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Review

# Trinuclear molybdenum cluster sulfides coordinated to dithiolene ligands and their use in the development of molecular conductors

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ABSTRACT

The present article reviews synthetic approaches to efficiently prepare $Mo_3S_7$ clusters coordinated to 1,2-bis-dithiolene ligands of general formula $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ where dithiolene stands for tfd (bis(trifluoromethyl)-1,2-dithiolene), bdt (1,2-benzenedithiolene), mnt (maleonitriledithiolene), tdas (1,2,5-thiadiazole-3,4-dithiolene), dmid (1,3-dithia-2-one-4,5-dithiolene), dmit (1,3-dithia-2-thione-4,5-dithiolene) and the diselenolene dsit (1,3-dithia-2-thione-4,5-diselenolene). These $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ dianions serve as starting materials to access new dithiolene clusters featuring $Mo_3S_4$ and $Mo_2O_2S_2$ cluster cores. The electrochemical and spectroscopic properties as well as solid state structures of $Mo_3S_7$/dithiolene compounds are also described. These $C_3$-symmetry $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ molecules inherently possess degenerate frontier orbitals and display a rich structural diversity due to the electrophilic character of the three sulfur atoms in axial positions. These characteristics make the $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ dianions, versatile targets for the development of new molecular conductors. Several examples of hybrid charge-transfer salts based on TTF-donors and $[Mo_3S_7(\text{dithiolene})_3]^{2-}$/$[Mo_3S_7X_6]^{2-}$ dianions (X = Cl, Br) are discussed as well as the preparation of the first family of cluster-based single-component magnetic conductors of formula $Mo_3S_7(\text{dithiolene})_3$.

## 1. Introduction

The chemistry of transition metal 1,2-bis-dithiolene complexes has long been motivated by its bioinorganic significance and its connections to material science [1,2]. In this last field, metal bis 1,2-dithiolene complexes have been intensively studied as building blocks of molecular conductors and have provided unconventional physical properties that include semiconductors, metals or superconductors [3], thus representing a separate category of conducting materials intensively explored in the last two decades [4–12].

Most efforts have been concentrated in square planar transition metal $[M(\text{dithiolene})_2]^{n-}$ complexes which possess a delocalized electron system at the $M(C_2S_2)_2$ planar central core and may exist in different formal oxidation states for the same metal ion. The minimal requirements for the design of molecular conductors are the formation of conduction bands and the generation of charge carriers. In a molecular systems based on $[M(\text{dithiolene})_2]^{n-}$ anionic components, this can be achieved by arranging open-

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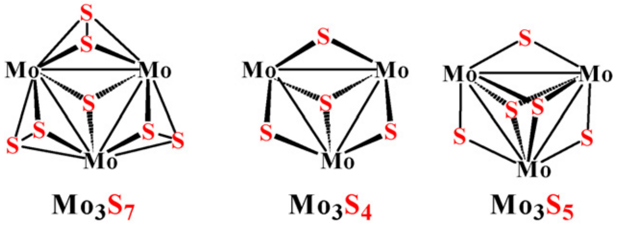
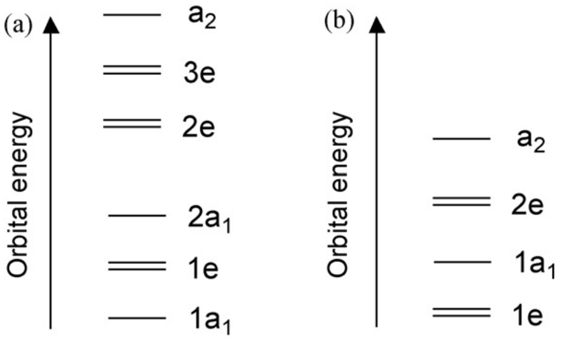


**Fig. 1.** Structural types of sulfur-rich trinuclear $Mo_3$ clusters.



**Scheme 1.** Simplified MO diagram for $Mo_3S_4$ (a) and $Mo_3S_7$ (b) clusters with an idealized $C_{3v}$ symmetry.

shell molecules (radicals) in the solid state so as to enable intermolecular electron transfer and a great deal of work has been reported using different charge compensating cations. Up to now around 10 two-component dithiolene-based compounds, all of them comprising $[M(dmit)_2]^{n-}$ anions, have been reported to exhibit superconductivity. In this decade, Kobayashi's group have described various conducting neutral $M(dithiolene)_2$ complexes containing TTF dithiolene ligands [3,13], which illustrate that charge carrier generation is also possible in single-component molecules with small HOMO–LUMO gaps.

Despite the use of mononuclear metal centers is still dominant in the preparation of molecular conductors, continuous efforts of cluster chemists are being made to open this field. In the past years, our group has been involved in the development of synthetic strategies for the preparation of highly symmetrical new cluster topologies functionalized with electroactive ligands on the basis of the rationale that their large size combined with structural and electronic diversity may lead to novel structural and physicochemical properties. In this sense, group 6 metal cluster chalcogenides constitute a large and rapidly growing family of inorganic compounds with applications in multidisciplinary fields [14]. Most of the research presented in this review involves dithiolene trinuclear clusters containing a $Mo_3S_7$ core with a $C_{3v}$ symmetry and a capping sulfur atom and to a lesser extend the topologically related $Mo_3S_4$ cuboidal clusters. In general, triangular $Mo_3$ clusters can be classified depending on the number of capping ligands. Two different structural types exist for complexes with one capping ligand and these are represented in Fig. 1.

The main difference between complexes $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3]$ (or $Mo_3S_7$) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3]$ (or $Mo_3S_4$) is the nature of the bridging ligands, dichalcogenides ($\mu$-$S_2$) or chalcogenides ($\mu$-S), respectively. In addition, the chalcogen atoms in axial positions in $Mo_3S_7$ complexes (depicted above the $Mo_3$ plane), represented in Fig. 1 (left), have an electrophilic character not observed for the $Mo_3S_4$ complexes, shown in Fig. 1 (middle). The central core in $Mo_3S_4$ compounds adopts an incomplete cubane-type structure with the molybdenum atoms located in most cases in an octahedral environment of three chalcogen atoms and different outer ligands except for the dithiolene complexes in which the coordination number around the metal equals five if one neglects the metal–metal bond. A third structural type has recently been found for molybdenum trinuclear sufides coordinated to dithiolene ligand with two capping chalcogen atoms as seen for the $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3]$ structure type (see Fig. 1 right).

In all complexes included in this review article, the metal has a formal oxidation state of +4 that for the molybdenum trinuclear clusters leaves six metal electrons for the formation of the intermetallic bond [15,16]. A simplified description (see Scheme 1a) of the metal to metal bonding in the $Mo_3S_4$ trinuclear complexes showed that the molecular orbitals concerned are as follows: three bonding $1a_1$ and 1e orbitals, one $2a_1$ orbital which is essentially M–M non-bonding and five antibonding (2e, 3e and $1a_2$) orbitals [15]. For $Mo_3S_7$ clusters in a strictly $C_{3v}$ symmetry, the molecular orbital scheme features three bonding 1e and $1a_1$ orbitals, and three antibonding (2e and $1a_2$) orbitals (see Scheme 1b) [15]. According to these schemes, these trinuclear $Mo_3S_7$ and $Mo_3S_4$ clusters should be stable when there are six metal "d" electrons available to enter the low energy $1a_1$ and 1e metal based orbitals, which correspond to three metal–metal bonds. The electronic nature of the outer ligands may alter the orbital energy ordering of this simplified scheme.

While some comprehensive reviews dealing with $Mo_3S_7$ and $Mo_3S_4$ cluster chemistry can be found elsewhere [17–22], the present review deals with the combination of dithiolene ligands to these $Mo_3S_7$ and $Mo_3S_4$ cluster units. This review attempts to summarize all the work that has been carried out on molecular materials that combine trinuclear $Mo_3$ cluster sulfides with 1,2-bis-dithiolene ligands or with TTF-derivatives. Aspects such as synthesis, structure, reactivity, electrochemical and electronic properties of these compounds are included. In the last part, we summarize the application of these complexes for the construction of molecular conducting radical salts and single-component molecular conductors.

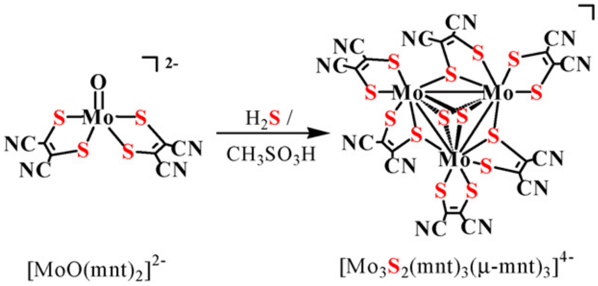
## 2. Coordination of dithiolene ligands to trinuclear $Mo_3$ cluster units and their transformations to other cluster cores

Among the wide spectrum of preparation routes to transition metal dithiolenes, two general synthetic approaches have been highlighted by Rauchfuss [23]; one of them comprises coordination of previously generated dithiolene ligands to metal centers and the second one involves the participation of transition metals in the assembly of the dithiolenes, usually by the reaction of metal sulfides or disulfides with alkynes. These two approaches also apply to transition metal cluster complexes when replacing the metal center by a cluster core, as we will detail later on in this section, although their chemistry remains less developed and has yet to reach the level of efficiency attained with their mononuclear congeners.

In addition, a significant number of synthetic entries to polynuclear transition metal complexes bearing dithiolene ligands have been reported that involve the self-assembly of lower nuclearity species or the fragmentation of compounds of higher nuclearity. This can be attributed to the tendency of the dithiolene ligands to coordinate in several (and often unexpected) fashions, thus decreasing or increasing the nuclearity of the initial complex. Some examples illustrating these two possibilities are briefly introduced in this section. In certain cases the dithiolene ligand may act as a source of sulfide ligand that bridges two or more metal atoms as in

$(n\text{-}Bu_4N)_2[Nb_2(dmit)_4(\mu\text{-}S_2)_2]$ prepared via reaction of $NbCl_5$ with $(n\text{-}Bu_4N)_2[Zn(dmit)_2]$ [24].

The assembly of polynuclear metal complexes starting from lower nuclearity precursors, usually mononuclear complexes, is illustrated with examples such as the dinuclear rhenium $(PPh_4)_2[Re_2(\mu\text{-}dmit)(dmit)_4]$ [25], or thallium $(Et_4N)_2[Tl(\mu\text{-}bdt)_2]_2$ compounds [26], several tri- or tetranuclear $[Au_3(\mu_3\text{-}dmit)(PPh_3)_3]^+$ or $Au_4(\mu\text{-}dmit)_2(\mu\text{-}dppm)_2$ [27], $(n\text{-}Bu_4N)_4[Ag_4(\mu\text{-}mnt)_4]$ [28], and $(Cation)_2\{Cu_4(dithiolene)\}$ [29–32] clusters or a hexanuclear homoleptic $Pd_6$ dithiolene-bridged complex reported by Stiefel [33]. The synthesis of all these compounds starts from previously generated dithiolenes and in all cases, the ligand acts in a bridging mode in the final compound. Of special relevance in the context of this review article is the synthesis of the $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ cluster via reaction of $[MoO(mnt)_2]^{2-}$ with $H_2S$ in the presence of methanesulfonic acid, featuring three terminal and three bridging dithiolene ligands as represented in Eq. (1) [34].

