Clathrates

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Tetrahedral Mo_4 Clusters as Building Blocks for the Design of Clathrate-Related Giant Frameworks**

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The Mo_4 cluster based solid-state family with the general formula $A_xM_4Q_4X_4$ (A = trivalent cation; M = Mo, Nb, Ta, or V; Q = chalcogen; X = chalcogen or halogen), was discovered and characterized in the early 1970s.[1–3] These materials were subsequently widely studied for their ferromagnetic properties, high-pressure-induced superconductivity, and their Mott insulator behavior, with electric-pulse-induced resistive switching making them relevant candidates for nonvolatile memory (RRAM) applications.[4–7] Their crystal structures differ from that of spinels by a shift of M atoms along the threefold axis of the cubic unit cell. This displacement induces contractions of some M–M distances and leads to the formation of tetrahedral Mo_4 clusters characterized by metal–metal bonds. The Mo_4 cluster is linked to four face-capping chalcogens, and each Mo_4 apex is bonded to three additional ligands to form a $M_4Q^i_4X^a_{12}$ building block (^{i} for inner and ^{a} for apical, Figure 1 a). In $A_xM_4Q_4X_4$ structures, every X^a ligand is shared by three adjacent cluster building blocks to form a polymeric framework with the $M_4Q^i_4X^{a\text{-}a\text{-}a}_{12/3}$ developed formula according to Schäfer notation.[8]

To date, no other structure type based on $M_4Q^i_4X^a_{12}$ building blocks has been reported in solid-state chemistry. However, the tetrahedral geometry of the $M_4Q^i_4X^a_{12}$ scaffold is favorable to the formation of clathrate-related structures.[9] Clathrates have been known since the discovery of an atypical gas hydrate at the beginning of the 19th century. For a long time, the challenging issue was to understand how water molecules could be organized to build a framework enabling encaging of large guest molecules. Furthermore, Clausen's studies evidenced two structural models for clathrates, simply differentiated as type I for gas hydrates and type II for liquid hydrates or double hydrates.[10] Herein we consider only the type II clathrate whose structural model was confirmed in 1964 by single-crystal X-ray diffraction investigations.[11] In the original structure, it is shown to crystallize in the $Fd\bar{3}m$ space group and is characterized by a framework of 136 water molecules located on 8*a*, 32*e*, and 96*g* Wyckoff positions and held together by hydrogen bonds, thus leading to a giant structure with 16 dodecahedral cavities (G) and eight hexacaidecahedral larger cavities (L) that could receive gas and liquid molecules, respectively. Considering a full occupation of the G and L hosting cavities, the ideal composition is $G_{16}L_8(H_2O)_{136}$. The dodecahedral cavities (Figure 1 b) are built from 20 oxygen atoms forming a polyhedron with 12 pentagonal faces [5^{12}] and 30 edges. The hexacaidecahedral cavities are built from 28 oxygen atoms forming a polyhedron with 12 pentagonal and four hexagonal faces [$5^{12}6^4$] with 42 edges. Replacing the water molecules by tetrahedrally coordinated Si atoms within the clathrate framework led to original inorganic solid-state compounds such as Na_xSi_{136}, first reported in 1965.[12] These periodic solids contain the two above-mentioned types of cages that surround alkali metal ions, as found further for $Cs_8Na_{16}Si_{136}$ or $Rb_8Na_{16}Si_{136}$.[13] The thermal conductivity, transport, and thermoelectric properties of these materials have been widely studied.[14–16]

