

How Solids Can Be Obtained from the Molecular $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ Building Block

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Self-condensation of the $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ building unit under addition of OH^- ions gave the neutral cyclic $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_6]$ wheel. In the presence of assembling groups such as phosphates, arsenates, and oxalates, the Mo_2 -building unit led to anionic wheels differing by their nuclearity, shape, and charge. Solids were derived by tuning the type of associated cations ranging from isolated species to 3D arrangements and layered structures. By functionalization of the $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ precursor by oxalate, discrete compounds having open or cyclic structures as well as infinite solids were specifically designed. © 2000 Academic Press

INTRODUCTION

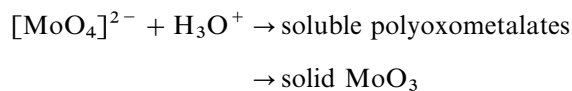
Until recently the domains of molecular chemistry and solid state chemistry were considered as clearly separated, the natures and sizes of the objects manipulated in each field being as different as the concepts developed to describe them. Induced by the need for energy economy and in the interest of using more rational routes for the design of new types of solids, solid state chemistry is evolving from traditional ways of syntheses under extreme conditions of temperature and pressure to using mild conditions, RT reactions, use of soluble precursors (chimie douce), and hydrothermal and solventothermal syntheses. Great attention is being placed on the design of the shape of inorganic molecules to tailor properties for specific applications. Thus the syntheses and characterization of sulfur-containing compounds are of current interest for their implications in modern trends of chemistry related to the hydrodesulfurization process (1), hydrogenation catalysis (2), and inorganic and bioinorganic fields (3). Recent works in the field of metal chalcogenides have been reported in connection with the design of microporous and mesoporous materials, polymer-layered containing sulfides, syntheses of MoS_2 nanotubes (4).

The building block method can really be used to elaborate new solids based on molecular materials under the

condition of possessing a chemically stable and geometrically adapted building block and having a convenient and easily reproducible method of preparation of the building unit.

A good illustration of the relation which can exist between soluble species relevant to molecular chemistry and solid state chemistry is the acidification of metalates with a view to preparing sophisticated oxide frameworks built on 3D-directing agents. The driving force of the reaction is the lowering of the charge through an acidobasic process which makes the formation of the neutral solid possible.

Between the anionic precursor and the final neutral solid, an intermediate domain exists, namely the domain of polyoxometalates, comprising a large number of complex anions resulting from the connections via corners, edges and/or faces of MO_6 octahedra (5). The enchainments between metallic centers and oxygen are generally of oxo type ($M\text{-O-M}$) for $M = \text{Mo}, \text{W}$ (d^0 configuration), or hydroxo type for lower oxidation states (6).



A symmetric method of condensation consists of carefully adding a base to a solution of a cationic precursor in order to induce and control the decrease of the initial positive charge.

We have transposed this type of reaction to sulfur chemistry with the aim of preparing soluble polythiometalate precursors of sulfur-containing solids. The first challenge was to design the good building block susceptible to generate the expected precursors by polycondensation. According to our experience in Mo–S chemistry (7), the $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ dication was chosen as starting material, the lowering of the initial charge being induced by addition of KOH or NaOH. A Mo–OH–Mo bonding scheme is thus expected starting from a reduced Mo(V) ion.

We have chosen to present here a minireview limited to our recent contributions centered on the elaboration of

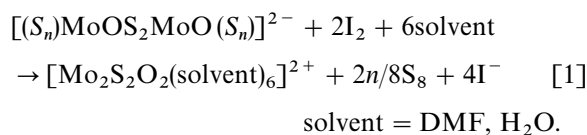
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solids derived from soluble molecular precursors and relevant of the building block method.

PREPARATION AND CHARACTERIZATION OF THE [Mo₂S₂O₂]²⁺ BUILDING UNIT

Many complexes of molybdenum containing the formal {Mo₂S₂O₂}²⁺ central core have been published since the pioneering works of Spivack *et al.* (8). The chemistry of these complexes has been widely studied on the basis of molecular chemistry and was recently reviewed by D. Coucouvanis, one of the main actors in this field (9).

The [Mo₂S₂O₂]²⁺ precursor was obtained from the selective oxidation of the terminal (S_n)²⁻ n = 2, 4 ligands in the [(S_n)MoOS₂MoO (S_n)]²⁻ anion by iodine, in aqueous solution, according to equation [1]. This protocol was initially described for DMF medium (10) and adapted by us to aqueous solutions.



This redox reaction is remarkable for transforming the [(S_n)MoOS₂MoO (S_n)]²⁻ nucleophile into the strong [Mo₂S₂O₂(H₂O)₆]²⁺ electrophile. The dithiocation represents a quite perfect example of reactive building block with respect to its geometry, electronic structure, and chemical stability. As expected, the [Mo₂S₂O₂(H₂O)₆]²⁺ cation is stable in acidic medium down to weak values of pH. Figure 1a shows the overall geometry of the dithiocation in its soluble form in water and Fig. 1b shows the orbital arrangement within the {Mo₂S₂O₂} core. The orbital arrangement was deduced from the results of the calculations of Chandler *et al.* (11) and from our own recent calculations (12) carried out on γ-[SiW₁₀O₃₆Mo₂O₂S₂]⁶⁻ (13a) and from the reactivity of derivatives structurally based on this fragment (13b).

