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A second sphere coordination adduct containing one-dimensional water/methanol channels: X-ray structures, thermal stability and single crystal impedance spectroscopy analysis.†‡

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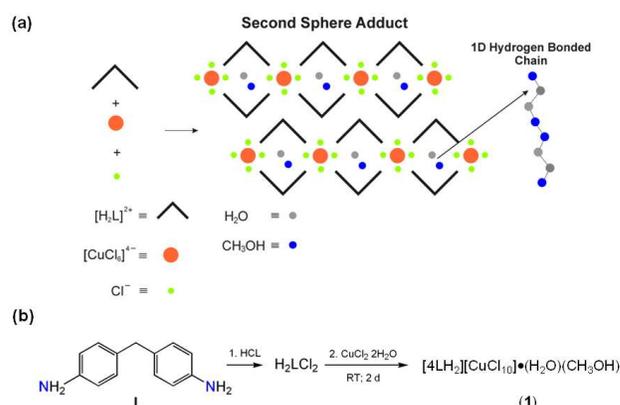
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Using second sphere coordination, a new metal complex has been synthesized, self-assembling a bent shaped organic dication with $[\text{CuCl}_6]^{4-}$ and Cl^- anions, yielding a network with one-dimensional channels. The salt encapsulates water and methanol forming a well defined hydrogen bonding array. The framework is thermally stable (190 °C) whilst keeping the channels. It can uptake dichloromethane but not chloroform from a dichloromethane/chloroform mixture. The solid serves as a support matrix for ionic conductivity via the included water/methanol molecules as shown by single crystal impedance spectroscopy.

Crystal engineering of a new molecular adduct where two or more molecular components are self assembled together is a powerful approach to form new functional materials. Although known for many years, second sphere coordination has been used in various scientific areas such as biological reception¹ and supramolecular self-assembly.² Only recently has been revisited showing a good potential for developing solids with applications in separation³ and gas storage.⁴

Second-sphere coordination, refers to any intermolecular interaction with the ligands directly bound to the primary coordination sphere of a metal ion.⁵ In this way, metal ions acting as connectors and cationic organic ligands as linkers, can form extended frameworks.⁶ Bringing together molecules having concave/convex surfaces can self-assemble in such a way that voids/channels are generated and therefore solvent molecules tend to fill up such empty spaces. However, the precise control on the self assembling of molecules is still a difficult task and only few functional materials have been reported using second sphere coordination.^{3,4}

Here we report a new second sphere coordination complex using a V-shape diamino ligand (4,4'-methylene dianiline) (**L**) which is doubly protonated and further self assembled with two differently charged anions: $[\text{CuCl}_6]^{4-}$ and Cl^- by means of



Scheme 1. (a) Cartoon displaying the synthesis of complex **1** using V-shaped ligand **L** through the formation of the chloride salt $\text{H}_2\text{L}_2\text{Cl}_2$ using second sphere coordination. Note that the guest molecules form a 1D hydrogen bonded $\text{H}_2\text{O}\cdots\text{MeOH}$ chain. (b) Synthesis of **1**.

charge assisted hydrogen bonds (Scheme 1). The new second sphere adduct (**1**) forms one-dimensional channels encapsulating water and methanol molecules connected via hydrogen bonds. The network displays moderate thermal stability up to 190 °C after guest release, and maintains the channel structure suitable for selective guest inclusion based on molecular size. Moreover, the ionic nature of the solid gives a highly crystalline material, allowing single crystal ionic conductivity measurements at ambient conditions. We demonstrate that conductivity is water/methanol mediated as the guest-free crystal shows no conductivity.

