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LETTER

Synthesis of a Novel Hybrid Metal Organic Salt and its Solid-State Transformation.

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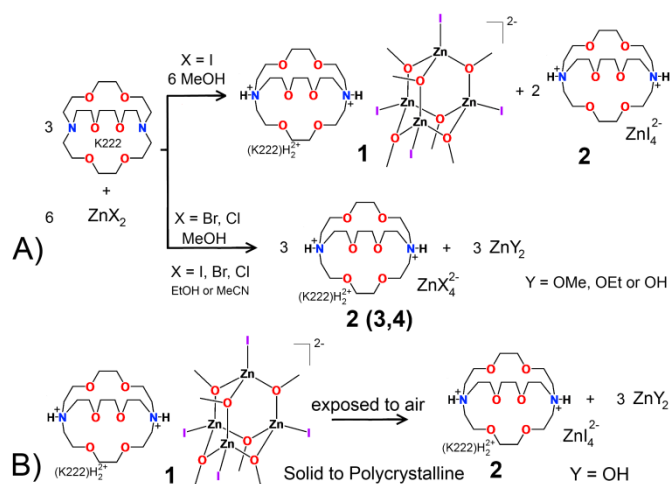
A new non-centrosymmetric adamantanoid metal cluster has been synthesized by combining macrocyclic K222 cryptand and ZnI_2 . Its solid-state crystal-to-polycrystalline transformation involves only the anionic adamantanoid cluster, while the cationic cryptand remains virtually unchanged as shown by single crystal and powder X-ray crystallography.

Chemical reactivity in the solid state is an interesting research field and its understanding quite underdeveloped, especially if compared to the solution state.¹ Hybrid metal organic salts built by a network of weak hydrogen bonding interactions are one type of solids that are displaying various interesting properties.² Particularly, in the solid state hydrogen bonding metal organic salts have shown potential applications in areas such as gas adsorption,³ separation,⁴ and magnetic properties.⁵ The retention of crystallinity of such hybrid metal organic salts is crucial to visualize the structural changes taking place in the solid-state.

Solid state reactivity in metal organic complexes has been focused mainly on small ligands containing nitrogen bases showing the conversion from salt complexes into coordination networks and *vice versa*.⁶ Only recently larger organic ligands have been investigated *via* mechanochemical dehydrochlorination reactions.⁷ Macrocyclic K222, also, received attention in the synthesis of hybrid metal organic complexes.⁸ However, the structural reactivity of complexes involving K222 and tetrahalide counterions has received less attention. Typically, solid-state reactions in porous hybrid metal organic complexes are guest inclusion/release processes that tend to occur *via* single-crystal-to-single-crystal pathways without altering the host framework. However, in non-porous metal organic complexes reactions occurring either in metal anions and/or organic cations usually proceed disrupting single crystallinity due to the lack of voids along which molecules can diffuse. As a result, often interesting reactions are left unexplored, particularly reactions involving large structural transformations.

In this work, by combining macrocyclic K222 and ZnI_2 , we have obtained a crystalline material of formula $[K222-H_2]^{2+}[Zn_4(MeO)_6I_4]^{2-}$

$\cdot(H_2O)$ (**1**) which is constituted by a doubly protonated K222 dication and a dianionic adamantanoid metal cluster, crystallizing in the non-centrosymmetric space group $P2_13$ (Scheme 1, a). Although several structures containing adamantanoid metal clusters can be found in the literature,⁹ to the best of our knowledge, compound **1** represents the first *d*-block metal cluster with adamantanoid topology containing μ -oxygen atoms.¹⁰ We also report, for the first time, the solid-state transformation of **1** into a trigonal complex of formula $[ZnX_4]^{2-}[K222-H_2]^{2+}\cdot(H_2O)$ (**2**) (Scheme 1, b). The solid state reaction occurs *via* a single-crystal-to-polycrystalline transformation which involves major anionic structural changes. The structural analysis has been carried out combining single crystal and powder X-ray diffraction. Interestingly, the adamantanoid metal cluster only forms with the iodide salt, while bromide and chloride Zn metal salts only form the trigonal phase (Scheme 1).



Scheme 1. Synthesis of complex salts **1** - **4** (a) and the solid-state conversion of **1** into **2** (b).