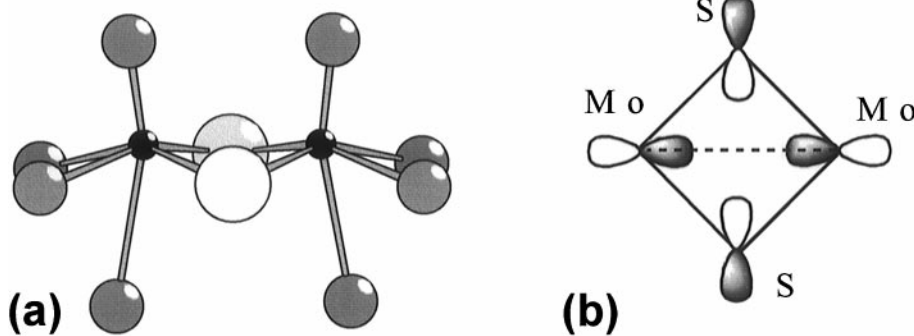
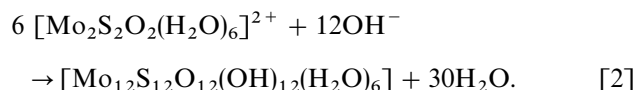


FIG. 1. (a) Representation of the [Mo₂S₂O₂(H₂O)₆]²⁺ building block: Mo atoms, black spheres; S atoms, white; O atoms, medium gray. (b) Schematic representation of the orbital overlapping in the Mo–Mo bond.

SELF-CONDENSATION OF THE [Mo₂S₂O₂(H₂O)₆]²⁺ BUILDING UNIT

Characterization of the Neutral [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆] Cluster

Soluble polyoxoanions are generally obtained by acidification of monomeric oxoanions, WO₄²⁻, MoO₄²⁻, VO₄³⁻. The polycondensation reaction can be carried out in the presence of templating agents (PO₄³⁻, SiO₄²⁻) which led the so-called Keggin anion family (5). The reaction we propose here is symmetric for being based on the addition of a base to the cationic [Mo₂S₂O₂(H₂O)₆]²⁺ precursor and is illustrated by



A microcrystalline powder was obtained by direct addition of KOH to a mixture of [Mo₂S₂O₂(H₂O)₆]²⁺ and KI (10) until pH 2.5–3. After recrystallization in water, yellow crystals were isolated and their structure established by single-crystal X-ray diffraction study (14). The most striking feature of the structure of the neutral dodecameric [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆], represented in Fig. 2, is the cyclic arrangement of the 12 Mo atoms. Six {Mo₂S₂O₂} building units are connected via hydroxo-double bridges delimiting a central cavity of 11 Å. The pocket of the cavity is lined by six water molecules which are labile enough to be easily and rapidly replaced by anionic groups (see Reaction with Phosphates, below). The formation of the wheel really represents a nice example of the building block process since the acidification of the wheel regenerates the [Mo₂S₂O₂(H₂O)₆]²⁺ precursor.

Reaction with Phosphates

The reaction of [Mo₂S₂O₂(H₂O)₆]²⁺ with phosphates is closely dependent on the stoichiometry. We first examine

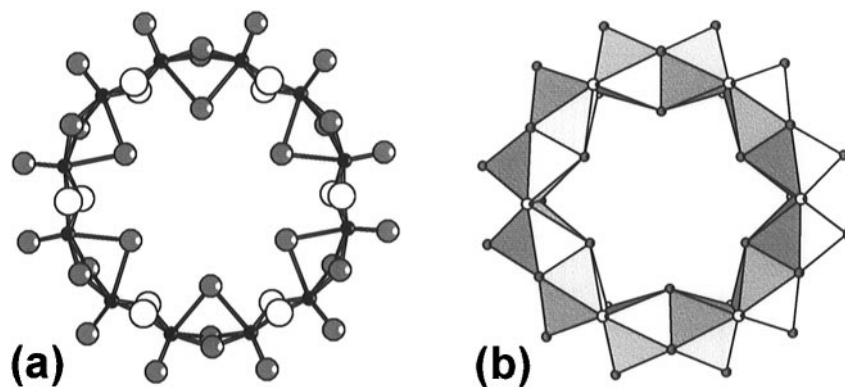
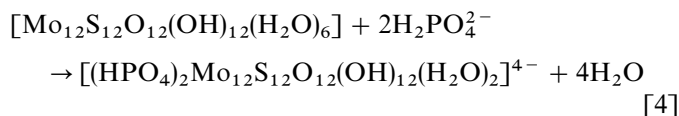
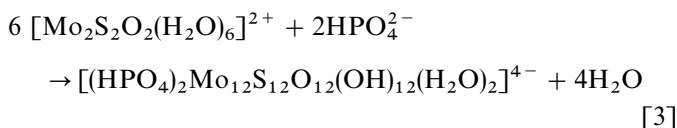


FIG. 2. Representation of $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_6]$ wheel: (a) ball and stick view; (b) polyhedral view showing the edge- and face-sharing connections.

the results obtained with low phosphate/precursor values, $2 < \text{PO}_4/\text{Mo}_2 < 4$.