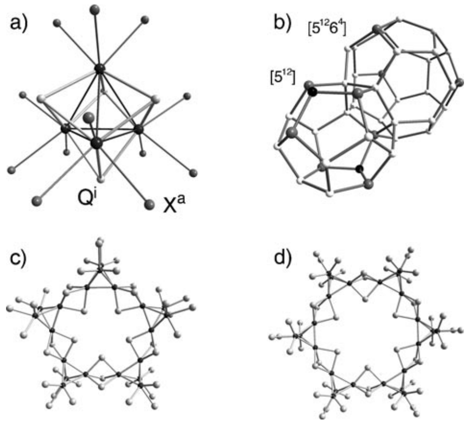

Figure 1. a) A $M_4Q^i_4X^a_{12}$ building block and b) dodecahedral [5^{12}] and hexacaidecahedral [$5^{12}6^4$] cavities in type II clathrates. The 8*a*, 32*e*, and 96*g* Wyckoff positions that are occupied in **1** by the centroids of the A, B, C cluster units are represented as black, gray, and white spheres, respectively. c) Interconnections of adjacent Mo_4 clusters in **1** through three $Cl^{a\text{-}a}$ bridges building pentagonal faces and d) hexagonal faces of the cavities. S^i atoms are omitted for clarity.

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Herein we show that tetrahedral $Mo_4S^i_4Cl^a_{12}$ building blocks can be fruitfully assembled in situ by a solid-state chemistry approach to design a giant inorganic clathrate framework with magnetic and semiconducting properties. In $[(Cs_2Mo_6Cl_{14})_{4.77}(CsCl)_{138}Cs_{47}][(CsCl)_{97}Cs_{24}][Mo_4S_4Cl_6]_{136}$ (**1**), the $Mo_4S^i_4Cl^a_{12}$ cluster building blocks share apical ligands to form a $Mo_4S^i_4Cl^{a\text{-}a}_{12/2}$ framework strongly related to that of type II clathrate.

The structure of **1** has been solved by single-crystal X-ray diffraction techniques. Compound **1** exhibits a giant crystal structure with a huge unit cell volume of 78491 Å^3, one of the largest reported so far for a pure inorganic compound synthesized by conventional solid-state chemistry techniques. However, an accurate structural determination could be achieved using the state-of-the-art maximum entropy method (MEM).

Compound **1** is built of three crystallographically independent $Mo_4S^i_4Cl^a_{12}$ building blocks (referred to as A, B, and C; see the Supporting Information) that are centered on 8*a*, 32*e*, and 96*g*, Wyckoff positions, respectively (Figure 1 b). Each face of Mo_4 clusters is capped by one sulfur atom, and each Mo apex is additionally bonded to three chlorine atoms. Molybdenum atoms of two adjacent clusters share their three apical chlorine atoms (Figure 1 c and d) to form a $Mo_4S^i_4Cl^{a\text{-}a}_{12/2}$ framework containing 136 $Mo_4S^i_4Cl^a_{12}$ units per unit cell. Adjacent clusters are always in an eclipsed configuration. Besides this ordered architecture, it is worth pointing out that cesium cations, chlorine anions, and $[Mo_6Cl_{14}]^{2-}$ octahedral cluster units occupy the dodecahedral and hexacaidecahedral cavities with a strong disorder and small value of their site occupancy. Pentagonal and hexagonal faces of the cavities are statistically capped by cesium cations which are ionically linked to the $Cl^{a\text{-}a}$ chlorine atoms shared between adjacent clusters. The characterization of giant crystal structures with unit cell volumes higher than 50000 Å^3 remains scarce, especially for purely inorganic compounds synthesized at high temperature. To our knowledge, the largest unit cell for inorganic solids prepared at high temperature was found for ACT-71, an intermetallic compound with an unprecedented complexity exhibiting a unit cell volume of 365372 Å^3.[17] Huge unit cell volumes have also been reported for polyoxometallates prepared by solution chemistry.[18,19] In all these giant crystal structures, part of the molecules or atoms is often submitted to a huge disorder or to anharmonic displacements, thus increasing the difficulties of the structural determination. In such utmost cases, the MEM is a useful alternative method to model-based refinements for the elucidation of advanced structural features through the reconstruction of the most probable electron density against phased observed structure factors.