Crystallization of **1** was carried out by first protonation of **L** to form the salt $[\text{H}_2\text{L}]^{2+}\cdot 2\text{Cl}^-$ which was further crystallized in the presence of $\text{CuCl}_2\cdot 2(\text{H}_2\text{O})$ in MeOH.⁷ After two days, yellow block single crystals precipitated (Yield 69.7%). A single crystal was removed from the mother solution, covered with protectant (Paratone) oil and mounted for X-ray structure analysis. Single crystal X-ray diffraction measured at 100 K confirmed that the second sphere coordination adduct with formula $[\text{4LH}_2][\text{CuCl}_{10}]\cdot(\text{H}_2\text{O})(\text{CH}_3\text{OH})$ (**1**) was formed.⁷

The structure of **1** contains 4,4'-methylene dianiline H_2L^{2+} cations, an isolated $[\text{CuCl}_6]^{4-}$ anion (located in a crystallographic inversion center) and lattice Cl^- anions, one water and one methanol molecules. Regarding the $[\text{CuCl}_6]^{4-}$ anion, the in-plane $\text{Cl}-\text{Cu}-\text{Cl}$ angles are 89.68(2) ° and the out-plane angles are 87.71(2) °. The three different $\text{Cu}-\text{Cl}$ distances are (2.2703(6); 2.3148(8); 3.1196(9) Å). Therefore, the anion is approximately an elongated rhombic octahedron

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† Electronic supplementary information (ESI) available: CCDC 1008245 (**1**) and 1026237 (**1•DCM**), (contain supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x.

due to the Jahn-Teller effect.⁸ It is worth noticing that the two dications have different geometries differing in the phenyl-phenyl torsion angles and the N-CH₂-N angle (Figure S3). These features are important as this might help the network to accommodate/self repair in response to external stimuli (*i.e.*, T, P or new guest molecules). As expected, the charge assisted hydrogen bonds hold the supramolecular framework which forms a column along the *a*-axis, where the rhombic octahedron [CuCl₆]⁴⁺ interacts with four surrounding NH₃⁺ groups through Cu-Cl...H⁺ hydrogen bonds (Figures 1a,b and Table S1). The two free Cl⁻ anions, Cl3 and Cl4 (*i.e.*, not coordinated to Cu) have important roles as they are hydrogen bonded to the NH₃⁺ groups (Cl3⁻, Cl4⁻) (Table S1 and Figure S4) and also interact via C-H...Cl⁻ contacts (Cl3⁻) ($d_{C...Cl3^-} = 3.681(2)$ Å) with neighbour cations *via* the central -CH₂- group (Figure 1).

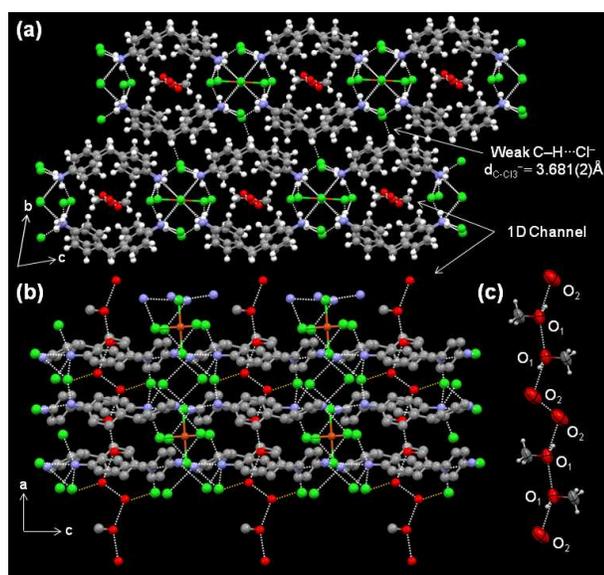


Figure 1. Crystal structure of **1**. (a) View of the 1D channels along the *a*-axis showing the charge assisted hydrogen bonding interactions involving H₂L cations, [CuCl₆]⁴⁺ and Cl⁻ anions. Water and methanol guest molecules are included in the channels. No interactions between the host-guest molecules are shown in this image. (b) Packing of **1** viewed along the *b*-axis showing the alternation of cations and metal ions interacting via charged hydrogen bonds. Guest molecules form 1D hydrogen bond arrays (white dash lines). Yellow dash lines indicate host-guest water...Cl⁻ hydrogen bonds. (c) Hydrogen bonding interactions between water and methanol molecules included in the channel are shown in white dash lines. Colour code: Carbon (grey); Nitrogen (blue); Copper (brown); Chloride (green); Oxygen (red).