Characterization of $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_2]^{4-}$

Synthesis. The diphosphato $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_2]^{4-}$ anion was obtained in aqueous solution by direct addition of $\text{H}_2\text{PO}_4^{2-}$ phosphate ions, abbreviated to P_2Mo_{12} , on the preformed wheel $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_6]$ or by direct condensation of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ with the assembling $\text{H}_2\text{PO}_4^{2-}$ group, by addition of sodium hydroxide. Both solutions exhibit about pH 5 the same ^{31}P NMR spectrum and led after crystallization to the same compound in comparable yield (15). Equations [3] and [4] represent the two reaction schemes:



Another phosphato-species exists in solution in equilibrium with P_2Mo_{12} . After being characterized in solution by ^{31}P NMR measurements (15), $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_2]^{4-}$ was obtained as single monocystals.

Molecular description. The molecular structure of $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{11}(\text{H}_2\text{O})_2]^{4-}$ is represented in Fig. 3a. The $\{\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}\}$ cyclic skeleton of the wheel has been retained after the direct substitution of water by phosphates, and the same result could be obtained by direct self-condensation of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ in the presence of phosphates.

As observed in the Mo_{12} wheel, two types of Mo–Mo distances are observed, short metallic separations (2.8002–2.8153 Å) within the $\text{Mo}_2\text{S}_2\text{O}_2$ building block, confirming that the metal–metal bond has been retained, and

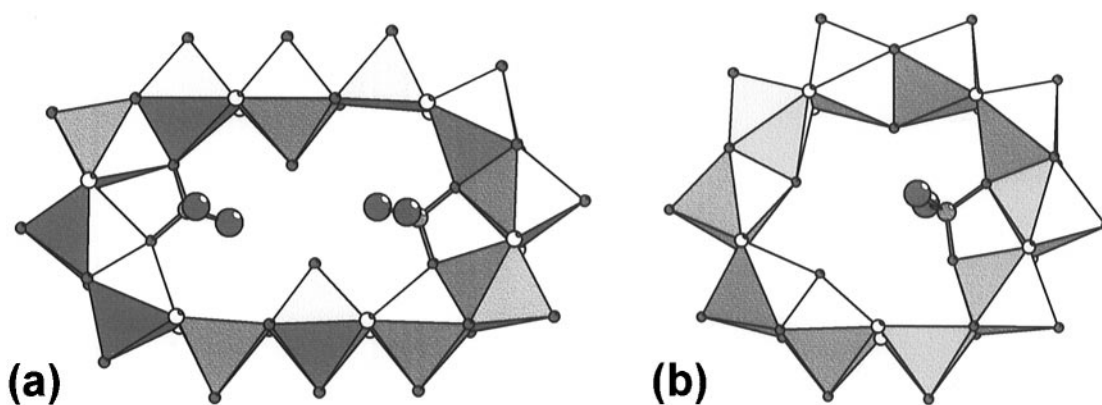


FIG. 3. Molecular representations of: (a) $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{11}(\text{H}_2\text{O})_2]^{4-}$ and (b) $[(\text{H}_2\text{PO}_4)[\text{Mo}_{10}\text{S}_{10}\text{O}_{10}(\text{OH})_{10}(\text{H}_2\text{O})_2]^{2-}$.

longer interblock Mo–Mo distances of 3.226–3.299 Å. Two phosphate ions are symmetrically located in the cavity, each phosphato-group being bonded to four adjacent Mo atoms through two equivalent P–O–Mo bridges. Of the two terminal P–O bonds, one is protonated (1.576 Å), while the other is free of proton with respect to the short P–O bond (1.423 Å). The mode of coordination of these phosphates induces a strong deformation of the 12-membered ring from strictly circular in the parent wheel to elliptical. This deformation can be attributed to two concomitant effects, one is the pincer effect of the phosphates acting as chelating groups, and the other is related to the electrostatic repulsion between the diametrically opposite phosphates. Because of steric constraints due to the presence of phosphates, two Mo atoms have lost their trans water molecule and display a pyramidal geometry. Those geometrical features, namely the cyclic deformation and variable geometry sites, illustrate

the great adaptation of the ring due to the flexible edge–edge connections within the building blocks.

The molecular arrangement of $[(\text{HPO}_4)\text{Mo}_{10}\text{S}_{10}\text{O}_{12}(\text{OH})_{11}(\text{H}_2\text{O})_2]^{2-}$ is represented in Fig. 3b. It corresponds to a new cyclic monophosphato-wheel in which the neutral $\{\text{Mo}_{2n}\text{S}_{2n}\text{O}_{2n}(\text{OH})_{2n}\}$ backbone has been retained. As for P_2Mo_{12} , an inner molecule of water has been displaced, but the geometry of the 10-membered ring remains close to that of the Mo_{12} parent for displaying edge- and face-sharing connections.