The synthesis of complex **1** was prepared by mixing a solution of K222 in (MeOH; 1 ml) and ZnI_2 (MeOH; 1 ml) in a 1:2 molar ratio; (0.053

mmol : 0.106 mmol). The ZnI_2 solution was added dropwise, and after 1 day colorless block crystals suitable for single X-ray analysis were obtained.¹¹ X-ray crystallography demonstrated that **1** crystallizes in the cubic noncentrosymmetric space group $P2_13$ (198) with the formula $[\text{Zn}_4(\text{MeO})_6\text{I}_4]^{2-}[\text{K222-H}_2]^{2+} \cdot (\text{H}_2\text{O})$. The crystal structure of the complex salt **1** is shown in Figure 1.¹² In **1**, the K222 is doubly-protonated and adopts the *endo-endo* type conformation where the N atoms are directed towards the cavity of the macrocycle (Fig 1a). Likewise, the O atoms point inwards the inner cavity of the macrocycle where weak $\text{N}^+-\text{H}\cdots\text{O}$ hydrogen bond interactions are observed. The nonbonding $\text{N}\cdots\text{N}$ separation (6.127(9) Å) is markedly shorter than that of neutral cryptand (6.871(4) Å).¹³

The dianion adamantanoid is formed by four Zn metal centers located at the vertices of a tetrahedron in which each metal is tetrahedrally coordinated by three O atoms, from deprotonated methanol molecules, and one I atom. The four assembled Zn metal centers give rise to three fused hexagonal rings (Fig 1b). Thus, the dianion can be described as an adamantanoid structure with four peripheral iodide groups. The dianion interacts with neighbour K222- H_2^{2+} dications in two different ways. First, three I atoms (*i.e.*, I1, I2 and I3) establish a weak $\text{C-H}\cdots\text{I}$ interaction (4.009(9) Å) (Fig. 1c). A second type of weak interaction corresponds to the $\text{C-H}\cdots\text{O}$ (3.66(3) Å) where the H atom in the K222- H_2^{2+} is hydrogen bonded to the coordinating oxygen in the adamantanoid cluster (Fig. 1d). The iodide (I4) atom at the upper part of the adamantanoid cluster does not interact with any surrounding atom. Finally, the overall structure adopts an *isomer IV* type of conformation.^{9e}

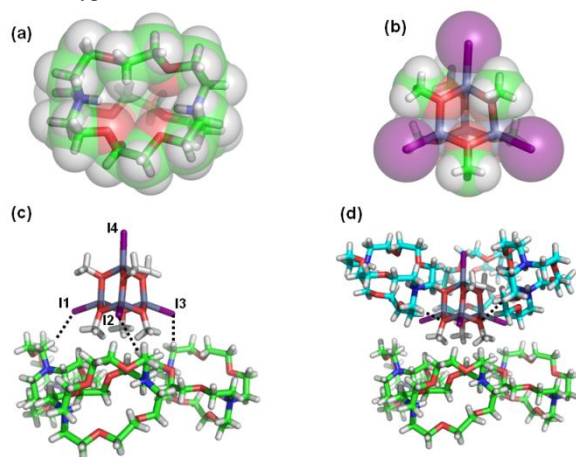


Figure 1. Single crystal X-ray structure of complex **1**. View of (a) the dication and (b) dianion. (c) Side view of the adamantanoid cluster surrounded by the dications establishing hydrogen bond interactions via $\text{C-H}\cdots\text{I}$; (d) same view of (c) but with the $\text{C-H}\cdots\text{O}$ interactions with the adjacent layer of cations. Different colours have been given to K222 for the sake of clarity. Disordered H_2O molecule is not shown.

In the mother solution, we also observed the presence of a second type of crystal together with **1**. X-ray structure determination showed that this crystal (**2**) is isostructural to the reported trigonal $R\bar{3}c$ (167) ZnCl_2 version,¹⁴ where the K222 is also doubly-protonated and adopts the *endo-endo* type conformation.¹⁵ The $[\text{ZnI}_4]^{2-}$ anions, lying in the 3-fold crystallographic axis, have tetrahedral coordination (Fig. S2).¹⁶ Interestingly, when the bulk of the sample containing both type of crystals (**1** and **2**) was dried and grinded for powder X-ray diffraction

analysis (PXRD), the resulting powder diffraction pattern showed the presence of a single phase which corresponded to complex **2** (Fig. 2d). Puzzled by this initial finding, we considered that two options were possible: *i*) complex **1** is unstable in contact with air and transforms to **2**; or *ii*) grinding process induced a mechanochemical structural transformation of **1** to **2**.

