Bull Soc Chim Fr (1996) 133, 783-794
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A concave, cubic diamond coordination polymer in the versatile chemistry of the aqua-alkaline-earth complex salts of molecular hexanuclear chalcohalide rhenium clusters, $[Ca(H_2O)_n]Re_6Q_6Cl_8{\bullet}mH_2O$ and $[Mg(H_2O)_6]Re_6S_6Cl_8{\bullet}2\ H_2O$ (Q = S, Se)[†]

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(Received 24 May 1996; accepted 28 June 1996)

Summary — The high temperature solid-state synthesis of the alkaline-earth salts of molecular chalcohalide rhenium cluster dianions, $CaRe_6S_6Cl_8$, $CaRe_6Se_6Cl_8$, $MgRe_6S_6Cl_8$, and $MgRe_6Se_6Cl_8$ is described. The compounds exhibit a high solubility in a variety of organic solvents which allows a ready access in high yields to the tetrabutylammonium salts $(n\text{-}Bu_4N)_2Re_6Q_6Cl_8$ (Q = S, Se). It is further demonstrated that the dissolution of the calcium and magnesium salts and their subsequent crystallization out of organic solvents provides high-quality single crystals of a series of inner-sphere, heptaaqua- and pentaaqua-calcium(II) and hexaaqua-magnesium(II) complex salts, $Ca(H_2O)_7Re_6Q_6Cl_8{\cdot}3H_2O$ (Q = S, Se), $Ca(H_2O)_8Re_6S_6Cl_8$ and $Mg(H_2O)_6Re_6S_6Cl_8{\cdot}2H_2O$. The latter are fully characterized by liquid secondary ion mass spectroscopy and determination of their crystal structures which reveal remarkable, hydrogen-bonded, one- and three-dimensional associations of the molecular sub-units with unique topologies in coordination chemistry.

aqua-alkaline earth cation / water cluster / rhenium chalcohalide cluster / 3D coordination polymer

Résumé — Un polymère de coordination convexe de structure diamant cubique dans la chimie versatile des sels de complexes aqua-alcalino-terreux de chalcohalogénures de rhénium à clusters octaédriques, $[Ca(H_2O)_n]Re_6Q_6Cl_8{\cdot}mH_2O$ et $[Mg(H_2O)_6]Re_6Q_6Cl_8{\cdot}2\ H_2O$, (Q = S, Se). *La synthèse en phase solide à haute température des sels de chalcohalogénures de rhénium à clusters octaédriques de cations alcalino-terreux,* $CaRe_6S_6Cl_8$, $CaRe_6Se_6Cl_8$, $MgRe_6S_6Cl_8$ *et* $MgRe_6Se_6Cl_8$ *est décrite. Ces composés sont solubles dans une variété de solvants organiques ce qui permet l'accès avec des rendements élevés aux sels* $(n\text{-}Bu_4N)_2Re_6Q_6Cl_8$ *(Q = S, Se). Nous démontrons par ailleurs que la cristallisation des sels de calcium et de magnésium à partir de solvants organiques permet d'obtenir des monocristaux de grande qualité des sels de complexes heptaaqua-, and pentaaqua-calcium(II) et hexaaqua-magnesium(II),* $Ca(H_2O)_7Re_6Q_6Cl_8{\cdot}3H_2O$ *(Q = S, Se),* $Ca(H_2O)_8Re_6S_6Cl_8$ *and* $Mg(H_2O)_6Re_6S_6Cl_8{\cdot}2H_2O$*. Ces derniers ont été caractérisés par LSIMS et détermination de leurs structures cristallines. Celles-ci révèlent des topologies inusitées en chimie de coordination, résultant d'associations mono- et tri-dimensionnelles des sous-unités moléculaires par liaisons hydrogène.*

cation aqua-alcalino-terreux / cluster d'eau / chalcohalogénure de rhénium à cluster octaèdrique / polymère de coordination tridimensionnel

Introduction

The solid-state and solution chemistries of molecular forms of hexanuclear chalcohalide rhenium clusters have recently undergone a spectacular acceleration motivated by the prospects of unravelling the reactivity of these small, discrete fragments of extended solid-state arrays [1–7] and constructing novel, electroactive molecular architectures [8]. A particularly striking example of the former is the transformation upon thermal treatment in solution of the cluster monoanions $[Re_6Q^i_5Cl^i_3(Cl^a_6)]^-$ (where i stands for an inner ligand bridging a face of the Re_6 octahedron and a stands for an outer, axial ligand linked to a single rhenium atom) [4] into the chalcogen-enriched dianions, $[Re_6Q^i_6Cl^i_2(Cl^a_6)]^{2-}$, the thermodynamically most stable cluster form, both for the selenium (Q = Se) [3] and the sulfur (Q = S) [4] series. This particular core

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[†] Dedicated to Prof Raymond Weiss.

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conversion reaction provides the rhenium chalcohalide cluster dianions in low yields only and served as an incentive for extensive studies of the reactivity of the cluster monoanions, $[Re_6Q^i_5Cl^i_3(Cl^a_6)]^-$, reported separately [5, 6]. Here, we report the direct solid-state synthesis of the molecular rhenium cluster dianions in the form of their alkaline-earth salts, $CaRe_6S_6Cl_8$, $CaRe_6Se_6Cl_8$, $MgRe_6S_6Cl_8$, and $MgRe_6Se_6Cl_8$. They are obtained as neat single-phase compounds, which exhibit high solubility in a variety of organic solvents, thereby providing a ready access in high yields to the tetrabutylammonium salts $(n\text{-}Bu_4N)_2Re_6Q_6Cl_8$, a much needed step in this chemistry.

In addition, this paper discloses our discovery of a remarkable, prompt organomineralization phenomenon which readily transforms, by virtue of their dissolution and subsequent crystallization out of organic solvents only, the native mineral polycrystalline alkaline-earth phases into high quality single crystals of a series of inner-sphere, heptaaqua-, and pentaaqua-calcium(II) and hexaaqua-magnesium(II) complex salts, $Ca(H_2O)_7Re_6Q_6Cl_8{\cdot}3H_2O$ (Q = S, Se), $Ca(H_2O)_8Re_6S_6Cl_8$ and $Mg(H_2O)_6Re_6S_6Cl_8{\cdot}2H_2O$, where clusters of water molecules encapsulate the alkaline-earth metal cations. These series of crystalline alkaline-earth aqua complexes, whose first hydration shells and second coordination spheres are characterized here, add to the recent pronounced interest in the emerging chemistry and physical chemistry of such cationic water cluster complexes of calcium and magnesium [9–14].

Finally, it is demonstrated that, whenever discrete water molecules appear in the formulation of the compounds, they serve to link the metal water cluster cations within topologically precise, hydrogen-bonded polymeric coordination networks. Of particular interest is the unprecedented, three-dimensional, concave cubic diamond coordination polymer described in the present contribution.

Results and discussion

Solid-state synthesis

The alkaline earth salts of these all-inorganic molecular cluster anions are prepared by high temperature (typically 825 °C) solid-state reaction of mixtures of Re(0), Q (S or Se), $ReCl_5$ and $ZnCl_2$, $CaCl_2$ or $MgCl_2$. This high temperature process essentially achieves a redox reaction between metallic rhenium and Re(V) which yields metal-metal bonding between Re(III) atoms stabilized by donor ligands. It is of interest to note that 12 Re-Re bonds, 24 Re-Cl^i and Re-S(Se)^i bonds and 6 Re-Cl^a bonds, ie, a total of 42 covalent bonds, are formed simultaneously in the course of this one-pot reaction.

Since no single crystals of $CaRe_6S_6Cl_8$ **1**, $CaRe_6Se_6Cl_8$ **2**, $MgRe_6S_6Cl_8$ **3** or $MgRe_6Se_6Cl_8$ **4** could be grown under the reaction conditions, we turned to the hitherto unknown synthesis under similar conditions of $ZnRe_6S_6Cl_8$ **5** for which single crystals were obtained and the structure determined. The X-ray powder patterns for **1**–**4** are isomorphous and can be properly indexed on the basis of the crystal structure of $ZnRe_6S_6Cl_8$ and the powder diffraction data for $PbRe_6Se_6Cl_8$ prepared earlier [15]. The powder diffraction diagram for **1** is given in figure 1. Refinement of the powder diffraction data yield the following lattice parameters for the cubic unit cells: a = 12.6796(4) Å for **1**; a = 12.8578(4) Å for **2**; a = 12.4421(6) Å for **3**; and a = 12.6197(7) Å for **4**.