3-D description. $\text{Na}_4[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_2] \cdot 27\text{H}_2\text{O}$ exhibits a three-dimensional arrangement in which sodium cations and anions are mutually connected. In Fig. 4 are given two representations of the 3D structure along the c and b axes, respectively. In the ab plane, sodium atoms and phosphato-wheels are connected

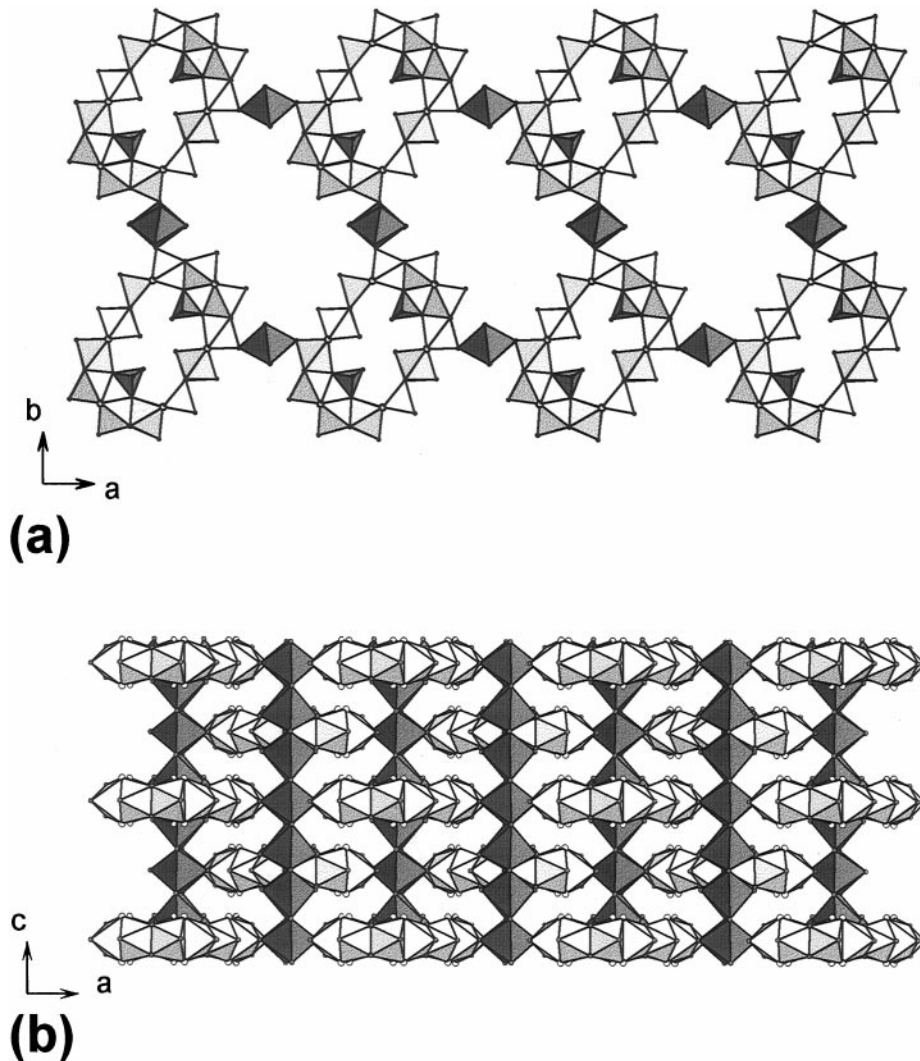


FIG. 4. Three-dimensional arrangement of P_2Mo_{12} : (a) view in the ab plane; (b) view along the b axis showing the Na pillars.

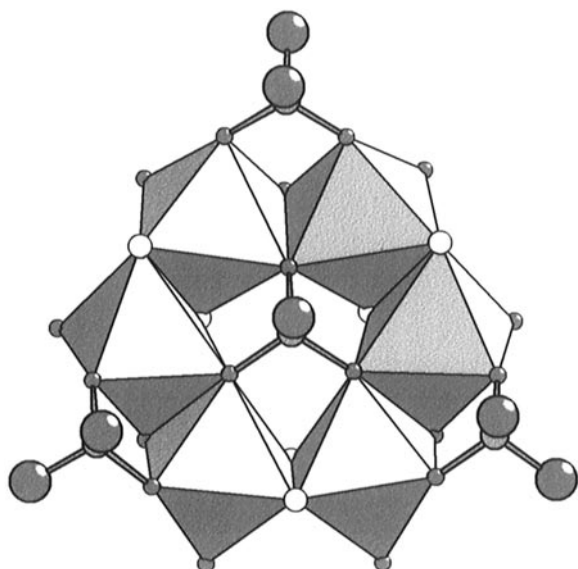


FIG. 5. Molecular geometry of the $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ anion.

through oxo groups, the octahedral coordination at the Na^+ ions being achieved by water molecules.

The connections between polyanionic wheels and sodium atoms delimit large cavities of $15 \times 9 \text{ \AA}$ forming 20-membered rings. Sodium atoms are arranged in infinite chains parallel to the c axis, the $[(\text{HPO}_4)_2\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_2]^{4-}$ polyanions being distributed along the Na^+ pillars.

Characterization of $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$

In the presence of large excess of phosphate ($\text{PO}_4/\text{Mo}_2 = 180$) and at pH 5, ^{31}P NMR analyses revealed that only a single phosphate-containing species is present in solution, single crystals of which were obtained by addition of RbCl (16).

Molecular structure. The molecular structure of $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ is comparable to that of the fully oxygenated compound $[(\text{HPO}_4)_4\text{Mo}_6\text{O}_{12}(\text{OH})_3]^{5-}$ widely described in the literature (17). Three equivalent $[\text{Mo}_2\text{S}_2\text{O}_2]^{2+}$ building units are mutually connected by an outer phosphate and by a hydroxo group.