Most notably, contrary to Fourier syntheses, MEM maps exhibit very low noise and are free of the uncertainties arising from series termination effects.[20] In the course of the structure solution of **1**, 3D MEM maps were used extensively—along with crystal chemistry arguments in terms of relevant contact distances and local environment—for locating and further identifying the Mo, Cl, and Cs disordered atoms (representing ca. 60 % of the asymmetric unit), preliminary found by a combination of least-squares refinements and classical difference Fourier syntheses. Whenever large atomic displacement parameters were found, the possibilities of split positions or strong anisotropic atomic displacement parameters were carefully checked against the MEM maps (Figure 2). The correctness of the latter combined approach is corroborated by the refined formula, $[(Cs_2Mo_6Cl_{14})_{4.77}(CsCl)_{138}Cs_{47}][(CsCl)_{97}Cs_{24}][Mo_4S_4Cl_6]_{136}$, which is in excellent agreement with the results of energy-dispersive spectroscopy (EDS) analyses.

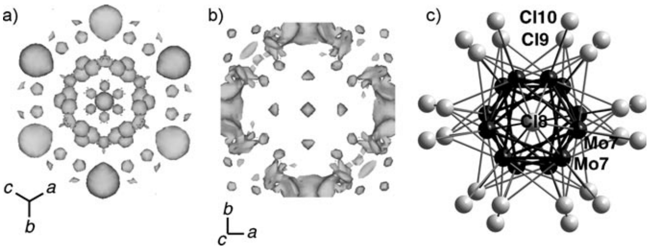

Figure 2. Close-up view of MEM electron-density distribution around the center of: a) cavity G and b) cavity L, showing the strong delocalization of Mo, Cl, and Cs atoms in G and Cs and Cl atoms in L. Isosurface level of 6.5 and 0.9 for (a) and (b), respectively ($F_{max} = 632.73$). c) The two positions statistically occupied by the Mo_6Cl_{14} cluster unit in cavity G. They are related to each other by a mirror plan; Cs^+ and Cl^- positions are not shown.

In metal-atom cluster compounds, the M−M distances are related to the number of valence electrons involved in the metal–metal bonds, the so-called valence electron count (VEC) value, owing to the metal–metal bonding character of the highest occupied molecular orbital (HOMO) level of the cluster unit molecular orbital diagram. For instance, the VEC and Mo−Mo bond lengths are 12 and 2.7973 Å for $Mo_4S_4Cl_4$ and 11 and 2.82 Å for $GaMo_4S_8$, two compounds belonging to the $A_xM_4Q_4X_4$ family. In **1**, the symmetry of $M_4Q^i_4X^a_{12}$ units and average Mo−Mo bond lengths depend on the Wyckoff position at which they are centered. For A, B, and C building blocks, the symmetry is T_d, C_{3v}, and C_s, respectively, while the average Mo−Mo bond lengths are 2.754, 2.779 and 2.791 Å. Discrepancies in the latter values indicate that clusters with different VEC are present in the structure. Indeed, for a neutral $Mo_4S_4Cl_{12/2}$ framework the VEC value per Mo_4 cluster is calculated to be 10 for the 136 units. The excess of 71 Cs^+ ions within the unit cell implies that 71 clusters out of 136 exhibit a VEC value of 11. The presence of magnetic clusters was demonstrated by susceptibility measurements that evidence a paramagnetic behavior with $\mu_{eff} = 1.62\ \mu_B$ (see the Supporting Information). However, the quantification of the number of magnetic clusters among the 136 constituting the structure remains quite tricky. Mo_4 clusters with 11 electrons are necessarily magnetic and carry one spin whatever the local symmetry. For Mo_4 clusters with 10 electrons, the interpretation is more intricate, as depending on the local symmetry of the $M_4Q^i_4X^a_{12}$ units and more precisely on its deviation from the ideal T_d, clusters can be nonmagnetic or magnetic with two unpaired electrons owing to the removal of the three-fold degeneracy of the HOMO level.[5] Electron transport measurements performed on a single crystal evidenced a semiconducting behavior with an activation energy of 0.16 eV (see the Supporting Information).