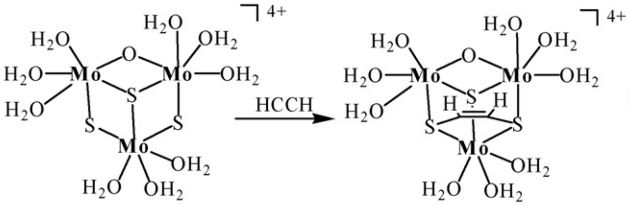


(1)

In contrast to the abundance of sulfur-monocapped $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ and $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cluster types, examples of molybdenum trinuclear cluster compounds with two capping sulfur atoms are restricted to a few examples. Compound $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ is the only dithiolene trinuclear cluster in which the $Mo_3$ triangle is sulfur capped on both sides. The other examples belong to the $Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3$ cluster type with their terminal positions occupied by phosphine ligands [35,36]. Mononuclear metal sulfides such as tetrathiometallates are also useful precursors for the formation of high nuclearity aggregates since terminal sulfur atoms possess a strong tendency to increase their coordination number. Various examples of transition metal cluster dithiolenes are known through reaction of tetrathiometallates of Re [37,38], Mo or W in the presence of alkynes with the concomitant generation of the dithiolene ligand [39]. Although no molybdenum trinuclear cluster sulfide has been obtained by this route, its potential should not be ignored.

Other synthetic entries to polynuclear complexes are conceptually opposite to that illustrated in the previous paragraphs in which the chelating ability of dithiolene ligands is used to break the cluster cores and form reassembled coordination compounds of lower nuclearity. Several dinuclear dithiolene palladium complexes have been synthesized from one-dimensional palladium polymers in the presence of dithiolenes using this procedure [40]. It has to be pointed out that the unsymmetrically dithiolene substituted $[Cd(dmit)(SPh)_2]^{2-}$ complex has also been prepared starting from tetranuclear $[Cd_4(SPh)_{10}]^{2-}$ dianions and "in situ" generated $(dmit)Na_2$, a synthetic approach that the authors refer to as "cluster cracking" reactions [41].

A more rational way to prepare polynuclear/dithiolene complexes relies on the functionalization of preassembled robust polynuclear entities with dithiolene ligands. This functionalization may proceed via addition of alkynes to sulfur-rich polynuclear entities such as dimeric [42,43], or trimeric sulfur-rich molybdenum species [44], or through ligand substitution reactions at the cluster core metal sites, as we shall illustrate below for the $Mo_3S_7$ complexes. Shibahara et al. have reported the preparation of alkenedithiolenes incomplete cubane-type clusters through the reaction of the $[Mo_3S_3O]^{4+}$ aqua ion with acetylene in acidic media according to Eq. (2) (note that metal–metal bonds have been omitted for clarity) [44]. The dithiolene ligand in the resulting $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ cation bridges two Mo atoms through each dithiolene sulfur atom. This synthetic route can also be extended to other $[Mo_3S_4]^{4+}$ clusters with dithiophosphates [45,46] or nitrilotriacetic ligands [47] and their tungsten analogs [48,49].

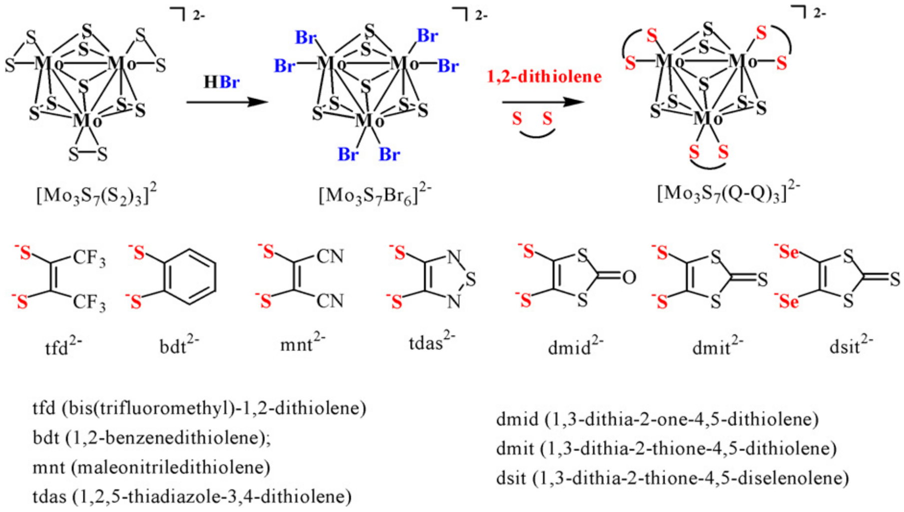


(2)

Derivatives with $Mo_3S_7$ units are readily accessible by ligand exchange reactions on the $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_2Br_6]^{2-}$ cluster anions, both in the solid state and in solution, due to the lability of the bromine ligands. The $[Mo_3S_7X_6]^{2-}$ (X = Cl, Br) starting material can be conveniently prepared by treating molecular $(NH_4)_2[Mo_3S_7(S_2)_3]$ [50], with HBr [51], or by dimensional reduction of polymeric $\{Mo_3S_7X_4\}_n$ phases with molten $PPh_4X$ salts, with $Br_2$ or $Cl_2$, or by mechanochemical activation or gamma-radiolysis in the presence of $Et_4NBr$ salts [52,53]. Among the wide diversity of synthetic routes to transition metal dithiolenes [23], the most general synthetic procedure for dithiolene coordination relies on the use of bis-thioester compounds in the presence of $NaOCH_3$ with metal halides, followed by precipitation with tetralkylammonium salts. However, by using this approach, the synthesis $Mo_3S_7$/dithiolene complexes produces low yields and tedious purification steps in part due to the limited stability of $Mo_3S_7$ clusters in the presence of strong bases.

Ligand substitution on the $[Mo_3S_7Br_6]^{2-}$ dianion using zinc salts of general formula $(n\text{-}Bu_4N)_2[Zn(dithiolene)_2]$ or the $Na_2(mnt)$ sodium salt circumvents the limitation of stability in basic media and usually yields the desired $[Mo_3S_7(dithiolene)_3]^{2-}$ complexes in moderate yield [54–56]. This procedure is also extended to diselenolenes such as dsit by the reaction of the $[Mo_3S_7Br_6]^{2-}$ dianion and $(n\text{-}Bu_4N)_2[Zn(dsit)_2]$ to yield $[Mo_3S_7(dsit)_3]^{2-}$ [57]. Recently, we have reported an improved method for preparing $Mo_3S_7$/dithiolene complexes that relies on the treatment of $(n\text{-}Bu_4N)_2[Mo_3S_7Br_6]$ with an excess of the corresponding tin $(n\text{-}Bu)_2Sn(dithiolene)$ complex to afford the ligand substitution $[Mo_3S_7(dithiolene)_3]^{2-}$ products which are readily isolated in analytically pure form by simple precipitation with diethylether [57]. In this way, the series of $[Mo_3S_7(dithiolene)_3]^{2-}$ dianions, represented in Scheme 2, have been obtained.

Complexes $(n\text{-}Bu_4N)_2[Mo_3S_7(dithiolene)_3]$ having a $Mo_3S_7$ core can be easily transformed to $Mo_3S_4$ complexes. In the presence of reducing agents such as $PPh_3$, $[Mo_3S_7(dithiolene)_3]^{2-}$ dianions undergo conversion of the three disulfide-bridged to sulfur-bridged ligands to yield $[Mo_3S_4(dithiolene)_3]^{2-}$ complexes together with $PPh_3{=}S$ as represented in Scheme 3. These $Mo_3S_4$ complexes degrade in air in almost quantitative yield to afford a series of Mo(V) dimers of formula $[Mo_2O_2(\mu\text{-}Q)_2(dithiolene)_2]^{2-}$ where the oxygen atoms are in a *syn* configuration [58]. This degradation step constitutes an alternative synthetic entry to the ligand substitution approach starting from the dinuclear $[Mo_2O_2(\mu\text{-}S)_2(DMF)_6]I_2$ (DMF = dimethylformamide) and allowed us to access the full series of members encompassing M = Mo, W; Q = S, Se and several dithiolene ligands [58]. Of particular interest is the synthesis of a $[W_2Se_2O_2(dithiolene)_2]^{2-}$ dianion for which dinuclear precursors with labile ligands are not available, thus



tfd (bis(trifluoromethyl)-1,2-dithiolene)
bdt (1,2-benzenedithiolene);
mnt (maleonitriledithiolene)
tdas (1,2,5-thiadiazole-3,4-dithiolene)

dmid (1,3-dithia-2-one-4,5-dithiolene)
dmit (1,3-dithia-2-thione-4,5-dithiolene)
dsit (1,3-dithia-2-thione-4,5-diselenolene)

**Scheme 2.**

highlighting the importance of this cluster degradation synthetic approach.

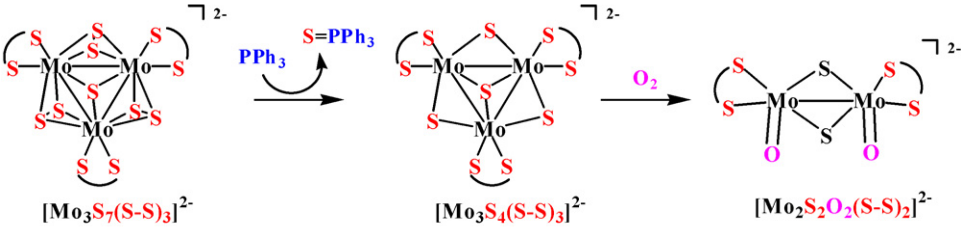
Electrospray ionization mass spectrometry has proved to be a very useful technique to characterize the integrity of the $Mo_3S_4$/dithiolene clusters in solution as well as to unravel mechanistic insights on the degradation step from $Mo_3S_7$ to $Mo_3S_4$ and ultimately to $Mo_2S_2O_2$ clusters highlighted in Scheme 3 [58]. Typically, the transformation of $Mo_3S_7$ to $Mo_3S_4$ cluster cores is immediate as evidenced by the disappearance of the peaks attributed to the $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ dianions in the ESI mass spectrum concomitant with the appearance of the characteristic $[Mo_3S_4(\text{dithiolene})_3]^{2-}$ dianions at lower $m/z$ values. Subsequently, the $Mo_3S_4$ to $Mo_2S_2O_2$ cluster core degradation proceeds much more slowly (ca. 1 h upon stirring in air). A detailed investigation of the gas-phase dissociation of dmit-coordinated complexes with $Mo_3S_4$ and $Mo_2S_2O_2$ cores has also been reported revealing a dominant fragmentation pathway that consists of a two-step breaking (evolving $CS_2$ and $C_2S_2$) of each dmit ligand that can be used as a tool for structural elucidation in related systems. No degradation of the trinuclear $Mo_3S_4$ unit is observed for dmit-coordinated complexes while a symmetric degradation of the metal $Mo_2S_2O_2$ dimer is observed under similar conditions, indicating a more robust $Mo_3S_4$ cluster unit in comparison with its dinuclear homologues. Analogous conclusion has been reported for several $M_3S_4$ clusters decorated with diphosphane [59–61], and methanol ligands [62].