Solution chemistry

Although **1**–**4** proved to be insoluble in water, they were found to be highly soluble in a variety of solvents such as acetone, acetonitrile, THF, dioxane, DMF, methanol and ethanol, whereas $ZnRe_6S_6Cl_8$ is not soluble in any of these. The solubility of **1**–**4** allows for straightforward metathesis reactions with tetraalkylammonium halides to give, for example, $(n\text{-}Bu_4N)_2Re_6Q_6Cl_8$ (Q = S, Se), in high yields. This novel, efficient alkaline-earth cluster salt route to the latter molecular cluster forms is particularly valuable since neither of those two cluster dianions have been obtained directly before. Indeed, $[Re_6Se_6Cl_8]^{2-}$ was obtained indirectly either by excision out of the bidimensional solid $Re_6Se_6Cl_6$, or by reacting $(n\text{-}Bu_4N)Re_6Se_5Cl_9$ with Li_2Se [3, 16]; $[Re_6S_6Cl_8]^{2-}$ was prepared in low yields only by thermal treatment of $RbRe_6S_5Cl_9$ in ethanol [4]. Recent progress in the substitution chemistry of the cluster monoanions has allowed the preparation of both $(n\text{-}Bu_4N)_2Re_6S_6Cl_8$ and $(n\text{-}Bu_4N)_2Re_6Se_6Cl_8$ in good yields, albeit again indirectly, by reacting the corresponding cluster monoanions $(n\text{-}Bu_4N)Re_6Q_5Cl_9$ with $[(CH_3)Si]_2Q$ (Q = S, Se) [5].

Liquid secondary ion mass spectroscopy for $Re_6Q_6Cl_8^{2-}$ (Q = S, Se)

The solubility of **1**–**4** in organic solvents also made it possible to use liquid secondary ion mass spectroscopy (LSIMS) to characterize the anionic clusters. The experiments were carried out with tiny amounts of the crude pellets of **1**, **3** and **4** as well as single crystals of the hydrates **6** and **7** and $(Bu_4N)_2Re_6Q_6Cl_8$ (Q = S, Se), obtained from the former alkaline salts. LSIMS has been successfully applied to the characterization of molybdenum halide clusters [17] and more recently to rhenium chalcohalide clusters [5–6].

Attempts to record positive LSIMS mass spectra of compounds **1**–**7** were unsuccessful. The negative LSIMS data are gathered in table I and the formulation of the fragments reported therein are supported by the good agreement of experimental and calculated isotopic ion distributions [18]. The spectra are analogous to those previously described for heterosubstituted hexanuclear rhenium dianions [5]. Moreover, the cluster anion peaks are identical regardless of the nature of the cation (fig 2). Singly charged cations are characterized by the presence of $[(Bu_4N)Re_6Q_6Cl_8]^-$ ions (m/z = 1835 in fig 2) while the presence of Na^+ cations in the MNBA matrix [19] accounts for the $[Na(Re_6Q_6Cl_8)]^-$ ions (m/z = 1616 in fig 2) in the spectra of alkaline-earth salts.

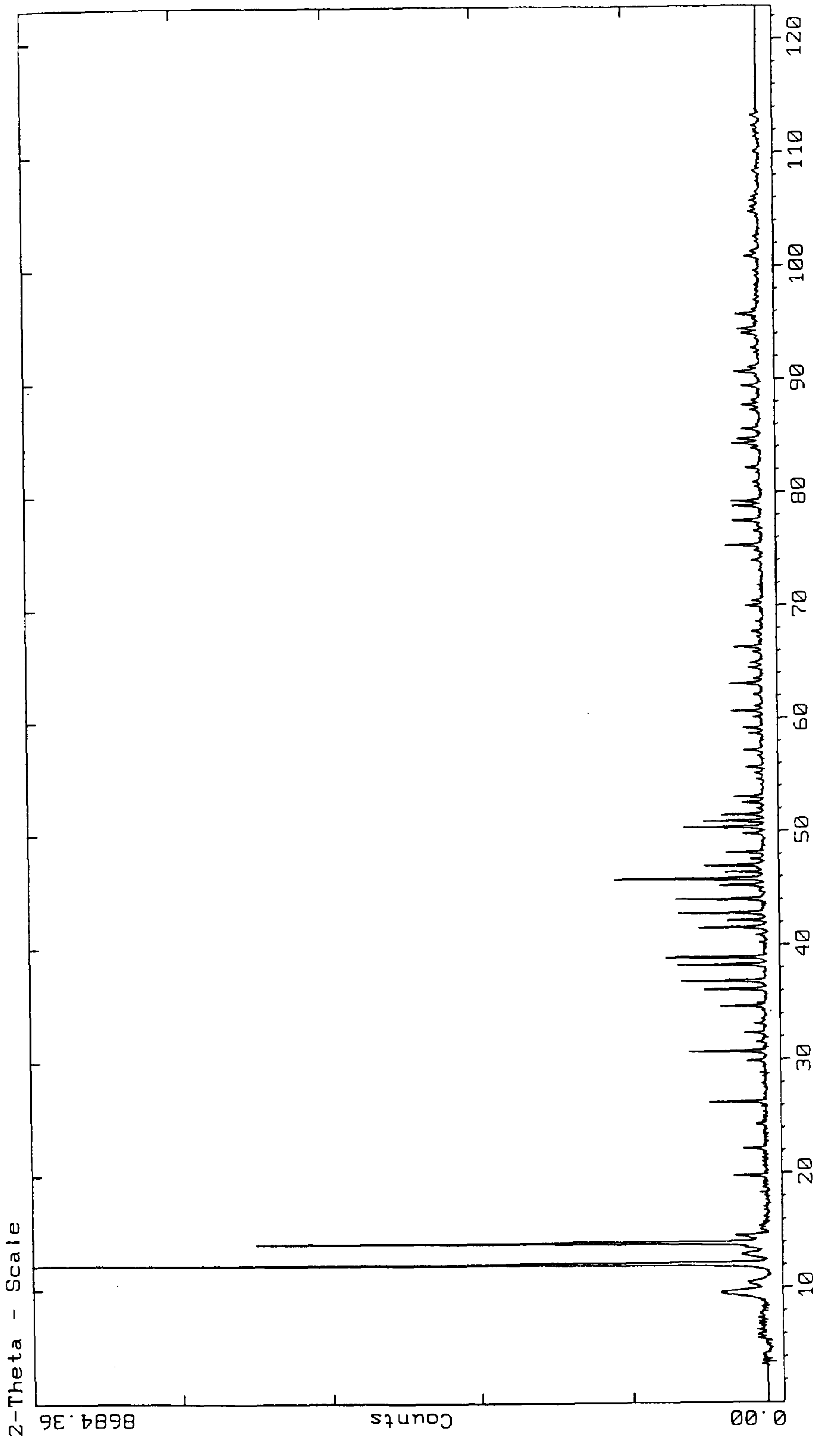


Fig 1. X-ray powder diffraction diagram for $CaRe_6S_6Cl_8$ 1.

Table I. Negative ion LSIMS of octahedral rhenium clusters anions: m/z^a (relative abundance).

