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# Tuning the Inclusion Properties and Solid-State Reactivity of Second Sphere Adducts Using Conformationally Flexible Bidentate Ligands

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### Abstract

Second-sphere coordination refers to any intermolecular interaction with the ligands directly bound to the primary coordination sphere of a metal ion. In this article, we have successfully applied the second-sphere coordination approach in the construction of versatile host frameworks that can accommodate various guest molecules. We have used a family of bidentate flexible molecules as second-sphere ligands, and the tetrachlorometalate anion  $[MCl_4]^{2-}$  (where M = Cu, Co, Cd, Zn and Hg) as the primary coordination sphere to synthesize new second sphere adducts. By introducing an alkyl spacer  $-(CH_2)_n - (n = 1, 2, 3, 3)$ 4) to bibenzylamine ( $L^0$ ), the ligands  $L^1$ ,  $L^2$ ,  $L^3$  and  $L^4$ , with higher degree of flexibility were synthesized. Different guest molecules such as alcohol, acetic acid, acrylic ester or acetonitrile can be included in the host framework self-assembling diprotonated  $L^{1}-L^{4}$  and  $[MCl_4]^{2-}$ , leading to a novel type of supramolecular assemblies: CH<sub>3</sub>CH<sub>2</sub>OH  $\subset$  $[L^{2}]2H^{+} \cdot [CuCl_{4}]^{2-}$  (2),  $CH_{3}OH \subset [L^{3}]2H^{+} \cdot [MCl_{4}]^{2-}$  (3),  $CH_{3}COOH \subset [L^{3}]2H^{+} \cdot [CuCl_{4}]^{2-}$  (4), CH<sub>2</sub>CHCOOCH<sub>3</sub> $\subset$ [L<sup>3</sup>]2H<sup>+</sup>·[MCl<sub>4</sub>]<sup>2-</sup> (5-7), CH<sub>3</sub>CN·H<sub>2</sub>O  $\subset$ [L<sup>4</sup>]2H<sup>+</sup>·[MCl<sub>4</sub>]<sup>2-</sup> (8-9), and CH<sub>3</sub>OH  $\subset$  [L<sup>4</sup>]2H<sup>+</sup>·[MCl<sub>4</sub>]<sup>2-</sup> (10). L<sup>2</sup> forms the *quasi*-chelating charge-assisted N-H···Cl hydrogen bonds with  $[MCl_4]^{2-}$  that can transform in the solid-state to a chelated coordination complex following a mechanochemical dehydrochlorination reaction. By increasing the number of methylene groups, ligands  $L^3$  and  $L^4$  exhibit considerable conformational diversity due to the higher flexibility induced by the backbone chains. The  $-(CH_2)_n$ - spacer lengths of the ligands influences the structural dimensionality and its solid-state mechanochemical

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reactivity preventing the transformation from salt  $[L^{3-4}]2H^+ \cdot [MCl_4]^{2-}$  to chelating coordination complex  $[(MCl_2)(L^{3-4})]$ . Moreover, the thermal stability of the second sphere adducts has been monitored by thermogravimetric analyses and X-ray powder diffraction (PXRD). We demonstrate that some of the second sphere adducts are dynamic showing reversible guest release/uptake involving crystalline-to-amorphous-to-crystalline phase transformations. Quantum/Mechanical (QM) demonstrate that ligands with backbone lengths longer than  $-(CH_2)_2$ - are reticent to react via dehydrochlorination reaction because of the backbone chain length, the symmetry and orientation of the frontier molecular orbitals (FMOs), while for the  $-(CH_2)_2$ - the length and orientation of the FMOs is optimal for the reaction to occur.

### Keywords

Second Sphere Coordination, Host-Guest Superstructures, Conformational Flexible Ligands, Hydrogen Bonding, Self-Assembly, Quantum-Mechanical Calculations, DFT Frontier Molecular Orbitals.

### Introduction

Chemical reactions carried out in the solid state induced by external stimuli are important to gain insights on how chemical reactions occur.<sup>1,2,3,4,5,6,7,8,9,10</sup> An important aspect is on the ability to bring the reacting molecules into an optimal orientation and distance allowing the

reaction partners to interact and react. Molecular recognition is crucial to bring the reactants together, but such control is often difficult in the solid-state. Crystal engineering is one of the most important routes to achieve molecular recognition by proper combination of functional groups present in molecules or ions.<sup>11,12</sup> One way to achieve selectivity and effective binding of ions can be obtained by using the concept of second sphere coordination.<sup>13</sup>

Second sphere coordination was described by Alfred Werner over a century ago by describing how the first coordination sphere of a transition metal complex can interact with neutral or charged species to give a second sphere coordination. In the early 80's studies aimed to get insights into the nature of second sphere coordination were carried out,<sup>14,15,16,17</sup> and more recently has been exploited to study metal-based anion receptors.<sup>18,19,20</sup> The first sphere ligands can form second-sphere adducts with the whole range of noncovalent bonding interactions, such as electrostatic, hydrogen bonding, halogen bonding, charge transfer and van der Waals interactions. The contribution of second sphere coordination has been important in supramolecular chemistry,<sup>21</sup> including biological recognition.<sup>22</sup>

Solid-state chemistry knowledge of hybrid metal organic compounds (i.e., self-assembled via electrostatic interactions) is very important in order to design new functional materials. However, the solid state chemistry of second sphere coordination has not been studied very much. Only recently, second sphere coordination has demonstrated that is a suitable approach to synthesize functional materials for gas adsorption,<sup>23</sup> separation of metal

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ions<sup>24,25,26,27</sup> for the extraction of auric anions using  $\alpha$ -cyclodextrin,<sup>28</sup> to study solid-state mechanochemical dehydrochlorination reactions,<sup>29</sup> crystalline-to-polycrystalline reactions,<sup>30</sup> and to form permanent porous networks showing single-crystal-to-single-crystal guest exchange and ionic conductivity.<sup>31</sup> Halogen bonds have been used in second-sphere coordination complexes to form 6,3-networks.<sup>32</sup>

Using large and flexible molecules having bulky groups can be a good crystal engineering strategy to synthesize new host-guest systems,<sup>33</sup> because such molecules would not organize efficiently and therefore alternative crystal packing modes (using molecule's flexibility) might be achieved by inclusion of guests with good size and shape complementarity.<sup>34</sup>

Our recent research has focused on the construction of new type of supramolecular inclusion system that cooperatively utilizes secondary sphere coordination interactions, in which a series of N-bidentate flexible ligands have been designed as second-sphere ligands and self-assembled with tetrahedral anions like  $[MCl_4]^{2-}$  (M = Cu, Co, Mn and Zn) as the primary coordination sphere.<sup>35</sup> Herein, we have used bibenzylamine ( $L^0$ ) as an organic moiety, to which we introduced  $-(CH_2)_{n-}$  (n = 1, 2, 3, 4) alkyl chains on the bibenzylamine ligand to synthesize a series of ligands  $L^1-L^4$  differing only in the backbone chain separating the two aromatic moieties (Scheme 1).