## 3. Structural diversity in $Mo_3S_7$ and $Mo_3S_4$ dithiolenes

The geometry of the $Mo_3S_7$ cluster core in $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ complexes can be described as an equilateral $Mo_3$ unit capped by a $\mu_3$-$S^{2-}$ atom that lies above the metallic plane as illustrated in Fig. 2a for the $[Mo_3S_7(\text{tdas})_3]^{2-}$ dianion [56]. In addition, each side of the triangle is bridged by a $\mu$-$S_2{}^{2-}$ group with three sulfur atoms occupying an equatorial position ($S_{\text{equatorial}}$), essentially in the $Mo_3$ plane, and three axial sulfur atoms ($S_{\text{axial}}$) located out of the metal plane. The metal–metal distance in this cluster unit ranges between 2.76 and 2.79 Å, consistent with the presence of a single Mo–Mo bond and a Mo(IV) oxidation state for the metal.

All $(n\text{-}Bu_4N)_2[Mo_3S_7(\text{dithiolene})_3]$ salts crystallize in space groups without a crystallographically imposed $C_3$-symmetry and consequently the three dithiolene ligands are not equivalent in the solid state [54–57]. This fact is discussed in detail below in terms of the distinctive participation of each of the three ligands in the $[Mo_3S_7(\text{dithiolene})_3]^{2-}$ dianions in short contacts with neighboring clusters. The dithiolene group fills the remaining two positions on the seven-coordinated molybdenum atoms and is oriented almost perpendicular to the $Mo_3$ plane which results in idealized $C_{3v}$-symmetrized cores. This stereochemical disposition is reminiscent to that found in mononuclear tris-dithiolene molybdenum $[Mo(\text{dithiolene})_3]^{n-}$ ($n = 0$–2) complexes (if one assumes replacement of Mo in the mononuclear fragment by the $Mo_3S_7$ cluster core) displaying a trigonal prismatic geometry [63]. This parallelism is evidenced by the characteristic trigonal twist $\theta$ angle close to 0° [64], the average dihedral $\phi$ angle between the S–M–S plane and the S–S–S plane close to 90° [65], or the $\delta$ angle values between the trigonal planes which are close to 0° for the whole series of $(n\text{-}Bu_4N)_2[Mo_3S_7(\text{dithiolene})_3]$ salts. Fig. 2b describe in detail the depiction of the $\theta$ angle and the dihedral $\phi$ and $\delta$ angles.

An additional characteristic of the $Mo_3S_7$ cluster compounds is the electrophilic character of the axial chalcogen atoms, those out of the $Mo_3$ plane, which provides them with the ability to bind different anions. This intrinsic feature of the $Mo_3S_7$ clusters makes them versatile building blocks for the construction of more complex architectures in the solid state. Some examples that illustrate the great variety of solid state arrangements arise due to the binding of: (i) monoanions such as halogens



**Scheme 3.**

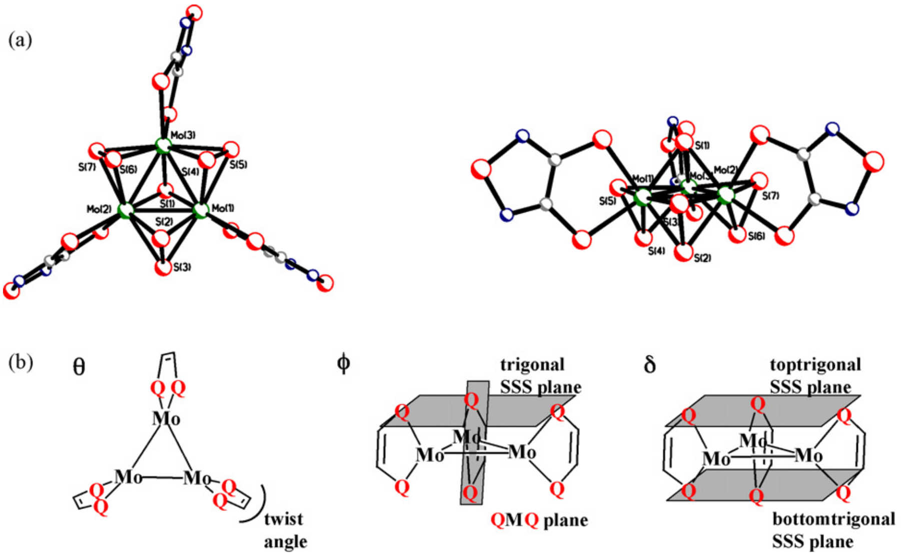


**Fig. 2.** (a) Two different representations of the $[Mo_3S_7(tdas)_3]^{2-}$ dianion. Reproduced with permission of the Royal Society of Chemistry [56]; (b) schematic representation of the $\theta$ (twist angle between $Q_{dithiolene}$ atoms projected perpendicular to the molecular threefold axis); $\phi$ (dihedral angle between the top SSS trigonal plane and the plane defined by the $Q_{dithiolene}$–M–$Q_{dithiolene}$ plane) and $\delta$ (dihedral angle between the top and bottom SSS trigonal planes) angles in $[Mo_3S_7(dithiolene)_3]^{2-}$ clusters.

[66–68], $ClO_4^-$ [69], 7,7,8,8-tetracyanoquinodimethane [70], (ii) dianions ($SO_4^{2-}$ [69], $S^{2-}$ [69,71]), (iii) the trihapto sulfur atom from another cluster to afford chain structures [72], or (iv) sulfur atoms from the peripheral ligands of neighboring cluster to form dimers. A comprehensive collection and analysis of structural trends of $Mo_3S_7$ clusters can be found elsewhere [73,74]. The electronic nature of this interaction has also been investigated by density functional theory and semiempirical calculations for the systems $\{Mo_3S_7(dtc)_3\cdots X\}$ (dtc = diethyldithiocarbamate; X = $NO_3^-$, $ClO_4^-$, $I^-$, $S^{2-}$) [69] and it was proposed that electrostatic interactions dominated the $S_{axial}\cdots X$ contacts for hard counterions such as $NO_3^-$ and $ClO_4^-$ whereas for soft nucleophiles such as $I^-$ and $S^{2-}$ significant covalency is observed. The series of $\{Mo_3Q_7X_6\cdots X\}^{3-}$ (Q = S, Se, Te; X = Cl, Br, I) trianions have also been investigated by DFT calculations and the topological AIM theory [75]. In this later case, the origin of the $S_{ax}\cdots X$ interaction results from a joint effect of shared halogen–chalcogen interactions and electrostatic halogen–halogen repulsion between adjacent clusters. Moreover, the nature of the outer dithiolene ligands in these $(n\text{-}Bu_4N)_2[Mo_3S_7(dithiolene)_3]$ complexes also plays an important structural role because of the potential formation of short interligand S···S or ligand-cluster S···S contacts between neighboring clusters. As a whole, the combined involvement of sulfur atoms from the cluster $Mo_3S_7$ core and the dithiolene ligands in the formation of supramolecular furnishes a high structural diversity to these $Mo_3S_7$/dithiolene complexes.

As we mentioned above, compounds $(n\text{-}Bu_4N)_2[Mo_3S_7(dithiolene)_3]$ do not strictly possess imposed $C_{3v}$ symmetry (even though small variations within the cluster $Mo_3S_7$ core evidence such $C_{3v}$ symmetry) and consequently the three dithiolene ligands are not crystallographically equivalent. One way to rationalize the crystal ordering in these dithiolene cluster salts consist of considering the distinctive participation of the three non-crystallographically equivalent dithiolene ligands (labeled as **I**, **II** and **III**) in short contacts with neighboring clusters. Hence, $Mo_3S_7$/dithiolene dianions were all found to dimerize in the solid state through an inversion center held together by short S···S contacts (typically below 3.7 Å) between the three axial sulfur atoms and the S atoms of one dithiolene ligand, labeled as **I**, belonging to a neighbor cluster. These interactions formally result in the dimerization of the trimetallic dianion as illustrated for $\{[Mo_3S_7(mnt)_3]_2\}^{4-}$ and $\{[Mo_3S_7(dmit)_3]_2\}^{4-}$ in Fig. 3 [54,55].

For those compounds lacking of a dmit framework in the dithiolene moiety, the other two dithiolene ligands remain non-interacting, thus leading to discrete dimerized $Mo_3S_7$ clusters

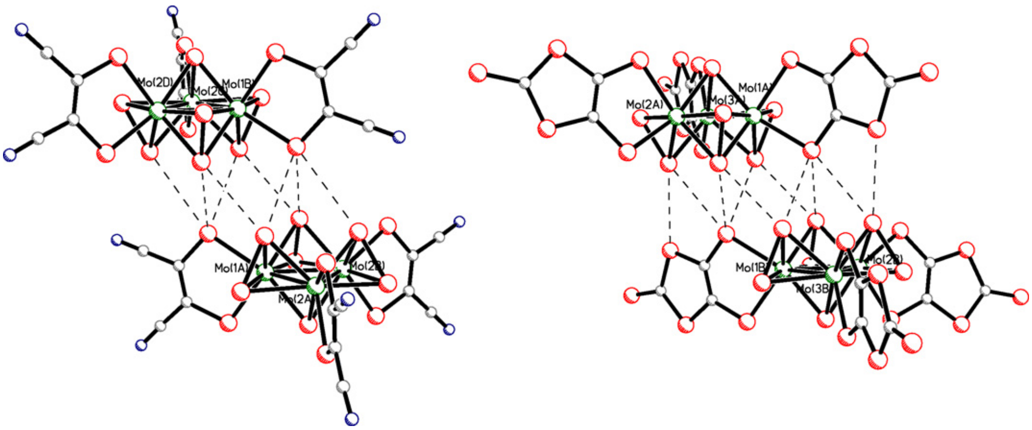


**Fig. 3.** Dimer formation in $[Mo_3S_7(mnt)_3]^{2-}$ and $[Mo_3S_7(dmit)_3]^{2-}$ through short intercluster $S_{axial}\cdots S_{axial}$ and $S_{axial}\cdots S_{dithiolene}$ contacts and also applicable to the full $[Mo_3S_7(dithiolene)_3]^{2-}$ series [54,55].

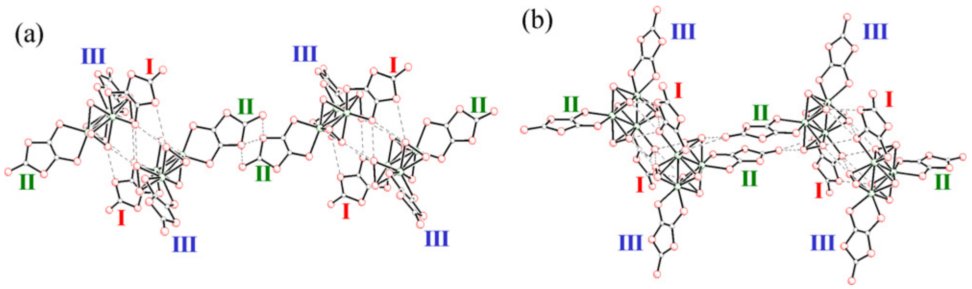


**Fig. 4.** Chain formation in the solid state structure of (a) compound $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ and (b) $(\text{Ph}_4\text{P})_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ [55].

in the solid state. However, for those dianions featuring dmit (or isologues) ligands, namely dmid or dsit, additional interactions between a second dithiolene (or diselenolene) ligand, labeled as **II**, give rise to the formation of infinite chains through short contacts between crystallographically equivalent dithiolene ligands. This chain formation involving coplanar **II** dithiolenes is shown in Fig. 4a for the $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ salt and it is also applicable to the isostructural tetrabutylammonium $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dsit})_3]$ salt and closely related to the crystal structure of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dmid})_3]$. The third dithiolene ligand labeled as **III** appears non-interacting in the dmit, dmid and dsit series.