Assignment	$(Bu_4N)_2Re_6S_6Cl_8$	$(Bu_4N)_2Re_6Se_6Cl_8$	$Ca(H_2O)_n$ $Re_6S_6Cl_8$	$Ca(H_2O)_n$ $Re_6Se_6Cl_8$	$Mg(H_2O)_6$ $Re_6S_6Cl_8$	$Mg(H_2O)_6$ $Re_6Se_6Cl_8$
$(Bu_4N)Re_6Q_6Cl_8]^-$	1835.6 (35)	2117.3 (25)				
$(Bu_4N)Re_6Q_6Cl_7]^-$	1800.6 (7)	2082.3 (4)				
$[Re_6Q_6Cl_8]^-$	1593.3 (45)	1875.0 (60)	1593.3 (43)	1875.0 (52)	1593.3 (45)	1875.0 (55)
$[Re_6Q_6Cl_7]^-$	1558.3 (100)	1840.0 (100)	1558.3 (100)	1840.0 (100)	1558.3 (100)	1840.0 (100)
$[Re_6Q_6Cl_6]^-$	1521.4 (32)	1805.0 (31)	1521.4 (30)	1805.0 (41)	1521.4 (30)	1805.0 (36)
$[Re_6Q_6Cl_5]^-$	1486.4 (25)	1770.1 (20)	1486.4 (25)	1770.1 (30)	1486.4 (20)	1770.1 (27)
$[Re_6Q_6Cl_4]^-$	1451.4 (10)		1451.4 (11)		1451.4 (13)	
$[Re_6Q_6Cl_8]^{2-}$	796.7 (7)	937.5 (3)	796.7 (10)	937.5 (16)	796.7 (10)	937.5 (11)

[a] m/z value of the most abundant ion in the isotopic distribution. Peaks above m/z = 300 and greater than 3% are included.

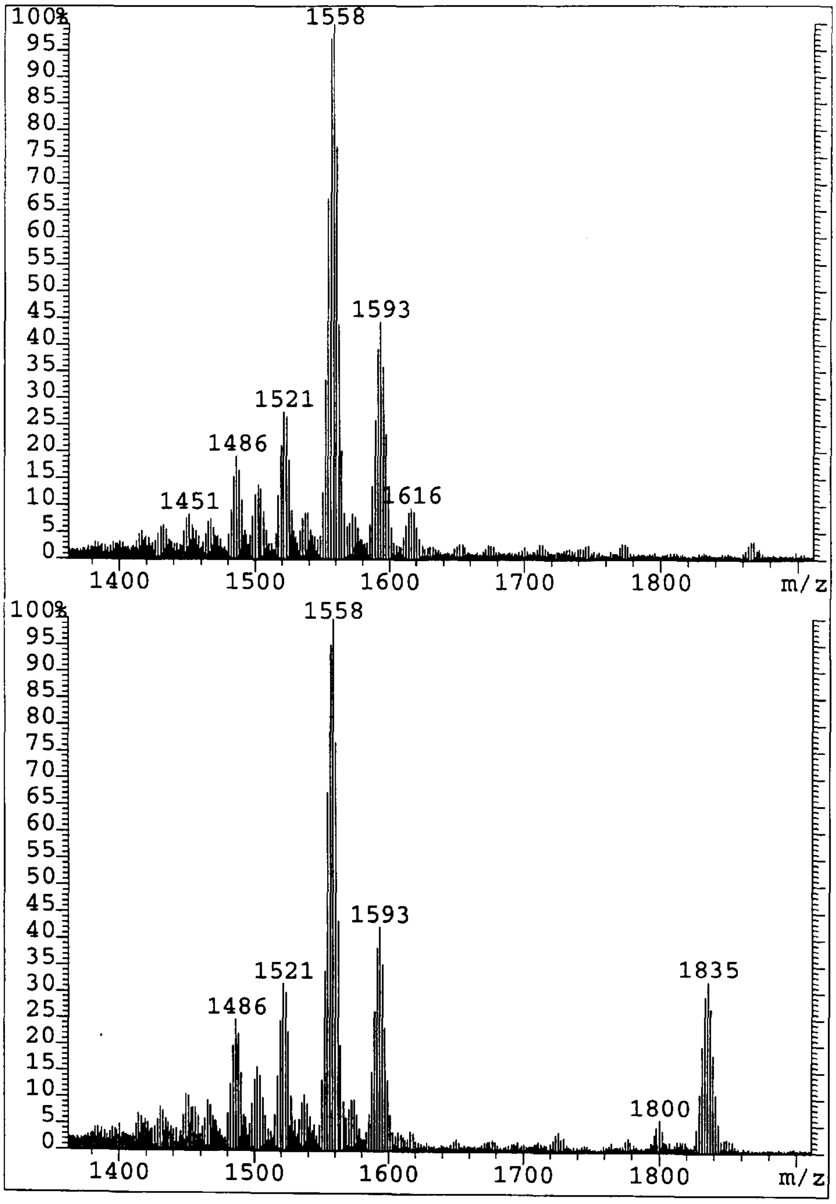


Fig 2. Negative LSIMS mass spectra of $Mg(H_2O)_6Re_6S_6Cl_8 \cdot 2H_2O$ **9** (top) and $(n\text{-}Bu_4N)_2[Re_6S_6Cl_8]$ (bottom).

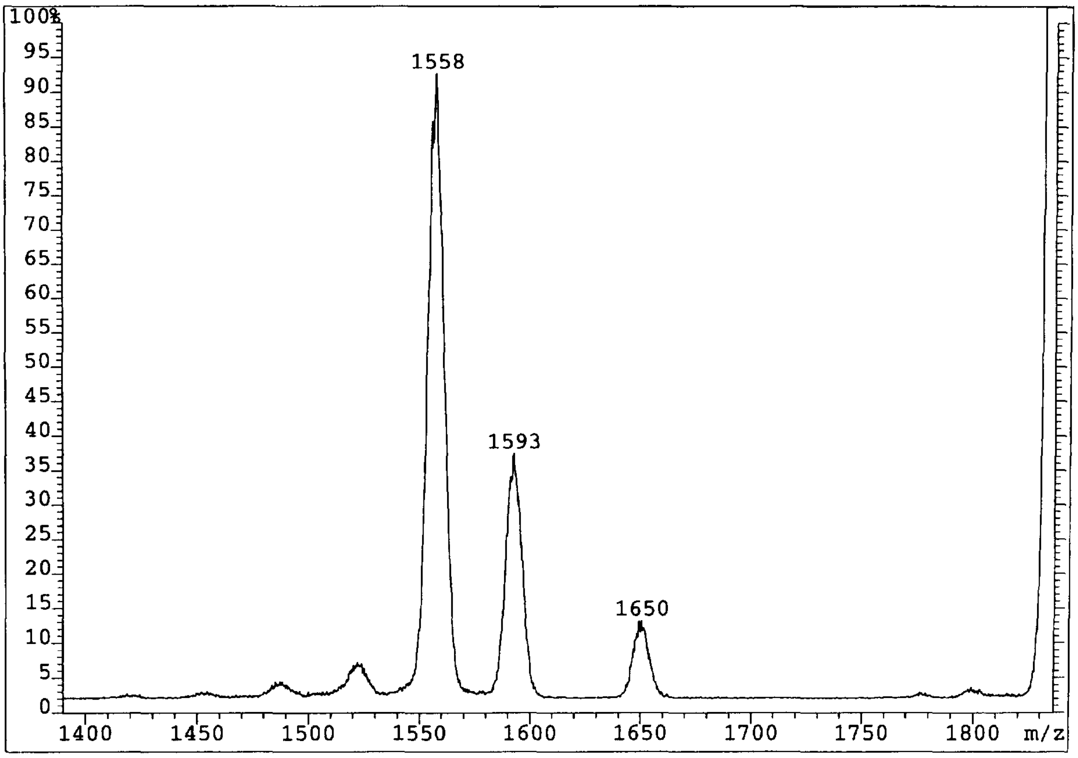


Fig 3. Daughter-ion collision induced dissociation from $[(n\text{-}Bu_4N)Re_6Q_6Cl_8]^-$ ions ($m/z = 1835$).

Collision-induced dissociation (CID) spectra of selected ions have also been recorded. Since CID spectra concern reactions occurring in the gas phase only, matrix processes, such as oxygen addition [5, 20], are not observed. The CID spectra of $[(Bu_4N)Re_6Q_6Cl_8]^-$ ions (fig 3) is of interest. Indeed, the presence of $[Re_6Q_6Cl_8]^-$ ions ($m/z = 1593$ in fig 3) demonstrates that these anions are formed by gas-phase decomposition of $[(Bu_4N)Re_6Q_6Cl_8]^-$ ions and not solely by matrix-induced oxidation of $[Re_6Q_6Cl_8]^{2-}$.