To elucidate the cause of the transformation, a single crystal of **1** was mounted in a Nylon loop without using protectant oil (*i.e.*, to allow direct exposition to air) for X-ray structural analysis. Indexing of its unit cell gave that corresponding of **1** (cubic; $P2_13$). Then, the crystal was left in contact with air for 3 days. Single crystal X-ray structural analysis showed that **1** transformed into a polycrystalline solid whose Debye-Scherrer-like diffraction plot matches that of **2** (Fig. 2b).¹⁷ This represents the first report of a solid state transformation which might imply the release of coordinated methanol molecules and the break-up of the adamantanoid cluster going from the $[\text{Zn}_4(\text{MeO})_6\text{I}_4]^{2-}$ to the $[\text{ZnI}_4]^{2-}$ ion (Fig. 2). In the process, the dication remains virtually unchanged and we note that the $\text{C-H}\cdots\text{I}$ interactions between the cations and anions (Fig. 1c & Fig. S2d) are of the same type in **1** and **2** and are somehow maintained after the transformation, suggesting their important role in the structures' stability.

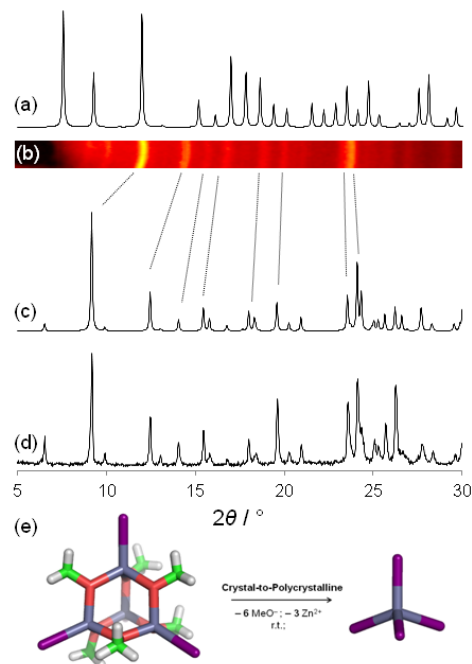


Figure 2. Comparison between PXRD patterns of **1** and **2**. (a) Simulated PXRD of **1**; (b) X-ray diffraction of a single crystal of **1** exposed to air for 3 days; (c) simulated PXRD of **2**; and (d) experimental PXRD of a polycrystalline sample of **1** exposed to air for 3 days and grinded. (e) Cartoon depicting the solid-state transformation of $[\text{Zn}_4(\text{MeO})_6\text{I}_4]^{2-}$ into $[\text{ZnI}_4]^{2-}$ at room temperature.

Mass balance indicates that other Zn-containing species, evidently lacking crystallinity, should form in the reaction. Elemental Analysis carried out on the bulk crystalline sample, after exposition to air, completely supports the occurrence of the solid-state transformation shown in Figure 2d and indicates that the final 1/2 of Zn(II) salts is composed of $\text{Zn}(\text{OH})_2$. This implies the replacement of OMe groups with OHs.¹⁸ Interested in this solid-state reaction we investigated the possibility that the adamantanoid structure could be formed with

smaller halides such as bromide and chloride. Notably, under the same experimental conditions, only trigonal phases isostructural to **2** were obtained (compounds **3** and **4**, see ESI).¹⁹ Hence, such solid-state transformation is possible only for the iodide case.

Similar crystallization experiments using K222 and ZnI₂ in ethanol, instead of methanol, did not form the adamantanoid cluster, but compound **2** as shown by PXRD and single crystal X-ray diffraction (see ESI). Furthermore, liquid assisted grinding (LAG) of the starting materials, using a drop of methanol, also resulted in the formation of **2** exclusively.

Moreover, experiments using aprotic MeCN solvent, working under similar conditions, resulted again in the formation of **2** only. As the formation of the adamantanoid cluster was not observed in the above mentioned cases, this strongly indicates that the presence of methanol is necessary for the self-assembly of the adamantanoid cluster. However, since the protonation of K222 is also observed in MeCN, we speculate that atmospheric water can also act as the source of protons in the system.²⁰

The different behaviour observed in methanol and that in ethanol can be simply explained by steric factors. At variance with the S-containing adamantanoid clusters, which are able to accommodate bulky substituents, the μ -O-based cluster is significantly smaller (Volumes and distances between opposite μ -O(S) atoms 382.5 Å³ – 4.32 Å and 446.5 Å³ – 5.44 Å for the μ -O and μ -S clusters, respectively)²¹ and an additional carbon on the alkoxide chain would probably lead to significant sterical clash with the apical I atoms.