Replacement of the countercation also affects the crystal packing as evidenced in Fig. 4 for the $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ (a) and $(\text{PPh}_4)_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ (b) salts; however, the main structural features regarding dithiolene involvement in intermolecular interactions remain. That is, dithiolene **I** holds together the $\{[\text{Mo}_3\text{S}_7(\text{dmit})_3]_2\}^{4-}$ dimers, dithiolene **II** is involved in the chain formation and dithiolene **III** remains non-interacting. Although we have not investigated the use of smaller countercations, the crystal structure of the neutral $\text{Mo}_3\text{S}_7(\text{dmit})_3$ compound reveals compact stackings of the $\text{Mo}_3\text{S}_7$ cluster units, thus suggesting that the large size of the $n\text{-Bu}_4\text{N}^+$ or $\text{PPh}_4{}^+$ counteractions prevent a closer stacking of the $\text{Mo}_3\text{S}_7$/dithiolene units in the corresponding dianions. The C=C distance in the free dmit ligand (**III**) is ca. 0.05 Å for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ and 0.08 Å for $(\text{PPh}_4)_2[\text{Mo}_3\text{S}_7(\text{dmit})_3]$ shorter that the C=C bond lengths found in the dithiolenes participating in the dimer (**I**) or chain formation (**II**).

As far as the structural chemistry of $\text{Mo}_3\text{S}_4$/dithiolene clusters is concerned, three derivatives have been structurally characterized so far, namely $[\text{Mo}_3\text{S}_4(\text{dmit})_3]^{2-}$ [58], $[\text{Mo}_3\text{S}_4(\text{dmid})_3]^{2-}$ or $[\text{Mo}_3\text{S}_4(\text{bdt})_3]^{2-}$ [76]. These compounds represent still rare examples, only observed before in the $[\text{Mo}_3\text{S}_4(\text{S}_2\text{C}_2\text{H}_4)_3]^{2-}$ complex [77], where each molybdenum atom appears pentacoordinated, if one ignores the metal–metal bond, instead of its more common octahedral environment. The $\text{Mo}_3\text{S}_4$ cluster core can be described as an equilateral triangle of Mo atoms, a single capping $\mu_3$-sulfido, and three bridging $\mu$-sulfido ligands. The Mo–Mo distances in these three complexes are in the 2.75–2.83 Å range and, as emphasized for the $\text{Mo}_3\text{S}_7$ dithiolene complexes, agree with the presence of a single metal–metal bond and a +4 oxidation state for the Mo atoms.

The pentacoordinated environment of each metal in $[\text{Mo}_3\text{S}_4(\text{dithiolene})_3]^{2-}$ is completed by a chelating bdt ligand and as illustrated in Fig. 5 for the $[\text{Mo}_3\text{S}_4(\text{bdt})_3]^{2-}$ dianion. It is remarkable that in all $\text{Mo}_3\text{S}_4$/dithiolene complexes, the dithiolene disposition is not completely perpendicular to the $\text{Mo}_3$ plane as previously found for $\text{Mo}_3\text{S}_7$/dithiolene complexes, as judged by the analysis of the values of the $\theta$ angle and the dihedral $\phi$ and $\delta$ angles. By analogy with the stereochemical orientation of some Mo tris(dithiolene) complexes [78], the relative orientations of the three dithiolene ligands in $\text{Mo}_3\text{S}_4$/dithiolene complexes are half way between trigonal prismatic and octahedral geometries if one replaces the $\text{Mo}_3\text{S}_7$ cluster unit by a single metal atom.

The structural change from $\text{Mo}_3\text{S}_7$ to $\text{Mo}_3\text{S}_4$ clusters is not only topological, but also affects the intrinsic electronic characteristics of the bridging sulfur atoms. Hence, the electrophilic character of the axial sulfur atoms is not preserved on going from $\text{Mo}_3\text{S}_7$ to $\text{Mo}_3\text{S}_4$ clusters. Consequently, dimerization of $\text{Mo}_3\text{S}_4$/dithiolene complexes is not observed in the solid state for $[\text{Mo}_3\text{S}_4(\text{dithiolene})_3]^{2-}$ salts and only the outer dithiolene ligand does participate in short contacts between neighbor clusters in the solid state. Moreover, these $\text{Mo}_3\text{S}_4$/dithiolenes are air-sensitive in solution and they readily degrade to dimeric species of general formula $[\text{Mo}_2\text{S}_2\text{O}_2(\text{dithiolene})_2]^{2-}$. Fig. 5b shows a schematic representation of the dimeric $[\text{Mo}_2\text{S}_2\text{O}_2(\text{dmit})_2]^{2-}$ compound. In this dianion, the two molybdenum centers are connected through two doubly bridged sulfide groups where each molybdenum atom appears five-coordinated without considering the metal–metal interaction, in a square pyramidal environment. The remaining positions are occupied by the two sulfur atoms of the dithiolene ligand and a terminal oxygen atom. The oxygen atoms are in a *syn* configuration. The Mo–Mo bond distances (ca. 2.82 Å) in these dimetallic anions are consistent with an oxidation state of +5 for the metal and the presence of a single metal–metal bond.

The structure of $(\text{Et}_4\text{N})_4[\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-mnt})_3(\text{mnt})_3]$ represents the first and only example of a sulfur bicapped trinuclear molybdenum cluster [34]. The Mo–Mo distance of 2.84 Å for this

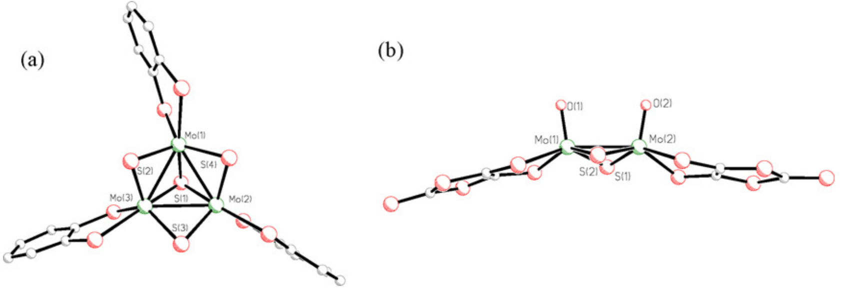


**Fig. 5.** Representation of the (a) $[\text{Mo}_3\text{S}_4(\text{bdt})_3]^{2-}$ and (b) $[\text{Mo}_2\text{S}_2\text{O}_2(\text{dmit})_2]^{2-}$ dianions [58].

Mo(IV)$_3$ triangular complex lies in the range found in other $Mo_3S_7$ and $Mo_3S_4$ clusters but is larger than that reported (2.71 Å) by Saito et al. for the $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ complex [35,36]. These differences in the intermetallic distances can be attributed to variations in the metal electron populations. While all triangular dithiolene $Mo_3$ complexes, mono- and bicapped, are electron precise with six metal electrons and a single Mo–Mo bond between adjacent metal atoms, complex $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ contains eight metal electrons and a formal oxidation state of +3.33 for the Mo atom. The coordination environment in this last complex is octahedral while the Mo atoms in $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ are seven coordinated. It is remarkable that all reported dithiolene monocapped $Mo_3S_4$ clusters and the $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ bicapped compound present unusual coordination environments, five and seven coordinated, respectively, in front of the most usual octahedral coordination found for the metal in other monocapped $Mo_3S_4$ and bicapped $Mo_3S_5$-type clusters bearing phosphane ligands.

Both series of dithiolene $Mo_3S_7$ and $Mo_3S_4$ clusters can be conveniently identified by Raman and infrared spectroscopy. IR spectra reveal, besides the characteristic bands due to the dithiolene itself, characteristic signals of the trinuclear $Mo_3S_7$ and $Mo_3S_4$ cluster unit with medium intensity frequencies in the 250–500 $cm^{-1}$ range attributed to the Mo–(μ-S) and Mo–($\mu_3$-S) stretching vibrations [79]. The most salient feature of the Raman spectra of the $[Mo_3S_7(dithiolene)_3]^{2-}$ anions is the presence of very strong signals attributed to the $S_2^{2-}$ bridging ligands [79]. A decrease of the $S_{ax}$–$S_{eq}$ stretching frequency wavenumber has been correlated with an increase of the $S_{ax}$–$S_{eq}$ bond distances in several $Mo_3S_7$ clusters [69]. Upon chemical transformation from $Mo_3S_7$ to $Mo_3S_4$ clusters, this Raman spectroscopic signature becomes absent.

## 4. Electrochemical properties and electronic structure of $Mo_3$ cluster sulfides with outer dithiolene groups

The coordination of non-innocent ligands such as dithiolenes, diselenolenes or dioxolenes to the $Mo_3S_7$ or $Mo_3S_4$ cluster units furnishes oxidation activity at accessible potentials to the new complexes. The number and reversibility of these processes have been investigated using cyclic voltammetry techniques. A summary of electrochemical data for trinuclear $Mo_3$ cluster sulfides containing dithiolene or diselenolene ligands is collected in Table 1. Data for the dithiolene $Mo_3S_7$ precursors are also included for comparative purposes.

In general, all $Mo_3S_7$ complexes undergo one reduction process regardless the charge state as well as the identity of the peripheral ligands [80,81]. This process is attributed to the reduction of three dichalcogenide ligands to afford the homologous sulfur-bridged complexes with a $Mo_3S_4$ core, as evidenced by the isolation of $[Mo_3S_4(dithiolene)_3]^{2-}$ upon treatment of $[Mo_3S_7(dithiolene)_3]^{2-}$ anions with reducing agents such as $PPh_3$ (see previous section). This observation was also confirmed by molecular orbital calculations. The LUMO orbital for these $Mo_3S_7$ systems is mainly located on the bridging $S_2^{2-}$ ligand and has antibonding $p$–$\pi^*/\sigma^*$ character on the S–S bond [15,69].

Cyclic voltammograms of $Mo_3S_4$ complexes are dominated by the reduction of the central metal core through monoelectronic processes: $Mo_3^{IV} \rightarrow Mo^{III}Mo_2^{IV} \rightarrow Mo_2^{III}Mo^{IV}$ [20]. However, except for the $Mo_3S_4Cl_3(dppe)_2(PEt_3)_2$ neutral compound with seven metal electrons [82], all other $Mo_3S_4$ cluster complexes are electron precise with six metal electrons for the formation of three metal–metal bonds. In the case of the $Mo_3S_4$/dithiolenes, the irreversible reduction processes are observed at nearly the same potential to those of $Mo_3S_7$/dithiolene involving the disulfide ligands (see Table 1). Electrochemical studies on the sulfur bicapped $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ trinuclear tetraanion show one irreversible reduction at $E_{pc} = -0.97$ V that the authors tentatively assigned to a two-electron process [34].