The formation of $[Re_6Q_6Cl_8]^-$ ions in the gas phase by a two-step mechanism involving the successive loss of Bu_3N and the butyl radical is supported by the presence of $[(Bu)Re_6Q_6Cl_8]^-$ ($m/z = 1650$ in fig 3) ions in both the daughter ion spectrum of the $[(Bu_4N)Re_6Q_6Cl_8]^-$ and the parent ion spectrum of $[Re_6Q_6Cl_8]^-$ ions. This fragmentation may formally be regarded as an oxidation of the rhenium cluster dianion and a reduction of the Bu_4N cation. It is interesting to note that the proposed two-step fragmentation of Bu_4N resembles the well-known electrochemical reduction of tetralkylammonium salts [21].

The aqua-alkaline-earth complex salts

When methanol, acetonitrile/THF or acetonitrile solutions of $CaRe_6Q_6Cl_8$ (Q = S, Se) and $MgRe_6S_6Cl_8$ are allowed to evaporate, single crystals are quickly obtained and formulated as: $Ca(H_2O)_7Re_6S_6Cl_8{\cdot}3H_2O$ **6**, $Ca(H_2O)_7Re_6Se_6Cl_8{\cdot}3H_2O$ **7**, $\{Ca_{1/2}(H_2O)_3(H_2O)_{2/2}\}_2Re_6S_6Cl_8$ **8**, and $Mg(H_2O)_6Re_6S_6Cl_8{\cdot}2H_2O$ **9**, by resolution of the crystal structures of **6**, **8** and **9** (table II) and LSIMS (table I). The novel mineral hydrates **6**–**9** are highly soluble in water, whereas the initial phases **1**–**4** were insoluble in water and not even slightly hygroscopic.

- *Crystal chemistry results*

The analysis of the crystal structures of **6**, **8** and **9** reveals the presence of inner-sphere aqua-alkaline-earth complex ions, whose first hydration shells and second coordination spheres were identified by applying the metal-to-water oxygen atom and first shell water oxygen atom-to-atom X of the second coordination sphere bond lengths criteria recently determined by Carugo, Djinovic and Rizzi [9].

■ *$Ca(H_2O)_7Re_6S_6Cl_8{\cdot}3H_2O$* **6**: *strings of octahedral Re_6 clusters within a 3D, concave cubic diamond frame of [heptaaqua-Ca]$^{2+}$ ions linked by water molecules*

The description of the remarkable architecture of this series of two compounds, **6** and **7**, begins by observing that the calcium ion in figure 4 is hepta-coordinated by water oxygen atoms O1 to O7. The Ca-water oxygen atom average bond length of 2.440 Å is in agreement with the expected experimental distance of 2.403 Å for coordination number seven [10] and that of 2.452 Å obtained by density functional calculations of the opti-

Table II. Crystallographic data for $Zn[Re_6S_6Cl_8]$ **5**, $Ca(H_2O)_7[Re_6S_6Cl_8]\cdot 3H_2O$ **6**, $Ca(H_2O)_8[Re_6S_6Cl_8]$ **8**, and $Mg(H_2O)_6[Re_6S_6Cl_8]\cdot 2H_2O$ **9**.

	5	***6***	***8***	***9***
Formula	$Cl_8Re_6S_6Zn$	$H_{20}CaCl_8O_{10}Re_6S_6$	$H_{16}CaCl_8O_8Re_6S_6$	$H_{16}Cl_8MgO_8Re_6S_6$
Formula weight	1658.58	1813.44	1777.41	1761.64
Crystal system	cubic	triclinic	triclinic	triclinic
Space group	$P_n\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	12.433 (2)	12.779 (3)	9.033 (2)	11.902 (2)
b, Å		13.639 (5)	9.923 (3)	13.758 (2)
c, Å		11.320 (2)	8.987 (2)	9.074 (3)
α, deg		114.51 (2)	99.72 (2)	107.56 (2)
β, deg		116.27 (1)	114.70 (2)	90.10 (2)
γ, deg		62.67 (2)	85.54 (2)	83.29 (1)
V, Å^3	1921.9 (9)	1515.2 (1.2)	721.3 (7)	1406 (1)
Z	4	2	1	2
d(calc), g.cm^{-3}	5.73	3.97	4.09	4.16
μ, cm^{-1}	411.6	255.1	267.9	273.3
R^a	0.033	0.043	0.046	0.037
R_w^b	0.042	0.073	0.064	0.051
Goodness of fit Sc	1.117	0.907	1.204	1.035

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma^2(I) + (p.F_o^2)^2]^{-1}$; [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - v)]^{1/2}$.

mized geometry for $[Ca(H_2O)_6...H_2O]^{2+}$ [11]. As exemplified in figure 4, the first hydration sphere geometry for $[Ca(H_2O)_7]^{2+}$ in **6** is essentially that predicted by the former calculations [11] and can be thought of as a distorted octahedron which the additional water oxygen O7 has broken into, repelling the vertex water oxygen O6. It is also similar to the calcium heptacoordination geometry simulated for calcium-dependent mammalian lectins [14].

Within the structure, any $[Ca(H_2O)_7]^{2+}$ ion is connected to four other aqua-calcium ions by a precise set of four hydrogen-bonded water molecules belonging to its second coordination sphere (O10, O11, O12 and O13 in fig 4). Thus, two types of centrosymmetrical linkages are identified which involve either one (O12 and O13) or two (O10-O10 and O11-O11) water molecules. It is interesting to note that this set of directional hydrogen bonds provide the connecting code for the three-dimensional assemblage of the calcium-water cluster dications. Indeed, we can consider the construction of a polymeric 3D coordination framework out of a unique, four-connected structure generator, the concave node shown in figure 5, where all links connect at angles lower than 90°. Thus, by considering the motif obtained by drawing the calcium atoms only within the structure of **6** and linking them by applying the above connection principle, we obtain the fascinating frame shown in figure 6a and identify a rare, perhaps unprecedented topological type. Six-membered rings with a chair conformation are formed and connected within one layer by equatorial links. Thus, the axial links serve to join these particular layers with each other. The topology of the prototypical diamond structure can then be recognized and, since the six-membered rings created by the axial links junctions also have a chair conformation (fig 6a), there is no symmetry plane between the layers, which qualifies the present construction as belonging to the cubic diamond structure type [22].

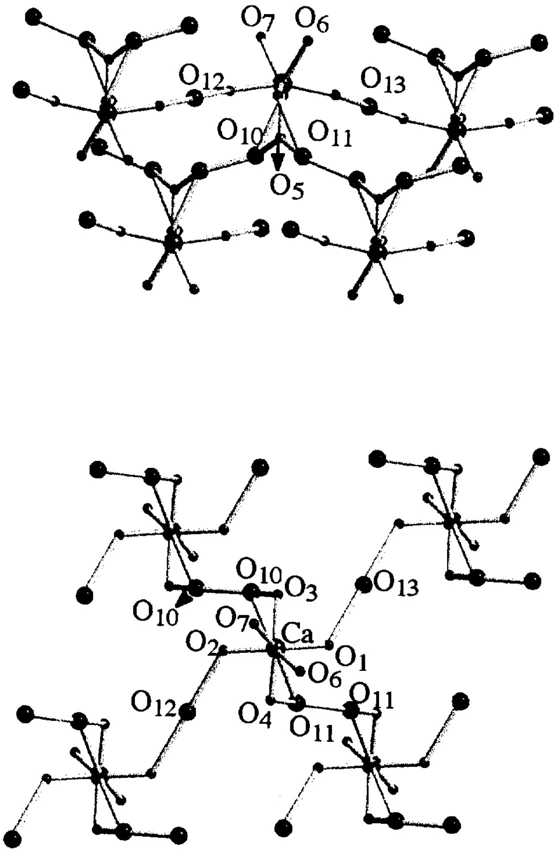


Fig 4. Two orthogonal views, normal (top) and along (bottom) the Ca-O5 direction of the first hydration shells of $[Ca(H_2O)_7]^{2+}$ ions in **6** and their connecting pattern. Selected bond lengths (Å): Ca-O1, 2.431; Ca-O2, 2.382; Ca-O3, 2.487; Ca-O4, 2.391; Ca-O5, 2.408; Ca-O6, 2.438; Ca-O7, 2.540; O1...O13, 3.177; O2...O12, 3.213; O3...O10, 2.981; O4...O11, 2.945; O5...O10, 2.845; O5...O11, 2.789.