The six Mo atoms are coplanar and are engaged in alternating short Mo–Mo intrablock distances (2.8 \AA) and long Mo–Mo extrablock distances (3.2 \AA). The connections between the building units are all edge-sharing conversely to the enchainments described for $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_6]$ in which face-sharing connections were observed. The overall geometry, represented in Fig. 5, can be described as a hexanuclear wheel encapsulating a central phosphato group stabilized by three additional peripheral phosphates. The four PO_4 groups are stereospecifically distributed on the same side of the plane defined by the six Mo-atoms. A P–O bond of the peripheral phosphate is protonated while the remaining one is attributed to a non-protonated P=O on the basis of the bond lengths. The central phosphate is monoprotonated in agreement with the chemical analysis.

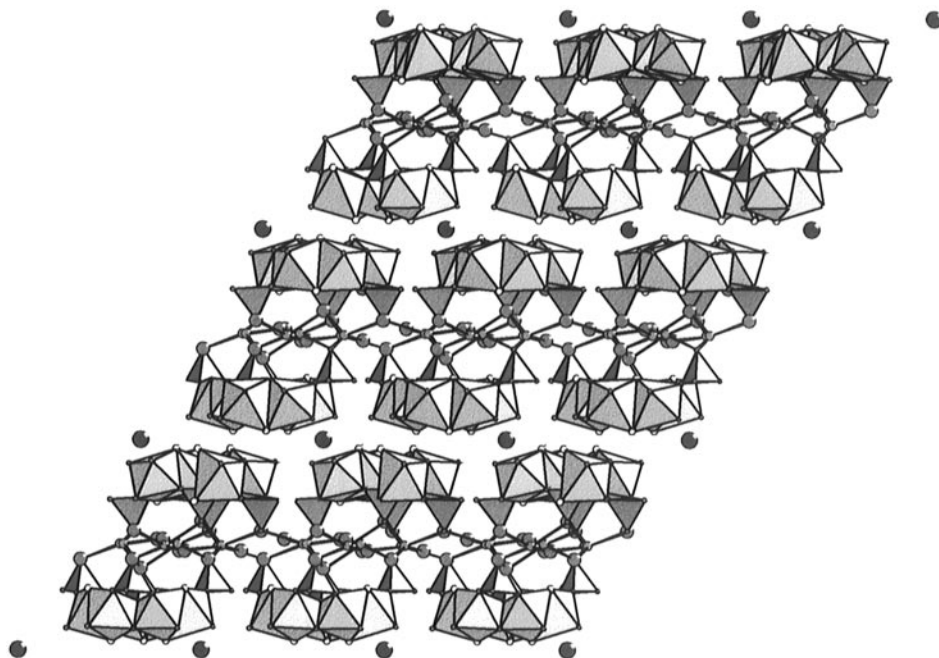


FIG. 6. Evidence of the layered structure in $\text{Na}_{1.75}\text{Rb}_4\text{Cl}_{0.75}[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]$. Cl atoms, gray spheres. Interleaved Rb atoms have been omitted for clarity.

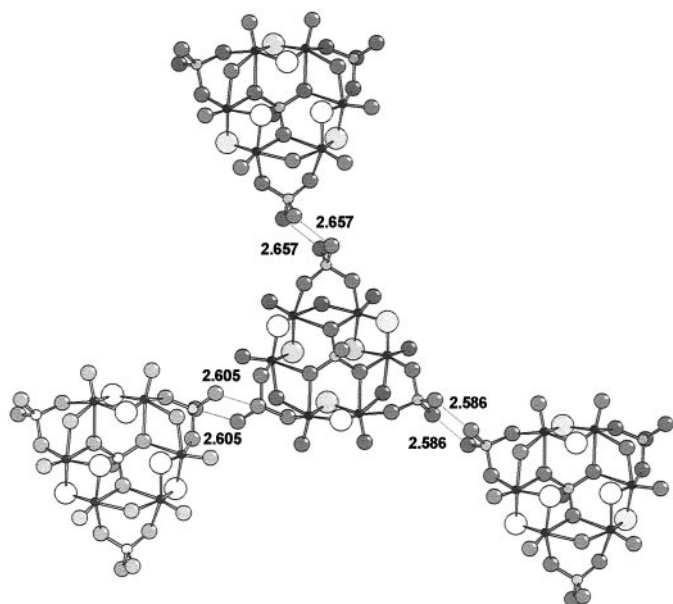


FIG. 7. Hydrogen bonding pattern in $\text{Rb}_{3.5}\text{Na}_{1.5}[(\text{AsO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]$.