Scheme 1. Ligands used in this work (a); and cartoon showing the metals used as first coordination sphere which are self-assembled with ligands  $L^{1-4}$  via second coordination sphere interactions (b).

The two N atoms in the flexible backbone can be protonated. They can act as hydrogen bonding donors (outer sphere), playing a key role in the anion recognition of the primary coordination sphere of tetrachlorometallates such as  $[MCl_4]^{2-}$ , but also might act as an anchoring point for guests molecules. Moreover, the bulky phenyl rings may also act as molecular recognition site and contribute to the formation of voids to accommodate small/medium guests such as methanol, ethanol, acetic acid, acrylic ester or acetonitrile. In

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some complexes, the host structure upon heating, is robust enough to allow guest release/uptake whilst maintaining their crystallinity or via an amorphous phase. Up to now, studies of inclusion complexes involving thermal stability, solid-state mechanochemical dehydrochlorination reactivity, and their guest behavior self-assembled via second-sphere coordination using bidentate ligands with different backbone lengths (i.e., the effect of  $-(CH_2)_n$  spacers) are uncommon. Additionally, we provide Quantum Mechanical calculations (QM) including methods for solid phases, which have been carried out to gain information about the electronic density distribution of frontier molecular orbitals (FMOs) in ligands  $L^2-L^4$  in order to better understand their solid-state reactivity. The QM results indicate that the orientation and symmetry of the HOMOs (which resulted concentrated mainly at the N atoms) need to be considered as well as the backbone N–(CH<sub>2</sub>)<sub>n</sub>–N distance in order to achieve dehydrochlorination reactions followed by chelation upon mechanochemical grinding.

### **Experimental section**

**Materials and Methods.** All chemicals were obtained from commercial sources and used without further purification. IR spectra were obtained with a Perkin Elmer 100 FT-IR spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25 °C with TMS as the internal reference. Powder

X-ray diffraction were recorded using a D8 Bruker and D2 PHASER diffractometer ( $\lambda = 1.54056$  Å).

### Synthesis of ligands L<sup>1</sup>–L<sup>4</sup>

**Synthesis of L<sup>1</sup>:** For the synthesis of L<sup>1</sup>, 8g (0.04 mol) of bibenzylamine were added into 40 mL ethanol, and slowly stirred at 40 °C. Subsequently 1.62 g ((0.02 mol) 37 % purity) formaldehyde was then continuously (2–3 drops) added into the mixture solution. The reaction was stirred for 2 h, and the mixture was cooled to room temperature. The white product was separated from ethanol, and then washed with distilled water. Recrystallization using anhydrous ethanol dryied under vaccum conditions produced a white crystalline solid 6.8982 g, yield 84.95 %, m.p. 101–103°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 3.09 (2H, s, CH<sub>2</sub>); 3.61 (8H, s, CH<sub>2</sub>); 7.22-7.33 (20H, m, ArH).

Synthesis of  $L^2$ : The synthesis of  $L^2$  was carried out by slowly adding 7 mL ethylene diamine into a solution of 8 g NaOH and 20 mL distilled water. Then 30 mL of benzyl chloride (2–3 drops) were continuously added into the mixture solution. The reaction was heated to 95°C and stirred for 4 h, and then the mixture was cooled to room temperature. The white product was separated from diethyl ether, and then washed with distilled water. Recrystallisation using anhydrous ethanol dried under vaccum conditions resulted in white crystals 12.43 g, yield 60.0%, m.p. 92-95°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) $\delta$ : 2.60 (4H, s, CH<sub>2</sub>), 3.50 (8H, s, CH<sub>2</sub>), 7.23–7.28 (20H, m, Ar–H).

Synthesis of L<sup>3</sup>: Ligand L<sup>3</sup> was prepared by adding 4.2 mL 1, 3-propanediamine into a solution of 8g NaOH and 18 mL anhydrous ethanol. Then, 27.5 mL benzyl chloride (2–3 drops/s) were continuously added into the solution. The reaction was heated to 80°C and stirred for 4 h, then cooled to room temperature. The white product was separated from ethanol, and then washed with distilled water for several times. Recrystallization using anhydrous ethanol dryied in vaccum conditions produced white needle crystals 14.06 g, yield 64.6 %, m.p. 50-51 °C. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300MHz)  $\delta$ : 1.71 (2H, s, CH<sub>2</sub>), 2.38-2.42(4H, t, CH<sub>2</sub>), 3.48 (8H, s, CH<sub>2</sub>), 7.21-7.28 (20H, m, Ar-H).

Synthesis of L<sup>4</sup>: The synthesis of L<sup>4</sup> was performed by adding 2 mL of 1,4-butanediamine into a solution of 7 g NaHCO<sub>3</sub> and 20 mL of distilled water. Then, 10 mL benzyl chloride (2–3 drops) were continuously added into the solution. The reaction was heated to 95°C and stirred for 8 h and cooled to room temperature. The white reaction product was separated from the mixture solution, washed with ethanol and distilled water several times. Drying in vacuum produced white needle crystals 4.87 g, yield 54.4 %, m.p. 138–140 °C. <sup>1</sup>HNMR (DMSO, 300MHz)  $\delta$ : 1.39 (4H, s, CH<sub>2</sub>), 2.25 (4H, s, CH<sub>2</sub>), 3.45 (8H, s, CH<sub>2</sub>), 7.20-7.30 (20H, m, Ar-H).

### Synthesis of $[L^0]2H^+ \cdot [CuCl_4]^{2-}(1)$

0.050 g (0.00012 mol)  $L^0$  and 5 mL ethanol were placed in a 50 mL Erlenmeyer flask, then 0.5 mL concentrated hydrochloric acid and 0.050 g (0.00029 mol) CuCl<sub>2</sub>·2H<sub>2</sub>O were slowly

added and shaken until the contents were dissolved. The flask was allowed to stand for one week at room temperature, giving rise to blue block crystal **1**. M.p. 193-195°C.