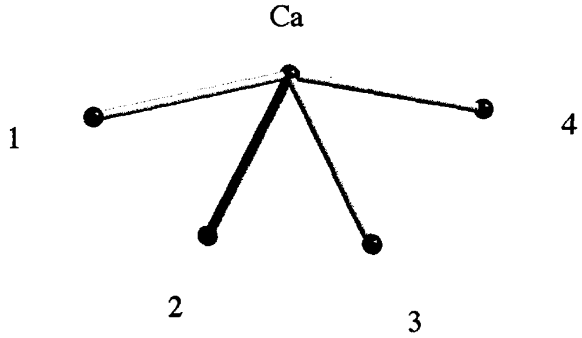


Fig 5. Geometry of the four-connected concave node of **6**: Ca-1, 9.94 Å; Ca-2, 10.08 Å; Ca-3, 10.07 Å; Ca-4, 9.88 Å; 1-Ca-2, 79.4°; 2-Ca-3, 86.1°; 3-Ca-4, 79.7°; 1-Ca-3, 86.0°; 2-Ca-4, 86.2°.

A further very interesting feature of this unprecedented, hydrogen-bonded 3D coordination polymer is its concave topology which originates in the geometry of its structure generator (fig 5) and is perhaps best exemplified by the following two observations. For any given six-membered ring (fig 6a), the axial and equatorial links at each node reside on the same side of the ring mean plane, alternately above or below the plane along the ring, a feature which differs strikingly from the usual above-and-below sequence for the axial and equatorial substituents at any carbon site of the cyclohexane framework in the chair conformation. Second, one should note the novel conformation for the concave six-membered rings, which is best appreciated by looking down the axial links and shown in figure 6b.

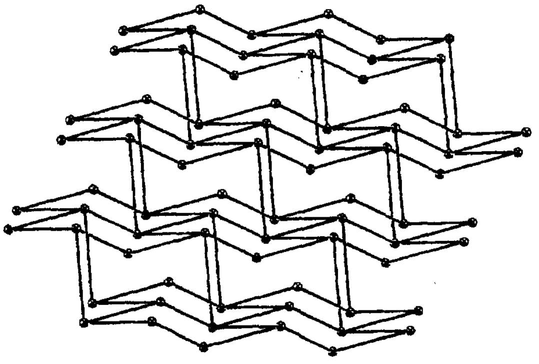
Novel networks with a variety of architectures have been obtained recently upon coordination of multifunctional ligands onto metal ions [23] and prototypical topologies, including interpenetrating diamontoid lattices [24a] and a lamellar phase with an anti-$CaSi_2$ architecture [24b], are being identified within networks of hydrogen-bonded organic ions. It should thus be noted that the present concave cubic diamond topology results from a precise combination of the two former construction principles, ie, organization of the water cluster complex within the inner sphere of the metal prior to the establishment of a hierarchy of hydrogen bonds within the second coordination sphere, here the concave "umbrella" structure generator.

■ *A retro-tectonic fragmentation of the cubic diamond coordination analog*

Strings of molecular inorganic octahedral cluster dianions, $Re_6S_6Cl_8^{2-}$, are encapsulated within the connected cavities of this unique 3D architecture (fig 7), where each link in figure 7 is typically of the order of 10 Å. Thus, the extended motif at the bottom view of figure 7 may be broken into a generic tecton shown in both views at the top of the figure. Finally, a drawing of one cavity made of eight, four-connected $[Ca(H_2O)_7]^{2+}$ cations and containing one single cluster anion is provided in figure 8.

■ $\{Ca_{1/2}(H_2O)_3(H_2O)_{2/2}\}_2Re_6S_6Cl_8$ **8**

There is no discrete water molecule interspersed within the crystals of **8** and, therefore, no connection occurs



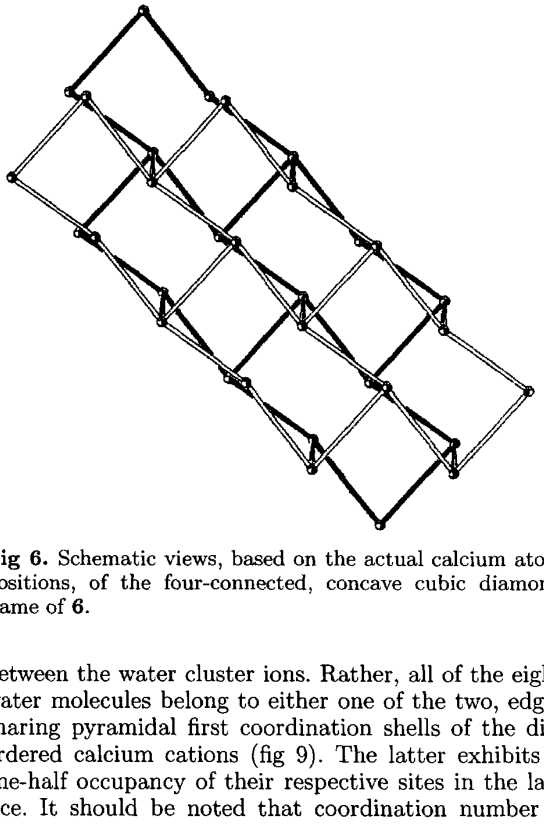


Fig 6. Schematic views, based on the actual calcium atom positions, of the four-connected, concave cubic diamond frame of **6**.

between the water cluster ions. Rather, all of the eight water molecules belong to either one of the two, edge-sharing pyramidal first coordination shells of the disordered calcium cations (fig 9). The latter exhibits a one-half occupancy of their respective sites in the lattice. It should be noted that coordination number 5 is highly unusual for calcium ions. This has been reported to occur only in those instances where the constraints in the ligand second coordination sphere force the cation to adopt a particular stereochemistry [9]. The present organization is a striking demonstration of this phenomenon.

■ $Mg(H_2O)_6Re_6S_6Cl_8 \cdot 2H_2O$ **9**

Since two additional water molecules are present in the formulation of **9**, one expects to identify some connectivity pattern between the aqua-magnesium cations within the crystal lattice. As shown in figure 10, two *trans*-coordinated, discrete water molecules indeed serve to connect the octahedral, first hydration shells of the $[Mg(H_2O)_6]^{2+}$ cations within one-dimensional, hydrogen-bonded coordination polymers. As demonstrated in the right-hand view of figure 10, it takes