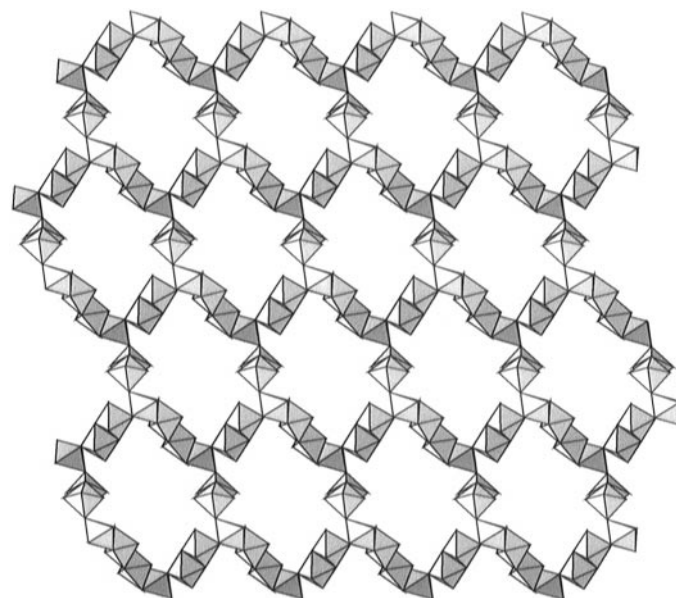


FIG. 9. Representation of the pseudohoneycomb array formed by the condensation of Na octahedra.

3-D description. The 3D-arrangement of $\text{Na}_{1.75}\text{Rb}_4\text{Cl}_{0.75}[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3] \cdot 8\text{H}_2\text{O}$ is quite complicated since the ionic stacking results from the presence of $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ and Cl^- anions balanced by Rb^+ and Na^+ cations. The Rb^+ cations ensure the connections between $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ anions, each

rubidium being bonded to polyanions by oxygen and sulfur atoms, defining planes parallel to the crystallographic (001) plane. The layers are interleaved alternately by sodium cations and chlorides located at the center of a perfect octahedron of Rb atoms. The Rb-Cl distances in the solid (3.26 Å) have values close to that of the close packed lattice of RbCl (3.28 Å).

Figure 6 shows the layered structure of $\text{Na}_{1.75}\text{Rb}_4\text{Cl}_{0.75}\text{Cl}_{0.75}[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3] \cdot 8\text{H}_2\text{O}$. The same type of molecular arrangement was obtained with arsenic replacing phosphorus (16). Because of a different distribution of protons among the peripheral XO_4 groups, the 3D structure is completely different. In this case, the dimensionality of the structure is ensured by strong hydrogen bonding involving the protonated AsO_4 peripheral groups. Each $[(\text{HASO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ is connected to three others through strong $\text{As}=\text{O} \cdots \text{H}-\text{O}-\text{As}$ (see Fig. 7).

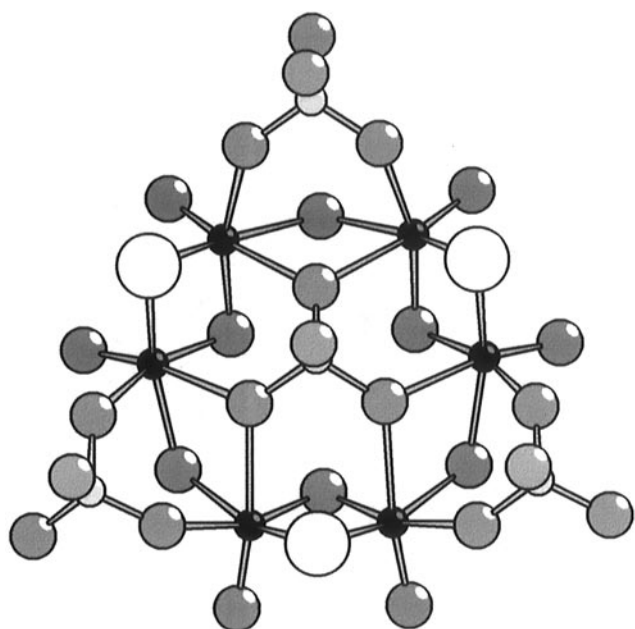


FIG. 8. Ball and stick representation of the half-substituted $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_3\text{O}_9(\text{OH})_3]^{5-}$ anion.

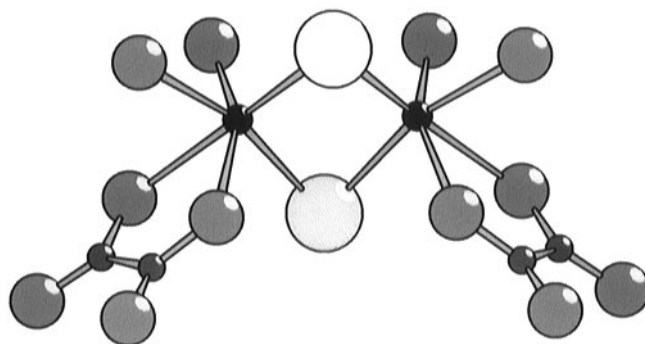


FIG. 10. Ball and stick representation of the discrete $[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ anion.