# Synthesis of $CH_3CH_2OH \subset [L^2]2H^+ \cdot [CuCl_4]^{2-}$ (2)

0.35 g (0.00083 mol) of  $L^2$  and 10 mL ethanol were placed in a 50 mL Erlenmeyer flask, then 1 mL concentrated hydrochloric acid and 1 mL of prepared K<sub>2</sub>[CuCl<sub>4</sub>] were added slowly and shaken until the contents were dissolved. The flask was left to stand for about 8-10 days at room temperature, giving rise to orange crystal **2**. M.p. 173-178°C.

# Synthesis of CH<sub>3</sub>OH $\subset$ [L<sup>3</sup>]2H<sup>+</sup>·[CuCl<sub>4</sub>]<sup>2-</sup> (3)

0.10 g (0.00023 mol) of  $L^3$  and 20 mL methanol were introduced into a 50 mL Erlenmeyer flask, then 0.19 g of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.0011 mol) and 1 mL concentrated hydrochloric acid were slowly added and shaken until the contents were dissolved. The flask was left for month at room temperature, giving rise to red block crystals **3**. M.p. 174-185 °C.

# Synthesis of CH<sub>3</sub>COOH $\subset$ [L<sup>3</sup>]2H<sup>+</sup>·[CuCl<sub>4</sub>]<sup>2-</sup>(4)

0.10 g (0.00023 mol) of  $L^3$  and 10 mL acetic acid were placed into a 50 mL Erlenmeyer flask, then 0.10 g of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.00059 mol) and 2 mL concentrated hydrochloric acid were slowly added and shaken until the contents were dissolved. The flask was allowed to stand for 5 days at room temperature, giving rise to orange-red crystals **4**. M.p.151-159°C.

# Synthesis of $CH_2CHCOOCH_3 \subset [L^3]2H^+ \cdot [MCl_4]^{2-}$ (5-7) (M = Zn, Co, Hg)

0.10g (0.00023 mol) of  $L^3$  and 10 mL acrylic ester were placed into a 50 mL Erlenmeyer flask, then 0.10 g ZnCl<sub>2</sub> (0.00073 mol) and 2 mL of concentrated hydrochloric acid were Page 11 of 42

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slowly added and shaken until the contents were dissolved. The flask was left for about one week at room temperature, giving rise to transparent block crystals **5**. M. p. 244–255°C. The same experiments were carried out using  $CoCl_2 \cdot 6H_2O/HgCl_2 \cdot 2H_2O$  yielding crystals **6** (m.p. 240-244°C) and **7** (m.p. 163–173°C).

### Synthesis of CH<sub>3</sub>CN·H<sub>2</sub>O $\subset$ [L<sup>4</sup>]2H<sup>+</sup>·[MCl<sub>4</sub>]<sup>2-</sup> (8-9) (M = Hg, Co)

0.10 g (0.00022 mol) of  $L^4$  and 4 ml dichloromethane and 20 ml acetonitrile were placed into a 50 ml Erlenmeyer flask, and then 0.10 g HgCl<sub>2</sub> (0.00037 mol) and 1 ml concentrated hydrochloric acid were slowly added and shaken until the contents were dissolved. The flask was allowed to stand overnight at room temperature, giving rise to transparent block crystals **8**. M.p. 106-115 °C. The same experiments were carried out using CoCl<sub>2</sub>·6H<sub>2</sub>O to produce blue block crystals **9**. M.p. 98-106°C.

# Synthesis of $CH_3OH \subset [L^4]2H^+ \cdot [CdCl_4]^{2-}$ (10)

0.10 g (0.00022 mol) of  $L^4$  and 4 ml dichloromethane and 20 ml methanol were placed into a 50 mL Erlenmeyer flask, then 0.10 g CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.00044 mol) and 1 mL concentrated hydrochloric acid were slowly added and shaken until the contents were dissolved. The flask was allowed to stand overnight at room temperature, giving rise to transparent crystals **10**. M.p.102-107 °C.

### Crystallography

Single crystal data collection were performed on a Bruker P4 diffractometer with Mo  $K\alpha$ radiation ( $\lambda = 0.71073$  Å) and Bruker X8 Prospector APEX-II/CCD diffractometer equipped  with a microfocusing mirror (Cu- $K\alpha$  radiation,  $\lambda = 1.54056$  Å). The structures were determined using direct methods and refined (based on F2 using all independent data) by full-matrix least-square methods (SHELXTL 97). Data were reduced by using the Bruker SAINT software. All non-hydrogen atoms were directly located from different Fourier maps and refined with anisotropic displacement parameters. Guest molecules were well resolved but disordered, with the thermal displacement parameters of some atoms being relatively large, partly owing to the loose packing in the void and partly because the atomic positions represent an average between the included guest molecules. The details of data collection, data reduction and crystallographic data are summarized in ESI Tables S1 and S2.

### Mecanochemistry

Liquid-assisted grinding (LAG) of 32 mg (0.047 mmol) of crystals **3** and 10.5 mg (0.094 mmol) of KOH in a 1:2 molar ratio, with the addition of 30  $\mu$ L of EtOH was performed. Upon grinding, a color change from orange to brown was observed within 5 min. Then the powder after grinding was recrystallized in anhydrous methanol.

Liquid-assisted grinding (LAG) of 29 mg (0.041 mmol) of crystals **10** and 4.6 mg (0.082 mmol) of KOH in a 1:2 molar ratio, with the addition of 30  $\mu$ L of anhydrous methanol was carried out. Upon grinding, a color change from colorless to white was observed within **10** min. Then the powder after grinding was recrystallized in anhydrous methanol.

### **Results and Discussion**

# Structure description of complexes using $L^0$ and $L^2$ : second sphere adducts 1 and 2.

In the absence of alkyl chain on the bibenzylamine ligand ( $L^0$ ), the bibenzylamine can directly react with  $[CuCl_4]^{2-}$  anion to produce the second-sphere coordination complex

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 $[L^0]2H^+ \cdot [CuCl_4]^{2-}(1)$ . Crystal structure analysis reveals that the asymmetric unit in 1 comprises half  $[CuCl_4]^{2-}$  anion and one diprotonated  $L^0$  ligand. The  $[CuCl_4]^{2-}$  anion adopts planar geometry, with the Cu–Cl bond lengths being 2.245 (1) Å and 2.279 (1) Å respectively. Each  $[CuCl_4]^{2-}$  anion is surrounded by four protonated  $L^0$  through N–H···Cl interactions (*i*, *ii*) and expanded into a linear hydrogen bonding chain along the crystallographic *a*-axis (Fig. 1). The second sphere adduct 1 does not include guest molecules.