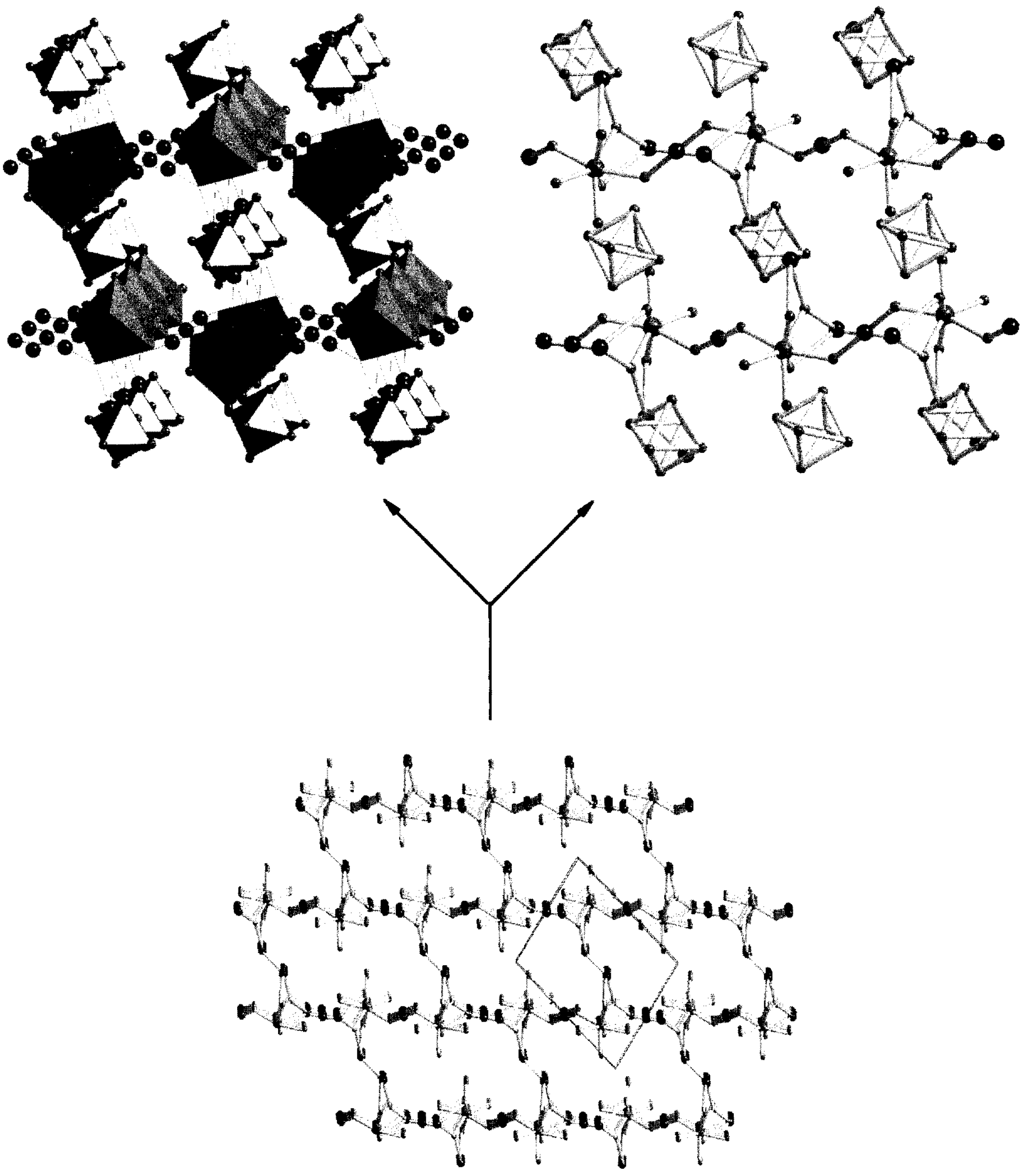


Fig 7. A retro-tectonic fragmentation of the structure of **6**. The chlorine and sulfur atoms of the cluster anions have been omitted for clarity.

eight metal water cluster cations from four different hydrogen-bonded chains to form a cavity which encapsulates a single inorganic cluster dianion.

Further comments on the organomineralization phenomenon

Thus, as a result of this remarkable process, small (water) molecules with strong coordinating abilities towards Ca^{2+} and Mg^{2+} and capable of complementary hydrogen bonding interactions readily self-organize within highly ordered networks in the solid state. Only one phase is obtained from **3**, namely, $Mg(H_2O)_6Re_6S_6Cl_8 \cdot 2H_2O$, in agreement with the well-documented Mg^{2+} preference for six coordination (fig 10). Interestingly, two types of aqua-calcium(II) complex salts, **6**, **7** and **8** (fig 4 and 9), with coordination numbers 7 and 5, are obtained from **1**, in agreement with the marked variability of the coordination numbers for Ca^{2+}, in the range 5–8, albeit with very few cases of coordination number 5 [9]. The latter thermodynamically favored formation of polymorphic crystalline forms is reminiscent of the well-known and presently much investigated biomineralization processes, which yields specific varieties of calcium carbonates in living organisms [25]. The present process requires the dissolution of

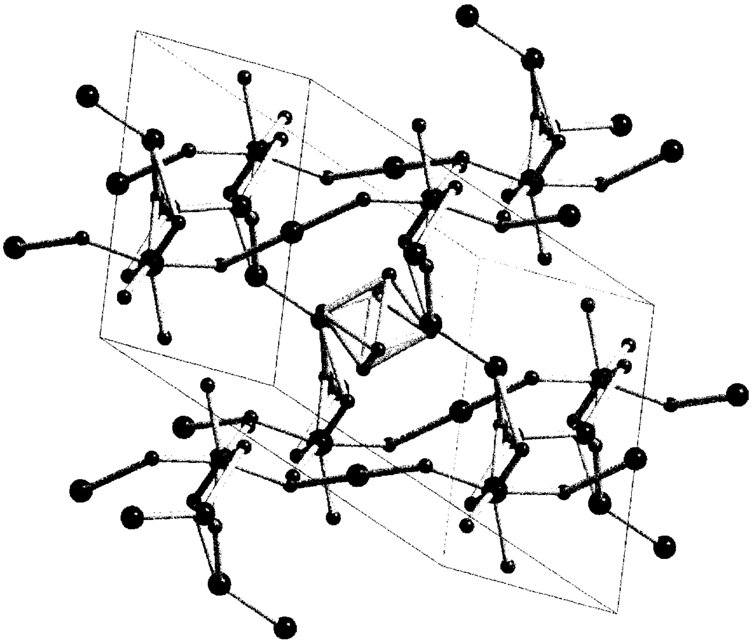


Fig 8. A perspective view of a single tecton made of eight, four-connected $[Ca(H_2O)_7]^{2+}$ ions.

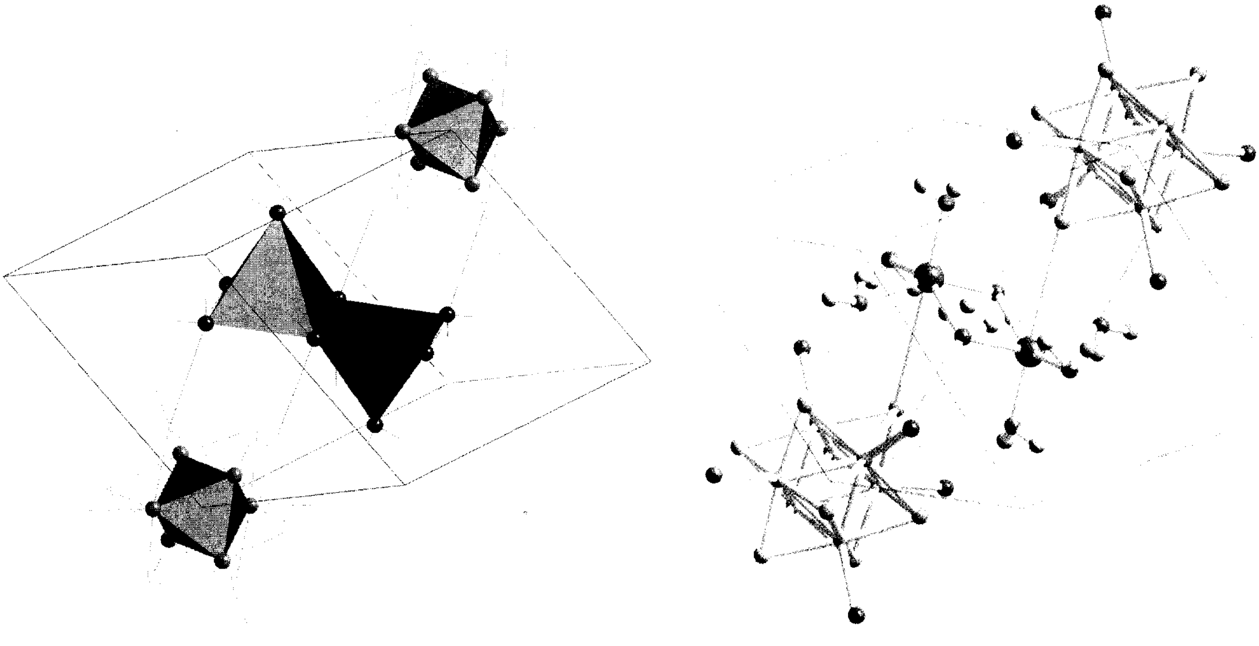


Fig 9. Polyhedral and ball-and-stick views of the first hydration shell and part of the second coordination sphere of the pseudo-$[Ca(H_2O)_5]^{2+}$ ions in the structure of **8**. Only two of the eight cluster anions centered at the vertices of the unit-cell have been represented. Note one μ^3-sulfur ligand of each Re_6 octahedral cluster reaching out to break into the pyramidal, first hydration spheres of Ca^{2+} ions (Ca1-S4 bond length, 4.083 Å). The displayed outer-sphere links between the water cluster oxygen atoms of the aqua-cations and the sulfur or chlorine atoms of the cluster anions are typical [9] of second coordination sphere binding interactions: O1...Cl1, 3.201 Å; O2...S1, 3.376 Å.

the native, anhydrous mineral phase in and subsequent crystallization out of organic solvents and is therefore define as an organomineralization phenomenon.