The common feature in the different kinds of type II clathrates reported in the literature is that their framework is built up from three crystallographically independent tetrahedra as building blocks with a ratio 8:32:96. In the following schematic description, we consider that the barycenter of the tetrahedron is occupied by an atom T. The latter that can be either bonded to a ligand R or carry lone pairs (E) or unpaired electrons for covalent bonding (C) to form the $TR_rE_eC_c$ moiety ($r+e+c=4$). In the original structure $G_{16}L_6(H_2O)_{136}$, the framework is built from H_2O water molecules as building blocks ($TR_2E_2C_0$, T = O and R = H) held together by hydrogen bonding thanks to the two lone pairs located on sp^3-hybridized oxygen atom. In clathrasil 3C, the building blocks are SiO_4 moieties ($TR_4E_0C_0$, T = Si and R = O).[21] The oxygen atoms are shared between adjacent tethrahedra to form a $SiO_{4/2}$ zeolite framework. In inorganic silicon clathrates, building blocks are sp^3-hybridized silicon atoms ($TR_0E_0C_4$, T = Si) tetracoordinated to adjacent silicon atoms. In the examples given above, it turns out that the main difference between inorganic solids and hydrates is that the cohesion of the framework is ensured by covalent bonding between T atoms in the former. Beginning in 2000, Férey et al. reported the structure of an unusual hybrid organic/inorganic compound $Cr_3F(H_2O)_2O[C_6H_4(CO_2)_2]_3$ (MIL-101). The structure of MIL-101 is based on supertetrahedra consisting of $Cr_3(OH)-(H_2O)_2(\mu_3\text{-}O)$ trimeric chromium units linked together via 1,4-benzendicarboxylate organic linkers.[22] The centroids of the latter supertetrahedra are centered on 8*a*, 32*e* and 96*g* Wyckoff positions. The trimeric chromium units are shared between supertetrahedra in a similar way as observed for the three apical chlorine atoms of $Mo_4S^i_4Cl^a_{12}$ building blocks in **1**. The latter thus exhibits a structure in between those of clathrasil 3D and MIL-101. Indeed, like in MIL-101 the tetrahedral building blocks are groups of atoms. The originality of **1** is the presence of metallic Mo_4 clusters in which valence electrons are fully delocalized. Like in clathrasil 3C, the connection is made through nonmetallic bridges. However, three chlorine atoms are shared between adjacent Mo_4 clusters instead of one oxygen atom between SiO_4 as in clathrasil 3C. The Si-O-Si bridge enables the staggered or eclipsed configuration of adjacent SiO_4 units. Such flexibility is not possible between adjacent $Mo_4S^i_4Cl^a_{12}$ units, as triply connected adjacent units are fixed in an eclipsed configuration.

An interesting aspect of these giant frameworks is that they contain large pores (i.e., 16 dodecahedral (G) and 8 hexacaidechedral (L) cavities) that could display interesting adsorption properties.[23] The nature of the tetrahedral building blocks as well as the type of connections between them (supramolecular interactions, covalent bonding between T, apex sharing) strongly influences the sizes of the G and L cages and consequently the value of the cubic unit cell parameter. It ranges from 14.5 Å in Na_xSi_{136} to an exceptional large value of 104.5 Å in MIL-101-NDC ($V \approx 1\,141\,166$ Å^3, NDC = naphthalene-2,6-dicarboxylate). In MIL-101-NDC,[24] the diameter of spherical volumes ascribed to G and L are approximately 39 and 46 Å. In **1**, the G and L cage diameters are roughly equal to 19 and 22 Å, respectively (from centroid to centroid). Owing to the steric hindrance of S and Cl atoms bonded to the Mo_4 clusters, the real accessible void must be smaller. The free apertures of the pentagonal and hexagonal faces are 13.5 and 18.2 × 20.3 Å in MIL-101-NDC, while in **1** the free apertures between chlorine atoms of the pentagonal and hexagonal faces are approximately 1.9 and 4.3 Å, respectively. As found recently for MIL-101, $Mo_6X^i_8X^a_6$ cluster units can be hosted in the framework of **1.** However, for **1** Mo_6 cluster units are incorporated in situ during the formation of the framework, while for MIL-101 they are incorporated by solution chemistry.[25] In the latter case, the incorporation of fluorinated $Mo_6Br_8F_6$ units in the framework allowed improvement of the hydrogen-storage performance of MIL-101.[25]