**Figure 1** Crystal structure of 1 showing the second-sphere coordination formed by  $L^0$  and  $[CuCl_4]^{2-}$ anions. N-H…Cl interactions (*i*, *ii*) showed as dashed lines.

Using  $L^1$  (one  $-CH_2$ - spacer), no second sphere adduct was obtained. In fact, the reaction between  $L^1$  and  $[MCl_4]^{2-}$  showed that the ligand  $L^1$  is unstable and decomposes into  $L^0$  and subsequently forms complexes with  $[MCl_4]^{2-}$ .

However, when the N–CH<sub>2</sub>–N backbone was expanded by introducing an extra CH<sub>2</sub> group to form the –(CH<sub>2</sub>)<sub>2</sub>– backbone, the ligand  $L^2$  was obtained. X-ray crystallography reveals that  $L^2$  crystallized in the *P*-1 space group with half molecule in the asymmetric unit.<sup>36</sup> The intramolecular N···N distance is 3.766 Å. The diffusion of CuCl<sub>2</sub>·2H<sub>2</sub>O in EtOH into a HCl/EtOH solution of  $L^2$  resulted in the second sphere adduct **2**, in which the host framework  $[L^2]2H^+$ ·[CuCl<sub>4</sub>]<sup>2–</sup> includes EtOH guest molecules. Single crystal XRD

shows that there are two  $[CuCl_4]^{2-}$  dianions, two doubly protonated  $L^2$  and one EtOH molecules in each asymmetric unit. The two protons in  $L^2$  are linked with the same  $[CuCl_4]^{2-}$  anion through two charge assisted N–H···Cl hydrogen bonds (*i*, *ii*), giving rise to a *quasi*-chelating<sup>37</sup> building block 1 (Fig 2a). The geometry of the  $[CuCl_4]^{2-}$  anion forms highly distorted tetrahedral coordination environment with Cl atoms. The neighbouring *quasi*-chelating building blocks further form a hydrogen bonded chain along the crystallographic *b*-axis through C–H···Cl interactions (*iii–v*, Fig. 2a) and then expanded into a cage-like along *c*-axis accommodating disordered ethanol (i.e., over two positions) guest molecules (Fig. 2b).



**Figure 2.** Crystal structure of **2** showing the *quasi*-chelating hydrogen bonded chain along the *b*-axis via C–H···Cl interactions (a). View along the *c*-axis of the included ethanol molecules (spacefilling) disordered over two positions (b).

Structure description of complexes using L<sup>3</sup>: second sphere adducts 3-7.

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Structure description of CH<sub>3</sub>OH $\subset$  [L<sup>3</sup>]2H<sup>+</sup>·[MCl<sub>4</sub>]<sup>2-</sup> (3). The insertion of an extra methylene in  $L^2$  formed a new ligand ( $L^3$ ). From single crystal X-ray diffraction data we observed that the intramolecular N···N distance increased from 3.766 Å in  $L^2$  to 5.113 Å in The diffusion of a methanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O into the HCl/MeOH solution of L<sup>3 37</sup> L<sup>3</sup>. gave good quality single crystals of the second sphere adduct  $CH_3OH \subset [L^3]2H^+ (CuCl_4)^{2-3}$ . X-ray crystallographic analysis reveals that **3** is monoclinic  $(P2_1/c)$  with one dianion  $[CuCl_4]^{2-}$ , one doubly protonated L<sup>3</sup> and one methanol molecule in the asymmetric unit. One double-protonated ligand  $L^3$  is linked with two different  $[CuCl_4]^{2-1}$ anions through N–H···Cl interactions (i, ii), forming the non-chelating dication-dianion building block which propagates along the *b*-axis (Fig. 3a). Methanol molecules are trapped in the concave region of the helical chain through the O-H…Cl interaction (3.165(4) Å) involving the hydroxyl groups and chloride atoms of [CuCl<sub>4</sub>]<sup>2-</sup> anions. The helical chains are linked further by weak C–H···Cl hydrogen bonds (*iii-v*) along the c-axis, constructing a 3D structure (Fig. 3b).



Figure 3. View along the *b*-axis of the hydrogen bonding interactions (dashed lines) between dianions, dications and solvent in 3 (a). View of the crystal packing of 3 accommodating methanol guest molecules (b).

We note that **3** is not isostructural to other two second sphere adducts crystallized using  $L^3$  [HgCl<sub>4</sub>]<sup>2–</sup> and [ZnCl<sub>4</sub>]<sup>2–</sup> which also include methanol as a guest.<sup>37</sup> This demonstrates the structural diversity of this type of second sphere complexes (Fig. 4a,b,c).



Figure 4. Different building blocks in crystals formed by  $L^3$  and metal chlorides in MeOH solvent: (a) crystal 3; (b) different building blocks previously reported in second sphere adducts (b) and (c).

**Structure description of CH<sub>3</sub>COOH**  $\subset$  [L<sup>3</sup>]2H<sup>+</sup>·[CuCl<sub>4</sub>]<sup>2-</sup> (4). It is known that weak interactions are crucial in the molecular self-assembling outcome. The effect of the solvent molecules can direct the crystallization affecting the stoichiometric ratio between the self-assembling building blocks (i.e., cations, anions and solvent molecules in this case). The following example is a proof on how by replacing methanol for acetic acid in the crystallization of L<sup>3</sup> and [CuCl<sub>4</sub>]<sup>2-</sup> results in a completely different second sphere adduct. This adduct was synthesized diffusing CuCl<sub>2</sub>·2H<sub>2</sub>O in acetic acid into a HCl/MeOH solution containing ligand L<sup>3</sup> to yield the salt CH<sub>3</sub>COOH  $\subset$  [L<sup>3</sup>]2H<sup>+</sup>·[CuCl<sub>4</sub>]<sup>2-</sup> (4). The metal organic hybrid complex 4 crystallizes in the monoclinic system in the *P*<sub>21</sub>/*c* space group, with two independent doubly-protonated L<sup>3</sup> ligands, two [CuCl<sub>4</sub>]<sup>2-</sup> dianions and one acetic acid in the asymmetric unit.