As far as the oxidation behavior of $Mo_3S_7$ complexes is concerned, the absence of oxidation processes for the $[Mo_3S_{13}]^{2-}$ anion has been explained taking into consideration the nature of its HOMO orbital which is mainly formed by weakly interacting $\pi^*$ orbitals from the terminal $S_2^{2-}$ ligand. Upon dithiolene coordination, $Mo_3S_7$ compounds become redox active on oxidation suggesting that the electrochemical response is mainly based on the ligand. This hypothesis has been confirmed by DFT calculations [57]. Fig. 6 represents the HOMO and HOMO-1 orbitals for the $[Mo_3S_7(bdt)_3]^{2-}$ cluster dianion, where an extensive mixing between the $Mo_3S_7$ unit based orbitals and the dithiolene ligands based orbitals exists. The same MO scheme applies for the rest of the $Mo_3S_7$ dithiolenes or diselenolenes complexes although with differences in the AOs contributions from the metal and sulfur cluster core orbitals and the ligand based orbitals.

The HOMO in these $[Mo_3S_7(dithiolene)_3]^{2-}$ dianions is a fully occupied e-type orbital, as expected for a $C_3$-symmetrized $Mo_3S_7$ cluster core. Ligand contributions to the HOMO vary from 61.67% for cluster $[Mo_3S_7(bdt)_3]^{2-}$ to 82.07% for the diselenolate $[Mo_3S_7(dsit)_3]^{2-}$ dianion so it can be considered as a ligand based orbital. The HOMO-1 with an "a" symmetry is mainly composed

**Table 1**
Redox potentials[a] (versus Ag/AgCl) for salts of several dithiolene $Mo_3S_7$ cluster dianions in dichloromethane.

| Cluster salt | Reduction $E_{p,c}$[b] (V) | Oxidation $E_{1/2}$, $\Delta E$[c] (V) or $E_{p,a}$ | Ref. |
|---|---|---|---|
| $(NH_4)_2[Mo_3S_7(S_2)_6]$ | −1.22 | – | [80] |
| $(n\text{-}Bu_4N)_2[Mo_3S_7Br_6]$ | −1.15 | – | [54] |
| $(n\text{-}Bu_4N)_2\,[Mo_3S_7(tfd)_3]$ | −1.22 | 0.51 (0.07) and 0.89 (0.06) | [57] |
| $(n\text{-}Bu_4N)_2\,[Mo_3S_7(bdt)_3]$ | −1.26 | 0.23 (0.07) and 0.41 (0.13) | [57] |
| $(n\text{-}Bu_4N)_2\,[Mo_3S_7(mnt)_3]$ | −1.04 | 0.77 (0.071) and 1.16 (0.068) | [54] |
| $(n\text{-}Bu_4N)_2[Mo_3S_7(tdas)_3]$ | −1.31 | 0.72 (0.076) | [56] |
| $(n\text{-}Bu_4N)_2[Mo_3S_7(dmid)_3]$ | −1.27 | 0.36 (0.10)[d] | [57] |
| $(n\text{-}Bu_4N)_2[Mo_3S_7(dmit)_3]$ | −1.20 | 0.38 (0.17)[d] | [55] |
| $(n\text{-}Bu_4N)_2[Mo_3S_7(dsit)_3]$ | −1.69 | 0.34 (0.18)[d] | [57] |
| $(n\text{-}Bu_4N)_2[Mo_3S_4(bdt)_3]$ | −.142 | 0.47[e] and 0.65[e] | [76] |
| $(n\text{-}Bu_4N)_2[Mo_3S_4(tdas)_3]$ | −1.36 | 0.89 (0.06) | [76] |
| $(n\text{-}Bu_4N)_2[Mo_3S_4(dmid)_3]$ | −1.10 | 0.57 (0.4)[d] | [76] |
| $(n\text{-}Bu_4N)_2[Mo_3S_4(dmit)_3]$ | −1.33 | 0.57 (0.4)[d] | [76] |
| $(Et_4N)_4[Mo_3S_2(mnt)_6]$ | −0.970 | 0.50[e] and 0.625[e] | [34] |

[a] Data for $(Et_4N)_4[Mo_3S_2(mnt)_6]$ were recorded in acetonitrile.
[b] Potentials measured at 100 mV $s^{-1}$.
[c] $\Delta E = |E_a - E_c|$.
[d] Asymmetric wave.
[e] Irreversible process.

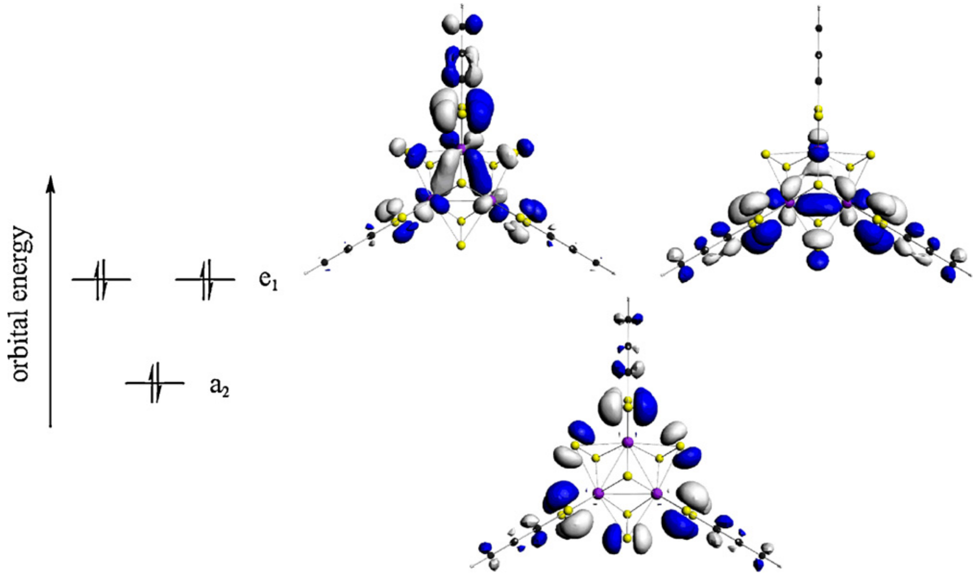


**Fig. 6.** Representation of the HOMO and HOMO-1 orbitals for the $[Mo_3S_7(bdt)_3]^{2-}$ dianion. Reproduced with permission of the American Chemical Society [57].

by the three outer ligands and the equatorial sulfur atoms of the cluster core, without participation of Mo atoms. Cluster dianions with a larger contribution from the ligands to the HOMO possess a smaller energy gap between the HOMO and HOMO-1 orbitals.

The number of observed oxidation processes for these $[Mo_3S_7(dithiolene)_3]^{2-}$ dianions or their diselenolene analogs depends on the nature of the outer ligand. In the case of the tfd, bdt, tdas or mnt derivatives, two successive reversible oxidations of equal intensity are observed. For the other cluster salts, only one oxidation process is registered that in the case of the dmid, dmit and dsit complexes are seen as an asymmetric wave (see Fig. 7). The asymmetry in the wave's shape is indicative of the deposition upon oxidation of conducting species at the electrode. As we shall discuss below, only for these dianions, we succeeded at preparing and isolating the neutral oxidized $Mo_3S_7(dmid/dmit/dsit)_3$ complexes. On the basis of the isolation of the neutral counterparts, the oxidation processes typically observed for $Mo_3S_7$/dithiolene complexes is proposed to occur via a two-electron process according to the $[Mo_3S_7(dithiolene)_3]^{2-} \rightarrow [Mo_3S_7(dithiolene)_3]$ process.

All attempts to isolate oxidation products from chemical or electrochemical oxidation reactions of compounds $(n\text{-}Bu_4N)_2[Mo_3S_7(dithiolene)_3]$ (dithiolene = tfd, bdt, tdas and mnt) were unsuccessful most likely, because of the decomposition of the $Mo_3S_7$ trinuclear core, the dismutation of the hypothetical $[Mo_3S_7(dithiolene)_3]^-$ monoanions to give the dianion and the neutral compounds or the active participation of the oxidizing reagent as entering ligand. This latter case has been recently reported upon oxidation of the closely related dioxolene $(PPh_4)_2[Mo_3S_7(tcc)_3]$ (tcc = tetrachlorocathecol) with iodine which by varying the reactions conditions lead to $(PPh_4)_2[Mo_3S_7I_6]$ or the cage complex $(PPh_4)_3[Mo_3S_7I_3(\mu\text{-}I)_3]_2\cdot I$ in which iodine ligands coordinate to the $Mo_3S_7$ cluster [83].

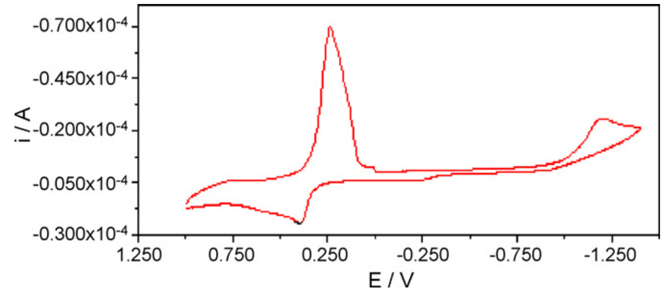


**Fig. 7.** Cyclic voltammogram of compound $(n\text{-}Bu_4N)_2[Mo_3S_7(dmit)_3]$ recorded in $CH_2Cl_2$ at a scan rate of 500 mV/s (versus Ag/AgCl) [55].

Sulfur abstraction from the disulfides bridging ligands in $Mo_3S_7$ dithiolene complexes to afford $[Mo_3S_4(dithiolene)_3]^{2-}$ dianions does not have a significant effect on the oxidation activity. These latest complexes also show oxidation processes at easily accessible potentials although there is an anodic shift of ca. 0.2 V on going from the $Mo_3S_7$ to the $Mo_3S_4$ dithiolene system. The electronic structure of these $C_3$-symmetrized $[Mo_3S_4(dithiolene)_3]^{2-}$ anions also shows an HOMO and HOMO-1 orbitals of the "e"- and "a"-type symmetry; however, the dithiolene ligand contribution to the HOMO decreases (between 4 and 10%) with regard to that of their $Mo_3S_7$ homologues. In spite of this the HOMO orbitals in all dithiolene and diselenolene $Mo_3$ sulfido complexes can be considered ligand based orbitals. This also applies to the oxidation of the $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}mnt)_3(mnt)_3]^{4-}$ trinuclear tetraanion with two irreversible processes at 0.50 and 0.62 V. In this complex, the ligand based highest molecular orbital (HOMO) is also associated to the observed irreversible oxidations.

The half wave potentials for the first oxidation process within dithiolene $Mo_3S_7$ and $Mo_3S_4$ series reveal that the easiness toward oxidation follows the trend bdt > dmid = dsit = dmit > tfd > tdas > mnt. This trend closely follows from previous observation for mononuclear molybdenum tris-dithiolene $[Mo(S_2C_2R_2)_3]^{z-}$ that decreases in the order of the electron-donating and -withdrawing ability of the R substituent groups for R = H, alkyl ≈ aryl > $CF_3$ > CN [84,85].

The analysis of the oxidation behavior in these dithiolene cluster complexes serves as a base towards the design of new molecular conductors. One key factor in this field is the formation of stable radicals combined with a solid state arrangement that favors intermolecular interactions without forming localized bonds. The molecules with low HOMO/LUMO gaps are of particular importance due to the ability to easily donate (from HOMO) or accept (on LUMO) an electron, which is the basic process in all molecular electronic devices. In the next section we will present a review of all charge-transfer salts obtained by combining TTF-donors molecules with $Mo_3S_7$ anions with outer halide or dithiolene ligand in which the cluster anion plays a structural role. Then we will review the use of dithiolene

$Mo_3S_7$ complexes in the formation of single-component molecular conductors.