To conclude, we have reported a novel member of the clathrate II structures based for the first time on tetrahedral metallic clusters. The unit cell comprises 136 tetrahedral $Mo_4S^i_4Cl^a_{12}$ cluster building blocks sharing apical chlorine atoms. Strong disorder appears in the cavities, which are statistically occupied by cesium cations, chlorine anions, and $[Mo_6Cl^i_8Cl^a_6]^{2-}$ octahedral cluster anionic units. Obvious correlations appear between this structure and those of inorganic clathrasil 3C and hybrid organic/organic MIL-101. Magnetic susceptibility data give evidence of paramagnetic behavior, and semiconducting behavior is detected by electrical resistivity measurements. Changing the nature of metal, the countercation, or the chalcogen or halogen ligands should lead to similar frameworks but with different electronic counts, as found earlier in the $A_xM_4Q_4X_4$ series, thus leading to a wide range of physical properties. Moreover, the development of M_4 hybrid organic/inorganic chemistry as already widely reported for the M_6 octahedral cluster should yield original open hybrid frameworks. In particular, the introduction by solution chemistry of large organic bidentate linkers around Mo_4 clusters should increase the sizes of cages and apertures, as in structures related to MIL-101, with potential intercalation and adsorption properties. Owing to the delocalization of electrons on Mo_4, original electronic transport properties are then expected.

Experimental Section

In a typical synthesis, powder samples were prepared by a solid-state route from a stoichiometric mixture of Mo, S, $MoCl_5$, and CsCl heated at 900 °C for 24 h. Single crystals suitable for structural determination were obtained from a reaction at 1000 °C with subsequent three days slow cooling. Chemical composition (atom %) were determined by energy-dispersive X-ray spectroscopic analysis: Cs 11.9, Mo 23.4, S 21.5, Cl 43.2; calculated from structural refinement: Cs 12.4, Mo 22.4, S 21.3, Cl 43.8. Crystal data for **1**: sample size = 0.11 × 0.10 × 0.07 mm^3, cubic system, space group $Fd\bar{3}m$, $a = 42.8160(13)$ Å, $V = 78\,490.7(3)$ Å^3, $Z = 136$ for $Cs_{2.32(4)}Mo_{4.210(4)}S_4Cl_{8.2(1)}$, $M_r = 1131.84$ g mol^{-1}, $\rho_{calcd} = 3.25$ g cm^3, $\lambda = 0.71069$ Å (Mo K_α), Bruker AXS APEX-II diffractometer, $T = 150(2)$ K, $\theta = 2.81$ to 34.97°, 51 398 reflections, 5696 independent reflections ($R_{int} = 0.0444$), SADABS absorption correction, 250 parameters, five constraints, full-matrix least-squares refinement on F (JANA2000 program[26]), final R_F ($I > 3\sigma(I)$) = 0.0424, final $wR_F = 0.0541$, $\chi^2 = 2.71$, largest difference peak and hole were +2.67 and −1.85 e Å^{-3}. Structure solution by direct methods using SIR97.[27] The MEM was used according to the Sakata

& Sato algorithm, using the program BayMEM.[28] The electron density was considered on a grid of 216 × 216 × 216, corresponding to a resolution of approximately 0.2 Å. All calculations were performed with an initial flat electronic density. 5697 F constraints were used, leading to $R_{MEM} = 3.26\,\%$ in the final state. The structural resolution is detailed in the Supporting Information. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-422712. All other experimental data are found in the accompanying Supporting Information.

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