the coordination sphere upon chemisorption of HCl; however the outer sphere adduct product does not contain MeOH.³² Interestingly, 1'. MeOH offers the opportunity to study the transformation of a hydrogen bonded second sphere adduct into a coordination complex via dehydrochlorination, and their reversibility back into a solvated second sphere coordination adduct.

Dehydrochlorination reaction using the chiral second sphere adduct 1'•MeOH was carried out using the LAG method by mixing 1'•MeOH and the strong base KOH in the presence of one drop of MeOH. During the LAG process the starting microcrystalline yellow powders transformed into a new green product. PXRD experiments on the green microcrystalline powders revealed that the PXRD pattern was different from that of 1'•MeOH, suggesting that a new phase (1"•MeOH) was obtained. The release of HCl is corroborated by the presence of KCl ($2\theta = 28^{\circ}$) which is formed as byproduct (Figure 3). Further grinding generates an amorphous phase but not 1• MeOH.

Recrystallization of 1"•MeOH in appropriate solvent was carried out until suitable green crystals for SC-XRD analysis



Figure 3. PXRD patterns of 1'·MeOH (a); the product obtained after LAG (1''·MeOH) (b) and simulated of 1''·MeOH obtained from SC-XRD (c).

were obtained. SC-XRD analysis reveals that $1'' \cdot \text{MeOH}$ crystallizes in the same orthorhombic space group $P2_12_12_1$. The match between the PXRD pattern resulting from grinding and that simulated from SC-XRD data suggests that the bulk powder has the same structure as the one obtained from the single crystal (Figure 4). In the dehydrochlorination reaction,



Figure 4. (a, b) Crystal structure of 1'·MeOH and the complex 1"· MeOH obtained upon dehydrochlorination reaction.

the release of H and Cl after covalent bond breaking takes place, and coordination bond formation with the chloride bridged coordination bond occurs to give the neutral complex 1''·MeOH. Interestingly, despite the dramatic atomic reorganization, methanol is also included in the structure.

The 1".MeOH crystal structure comprises a dimeric $(CuL_2Cl_2)_2$ unit, in which the geometry at each copper can be described as a distorted tetragonal-pyramidal arrangement. In the bridged metal core, the Cu atom is penta-coordinated forming a bidentate coordination sphere with the apical positions occupied by Cl ligands. The bridging Cu₂Cl₂ unit is constrained to be planar. The Cu-Cl terminal distances are 2.299(2) Å and 2.298(2) Å. The Cu–Cl bridging distances are in the range from 2.256(2) to 2.802(2) Å. Furthermore, the bridging angle Cu-Cl-Cu of 85.79(5)°/87.24(5)° and the Cu···Cu separation of 3.477(1) Å are in their respective ranges of this kind of dimeric copper complexes.⁴² The bond distances and angles of 1". MeOH are given in Supporting Information. Each dimeric moiety is linked with methanol solvent through N–H…O and O–H…Cl interactions $d_{N2...O1}$: 3.026(8) Å and $d_{O1\cdots Cl5}$: 3.125(6) Å as shown in Figure S7.

Therefore, via mechanochemical grinding, the chiral second sphere adduct 1'•MeOH can be transformed into the chiral neutral coordination complex 1". MeOH upon dehydrochlorination, but is it possible to reverse the reaction? In other words, is 1". MeOH able to respond dynamically and uptake HCl from the gas phase even being nonporous? To test that, experiments in which 1".MeOH where exposed to vapors of HCl were carried out. We note that the ratio of MeOH and $(CuL_2Cl_2)_2$ is not 1:1. Therefore, extra MeOH is needed to form the original second sphere adduct. Powders of 1".MeOH were exposed for 24 h to HCl in the presence of methanol at room temperature. During the vapors exposure process, 1".MeOH transformed from green to yellow. Further, PXRD experiments showed that the diffraction pattern is that of the initial second sphere adduct 1'·MeOH (Figure 5). This confirms the reversible transformation and the fact that a bimolecular uptake occurs by means of chemisorption and adsorption (i.e., HCl and MeOH). Such dynamic behavior in a densely packed nonporous structure is notorious as there are two molecules being adsorbed by microcrystalline 1"•MeOH.