This unique process appears to be kinetically fast, a feature shared also by biomineralization chemistries. Thus, a drop of an acetonitrile solution of **1** deposited on a glass slide evaporates readily and the concomitant, rapid formation of a thin crystalline film is observed. Analysis of the X-ray powder pattern of this film clearly demonstrates that the growth of thin crystals of $Ca(H_2O)_7Re_6S_6Cl_8 \cdot 2H_2O$ **6** has selectively occurred on the glass slide surface with a subsequent enhancement of the intensity of two reflections, namely (01-1) and (10-1) in the X-ray pattern of the crystalline film. Thus,

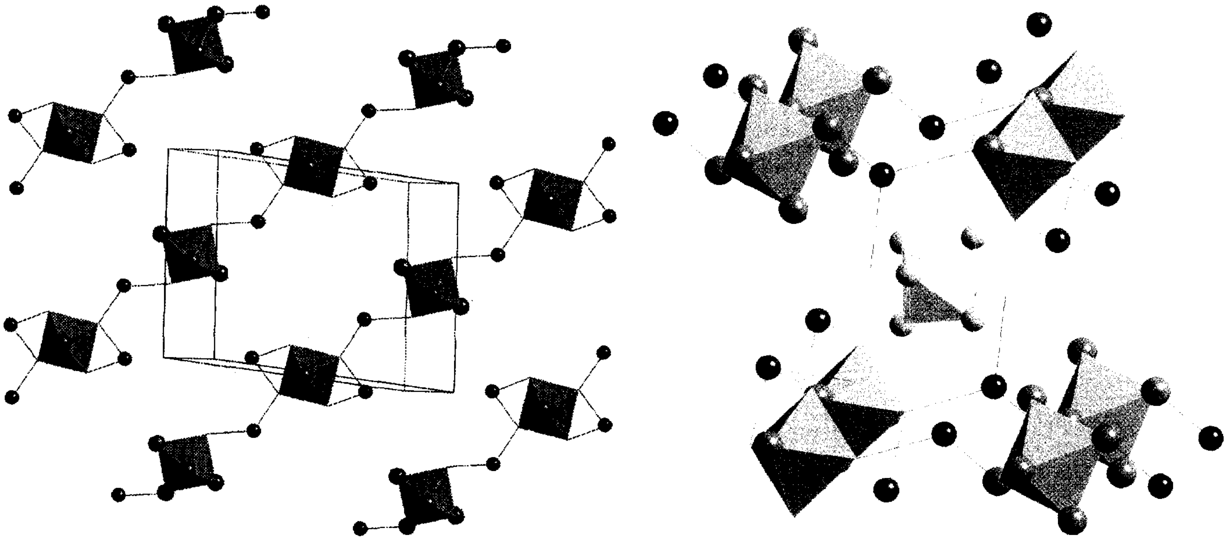


Fig 10. Polyhedral representation of the chains of $[Mg(H_2O)_6]^{2+}$ cations linked by hydrogen-bonded water molecules (left) and the cage encapsulating the $Re_6S_6Cl_8^{2-}$ cluster anion (right).

it is concluded that phase and crystal habit selectivities are associated with this novel organomineralization process.

Experimental section

High temperature synthesis of $CaRe_6S_6Cl_8$ **1**, $CaRe_6Se_6Cl_8$ **2**, $MgRe_6S_6Cl_8$ **3**, $MgRe_6Se_6Cl_8$ **4** *and* $ZnRe_6S_6Cl_8$ **5**

$ReCl_5$ and anhydrous MCl_2 (M = Ca, Mg, Zn), n-Bu_4NCl, Re(powder), sulfur and selenium were obtained from commercial sources and used as received. $MRe_6S_6Cl_8$ (M = Ca, Mg and Zn) and $MRe_6Se_6Cl_8$ (M = Ca or Mg) were prepared following slightly modified versions of our general procedure reported previously [4]. In the inert argon atmosphere of a dry box, stoichiometric quantities of Re (powder) (1.35 mmol), $ReCl_5$ (0.45 mmol), Q (Q = S, Se) (1.8 mmol) and anhydrous MCl_2 (M = Ca, Mg, Zn) (0.3 mmol) were mixed and pressed into pellets which were introduced in silica tubes closed with a valve. The bottom part of the tubes were cooled with liquid nitrogen to prevent $ReCl_5$ sublimation, evacuated to ca 10^{-5} torr of residual pure argon, sealed and placed in a vertical furnace. The sealed tubes have an inner diameter of 7 mm, an external diameter of 9 mm and are 45 mm long. The furnace temperature was raised first at 1 °C min^{-1} up to 450 °C and then at 0.5 °C min^{-1} to reach the final temperature of 825 °C. This temperature was maintained for 36 h prior to cooling down to room temperature at 2 °C min^{-1}. Dark-red, X-ray quality single crystals were obtained for $ZnRe_6S_6Cl_8$ **5** only and their structure determined (table I).

Solution-phase chemistry

- $(n\text{-}Bu_4N)_2[Re_6S_6Cl_8]$

Pellets of crude $CaRe_6S_6Cl_8$ or $MgRe_6S_6Cl_8$ prepared from 1.8 mmol of Re ($ReCl_5$ + Re) were ground and dissolved in methanol (500 mL) by stirring at room temperature for 2 h. The suspension was filtered to give an orange solution, which was concentrated in vacuo to 150 mL. Excess of solid n-Bu_4NCl was added to the solution and an orange precipitate immediately appears, which is collected on a glass frit, washed with methanol and dried in vacuo. The compound was recrystallized from acetonitrile to give 450 mg (78%) of $(n\text{-}Bu_4N)_2[Re_6S_6Cl_8]$. No significant difference in yields was observed starting from either calcium or magnesium pellets.

Anal calc for $C_{32}H_{72}N_2Re_6S_6Cl_8$: C, 18.49; H, 3.49; N, 1.35; Cl, 13.65. Found: C, 18.54; H, 3.14; N, 1.30; Cl, 13.40.

Unit cell dimensions determined by single-crystal X-ray crystallography at 20 °C: a = 12.402(8) Å, b = 11.809(7) Å, c = 18.47(1) Å, β = 90.61(6)°, V = 2706 $Å^3$ [4].

- $(n\text{-}Bu_4N)_2[Re_6Se_6Cl_8]$

The above procedure was applied to the preparation of this compound. The addition of tetrabutylammonium chloride to the methanolic solution gives a red-orange precipitate which yields 430 mg (70% calculated from 1.8 mmol of Re) of beautiful ruby red octahedra upon recrystallization in acetonitrile.

Anal calc for $C_{32}H_{72}N_2Re_6Se_6Cl_8$: C, 16.29; H, 3.08; N, 1.19; Cl, 12.02. Found: C, 16.14; H, 2.70; N, 1.12; Cl, 12.08.

Unit cell dimensions determined by single-crystal X-ray crystallography at 20 °C: a = 12.852(2) Å, b = 11.615(1) Å, c = 18.621(5) Å, β = 90.10(2)°, V = 2779 $Å^3$ [26, 27].

General procedure for the preparation of the aqua-alkaline-earth complex salts **6–9**

Crude $MRe_6Q_6Cl_8$ (M = Ca, Mg), (Q = S, Se) (50 mg) was dissolved in the appropriate solvent (20 mL). The solutions were filtered to eliminate a black residue and reduced to ca 5 mL. Good X-ray quality single crystals are readily obtained by slow evaporation.

- $Ca(H_2O)_7[Re_6S_6Cl_8]\cdot 3\ H_2O$ **6**

The solvent was methanol and the composition of the hydrate was determined by resolution of its crystal structure.