The two independent  $L^3$  ligands (labeled  $L^{3a}$ ,  $L^{3b}$ ) in the asymmetric unit interact with two independent  $[CuCl_4]^{2-}$  dianions ( $[CuCl_4]^{2-}_a$ ,  $CuCl_4]^{2-}_b$ ) through N-H…Cl interactions, constructing two individual building blocks (Fig. 5a). In one of the building blocks, one ligand  $L^{3a}$  is connected with two independent  $[CuCl_4]^{2-}$  anions ( $[CuCl_4]^{2-}_a$ ,  $CuCl_4]^{2-}_b$ )

through N–H···Cl interactions (*i* and *ii*); whereas in the other building block, the other ligand  $\mathbf{L}^{3\mathbf{b}}$  and the  $[\operatorname{CuCl}_4]^{2-}_{\mathbf{a}}$  anion via four N–H···Cl interactions (*iii* and *iv*) as shown in Fig. 5a. The building blocks are alternately arranged along the *c*-axis through C–H···Cl weak interactions (*v* - *ix*) to build a 3D structure (Fig. 5b), with acetic acid guest molecules filling the concave region through O–H···Cl interactions (3.148 Å).



Figure 5. Crystal structure of 4 showing the two different building blocks involving  $L^{3a}$  and  $L^{3b}$  (a). Crystal packing in 4 showing the inclusion of acetic acid as guest molecule (spacefilling).

Structure description of  $CH_2CHCOOCH_3 \subset [L^3]2H^+ \cdot [MCl_4]^{2-}$  (5-7). In order to test the guest inclusion ability of the second sphere adducts self-assembled using  $L^3$  we used larger guest molecules such as acrylic ester. When acrylic ester was added into a mixture of

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a solution of  $HgCl_2 \cdot 2H_2O/ZnCl_2 \cdot 2H_2O/CoCl_2 \cdot 2H_2O$  and  $L^3$  in HCl/EtOH, the  $CH_2CHCOOCH_3 \subset [L^3]2H^+ \cdot [MCl_4]^{2-}$  (M = Zn, (5); M = Co, (6), M = Hg, (7) inclusion complexes were formed. Since 5-7 are isostructural, the description of one (Zn) of the structures will suffice for all. The crystal structure of 5 crystallizes in the monoclinic  $P_{1/n}$  space group, with one doubly-protonated  $L^3$ , one  $[ZnCl_4]^{2-}$  dianion and half acrylic ester in each asymmetric unit. Each two  $L^3$  ligands and two  $[ZnCl_4]^{2-}$  dianions form a closed hydrogen bonded network through four N–H…Cl hydrogen bonds (*i*, *ii*), forming the building block (Fig. 6a). The neighboring building blocks are arranged nearly perpendicular giving a linear hydrogen bonded chain through weak C–H…Cl interactions (*iii-vi*) (Fig. S2 and 6b) and further expanded into a 3D structure, in which the acrylic ester adopts planar conformation and is accommodated inside the host framework formed by  $L^3$  and  $[MCl_4]^{2-}$  dianions through C–H…O interaction (3.070(3) Å). For the isostructural  $[HgCl_4]^{2-}$  and  $[CoCl_4]^{2-}$  second sphere adducts see ESI.





**Figure 6.** Single crystal structure of second sphere adduct **5**. View of the building block involving dianion and dications (a). Crystal packing showing the inclusion acrylic ester guest molecules (spacefilling) (b).

Structure description of complexes using L<sup>4</sup>: second sphere adducts 8-10.

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Structure description of  $CH_3CN \cdot H_2O \subset [L^4]2H^+ \cdot [MCl_4]^{2-}$  (8-9). To explore the guest behavior of this family of flexible molecules, we synthesized a new bidentate ligand  $L^4$  with longer  $-(CH_2)_4$ - backbone chain, and therefore higher conformational flexibility. The X-ray crystal structure shows that in the asymmetric unit there is half molecule of  $L^4$ . The molecule crystallizes in the *P*-1 space group. The N-(CH<sub>2</sub>)<sub>4</sub>-N distance increased to 6.266(4) Å to give a longer backbone.

Addition of HgCl<sub>2</sub>/CoCl<sub>2</sub> in a dichloromethane (DCM) solution containing  $L^4$  and HCl/CNCH<sub>3</sub> for four days, resulted in the isostructural second sphere adducts CH<sub>3</sub>CN·H<sub>2</sub>O  $\subset [L^4]2H^+ \cdot [MCl_4]^{2-}$  (M = Hg, (8); M = Co, (9)). The two complexes crystallize in the monoclinic  $P2_1/n$  space group, with one doubly-protonated  $L^4$ , one  $[HgCl_4]^{2-}$  dianion, one acetonitrile and one water molecule in the asymmetric unit. It is an enclosed hydrogen bonding interaction between  $L^4$  and  $[HgCl_4]^{2-}/[CoCl_4]^{2-}$  anion involving water molecules as linker (Fig. 7a).

The second sphere adduct **8** has a building block that involves three types of hydrogen bonds: the expected N–H····Cl interaction between N ligand and  $[HgCl_4]^{2-/}[CoCl_4]^{2-}$  (*i*), N–H···O interaction between ligand and linker water molecules (*ii*), and O–H····Cl interactions between water and  $[HgCl_4]^{2-}$  (*iii*). The acetonitrile molecule is encapsulated and stabilized by O–H···N interactions (*iv*) between the other remaining unused hydrogen atom of water and N atom of the CN group. Interestingly, the CH<sub>3</sub>CN molecules do not play a primary role in the host hydrogen bond network and are somehow acting as templates

to fill the empty space, while water is more directly involved in the host framework bridging the dication and dianion (Fig. 7a). The building blocks are further linked to each other through C–H…Cl interactions (*v-viii*) along *b-* and *c-*axis, constructing a 3D structure as seen in Fig. 7b, with the ligand molecules in a helical arrangement along *c-*axis.



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Figure 7. Crystal structure of second sphere adduct 8 showing the main hydrogen bonds between dications and dianions (*i.e.*, the building block) (a). (b) Crystal packing in 8 displaying also the hydrogen bonds between adjacent building blocks (b). The included acetonitrile guest molecules are shown as spacefilling model.

**Structure description of CH<sub>3</sub>OH** $\subset$ [L<sup>4</sup>]2H<sup>+</sup>·[CdCl<sub>4</sub>]<sup>2-</sup> (10). Using the above same conditions, the ligand L<sup>4</sup> can react with CdCl<sub>2</sub>·2.5H<sub>2</sub>O in methanol to produce the complex CH<sub>3</sub>OH $\subset$ [L<sup>4</sup>]2H<sup>+</sup>·[CdCl<sub>4</sub>]<sup>2-</sup> (10). The complex crystallizes in the monoclinic *P*2<sub>1</sub>/*n* space group, with one doubly-protonated L<sup>4</sup>, one [MCl<sub>4</sub>]<sup>2-</sup> dianion, one methanol in one asymmetric unit. One protonated NH in L<sup>4</sup> is connected with [CdCl<sub>4</sub>]<sup>2-</sup> dianion through N–H···Cl interaction (*i*), the other protonated NH in L<sup>4</sup> is linked with methanol molecule through N–H···O interaction (*ii*). Then the methanol acts as link further connecting with another [CdCl<sub>4</sub>]<sup>2-</sup> dianion through O–H···Cl hydrogen bonding (*iii*). The above three hydrogen bonds comprise a new building block. The building blocks are further linked to a linear chain along diagonal of *ac*-axis (Fig. 8a), and then expanded into a 3D structure through C–H···Cl (*iv*) (Fig. 8b).