Further experiments testing the dynamic behavior of 1• **MeOH** and 1"•**MeOH** were carried out exposing both crystals to EtOH instead of MeOH in the presence of HCl. This will





Figure 5. Experimental PXRD patterns of (a) $1'' \cdot MeOH$ and that obtained after exposing $1'' \cdot MeOH$ to vaporous HCl in MeOH; (b) and simulated from single crystal of $1' \cdot MeOH$ (c).

show clearly that the adsorption process as the exchanged guest is different. As shown in Figure 6, the color change indicates



Figure 6. Powders of 1·MeOH and the complex 1"·MeOH and the products after exposure to HCl and EtOH vapors. PXRD patterns of the described materials.

that a structural modification involving the coordination sphere of Cu takes place. The inclusion of EtOH in the structure is also confirmed by ¹H NMR analysis with the peak at ca. 3.17-3.15 ppm (Figures S14–S15). Moreover, a single crystal of the second sphere adduct containing EtOH grown after dissolving the obtained product clearly confirms that the adsorption of EtOH can also be carried out (see Supporting Information). As shown in Figure 6, the match between the experimental and simulated PXRD pattern corroborated the structural transformation.

In 1'•EtOH the interactions among the $[CuCl_4]^{2-}$ and the dications are different from that observed in 1'•MeOH as one dianion is linked to two adjacent dications forming a one-dimensional (1D) ribbon by means of hydrogen bonding interactions (Figure S10). The included ethanol molecule is interacting only with the dication in a chelated fashion acting as hydrogen bonding acceptor ($d_{N1\cdots O1}$: 2.854(7) Å and $d_{N2\cdots O1}$:

2.766(5) Å), whereas in 1'•MeOH the solvent molecule interacts additionally with the chloride ligand in the $[CuCl_4]^{2-}$ anion. Thus, the process again occurs via *chemisorption* and *adsorption* where in a cooperative effect HCl and EtOH are trapped in 1•MeOH and 1"•MeOH.

Interested to understand the adsorption process in **1·MeOH** and **1″·MeOH**, we performed more experiments by changing the solvents as this can provide additional information on the selectivity of the gas uptake. The same type of experiment but using *i*-PrOH, *n*-BuOH, CHCl₃, MeCN, THF, and ethyl acetate in HCl were carried out. The NMR experiments clearly show that there is the formation of the second sphere adduct as in the ¹H NMR it is possible to see the protonated N–H⁺ groups after adsorption of HCl, but there is no inclusion of solvent.

It is worth to mention that in the solution state using L and $CuCl_2$ in methanol/DCM solvent a mixture of **1·MeOH** and **1″·MeOH** crystals are obtained, whereas LAG yield pure amounts of **1″·MeOH**. The melting points of **1″·MeOH** and **1·MeOH** are markedly different, 165 and 144 °C respectively. This indicates that in the solid state via LAG, the obtained product, the denser **1″·MeOH** (2.199 g/cm³) prevails over **1·MeOH** (1.311 g/cm³).⁴³ This example confirms that mechanochemical LAG synthesis is *selective* toward the double core **1″·MeOH** coordination complex.

In order to prove that **1·MeOH** and **1"·MeOH** belong to nonporous materials, gas adsorption experiments using N_2 at 77 K were performed. As shown in Figure S30 and Figure S31, the isotherms correspond to a nonporous material and shows the capillary condensation of N_2 in the interparticle void space and not in the pores of the material. This is confirmed also by the pore volume obtained (see Table S1). Thus, this clearly confirms that the second sphere adducts reported here are nonporous.