In **1** the coordination sphere of [CuCl₆]⁴⁺ drives the ligands in such orientation that their concave side is facing each other and therefore a channel is generated (Figure 1a). The channels are delimited by the phenyl rings, the ligated Cl and the uncoordinated Cl⁻ anions. There is no interpenetration, thus leading to non-interconnected 5 Å × 6 Å 1D channels (Figure S5).⁹

In the as synthesized solid, along the channels, water and methanol molecules are encapsulated forming a 1D chain *via* O-H...O hydrogen bonds (Figure 1c). The distances $d_{O_{water}...O_{methanol}}$ (2.799(7)) and $d_{O_{water}...O_{water}}$ (2.396(8)) are

consistent with a hydrogen bonded chain similar to that observed in the water loaded narrow-pores in MIL-53(Cr).¹⁰ Interestingly, there are Cl4⁻...O2 ($d = 3.274(8)$ Å) interactions among the Cl⁻ anions and the water molecules which contribute to the stabilization of the guest molecules. The voids after manually removing the guest molecules account *ca.* 12 % of the total unit cell volume.¹¹

The thermal stability of **1** was monitored by XRPD, single crystal XRD and thermogravimetric (TG) analysis. As observed by XRPD analysis, the host framework in **1** upon heating to 190 °C is maintained as shown by the diffraction peaks (Figure 2a). TG analysis on a sample of **1** heated to 190 °C was carried out. As observed in Figure S7 (blue line) there is no weight loss until 190 °C while the as synthesized network (black line) shows a weight loss of *ca.* 5 %, that corresponds to the theoretical value for the included guests. Thus, a porous structure without guest molecules can be obtained upon heating.¹²

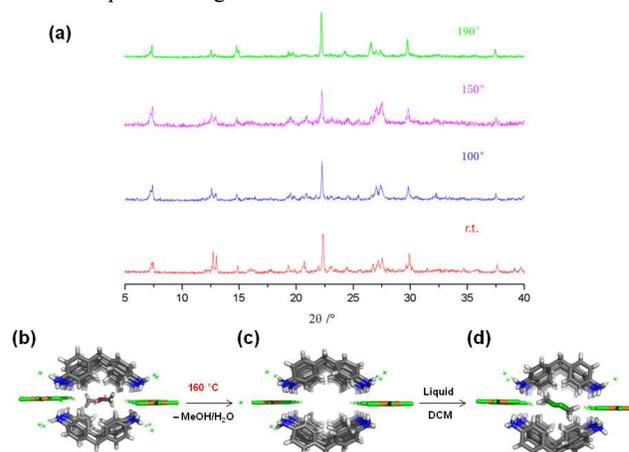


Figure 2. (a) XRPD patterns of **1** at different temperatures. (b) View of the channel containing MeOH and H₂O in **1**. (c) Empty host structure upon evacuation of MeOH and H₂O guest molecules after heating **1** to 160 °C for 2h. (d) View of the channel including DCM after immersing the empty framework of **1** in DCM. Color code as in Figure 1.

To test the robustness of the host framework in **1**, powders of **1** were heated to 160 °C for 2 hours (*i.e.*, to evacuate the channels), then immersed in a mixture of DCM/chloroform for 24 h. After removing the powders from the DCM/chloroform solvents, the microcrystalline solids were analyzed by ¹H NMR.⁷ As shown in Figure S11 and S12, DCM was selectively included in **1** but not chloroform. Bulkier solvents such as THF and toluene did not result in guest inclusion.⁷

Moreover, single crystal X-ray crystallography corroborated the DCM guest inclusion. Several pristine single crystals of **1** were heated to 160 °C for 2 hours then immersed in DCM for two days. Although the single crystals increased mosaicity we were able to pick up a small piece of crystal and analyzed it by single crystal X-ray diffraction.⁷ The inclusion of DCM although being disordered, can be clearly observed in Figure S8 and S9, reassuring that the host framework maintains the 1D channels after heating allowing guest inclusion to form **1•DCM**.¹³ The guest release with the subsequent empty host structure and the inclusion of DCM is shown in Figures 2b-d.