## 5. Molecular conductors based on $Mo_3S_7$ clusters

The preparation and comprehensive characterization of charge-transfer salts based on TTF-donors has provided a wide scope of transport properties ranging from semiconductors to metals and superconductors [86]. Due to the inherent two-component nature of these materials (a cationic TTF-based and an anionic part) a large variety of charge compensating anions have been employed and in particular metal-containing anions has been extensively investigated aimed at preparing hybrid inorganic/organic materials which can introduce multifunctionality (for example by combining a conducting organic network with an inorganic magnetic component), in the resulting molecular compound [87–90]. The charge distribution, distances, and relative orientations of the donor molecules are responsible for the collective physical properties, and this may be controlled by the packing of the compensating-charge anions. In this vein, it is expected that increasing interactions between the inorganic and organic sublattices will lead to an increase in the electronic dimensionality of the resulting molecular material so that the use of anionic complexes containing sulfur, selenium or halogens is preferred because of the relevance of Y–(S/H) (Y = Cl, Br, I, S, Se) intermolecular contacts between the inorganic and organic sublattices.

Besides these two-component molecular conductors, at the turn of this century it was realized that carrier generation was also possible between the HOMO and LUMO band even in neutral materials assuming that there was a small HOMO–LUMO gap. Canadell's group envisioned that metal–dithiolene complexes are expected to match the adequate electronic and structural requirements to internally promote electron transfer between two types of bands leading to single-component molecular metals [6,91]. By adopting extended tetrathiafulvalene (TTF) dithiolene ligands, Kobayashi's group was able to determine the first crystal structure of a metallic crystal based on neutral molecules, namely, $Ni(tmdt)_2$ (tmdt = trimethylenetetrathiafulvalenedithiolene), with a stable metallic state down 0.6 K and a room temperature conductivity of $\sigma = 400\,S\,cm^{-1}$ [92]. The existence of conduction paths was associated to a small energetic separation between the HOMO–LUMO orbitals and the formation of extended 3D networks through transversal S···S contacts involving sulfur π-orbitals [93–95]. These two topics represent the guideline principles to develop new single-component molecular conductors and the fulfillment of both criterions is a major challenge for the chemical and physical community. New single-component molecular conductors have been prepared by tailored-design of molecules with small HOMO–LUMO gap and in this context, the use of transition metal complexes with dithiolene ligands having a TTF skeleton has been preferred. The most relevant examples of single-component molecular conductors are the mononuclear $M(dithiolene)_2$ (M = Co, Ni, Cu, Pt, Au) complexes with extended TTF dithiolene [96–105] and more recently thiazole dithiolene [106] ligands, prepared by the oxidation of their corresponding anions. First-principles electronic-band calculations on most of these single-component molecular conductors have been recently reviewed [107]. However, control of the crystal ordering that will actually determine the intermolecular contacts in the extended solid and, hence, its collective properties is more difficult to anticipate, and single-component molecular conductors with semiconducting or metallic properties can be obtained.

Despite the growing interest in employing metal anions of higher nuclearity and complexity with different shapes, charges and electronic structures, the use of chalcogen or halide containing anions as well as bis-dithiolene complexes in the development of new charge-transfer salts or single-component molecular conductors is almost restricted to mononuclear species. Replacement of the transition metal by more complex polynuclear entities, such as the $Mo_3S_7$ cluster core, represents a very attractive and promising approach and might confer new electronic features associated to the tunable relative energy of the cluster core and the dithiolene ligand (as demonstrated for $Mo_3S_7$/dithiolene systems) [57], which might become available for extensive mixing leading to sizable electronic delocalization around the metallic core and the dithiolene ligand.

In this context, $Mo_3S_7$ clusters are attractive targets due to their chemical and structural versatility. The structural role of these $Mo_3S_7$ cluster complexes in the construction of TTF-based charge-transfer salts is analyzed next. We will continue with a detailed discussion on single-component molecular conductors based on $Mo_3S_7$ dithiolene complexes.

### *5.1. Hybrid charge-transfer salts based on $Mo_3S_7$ dianions and TTF-based donors*

The electrocrystallization of TTF-based donors such as bis(ethylenedithio)tetrathiafulvalene or BEDT-TTF or ET, and ethylenedithio-diodo-tetrathiafulvalene or EDT-$TTFI_2$ was attempted with the whole series $[Mo_3S_7X_6]^{2-}$ (X = Cl, Br) and $[Mo_3S_7(dithiolene)_3]^{2-}$ dianions bearing in mind the possibility to promote extensive contacts between the inorganic and organic sublattices through multiple short contacts between halogens and chalcogen atoms. Hybrid $Mo_3S_7$/TTF-donor phases with different stoichiometries were isolated by the electrooxidation technique depending on the solvent employed and the proper $Mo_3S_7$/TTF-donor combination. Their formulation, as determined on the basis of X-ray diffraction experiments, charge state of the donor molecules, general crystal packing and transport properties are collected in Table 2. Crystal structure descriptions are briefly described in this section, especially paying attention to the distinctive architectures of the inorganic part together with the global packing between the cluster anions and the ET donor molecules, especially by an inspection of the inorganic/organic interface in some of the salts depicted in Table 2.

Among all $Mo_3S_7$ cluster complexes, we succeeded at obtaining single crystals for the $[Mo_3S_7Br_6]^{2-}$, $[Mo_3S_7Cl_6]^{2-}$, $[Mo_3S_4Se_3Br_6]^{2-}$ and $[Mo_3S_7(tdas)_3]^{2-}$ dianions and TTF-based donors. The absence of redox activity upon oxidation in the all-halide $[Mo_3S_7X_6]^{2-}$, $[Mo_3S_4Se_3Br_6]^{2-}$ and the high oxidation potential found for the $[Mo_3S_7(tdas)_3]^{2-}$ cluster precludes any tuning of the band filling of the cation sublattice through anion oxidation. Two of the key factors determining the molecular and electronic structures of the final molecular solid are the size and charge carried out by the compensating anion. In the present case, despite the dianionic character of the $Mo_3S_7$ clusters, their solid state packing reveal more complex aggregates as a consequence of the well-known trend of the axial sulfur atoms to bind nucleophiles. As shown in Fig. 8, such aggregates display a variety of shapes and charges (from two to five minus or even polymeric anion sublattices) depending on the number of cluster units and halide ions involved. The structural predicting role in these systems, in relation to the preferred formation of a certain structural type, is not straightforward. A variety of factors such as the nature of the countercation or the inherent differences in the salts solubility seems to heavily determine the preferred halide intercalation into the cavities defined by the axial sulfur atoms and hence the ordering in the solid state.

As depicted in Fig. 8a, the three axial sulfur atoms may interact with one isolated bromine ion to produce the trianionic $\{[Mo_3S_7Br_6]Br\}^{3-}$ aggregate; on the other side, dis-

**Table 2**
Hybrid charge-transfer salts based on organic donor TTF-donors and $Mo_3S_7$ clusters.[a].

| Compound | ET donors (charge state) | Inorganic sublattice | Transport properties | Ref. |
|---|---|---|---|---|
| $(ET_A)_2(ET_B)[Mo_3S_7Br_6]_2{\cdot}CH_2Br_2$ | $ET_A(+1)$, $ET_B(+2)$ | $\{[\mathbf{2}]_2\}^{4-}$ | Insulator | [108] |
| $(ET_A)(ET_B)[Mo_3S_7Br_6]{\cdot}1.1CH_2Br_2$ | $ET_A(+1)$, $ET_B(+1)$ | $\{[\mathbf{2}]_2\}^{4-}$ | Semiconducting; $\sigma_{RT} = 4\ S\ cm^{-1}$;<br>$E_a = 27\ meV$ | [108] |
| $(ET_A)(ET_B)(ET_C)\{[Mo_3S_7Br_6]Br\}{\cdot}0.5C_2H_4Cl_2$ | $ET_A(+1)$, $ET_B(+1)$, $ET_C(+1)$ | $\{[\mathbf{2}]{\cdot}Br\}^{3-}$ | Insulator | [108] |
| $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$ | $ET_A(+1)$ | $\{[\mathbf{2}]_2\}^{4-}$ | Semiconducting; $\sigma_{RT} = 0.07\ S\ cm^{-1}$;<br>$E_a = 150\ meV$ | [108] |
| $(ET_A)(Ph_4P)[Mo_3S_7Br_6]{\cdot}0.5CH_3CN$ | $ET_A(+1)$ | $\{[\mathbf{2}]_2\}^{4-}$ | Insulator | [108] |
| $(ET_A)(ET_B)[Mo_3S_7(tdas)_3]$ | $ET_A(+1)$, $ET_B(+1)$ | $[\mathbf{6}]^{2-}$ | Semiconducting; $\sigma_{RT} = 4 \times 10^{-5}\ S\ cm^{-1}$;<br>$E_a = 280\ meV$ | [56] |
| $(ET_A)(n\text{-}Bu_4N)_2[Mo_3S_4Se_3Br_6]$ | $ET_A(+1)$ | $\{[Mo_3S_4Se_3Br_6]_2\}^{4-}$ | Insulator | [56] |
| $(ET_A)(ET_B)[Mo_3S_7Cl_6]_2{\cdot}CH_3CN$ | $ET_A(+2)$, $ET_B(+2)$ | $\{[Mo_3S_7Cl_6]_2\}_x^{4x-}$ | Insulator | [56] |
| $(ET_A)_2(ET_B)_2(ET_C)_2(ET_D)_2\{[Mo_3S_7Cl_6]_2{\cdot}Cl\}CH_3CN$ | $(+1) > ET_{A\text{–}D} > (+1/2)$ | $\{[Mo_3S_7Cl_6]_2{\cdot}Cl\}^{5-}$ | Metallic down 270 K; $\sigma_{RT} = 0.5\text{–}3.5\ S\ cm^{-1}$; semiconducting below 270 K following three different regimes | [56] |
| $(EDT\text{-}TTFI_2)_A(EDT\text{-}TTFI_2)_B(EDT\text{-}TTFI_2)_C(EDT\text{-}TTFI_2)_D$ $[Mo_3S_7Cl_6]{\cdot}CH_3CN$ | $(EDT\text{-}TTFI_2)_{A\text{–}C}(0)$,<br>$(EDT\text{-}TTFI_2)_D(+2)$ | $\{[Mo_3S_7Cl_6]_2\}^{4-}$ | Semiconducting; $\sigma_{RT} = 1 \times 10^{-4}\ S\ cm^{-1}$;<br>$E_a = 290\ meV$; insulator below 240 K | [113] |

[a] ET = bis(ethylenedithio)tetrathiafulvalene; EDT-TTFI$_2$ = ethylenedithio-diodo-tetrathiafulvalene.

crete supramolecular $\{[Mo_3S_7X_6]_2{\cdot}X\}^{5-}$ sandwich-type units (see Fig. 8b) are formed through binding a halide anion shared by two cluster units. Discrete supramolecular $\{[Mo_3S_7Br_6]_2\}^{4-}$ bicluster units may be also formed by interaction between the three axial sulfur atoms of one trimer with the bromine ligands of its neighbor trinuclear cluster to give tetraanions with an ellipsoidal shape and 4− charge (see Fig. 8c). For the all-chlorine derivative $\{[Mo_3S_7Cl_6]_2\}^{4-}$, these tetraanions are further connected through S···Cl interactions to give rise a 2D inorganic anion sublattice as exemplified in Fig. 8d.