Density Functional Theory (DFT) Solid-State QM Calculations. Energetic considerations are crucial to understand the solid-state chemistry among crystalline structures, and in this regard, DFT specific for the solid state can provide insights regarding the relative stabilities of the hybrid metal organic materials. In order to gain insights on the stabilities of 1.MeOH, 1'.MeOH, and 1".MeOH we used DFT suited for solid-state systems. A combination of numerical double- ζ quality basis set including polarization functions on all atoms (i.e., DNP) and an effective core potential for the metal atoms were adopted. In all the calculations, we used the experimental X-ray determined unit cells while relaxing atomic coordinates of all atoms. As for similar systems⁴⁴⁻⁴⁷ and for other organic crystalline phases,48-52 we employed the PBE functional as implemented into DMol³ code.⁵³ The inclusion of explicit van der Waals terms in the calculations has been chosen because of their importance when describing interparticle interactions.54-

The energetic stability of compounds 1·MeOH, 1'·MeOH, and 1"·MeOH was evaluated by comparing the average energy required to remove a cation ([2HL]²⁺) or a molecule (L) from the corresponding crystalline structures. This energy is obviously much higher in 1'·MeOH with respect to 1·MeOH and 1"·MeOH (i.e., about 200 kcal/mol) because of the ionic interactions in the second sphere adduct 1'·MeOH. However, when comparing neutral complexes, 1"·MeOH is more stable than 1·MeOH by about 20 kcal/mol. The latter results can be ascribed to the higher density of compound 1"·MeOH with respect to compound 1·MeOH and to the larger volume of the interacting particles constituting the crystalline structure of the former (1"·MeOH) that corresponds to a larger molecular polarizability. It can be concluded that the computational outcomes are in good accordance with the experimental results, thus furnishing a simple rationalization of the molecular transitions and transformations in terms of relative stabilities of the involved crystalline structures.

Potential Applications of 1·MeOH, 1'·MeOH, and 1"· MeOH as Functional Materials. Although we have not investigated the magnetic behavior in 1·MeOH, 1'·MeOH, and 1"·MeOH, the switch from antiferromagnetic to ferromagnetic induced by the changes from a first (coordination polymer) to second sphere (outer sphere adduct) transformation and vice versa, can be used to understand the mechanisms of those transformations and also to obtain magnetostructural correlations in a class of new dynamic nonporous materials. Such tunable magnetic materials that respond dynamically to the presence of external stimuli have a great potential to be used as switches and are attracting the attention of solid-state chemists in recent times.

The potential use of these materials in sensing also the dynamic behavior using HBr vapors instead of HCl opens the door to study such materials, allowing fundamental insights into this type of uncommon reactions to be discovered. While reactions as the ones described above are more common in porous materials, reports in nonporous materials are very rare.

CONCLUSIONS

In summary, we have reported a unique case in which a nonporous hybrid metal organic coordination complex is able to dynamically uptake HCl gas via chemisorption and MeOH/ EtOH upon molecular adsorption in a gas-solid process yielding a second sphere adduct sustained by ionic interactions. The chemisorption process involves dramatic atomic rearrangements as cleavage and formation of covalent and coordination bonds are needed for the incorporation of gaseous HCl into Cu-N bonds. The HCl molecules can be released from the second sphere adduct upon mechanochemical grinding following a dehydrochlorination reaction, to give in a selective manner a new bridged chloride coordination complex that also traps via concerted chemisorption and adsorption of two gas molecules: HCl, MeOH, and/or EtOH. Because of the coordination on the bridged halide complex, four N-Cu and two Cl- μ -Cl bonds are cleaved to form the outer sphere adduct which can include MeOH or EtOH guest molecules. Such bimolecular gas inclusion is notorious in this type of material. Gas-solid reactions in nonporous materials are rare, and further work on the topic is needed to understand better materials that might find application in areas such as magnetism, particularly in the form of molecular switches.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00698.

Further details on the synthesis and crystallographic information (PDF)

Accession Codes

CCDC 1524236, 1524244, and 1524246 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data request/cif, or by emailing data request@ccdc.cam.ac.

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Notes

The authors declare no competing financial interest.

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