A last comment is given on the behaviour of **1** in solution. The ¹H-NMR spectrum of **1**, shown in Figure S12, was recorded after dissolution of crystals of **1**, manually separated from those of **2** in the bulk, into a 2:1 deuterated DMSO:acetone solvent mixture. A preliminary analysis indicates that **1** is present as a 85:15 mixture of two species, namely the associated ion-pair and its dissociated form. The presence of singlet signals around 3.2 ppm, assigned to the μ -OMe groups and the comparison with the spectrum of an equimolar solution of **2**, strongly support the survival of the anionic adamantanoid structure of **1** under the investigated circumstances.

In summary, we have synthesized and characterized a new complex which displays an adamantanoid-type structure and a peculiar solid state reactivity. Although literature on salts composed of adamantane-like dianions of formulae $[(\mu\text{-SR})_6(\text{MSR})_4]^{2-}$, $[(\mu\text{-SR})_6(\text{MSR})_{4-n}(\text{MX})_n]^{2-}$ or $[(\mu\text{-SR})_6(\text{MSR})_{4+n}(\text{ML})_n]^{m-2}$ ($n = 1-4$; X = Cl, Br and I; L = neutral solvent; M = d-block metal, R = alkyl, aryl) is rich,⁸ to the best of our knowledge, structure **1** contains the first μ -oxo adamantanoid cluster.¹⁰ The process of formation of **1** was never described before and, notably, it was found to be specific for iodide, since bromide and chloride Zn salts formed only isostructural ZnX₄²⁻ type of material, **2** (and **3-4**, see ESI). An unusual solid-to-solid process which affords **2** by exposing **1** to air and which involves the break-up of the adamantanoid cluster was also observed and described.

The study of the properties of non centrosymmetric **1** in the solid state, in relation to non linear optical applications, and in solution are currently on-going.

Experimental

General

All the reagents and solvents were purchased from Sigma Aldrich and used without further purification. All single crystals used for X-ray analysis were checked using a Leica M165 C microscope equipped with a cross polarizer. ¹H-NMR spectra were recorded using a 500 MHz Bruker spectrometer at 25°C.

X-ray Diffraction Data

Single crystal X-ray diffraction data for **1**, **2** and **3** were recorded with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with an Incoatec I μ S_{Cu} microfocus X-ray source (CuK α radiation, $\lambda = 1.54056$ Å) and with a CCD detector. The low temperature experiments were collected using a Bruker Oxford Cryosystem device. SHELXL²² was used for structure solution and refinement. X-ray powder diffraction experiments were recorded on a Bruker D2 Phaser diffractometer ($\lambda = 1.54056$ Å). The 2θ scan range was 4.7° – 40° with a step size 0.02°. The exposure time was 2s. Simulated PXRD patterns were generated using Mercury Version 3.1 software program. Figures depicting the crystal packing were created using PyMol software.

Notes and references

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† Electronic supplementary information (ESI) available: CCDC 948435 (**1**), 948434 (**2**), 948436 (**3**), contain supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

Single crystal X-ray diffraction data for **1**: C₂₄H₅₈I₄N₂O₁₂Zn₄, Mr = 1335.8, crystal dimensions 0.13 × 0.07 × 0.06 mm³, cubic, space group, *P*2₁3, unit cell, *a* = 16.3228(18) Å, *V* = 4348.9(8) Å³, *T* = 100(2) K, *Z* = 4, Anisotropic least-squares refinement (148 parameters) on 2127 independent merged reflections (*R*_{int} = 0.0354) converged at $wR_2(|F|^2) = 0.0718$ for all data; *R*₁(*F*) = 0.0316 for 1972 observed data (*I* > 2σ(*I*)), GOF = 1.072. Single crystal X-ray diffraction data for **2**: C₁₈H₄₀I₄N₂O_{6.17}Zn₁, Mr = 956.16, crystal dimensions 0.13 × 0.11 × 0.02 mm³, trigonal, space group, *R*-3*c*, unit cell, *a* = 11.4410(7) Å, *b* = 11.4410(7) Å, *c* = 81.313(6) Å, *V* = 9217.6(11) Å³, *T* = 296(2) K, *Z* = 12, Anisotropic least-squares refinement (100 parameters) on 1797 independent merged reflections (*R*_{int} = 0.0901) converged at $wR_2(|F|^2) = 0.1760$ for all data; *R*₁(*F*) = 0.0617 for 1620 observed data (*I* > 2σ(*I*)), GOF = 1.127.

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