It is known that ionic conductivity can be facilitated by a carrier-mediated pathway such as water^{10, 14} or methanol¹⁵ molecules. Currently there are many reports on proton conductivity in metal organic frameworks¹⁶ but to the best of our knowledge, ionic conductivity in second sphere complexes seems ignored so far. Thus, in order to gain insight on structure-properties of this second sphere coordination complex, considering the included water/methanol chains observed in **1**, we evaluated its ionic conductivity by performing impedance spectroscopy on a single crystal with a two probe method.

A pristine single crystal of **1** was put in contact with planar, interdigitated gold electrodes, characterized by a channel length of 10 μm (Figure 3a and ESI).^{17, 18} Figure 3a shows the four orientations in which the impedance measurements were carried out on **1**. Orientations 1 and 4 clearly show that there is a resistive region within the explored frequency range, indicating conductivity. However, for orientations 2 and 3 there is no resistive behaviour at least down to 40 Hz (Figure 3b). We note that the pre-treatment of **1** by washing with chloroform and hexane clears out possible contamination from the mother solution. This is evident from the experiments carried out at different orientations which show that while orientations 1 and 4 show conductivity, orientations 2 and 3 do not show any conductivity. Clearly, if the crystal surface is contaminated we should observe also conductivity in orientations 2 and 3, as the overall interdigitated contact area is always fully covered due to the large crystal size. The results are reproducible, and very similar results (anisotropic ionic conductivity) have been observed for several crystals (See ESI).

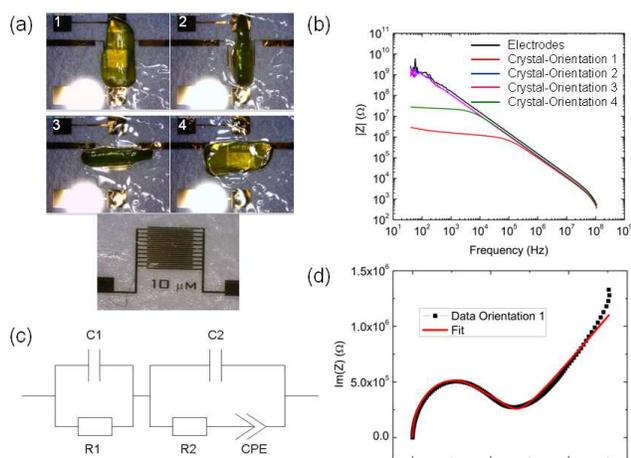


Figure 3. (a) Crystal orientations of **1** onto the interdigitated electrodes which have been covered with protectant oil. Inset: View of the interdigitated gold electrodes with 10 μm long channels. (b) Impedance spectroscopy results on the empty electrodes covered by oil and single crystal impedance spectroscopy measured at different orientations. (c) Equivalent circuit used for the fitting of the impedance measurements. (d) Typical Nyquist plot of **1** measured at room temperature in the orientation 1.⁷

The impedance data obtained from orientations 1 and 4 can be fitted with an RC parallel circuit in series (Figure 3c) with a Constant Phase Element (CPE) with $n = 0.4$.¹⁹ Figure 3d

demonstrates that the model used is representative of the electrodes-crystal device and can be used to obtain the conductivity values of **1**. The Nyquist plot obtained from fitting the impedance data from orientations 1 and 4, is qualitatively similar to what is usually obtained in solid-state ionic conductors. The semicircle in the higher frequency region indicates bulk conductivity (*i.e.*, conductivity arising from **1**) and the inclined vertical line in the lower frequency region suggests the accumulation of protons at the electrodes (Figure 3d). The impedance measurements allowed to extract a conductivity of 1.15×10^{-8} S/cm, dropping to 7.87×10^{-10} S/cm for the 90° rotated crystal.⁷ This suggests that the conductivity really depends on the crystal orientation with respect to the electrodes. Although the conductivity values are not high in absolute terms, they are of the same order of imidazole²⁰, solid I_2 ²¹, and some metal organic frameworks.^{16d}