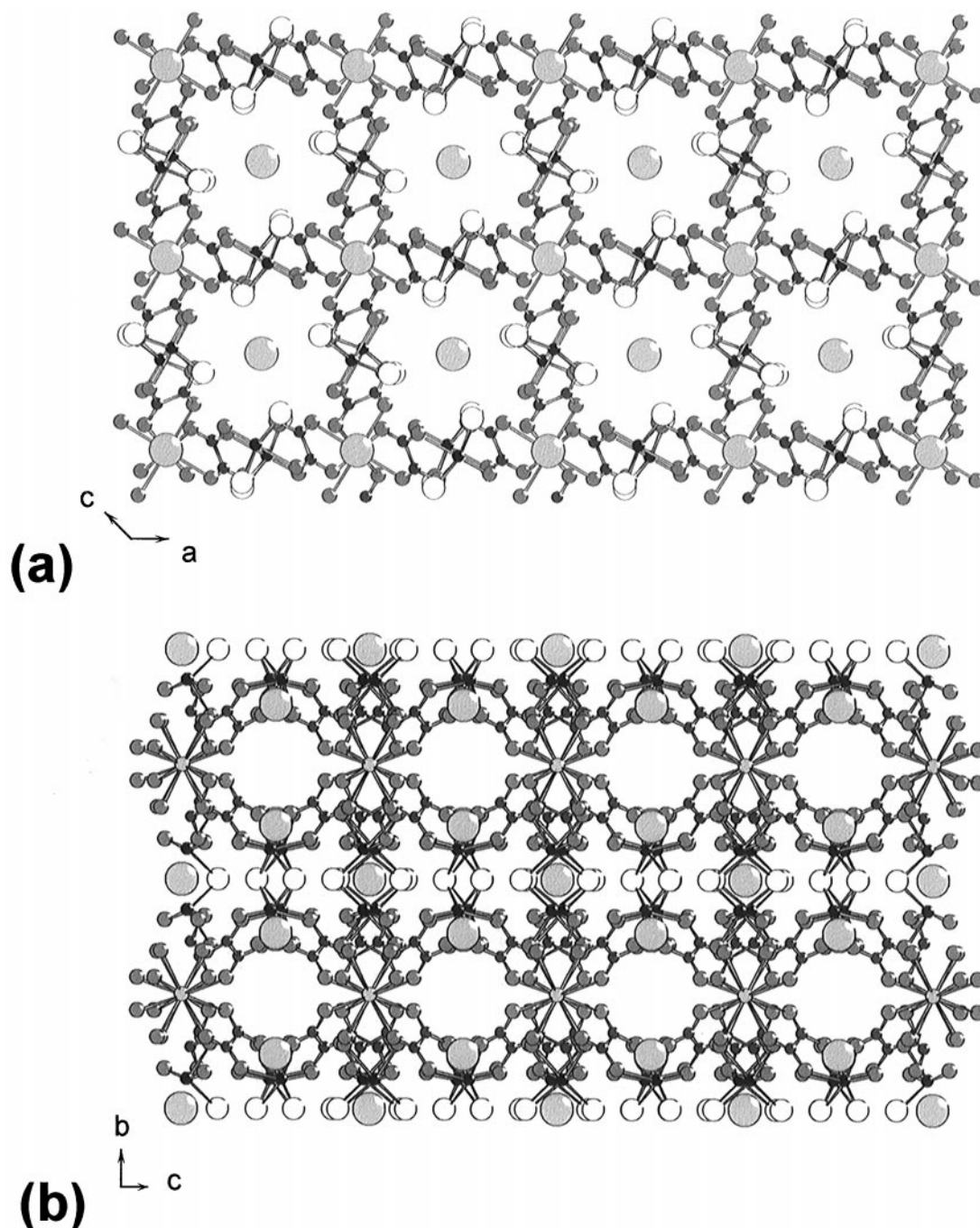


FIG. 11. Three-dimensional arrangement in $\text{NaCs}_3[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$. Cs atoms, large gray spheres. (a) View along the b axis; (b) view along the a axis.

Partial Desulfurization of $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$

When the synthesis solution of $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$ is heated for 17 h at 70°C , three sulfur atoms are successively removed to give the half-substituted $[(\text{HPO}_4)_4\text{Mo}_6\text{S}_3\text{O}_9(\text{OH})_3]^{5-}$ anion depicted in Fig. 8. A striking feature of the molecular arrangement is the distribution of the sulfur atoms on the same side of the plane

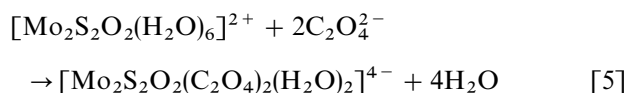
defined by the Mo atoms, at the opposite of the four phosphate groups. ^{31}P NMR experiments have shown the S/O substitution is progressive and regioselective (18).

3D structure. Sodium cations octahedrally coordinated by water molecules and terminal oxygen atoms of the $\text{Mo}=\text{O}$ and $\text{P}=\text{O}$ bonds of the anion ensure the connections between the hexanuclear anionic units. These Na^+ centered

octahedra condense to form a remarkable pseudohoneycomb array of 18 member rings, represented in Fig. 9.

Reaction with Oxalates

We have developed another rational approach to design infinite solids derived from the same $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$. This new approach consists in the functionalization of the precursor by strongly chelating ligands, oxalates for example (19). Equation [5] illustrates the stoichiometries used in the first example of functionalization:



The interest in modifying the $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ precursor by addition of anionic ligands lies in the control of the overall negative charge of the building unit with the aim of selecting the number (and type) of associated cations introduced in the solids. This possibility of controlling the charge is probably here the most important factor in the elaboration of 3D solids, since the stability of these solids is relevant to ionic interactions.