A general structural feature of most of these hybrid charge-transfer salts is the presence of alternating layers of dimerized organic donor molecules ($ET^{+}$:$ET^{+}$) and of inorganic clusters in the form of tri- or tetraanions (see Fig. 8a and c), where the long axis of the donor dimers runs almost parallel to the cluster layer, as represented in Fig. 9. This inorganic/organic arrangement is found in most of the obtained salts such as $(ET_A)_2(ET_B)[Mo_3S_7Br_6]_2{\cdot}CH_2Br_2$ and $(ET_A)(ET_B)[Mo_3S_7Br_6]{\cdot}1.1CH_2Br_2$, $(ET_A)(ET_B)(ET_C)\{[Mo_3S_7Br_6]Br\}{\cdot}0.5C_2H_4Cl_2$, $(ET_A)(Ph_4P)[Mo_3S_7Br_6]{\cdot}0.5CH_3CN$ or the isostructural $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$ and $(ET_A)(n\text{-}Bu_4N)[Mo_3S_4Se_3Br_6]$. This packing clearly illustrates the presence of numerous X···S and S···S contacts at the interface of the inorganic and organic sublattices.

The intimate crystal packing considering all ET donors, $Mo_3S_7$ clusters and in some cases solvent molecules is indeed more complex and it is not addressed in detail herein. For example for the $(ET_A)(ET_B)[Mo_3S_7Cl_6]_2{\cdot}CH_3CN$ salt, the dianion $[Mo_3S_7Cl_6]^{2-}$ forms $\{(Mo_3S_7Cl_6)_2\}^{4-}$ inorganic dimers of trimers; however, an extra contact is observed between one of the equatorial sulfurs and one outer chlorine ligand of a neighbor cluster to produce a ribbon-like structure as shown in Fig. 8d. Regarding the organic part, the two crystallographically inequivalent ET molecules in the $(ET_A)(ET_B)[Mo_3S_7Cl_6]_2{\cdot}CH_3CN$ salts are oriented almost perpendicularly forming channels down the *c* axis (see Fig. 10a) held together by short contacts exclusively between the sulfur atoms of the outer six-membered rings. Multiple contacts shorter than the sum of van

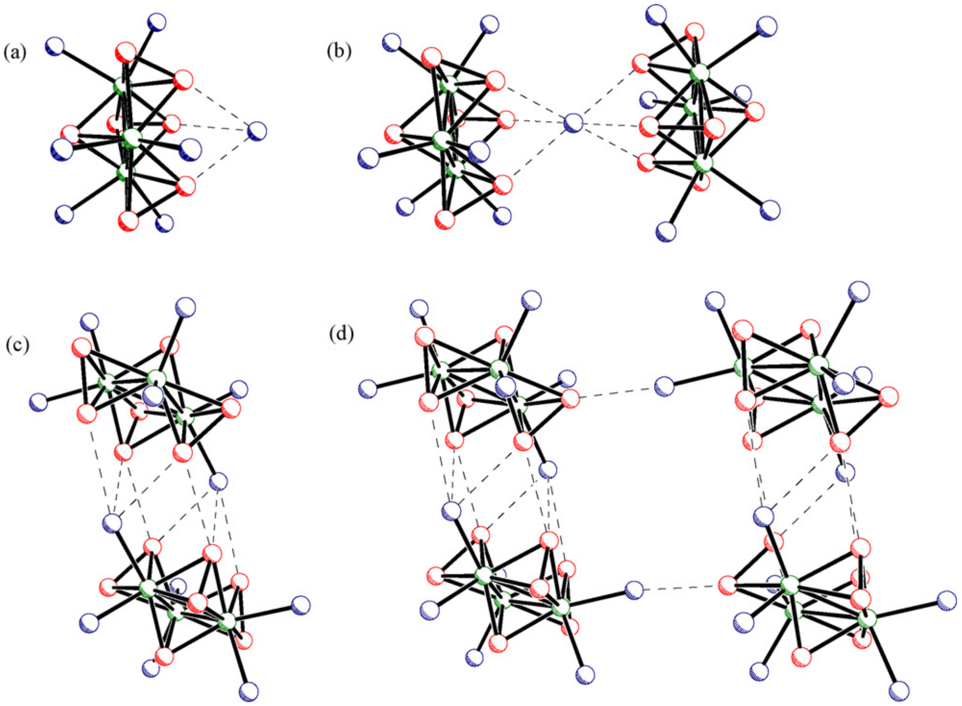


**Fig. 8.** Comparison of the inorganic cluster motifs at approximately the same scale present in anions incorporated into the ET and EDT-TTF-I$_2$ charge-transfer salts: (a) $\{Mo_3S_7Br_6{\cdot}Br\}^{3-}$ [108], (b) $\{[Mo_3S_7Cl_6]_2{\cdot}Cl\}^{5-}$ [56], (c) $\{[Mo_3S_7Br_6]_2\}^{4-}$ [108] and (d) $\{[Mo_3S_7Cl_6]_2\}_x^{4x-}$ [56]. Blue, halide; red, sulfur and green, molybdenum.

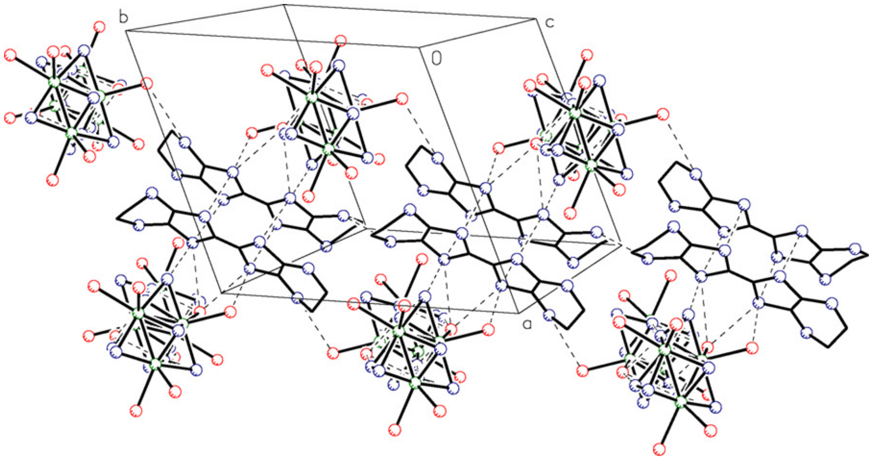


**Fig. 9.** General arrangement found in most hybrid charge-transfer salts illustrated for the $(ET_A)(ET_B)[\mathbf{2}]\cdot 1.1CH_2Br_2$ salt, where the inorganic and organic networks comprising $\{[Mo_3S_7Br_6]_2\}^{4-}$ and dimerized ET donors is clearly seen. Reproduced with permission of the American Chemical Society [108].

der Waals radii are observed between the inorganic clusters and the organic lattice where the ribbons of dimers previously described fit in the channel-like structures created by the packing of the ET molecules, thus forming an interpenetrated supramolecular structure.

It has to be pointed out that three of these salts, namely $(ET_A)(Ph_4P)[Mo_3S_7Br_6]\cdot 0.5CH_3CN$ or the isostructural $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$ and $(ET_A)(n\text{-}Bu_4N)[Mo_3S_4Se_3Br_6]$ contains an additional bulky component. The packing of the cluster:donor system in these three salts is analogous to that represented in Fig. 9 comprising $\{[Mo_3S_7Br_6]_2\}^{4-}$ or $\{[Mo_3S_4Se_3Br_6]_2\}^{4-}$ tetraanions and chains of dimerized $ET_A$ organic molecules. Fig. 10b shows the packing of the organic sublattice in $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$ phase including the bulky non-interacting cations (the whole packing considering the three components is complex). These results prove the versatility of the combination $\{[Mo_3S_7Br_6]\text{:ET}\}$ to yield new charge-transfer salts which accommodate a third bulky component. The third component in these $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$, $(ET_A)(n\text{-}Bu_4N)[Mo_3S_4Se_3Br_6]$ and $(ET_A)(Ph_4P)[Mo_3S_7Br_6]\cdot 0.5CH_3CN$ phases, namely the $n\text{-}Bu_4N^+$ or $PPh_4{}^+$ cation, comes from the supporting electrolyte. All these salts form alternate cationic layers where the $n\text{-}Bu_4N^+$ or the $PPh_4{}^+$ cation comes quite close to the organic donor layer making these systems very attractive as multicomponent materials, for example incorporating of magnetic and/or active NLO bulky cations with $n\text{-}Bu_4N^+$ or $PPh_4{}^+$-related topologies as an attempt to combine different properties within the same material. Recently, several systems have been reported which show the importance of this third component in the final properties of the charge-transfer salts incorporating for instance 18-crown-6 ether molecules which led to the first charge-transfer salts containing proton channels [109,110]. Iodine-containing neutral molecules act as a “template” within the family of ET charge-transfer salts with $Br^-$, $Cl^-$, $I^-$, and $AuBr_2{}^-$ as compensating anions to give a wide variety of solid phases with semiconductor and metallic behavior [111,112].

We have also faced the possibility to further increase the interaction at the inorganic/organic interface by using iodine-functionalized TTF-donors, thus promoting halide–halide contacts [113]. Hence, the salt formulated as $(EDT\text{-}TTFI_2)_{A-D}[Mo_3S_7Cl_6]\cdot CH_3CN$ was obtained which represents a still rare example of radical salts displaying a true interaction between the organic and inorganic sublattices which can be interpreted in terms of the presence of two iodine atoms in the donor molecules and several accessible acceptor atoms such as Cl and S in the $[Mo_3S_7Cl_6]^{2-}$ dianion.

A common feature of most of the compounds included in Table 2 is the presence of high oxidation states in the donor ET or EDT-TTF-$I_2$ molecules. All salts except $(ET)_8\{[Mo_3S_7Cl_6]_2\cdot Cl\}CH_3CN$ show the donor ET molecule in an integer oxidation state (see Table 2) as judged by X-ray analysis and Raman spectroscopy. For this latter salt, the asymmetric unit contains one $[Mo_3S_7Cl_6]^{2-}$ dianion, one chlorine atom in a special position, four crystallographically independent ET radical cations and a formal 5/8+ oxidation state for the ET donors is estimated. The isolated chlorine atom is sandwiched by two cluster dianions through interaction with the three axial sulfur atoms on each cluster with S···Cl contacts, thus producing the pentaanionic $\{[Mo_3S_7Cl_6]_2Cl\}^{5-}$ aggregate (see Fig. 8b). The whole packing including the inorganic and organic part consists of

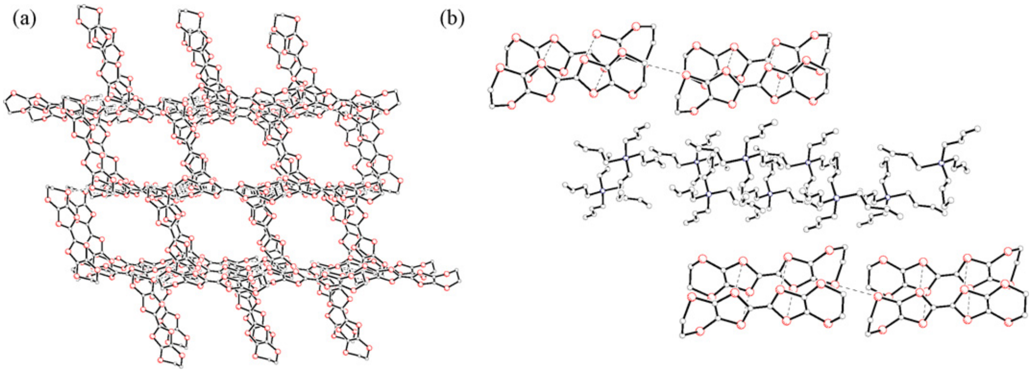


**Fig. 10.** Crystal packing of the organic part in the salt: (a) $(ET_A)(ET_B)[Mo_3S_7Cl_6]_2\cdot CH_3CN$ revealing an interpenetrated supramolecular structure and (b) $(ET_A)(n\text{-}Bu_4N)[Mo_3S_7Br_6]$. Reproduced with permission of the Royal Society of Chemistry [56], and the American Chemical Society [108].