To prove that the proton conductivity is mediated by the included water and methanol molecules, we carried out an experiment where a single crystal was heated to 110 °C and immediately covered by a thin film of protectant oil. Subsequent impedance measurements did not show any resistive region in the explored frequency range, corroborating the fact that the included guests mediate the proton conductivity (see Figure S22).

We recall that this is the first report on single crystal ionic conductivity of a second sphere coordination complex which allows anisotropic conductivity. The single crystal X-ray structure of **1** clearly shows that the 1D channels run parallel to the *a*-axis.²² Therefore when the large faces are in contact with the electrodes, most of the channels are directly interfaced with a metal contact. For orientations 2 and 3 we expect that the channels run parallel to the electrodes and therefore the possibility that the openings of channels are in contact with the electrodes are minimal. Considering the whole channel surface, the convex side of the channels, which do not contain water/methanol molecules, are in contact with the electrodes (Figure S24). This can explain why we do see conductivity only when the crystal is oriented with the channels opening facing the electrodes (*i.e.*, orientations 2 and 3 in Figure 3a).

Regarding the ion conduction mechanism, considering that it is difficult that a proton originates from the NH_3^+ group due to the strong $\text{N-H}\cdots\text{Cl}$ interaction, we believe that conductivity can be generated from H_3O^+ ions formed by moisture at the surface of **1**.²³ We cannot rule out that during the washing process some moisture is attached to the surface of the crystal being a source of protons at the openings of the channels. Upon application of an electric field, the H_3O^+ proton can be activated and hop to the water or methanol guest molecules which can further give the proton to the neighbour guest molecule, thus giving rise to ionic conductivity.

In conclusion, we have synthesized a second sphere coordination complex salt using the second-sphere coordination approach, self assembling a V-shaped dication, a $[\text{CuCl}_6]^{4-}$ and Cl^- anions. The charge assisted hydrogen bonding interactions drive the self assembly of the components yielding 1D channels including water/methanol

guests molecules. The framework is thermally stable and maintains the channel structure after evacuation of the original guest molecules upon heating, and can adsorb DCM guest molecules from solution. Single crystal impedance spectroscopy demonstrates that the second sphere coordination adduct including water and methanol shows ionic conductivity. We are currently working on the synthesis and structural characterization of new second sphere coordination complexes for ionic conductivity.

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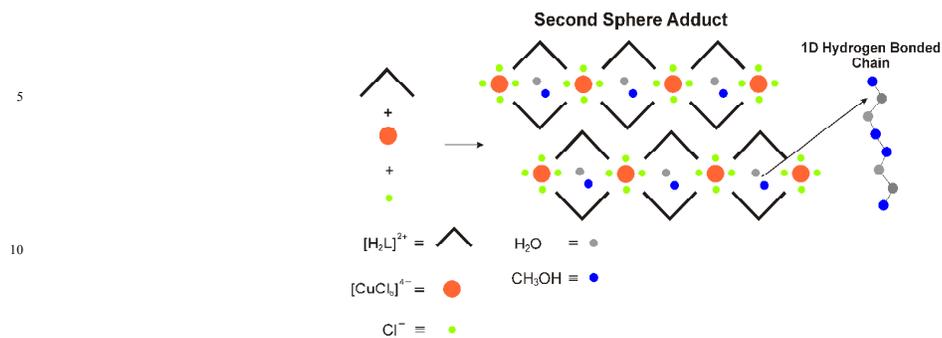
Notes and references