**Figure 8.** Single crystal structure of **10**. View of the building block involving dication, dianion and a water guest molecule (a); (b) Crystal packing showing the hydrogen bonding interactions perpendicular to the crystallographic *ac*-plane (b). Hydrogen bonds are shown as dash lines.

# Influence of $-(CH_2)_{n-}$ (n = 2, 3, 4) spacer lengths for inclusion property

The metal : ligand ratio can be an important parameter controlling the dimensionality of the resultant second sphere adduct. Herein, the metal : ligand ratio is constant (1 : 1) in crystals 2-10. Only 1 formed by  $L^0$  ligand give rise to the 1 : 2 ratio but does not show guest inclusion (i.e., due to the ligand size). The tetrachlorometallate dianion adopts a

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planar geometry in crystal **1**, but forms various distorted tetrahedral  $[MCl_4]^{2^-}$  dianions in **2-10** crystals. The alkyl chain length is an important factor determining the formation of second-sphere coordination giving rise to different guest molecules. Such versatility/flexibility allows keeping the 1:1 metal ratio even if the chain length increases from 3.766 to 6.266 Å.

QM calculations specific for solid state phases, particularly DFT approaches have demonstrated that for the ligand with two methyl groups in the backbone, the stability is higher than that with three methyl groups.<sup>37</sup> Moreover, the conformational freedom introduced by the addition of methylene groups has a strong influence in the conformational flexibility of the ligand when it self-assembles with the metal ions and solvent molecules. In the second sphere adduct 1 containing  $L^0$  (i.e., without alkyl), only one nitrogen donor, reacts with the dianion [CuCl<sub>4</sub>]<sup>2–</sup> through N–H···Cl interactions, constructing a linear second sphere adduct without included guests. Interestingly, the ligand  $L^1$  (–(CH<sub>2</sub>)<sub>*n*-</sup> *n* = 1) is unstable during the self-assembling reaction with [MCl<sub>4</sub>]<sup>2–</sup>, and decomposes into  $L^0$  and subsequently forms crystal 1.</sub>

In  $L^2$  the length between the two nitrogen atoms is *ca.* 3.76 Å, adopting a gauche conformation in crystal **2** (Fig. 9a) and forms a *quasi*-chelating N–H···Cl hydrogen bond with  $[MCl_4]^{2-}$ , including ethanol in the host framework.

By increasing the methylene chain length  $[(CH_2)_n (n = 3)]$ , the distance between the two nitrogen donors in  $L^3$  is *ca*. 5.11 Å.  $L^3$  exhibits higher conformational diversity due to the higher flexibility of ligand.  $L^3$  adopts antiperiplanar conformation or gauche conformation in this crystals (Fig. 9 b,c,d). The host framework takes different molecular arrangements to fit the demands of the same guest species (methanol). In **3**, methanol is not directly

involved in the connection between the ligand and  $[MCl_4]^{2-}$ . Additionally, acetic acid or acrylic ester can also be included in the host cavity formed by L<sup>3</sup> and  $[MCl_4]^{2-}$ , in which L<sup>3</sup> adopts gauche conformation in crystal **4** (Fig 9e) and crystal **5-7** (Fig. 9f).

With longer methylene chains ((CH<sub>2</sub>)<sub>n</sub> n = 4), acetonitrile and methanol molecules were included in the host framework formed by  $L^4$  and  $[MCl_4]^{2-}$ , due to length increase of N····N by (CH<sub>2</sub>)<sub>4</sub> spacer (6.34 Å), the interaction with  $[MCl_4]^{2-}$  is through water molecules, and acetonitrile.  $L^4$  also exhibit flexibility and can adopt gauche conformation in crystals 8-9 (Fig. 9g) whereas antiperiplanar conformation in crystal 10 (Fig 9 h).



Figure 9. Diversity in the conformations of  $L^2-L^4$  in crystals 2-10 viewed from the projection of the Newman-type overlay of two nitrogen atoms: (a)  $L^2$  in crystal 2; (b)  $L^3$  in crystal 3; (c,d)  $L^3$  in previous reported crystal structures; (e)  $L^3$  in crystal 4; (f)  $L^3$  in crystal 5-7; (g)  $L^4$  in crystal 8-9 (h)  $L^4$  in crystal 10.

### Thermal stability of supramolecular adducts 1-10.

The thermal stability and the reversible/irreversible properties (guest behavior) of complexes 2, 4 and 8 have been studied. The experimental PXRD patterns of complexes 1-10 are in agreement with the simulated diffraction patterns from their respective single crystal structures (Fig. S6-S13), thus confirming their phase purity.

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To begin with, we monitored the thermal stability of the second sphere adduct 2 which contains  $L^2$ . The release of the guest molecules has been monitored first by thermogravimetrical analysis (TGA), which showed that crystal 2 exhibits an initial weight loss (3.4 %) from RT to 137 °C, corresponding to the release of ethanol (calcd 3.5%). Further heating leads to the loss of ligand. Second, we have monitored the thermal stability of 2 by heating from RT to 150 °C by holding the sample at 100 °C for several hours. As shown in Figure S14, the crystallinity is practically lost after 15 h at 100 °C but seems that at 120 °C there is somehow a reorganization as weak diffraction is observed. However, at higher temperatures (i.e., 120-150 °C) the crystallinity is lost and the original crystalline structure (2) is not restored after immersing the heated powders of 2 in EtOH for 24 h.

The structural stability of **4**, formed using  $L^3$ , was also monitored upon heating. We found that heating complex **4** to 160 °C showed that after 140 °C, an amorphous phase is obtained and did not return to the original structure when it was immersed in acetic acid (Fig. S19). The structural transformation is probably too severe to allow the reconstruction of the framework. TG analysis reveals that **4**, the first weight loss (4.57 %) from 50°C to 170° C corresponds to the release of acetic acid (calcd 4.46 %).