$[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{4-}$ a New Building Block

Reaction of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}/\text{H}_2\text{C}_2\text{O}_4$ (1/4), NaOH, and CsCl at pH 1.5 and $T = 50^\circ\text{C}$ makes it possible to isolate in the solid state red cubic crystals of $\text{NaCs}_3[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]_2 \cdot 6\text{H}_2\text{O}$ (19). Each sodium cation is linked to four $[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ units through the oxygen atoms of the two terminal

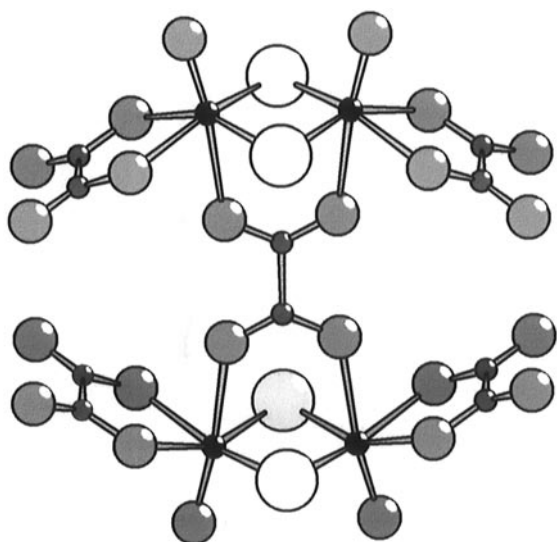


FIG. 12. View of the $[\text{Mo}_4\text{S}_4\text{O}_4(\text{C}_2\text{O}_4)_5]^{6-}$ anion illustrating the templating and chelating roles of oxalate.

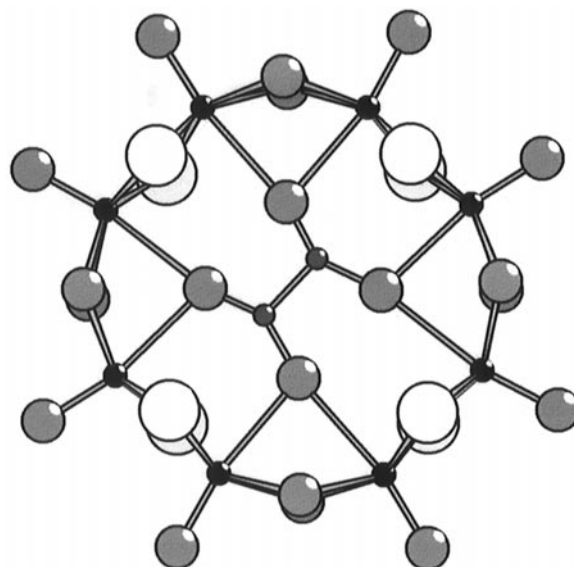


FIG. 13. Ball and stick view of the cyclic $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8]^{2-}$ anion.

oxalates. A representation of $[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ is given in Fig. 10.

The arrangement of the four molecular anions around the Na^+ cations results in interconnected chains which delimit cavities of about $16 \times 6 \text{ \AA}$. The center of the cavities is occupied by Cs^+ cations. The 3D structure is represented in Fig. 11.

By replacing sodium with cesium, the composition of the tetraanion remains unchanged but the resulting $\text{Cs}_2[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ compound is differently organized in the solid state. $[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ anions and Cs^+ cations are clearly separated without any bonding interactions, which leads to a zero-dimensional arrangement (20).

By changing the pH from 1.5 to 4 but conserving the same precursor/oxalate stoichiometry (1/4) another discrete species is obtained in the presence of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]^{2+}$ cations. The geometry of the anion is represented in Fig. 12.

In $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_3[\text{Mo}_4\text{S}_4\text{O}_4(\text{C}_2\text{O}_4)_5]$ (19) the central oxalato anion has the role of templating group as yet observed for the encapsulated phosphate, arsenate, and iodide anions (21), and in addition, it also acts as a chelating group as reported for $[\text{Mo}_2\text{S}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$. In the solid state the structure is viewed as the packing of discrete species, $[\text{Mo}_4\text{S}_4\text{O}_4(\text{C}_2\text{O}_4)_5]^{6-}$ anions, and cations having no contact.

The oxalato group can also be used as only a templating agent (19). To obtain this result it is obvious that the oxalate/ $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ ratio has to be lowered, but the pH also needs to be changed. For pH 5.5–6 and a $[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6]^{2+}$ /oxalate molar ratio of 4/1, the cyclic $[\text{Mo}_8\text{S}_8\text{O}_8(\text{OH})_8(\text{C}_2\text{O}_4)]^{2-}$ dianion anion

was obtained associated as K^+ or $[H_3N(CH_2)_3NH_3]^{2+}$ ions.

The structure consists of well separated dianions and cations. The anionic geometry represented in Fig. 13 is formed of a cyclic octagonal arrangement of Mo atoms delimiting a central cavity occupied by the templating oxalato group. Four $[Mo_2S_2O_2(H_2O)_6]^{2+}$ building units are connected by hydroxo-groups like in the former wheels encapsulating anions described above in this paper.

All these examples illustrate the versatility of the $[Mo_2S_2O_2(H_2O)_6]^{2+}$ building block which can generate different architectures by varying the pH of the solutions and/or the stoichiometry of additional anions. The wheels are relevant to molecular recognition for selectively encapsulating anions of various charge and shape but they also are relevant to solid state chemistry for giving organized solids exhibiting a true porosity.

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