Single crystal X-ray diffraction data for **1**: Triclinic space group *P*-1, $M_r = 711.49$, crystal dimensions $0.2 \times 0.07 \times 0.04 \text{ mm}^3$, unit cell, $a = 9.2374 (13) \text{ \AA}$, $b = 13.1931 (19) \text{ \AA}$, $c = 13.996 (2) \text{ \AA}$; $\alpha = 62.333 (4)^\circ$; $\beta = 87.519 (5)^\circ$; $\gamma = 89.003 (5)^\circ$ (4) \AA , $V = 1509.2 (4) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 1$, Anisotropic least-squares refinement (355 parameters) on 5395 independent merged reflections ($R_{\text{int}} = 0.031$) converged at $wR_2(|F|^2) = 0.112$ for all data; $R_1(F) = 0.041$ for 5098 observed data ($I > 2\sigma(I)$), GOF = 1.06. CCDC 1008245 (1).

The single crystal diffraction data for **1** were recorded with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a focusing mirror (Cu- $K\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$). Powder X-ray diffraction experiments were carried out using a D2 Bruker diffractometer ($\lambda = 1.54056$). The impedance measurements were performed using an Agilent 4294A 40 Hz-110 MHz Precision Impedance Analyzer instrument. The *EIS Spectrum Analyzer 1.0* software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values.

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- A CCD search containing ligand **L**, shows that there are no crystal structures having channels, despite the fact that coordination bonds and hydrogen bonds have been used in the self assembling process.

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- The voids considering contact surface area have been calculated using a 1.2 \AA probe radius, however the network still shows channel connectivity if a 1.2 \AA probe radius is used: L. J. Barbour, *Chem. Commun.* 2006, 1163.
- A single crystal of **1** heated to 160 $^\circ\text{C}$ was covered by protectant Paratone oil and mounted for single crystal XRD analysis. Although the data showed high mosaicity, it was still possible to index and solve the crystal structure. We note that the *R*-factor is high (*ca.* 24 %), however it is possible to clearly see that the main charge assisted hydrogen bonding interactions are still controlling the molecular arrangement keeping the 1D channels.
- The included DCM guest molecule interacts with the aromatic ring of the 4,4'-methylene dianilineH 2^{2+} via a C-H $\cdots\pi$ interaction ($d(\text{C1s}\cdots\text{C24}) = 3.4(2)$; angle $\text{C11s-H1s-C24} = 128(8)^\circ$), that contributes to its stabilization in the channel.
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- A single crystal of **1** was washed with chloroform to remove any of the mother solution. Then the crystal was immersed in protectant oil (i.e., the oil protection ensures that during the impedance measurements the crystal is not altered by external agents (humidity) and also avoids guest molecules escaping the channels), observed under optical microscope, washed again with hexane to remove the oil and put in a filter paper for a minute. After washing with hexane, the crystal was cleaned again several times with hexane/chloroform washing cycles.
- As a control experiment we put a drop of protectant oil on the electrodes and measured its impedance as a function of frequency. The result showed that there is no conductivity and therefore we can use the protectant oil to carry out impedance measurements (see ESI).
- The value of C1 is the geometric capacitance extracted from the high frequency region. Therefore, C1 is the capacitance of the interdigitated electrodes modified by the presence of the crystal and R1 is the resistance of the crystal, which is that needed to calculate the conductivity of the crystals. The second part of the circuit corresponds to the interface effects at the electrodes surface and do not indicate any property inherent to the ion conductivity through the channels of single crystal under measurement.
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- We indexed the crystal faces before carrying out the impedance measurements. As shown in Figure S23, the large faces (top and bottom) correspond to the (211) and (201) which are nearly perpendicular to the *a*-axis.
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- 15 Second sphere coordination has been used to synthesize a complex having 1D channels. The single crystal X-ray structures, thermal stability, selective guest inclusion and single crystal impedance spectroscopy are reported.