The investigation of reversible guest inclusion/release process of supramolecular second sphere adducts including ligand  $L^4$  and  $[MCl_4]^{2-}$  shows an interesting result for the second sphere adduct 8. The PXRD pattern of 8 shows that the positions and intensities of all peaks shifted upon heating at 100 °C, suggesting that the supramolecular host structure changed upon CH<sub>3</sub>CN release whilst maintaining the crystallinity (see ESI). Powder XRD indicates that a new phase is obtained at least for that period of heating time (as seen in Fig. 10d). Interestingly, when we put the polycrystalline powder in acetonitrile/water for 72h, the original structure was formed again (Fig. 10e).

TGA corroborates that **8**, shows two distinct weight losses corresponding to the  $CH_3CN$  and water respectively. The weight loss (4.90 %) fits with the release of  $CH_3CN$  molecules

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from RT to 120 °C (calcd. 4.82%) and the subsequent weight loss (2.32 %) from 120 to 170 °C corresponds to the release of water molecules (calcd. 2.22%). We note that the PXRD pattern obtained after 3 hours at 100 °C might be the one corresponding to the structure containing only H<sub>2</sub>O (as shown by TG and by the fact that there is no presence of **8** as the most intense peak at *ca*. 2-theta 12° is not present anymore Fig. 10d) and therefore, a stepwise guest release is observed. The restoration of **8** occurs as it might be helped by the presence of H<sub>2</sub>O in the crystal structure (Fig. 10e).



**Figure 10**. Experimental PXRD patterns of **8**: (a) Simulated PXRD from single crystal; (b) as synthesized PXRD pattern; (c) sample heated at 100 °C for 1h; (d) sample heated at 100 °C for 3h; (e) Immersing (d) sample in acetonitrile/water for 100 h. The diffraction peak highlighted in red corresponds to the most intense peak of **8** that does not appear after being heated to 100 °C for 3 hours.

In order to corroborate the dynamic behavior of adducts including  $L^4$ , we have prepared a new second sphere complex that includes ethanol and water as a guest  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$  (see ESI). We demonstrate that if  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$  is heated up to 100 °C for 1h, it becomes amorphous upon guest release (*i.e.*, corroborated by <sup>1</sup>H NMR) but if it is immersed again in

EtOH the desolvated adduct reverts to its initial structure as shown by PXRD (Figure 11). Thus the dynamic behavior in a second sphere adduct is observed following a crystalline-to-amorphous-to-crystalline transformation which is reminiscent to some coordination networks.<sup>9,38,39,40</sup> Such reconstruction of the original framework is indicative of a certain structural memory retained in the amorphous phase, clearly demonstrating that second sphere coordination adducts can be flexible and active upon external stimuli.



Figure 11. (a) Simulated PXRD (100 K) of  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ ; (b) Experimental PXRD (300 K) of  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ . (c) PXRD (300 K) corresponding to single crystals of  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$  heated up to 100 °C for 1h. (d) PXRD of the immersed amorphous phase obtained upon heating  $8 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$  to 100 °C in EtOH for 24h (d).

Influence of  $-(CH_2)_n$  (n = 2, 3, 4) spacer lengths on the solid-state mechanochemical dehydrochlorination reaction.

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Dehydrochlorination reactions consisting of the removal of HCl from crystalline salts are one type of reactions that have been rarely investigated in coordination molecular complexes.<sup>41,42</sup> Recently, we have studied the mechanochemical transformation of the  $[L]2H^+ \cdot [CuCl_4]^{2-}$ adduct (L second sphere = N. N, N', N'-tetra-p-methoxybenzyl-ethylenediamine) into a new discrete chelating metal coordination complex  $[(CuCl_2)(L)] \cdot 2(H_2O)$  via a dehydrohalogenation reaction.<sup>29</sup> Moreover, we expanded such studies showing that the chelating complexes resulting from the mechanochemical dehydrohalogenation reaction depend on the formation of *quasi*-chelating hydrogen bonding salts. The length of the bidentate backbone in this family of ligands is very important for the quasi-chelating motif formation. In the crystal structures we described above, only 2 formed by ligand  $L^2$  forms the quasi-chelating hydrogen bonding motif, which reacts via dehydrochlorination reaction to form  $[(CuCl_2)(L^2)]^{37}$ 

Increasing the length of the  $-(CH_2)_n-(n = 3, 4)$  backbone ( $L^3$  and  $L^4$ ), crystals **3** and **10** cannot form the *quasi*-chelating hydrogen bonding motif with  $[MCl_4]^{2^-}$  (*i.e.*, most likely due to the longer N···N distance). In our previous results we carried out the mechanochemical dehydrochlorination reaction involving  $CH_3CH_2OH\subset [L^3]2H^+ \cdot [CuCl_4]^{2^-}$  and we did not see the formation of a chelated complex.<sup>37</sup> Here we use a new second sphere adduct having different unit cell and guest molecule (**3**). Again using liquid assisted grinding (LAG) of **3** in presence of KOH did not show the formation of the chelated complex and only  $L^3$  and KCl were obtained (Fig. S29). This corroborates our previous results. Then we tested another complex having longer backbone chain  $-(CH_2)_4$ - by using the second sphere adduct **10**. In this case, upon grinding dehydrochlorination occurs but did not form the chelated complex but pure  $L^4$ , CdCl<sub>2</sub> and KCl in its crystalline form (Fig. 12).



Figure 12. (a) Experimental PXRD of crystal 10. (b) PXRD product of 10 grinded in the presence of KOH (298 K). (c) PXRD pattern of ligand  $L^4$ . It is interesting to note the formation of CdCl<sub>2</sub> and KCl as by-product.

### **Molecular Modelling Results**

The combination of experimental and theoretical calculations (using also methods specific for solid phases) can provide complementary insights in the rationalization of solid-state reactions. Density functional theory (DFT) approaches have been employed herein. The PBE (Perdew–Burke–Ernzerhof)<sup>43,44</sup> exchange-correlation functionals, has been used both for gas and solid phases (i.e., under periodical conditions). All the calculations were carried out using the DMol<sup>3</sup> software.<sup>45</sup>

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 was adopted. We assumed experimental X-ray determined geometries for heavy atoms while all the X–H (X = C, N, O) bond lengths were optimized because they are generally underestimated by crystal structure solution techniques. Large supramolecular complexes<sup>46,47,48,49</sup> systems also containing charged particles<sup>50,51</sup> and crystalline phases of thiophene-based oligomers and polymers, <sup>52,53,54,55</sup> have been successfully studied using a similar computational approach. The contribution of subtle inter- and intramolecular interactions (not included in standard Gradient Corrected DFT algorithms) has been accounted for by the Grimme scheme within a DFT-D approach<sup>56,57,58</sup> (i.e., PBE/DNP plus Grimme corrections).