- $Ca(H_2O)_7[Re_6Se_6Cl_8].3\ H_2O$ **7**

The solvent was methanol. The hydrate unit cell dimensions, determined by single crystal X-ray crystallography at 20 °C are: a = 12.856(4) Å, b = 13.865(4) Å, c = 11.343(5) Å, $\alpha = 114.10(3)°$, $\beta = 116.12(3)°$, $\gamma = 62.50(3)°$, $V = 1556$ Å^3; these are similar to those of **6**.

- $Ca(H_2O)_8[Re_6S_6Cl_8]$ **8**

The crude $CaRe_6S_6Cl_8$ pellet was first dissolved in acetonitrile. After concentrating the acetonitrile solution, dry THF (ca 2 mL) was added prior to crystallization. The composition of the complex salt was determined by resolution of its crystal structure.

- $Mg(H_2O)_6[Re_6S_6Cl_8]$ **9**

Compound **9** was crystallized out of an acetonitrile solution and its composition was determined by resolution of its crystal structure.

X-ray crystallography

Crystallographic data for compounds **5–6** and **8–9** are given in table II. Preliminary examination and data collection were performed on a κ-axis Enraf-Nonius CAD4-F diffractometer using graphite monochromatized Mo$K\alpha$ radiation. Unit cell dimensions and crystal orientation matrix were derived from least-squares refinement of setting angles of 25 reflections. Intensity data were collected using $\omega - 2\theta$ scan and were corrected for background, Lorentz, polarization and absorption effects. Absorption corrections were applied using empirical procedures based on azimuthal ψ scans of some reflections having an Eulerian angle χ near 90° ($\kappa > 100°$) [28] or Fourier procedures [29]. The structures were solved by Patterson method or direct methods and refined (on Fs) by full matrix least-squares calculations initially with isotropic and finally with anisotropic thermal parameters for non-H-atoms. The atomic scattering factors and anomalous dispersion corrections were from *International Tables for X-ray Crystallography* [30]. All calculations were performed on a microVAXII and IBM RS/6000 computers by using the Enraf-Nonius SDP/PLUS and XTAL3.2 systems of programs [31]. The similarity of the X-ray scattering power of sulfur and chlorine atoms makes it difficult to ascertain whether these atoms are localized or disordered over all crystallographically independent, face-capping sites. It was thus assumed that these sites are shared by S and Cl atoms with a statistical occupancy of 0.75 and 0.25, respectively. In the last refinement cycles these positions were refined independently or with an appropriately averaged scattering factor.

- $Zn[Re_6S_6Cl_8]$ **5**

An irregular plate-like ruby red crystal with dimensions 0.27 × 0.12 × 0.06 mm^3 was used. A total of 1905 intensities were recorded ($\theta \leqslant 26°$) at room temperature in the quadrants $+h$, $+k$, $+l$. An empirical absorption correction based on ψ scans procedure was applied (transmission ranged from 87.6 to 99.7) to the reflection data. Data reduction and averaging yielded 1182 independent reflections (R_{int} = 0.041) of which 642, with $I \geqslant 3\sigma(I)$, were used for the calculations. The Laue class was established to be $m3$ and the systematic extinctions were consistent with the centrosymmetric $Pn\bar{3}$ space group (space group number 201; origin choice 2). The structure was solved by direct-methods. All non-hydrogen atoms of the structure were refined anisotropically. The cluster core face-capping atoms were considered disordered and their positions were refined with site occupancies of 1/4Cl + 3/4 S. The asymmetric unit consists of one sixth cluster anion and one sixth zinc cation located on inversion centers.

- $Ca(H_2O)_7[Re_6S_6Cl_8]\cdot 3H_2O$ **6**

A parallelepiped red crystal with dimensions 0.24 × 0.21 × 0.15 mm^3 was used. A total of 6206 intensities were recorded ($\theta \leqslant 26°$) at room temperature in the quadrants $+h$, $\pm k$, $+l$. An absorption correction based on the DIFABS procedure was applied to the reflection data. Data reduction and averaging yielded 5924 independent reflections ($R_{\rm int}$ = 0.023) of which 4591 had $I \geqslant 3\sigma(I)$ and were used for the calculations. The structure was solved by Patterson method which revealed six independent rhenium atoms in general positions. The remaining atoms were found on successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The asymmetric unit consists of two half cluster anions located on inversion centers, one calcium cation surrounded by seven water molecules in general position and four more free water molecules in a general position, two of them having a site occupation factor of one half.

- $\{Ca_{1/2}(H_2O)_3(H_2O)_{2/2}\}_2[Re_6S_6Cl_8]$ **8**

A cubic red crystal with dimensions 0.19 × 0.19 × 0.18 mm^3 was used. A total of 3355 intensities were recorded ($\theta \leqslant 27°$) at room temperature in the quadrants $+h$, $\pm k$, $\pm l$. An empirical absorption correction based on ψ scans procedure was applied to the reflection data. Data reduction and averaging yielded 3151 independent reflections ($R_{\rm int}$ = 0.030) of which 2435 had $I \geqslant 3\sigma(I)$ and were used for the calculations. The structure was solved by Patterson method which revealed three independent rhenium atoms in general positions. The remaining atoms were found on successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The asymmetric unit consists of one half cluster anion. The cluster core face-capping atoms were considered disordered and their positions were refined with sites occupancies of 1/4 Cl + 3/4 S.

- $Mg(H_2O)_6[Re_6S_6Cl_8]\cdot 2H_2O$ **9**

A needle-shaped red crystal with dimensions 0.27 × 0.09 × 0.08 mm^3 was used. A total of 6694 intensities were recorded ($\theta \leqslant 27°$) at room temperature in the quadrants $+h$, $\pm k$, $\pm l$. An empirical absorption correction based on ψ scans procedure was applied to the reflection data (transmission ranged from 0.72 to 1.00) to the reflection data. Data reduction and averaging yielded 6191 independent reflections ($R_{\rm int}$ = 0.015) of which 4339 had $I \geqslant 3\sigma(I)$ and were used for the calculations. The structure was solved by Paterson method which revealed six independent rhenium atoms in general positions. The remaining atoms were found on successive difference Fourier maps. All atoms were refined anisotropically. The asymmetric unit consists of two half cluster anions located on inversion centers, two half magnesium cations also located on inversion centers, each of which is surrounded by three water molecules and two more free water molecules in a general position. The cluster core face-capping atoms were considered disordered and their positions were refined with sites occupancies of 3/4 for sulfur and 1/4 for chlorine atoms. Other crystallographic data are available as supplementary material.

Liquid secondary ion mass spectroscopy

The compounds were analyzed at the University of Zaragoza by using LSIMS. Negative LSIMS spectra were recorded on a VG-Autospect (VG Analytical, Manchester, UK) high resolution trisector EBE mass spectrometer. Ions were produced by a 30 keV primary beam of cesium ions, extracted and accelerated by a 8 keV potential. Samples were dissolved in acetonitrile and mixed with the m-nitrobenzyl alcohol (MNBA) matrix on the target. Scans were obtained in the 3000–300 mass range at ca 1500 resolving power (measured as peak width at 5% height) and at a scan rate of 10 s decade^{-1}. Mass calibration was achieved with the use of reference spectra of cesium iodide and a maximum error of 0.3 mass unit was obtained. Helium was used as the collision gas in collision-induced dissociation experiments [32] and the pressure was adjusted to reduce the main beam intensity to 50% of its original value. The CID spectra were recorded by linked scans [33] at constant B/E and B2/E for daughter-ion and precursor-ion spectra, respectively.

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No = SUP 90428 and is available on request from the Document Supply Center; material available: atom numbering, atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, hydrogen atoms parameters, bond lengths and angles, for $ZnRe_6S_6Cl_8$ (6 pages), $Ca(H_2O)_7Re_6S_6Cl_8 \cdot 3H_2O$ (11 pages), $\{Ca_{1/2}(H_2O)_3(H_2O)_{2/2}\}_2Re_6S_6Cl_8$ (9 pages) and $Mg(H_2O)_6Re_6S_6Cl_8 \cdot 2H_2O$ (12 pages).

Acknowledgments

A European Union Human Capital and Mobility postdoctoral fellowship (SU) and a Bourse de Formation par la Recherche of the Ministère de la Recherche et Enseignement Supérieur (JCG) are gratefully acknowledged.

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