The stability of  $L^4$  ligand in its crystalline form has been calculated by solid phase calculations at the PBE/DNP (plus Grimme corrections) level. The sublimation energy of  $L^4$ , is 56.8 kcal/mol, which is comparable to that of  $L^2$  and  $L^3$  molecules (60.5 kcal/mol and 51.9, respectively).

Gas phase calculations at the same level have been performed to investigate conformational energies and electron distribution of systems involved into the chelating reactions. First of all it should be underlined once more that in  $L^2$ ,  $L^3$  and  $L^4$  the low energy ligand structures possess different N–N distances both in crystal structures and in optimized geometries. In addition, the conformational freedom introduced by one or more extra methylene groups has a strong influence in cyclic intermediate transition states involved in the possible chelating reactions.

DFT-D calculations show that  $L^4$  ligand has a proton affinity (i.e., the difference in energy between neutral and protonated ligand) similar to that of  $L^3$  molecules (433 kcal/mol): 411 kcal/mol in 8 and 426 kcal/mol in 10. Thus, as in the case of  $L^2$ , in principle  $L^4$  can form complexes with metals as  $L^1$  ligand (which has a lower estimated proton affinity, 384 kcal/mol).<sup>37</sup> It is interesting to note that after deprotonation  $L^4$  ligands has an energy 2

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kcal/mol higher with respect to the corresponding neutral molecules in  $L^4$  crystal demonstrating the scarce tendency to form a chelate system (as  $L^1$  does) to lower its energy.

Furthermore, the interactions involved in H-bonded crystals have been analyzed by calculations on small clusters of particles extracted from the single crystal X-ray structures. The interaction energy of the dimer involving protonated  $[L^4]2H^+$  and a dianion (i.e,. one forming charge assisted H-bond) is about 252 kcal/mol in 8 and 261 kcal/mol in 10.. These interaction energies, although lower, are comparable to that observed in  $L^3$  system (272 kcal/mol).<sup>37</sup> Therefore, protonated  $L^4$  forms (at least locally) stronger H-bond interactions than those observed in the *quasi*-chelating motif in protonated  $L^2$  with an interaction energy of 158 kcal/mol for each of the charge-assisted hydrogen bonds.<sup>37</sup> Thus, such lower interaction energy might facilitate the disruption of the charge assisted hydrogen bond helping the formation of the N–Cu coordination bond upon grinding in presence of the strong KOH base.

Further analysis of DFT-D outcomes have shown that the more reactive electrons, (i.e., electrons in FMOs) in the ligand  $L^4$  (possessing the  $-N-(CH_2)_4-N-$  moiety) are mainly localized at the N atoms (Fig. 12). After N protonation the HOMO orbitals are displaced to the phenyl moieties as observed in  $L^2$  and  $L^3$  (Fig. 13). It should be emphasized that even if the HOMO orbitals of  $L^4$  reside mainly at the N atoms, the distribution does not allow the direct formation of a chelate without a relative rotation of the N groups to orient properly the HOMO lobes. In fact, due to symmetric reasons the lobes of the terminal N atoms have opposite signs at variance of the case of  $L^2$ . The number of  $CH_2$  groups between N atoms in stable conformations of  $L^2$ ,  $L^3$  and  $L^4$  not only influences the distance between them but also play a role in the symmetry of corresponding electron density distribution of HOMOs. Both these effects corroborate the experimental outcomes suggesting that  $L^3$  and  $L^4$  do not form atoms are suggesting that  $L^3$  and  $L^4$  do not form

the *quasi*-chelating motif that allows the formation of a chelated complex upon dehydrochlorination.<sup>37</sup>



Figure 13. Structures showing the calculated HOMOs in ligands (a)  $L^2$ , (b)  $L^3$ , and (c)  $L^4$ . View of the HOMOs after protonation in ligands (d)  $L^2$ , (e)  $L^3$  and (f)  $L^4$ .

### Conclusions

In this article, we have synthesized a new type of inclusion compounds based on second-sphere coordination through the deliberate design of various flexible bidentate ligands. A series of ligands based on dibenzylamine have been synthesized by inserting a methylene chain  $[(CH_2)_n (n = 1-4)]$  between two dibenzylamine moieties. Due to the presence of the  $-(CH_2)_n$ - alkyl chains between the biphenyl rings, the torsional freedom around the C–N bonds is higher the longer is the backbone chain. This results in different gauche conformation or antiperiplanar conformation of the ligands, thus forming different hydrogen bonding networks. In addition, the influence of the  $-(CH_2)_n$ - spacer length can have an effect on the inclusion property during the formation of second sphere coordination  $\frac{34}{24}$ 

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complexes. The complexes showing a reliable hydrogen bonding motif are those with  $L^2$  in which the *quasi*-chelating motif between  $L^2$  and  $[MCl_4]^{2-}$  is formed. Second sphere adducts self-assembled using diprotonated  $L^3$  and  $L^4$  with  $[MCl_4]^{2-}$  have shown a great diversity of crystal structures. The second sphere adducts formed by the longest  $-(CH_2)_4$ - chain ( $L^4$ ) and  $[MCl_4]^{2-}$  dianion have to use guest molecules connecting  $L^4$  and  $[MCl_4]^{2-}$  dianion and show dynamic guest uptake/release properties including crystalline-to-amorphous-to crystalline-transformations. Quantum mechanical calculations have shown that dehydrohalogenation reactions seem to occur only when there is a good size matching between the diprotonated N in the cation and the dianions. But not only size matching between reactants is important but also intermolecular interactions, conformational energies, and the symmetry of frontier molecular orbitals play a crucial role.

We believe that the strategy to synthesize new supramolecular second sphere adducts described in this work can be used to open a new family of host-guest compounds. The new second sphere adducts could find potential applications in various fields of materials science such as ion sequestration and gas adsorption. A better knowledge in their solid-state chemistry is needed to tune structure-function properties in the development of new functional materials. QM calculations can give an important input in such understanding.

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### **Supporting Information**

Details on the synthesis, mechanochemical reactions and crystallographic information can be found in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org/.

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### For TOC Only

Tuning the Inclusion Properties and Solid-State Reactivity of Second Sphere Adducts Using

Conformationally Flexible Bidentate Ligands

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Second-sphere coordination has been used to self-assemble various hybrid organic solids using a family of bidentate ligands. The second sphere adducts show dynamic behavior upon guest release-uptake. Experimental results and DFT calculations provide insights in their reactivity and stability.