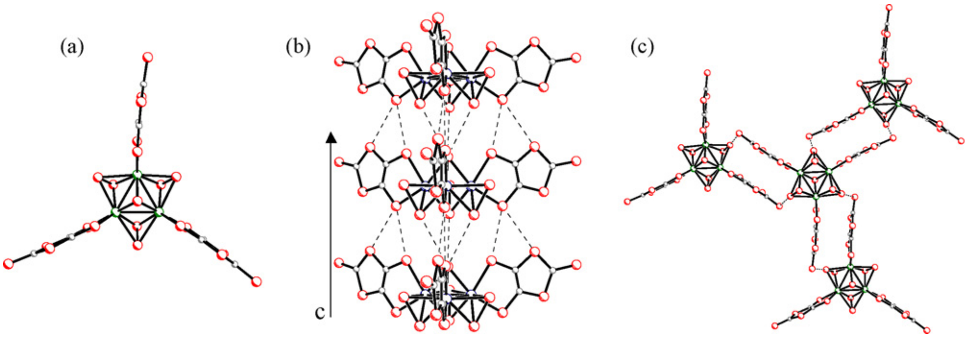


**Fig. 11.** Schematic representation of (a) the neutral $C_{3v}$-symmetrized $Mo_3S_7(dmit)_3$ (**9**) complex; (b) stacked packing of $Mo_3S_7(dmit)_3$ units running along the *c* axis and (c) view across the *bc* plane. Reproduced with permission of the American Chemical Society [55].

layers containing the $\{[Mo_3S_7Cl_6]_2\}^{5-}$ aggregate and acetonitrile molecules interleaved with ET layers perpendicular to the inorganic sublattice. The four crystallographically independent ET molecules depicted as A, B, C and D are almost parallel and are arranged in the β structural type, a distribution that has provided numerous examples of metallic and superconducting charge-transfer salts [114]. Compound $(ET)_8\{[Mo_3S_7Cl_6]_2{\cdot}Cl\}CH_3CN$ presents a room temperature conductivity (ca. $\sigma = 0.35–3.5\,S\,cm^{-1}$) and metallic behavior with a transition to an activated conductivity down ca. 270 K.

## 6. Single-component molecular conductors

The electrochemical properties of the trinuclear $Mo_3S_7$ and $Mo_3S_4$ dithiolene dianions evidence the ability of this system to generate stable radicals with $C_{3v}$ symmetry and the possibility of having a partially occupied orbital with an e-type symmetry, that is with one or two unpaired electrons. The resulting radical species can participate in multiple S···S interactions and a small HOMO–LUMO gap can be envisioned considering the small energy difference calculated between the HOMO and HOMO-1 orbitals in the $[Mo_3S_7(dithiolene)_3]^{2-}$ precursors. These ideas have prompted an extensive investigation on the oxidation chemistry of the dithiolene cluster dianions in an attempt to obtain cluster-based neutral $Mo_3S_7(dithiolene)_3$ and $Mo_3S_4(dithiolene)_3$ single-component conductors.

This goal was accomplished in 2004 by using the $(n\text{-}Bu_4N)_2[Mo_3S_7(dmit)_3]$ compound as target [55]. On the basis of the easily accessible oxidation of this dianion ($E_{1/2} = 0.38\,V$), we found that chemical or electrochemical oxidation of the dianion provides neutral paramagnetic $Mo_3S_7(dmit)_3$ species. Compound $Mo_3S_7(dmit)_3$ still represents the only example of a structurally characterized neutral complex made of cluster entities. Fig. 11 shows the crystal structure of this compound and its partial crystal packing.

Neutral $Mo_3S_7(dmit)_3$ crystallizes in a trigonal space group with the cluster units oriented along the *c* direction and connected through various S···S contacts as represented in Fig. 11b, to produce infinite chains. Parallel chains are related by an inversion center and connected through short contacts across the *ab* plane between the dmit sulfur atoms of one cluster chain and the bridging cluster sulfur on the c adjacent chain, as represented in Fig. 11c. This packing results in an extended hexagonal network (see Fig. 12) with threefold symmetry molecular units and partially filled molecular orbitals.

Powder diffraction techniques have shown the isostructurality of the $Mo_3S_7(dmid)_3$ and $Mo_3S_7(dsit)_3$ single-component materials, also prepared by chemical (with iodine) or electrochemical oxidation, with the dmit derivative.

All attempts to produce neutral paramagnetic $Mo_3S_7(dithiolene)_3$ complexes from their corresponding dianions derivatized with other dithiolene ligands (i.e. tfd, bdt, mnt, and tdas) using iodine, ferrocenium salt, lead acetate, 4-iodobenzene dichloride or electrochemically yield non-crystalline dark-fine insoluble powders whose compositions were dependent on the oxidation agent according to elemental analysis [57]. Similar results were obtained when oxidizing the $[Mo_3S_4(dithiolene)_3]^{2-}$ cluster dianions aimed at obtaining neutral $Mo_3S_4(dithiolene)_3$ species.

From an electronic point of view, oxidation of $[Mo_3S_7(dithiolene)_3]^{2-}$ to neutral $Mo_3S_7(dithiolene)_3$ results in a change from a $1a_1{}^2 1e^4$ to a $1a_1{}^2 1e^2$ ground-state, which leads to a partial occupation of the degenerate HOMO e-type orbitals with the concomitant production of radicals, a prerequisite in the formation of single-component molecular conductors. In addition, this two-electron oxidized molecule is also interesting from the magnetic point of view because it should have a spin $S = 1$. The magnetic susceptibility measured on polycrystalline samples of $Mo_3S_7(dmit)_3$ and their dmid and dsit homologues (see Fig. 13) shows a continuous decrease in the $\chi T$ versus $T$ plot upon cooling. At room temperature, the $\chi T$ values are clearly below the expected for a spin triplet (approx. $1\,emu\,K\,mol^{-1}$). These observations clearly indicate the presence of antiferromagnetic exchange interactions between the unpaired electrons of the

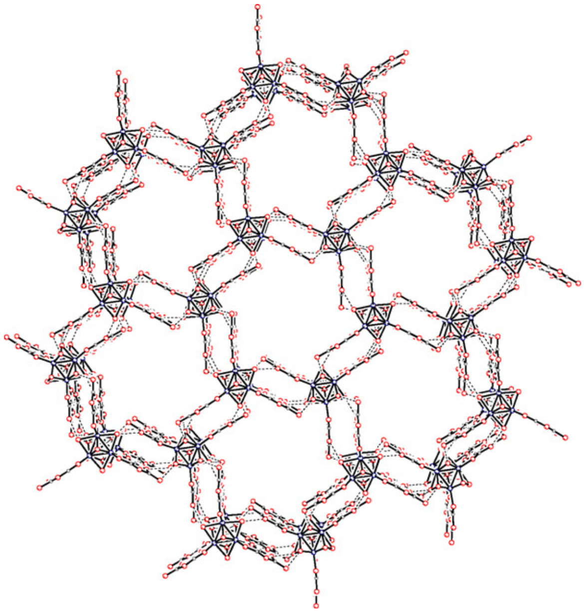


**Fig. 12.** Schematic representation along the *c* axis of the hexagonal honey-comb network defined by the $C_3$-symmetrized $Mo_3S_7(dmit)_3$ (**9**). Reproduced with permission of the American Chemical Society [55].

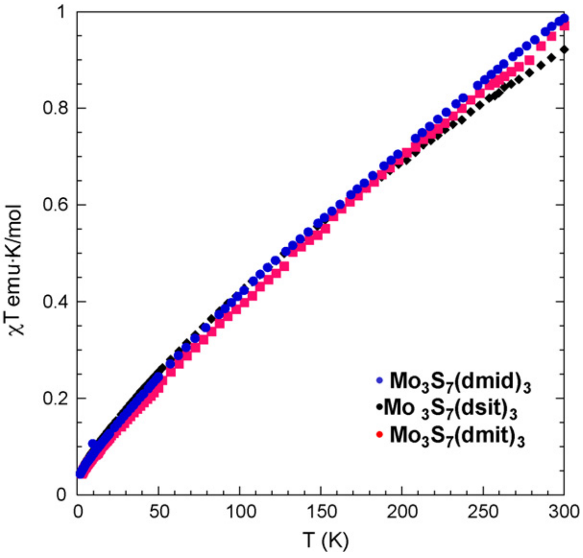


**Fig. 13.** Temperature dependence of the $\chi T$ product for polycrystalline samples of $Mo_3S_7(dithiolene)_3$ complexes [55,57].

neutral $Mo_3S_7(dithiolene)_3$ molecules. The magnetic behavior of these compounds can be explained as a one-dimensional exchange network formed by randomly distributed $S=0$ and $S=1$ spins, as we will detail later on in this section [55].

The dc electrical conductivities of dmit, dmid and dsit $Mo_3S_7$ neutral complexes have been measured by the four-probe method on compacted pellets and/or single crystal samples. A summary of the results is listed in Table 3. The resistivity of the neutral $Mo_3S_7(dmit)_3$ phases increases gradually with decreasing temperature, thus indicating a semiconductor behavior. The room temperature electric conductivity of single crystals of $Mo_3S_7(dmit)_3$ along the *c* axis is 25 S cm$^{-1}$, which is very high for a neutral molecular crystal and this value doubles at high pressures. The room temperature conductivity for $Mo_3S_7(dmid)_3$ measured on pressed pellets ($\sigma = 2\,S\,cm^{-1}$, $E_a = 90\,meV$) was comparable to that reported for $Mo_3S_7(dmit)_3$, while moderate conductivity was observed for $Mo_3S_7(dsit)_3$ ($\sigma = 9 \times 10^{-2}\,S\,cm^{-1}$, $E_a = 220\,meV$).

First-principles spin-polarized DFT-type calculations on the $Mo_3S_7(dmit)_3$ complex estimate the antiferromagnetic (AFM) state to be very close in energy to the ferromagnetic (FM) state, the AFM state being only 0.02 eV/molecule below the FM state in agreement with the susceptibility data [55]. Band structure calculation on the AFM state shows the existence of predominant electronic interactions along the *c* direction, represented in Fig. 14a, for the electrons near the Fermi level so that $Mo_3S_7(dmit)_3$ is a one-dimensional magnetic semiconductor with a small but non-negligible dispersion along *c*. In addition there is a small energy gap at the Fermi level (ca. 200 meV) in harmony with the activated although high conductivity of the system. The origin of this low energy gap is closely related to the small difference between the HOMO and HOMO-1 orbitals calculated for the dianionic clusters employed as precursors.

**Table 3**
Room temperature conductivity values for $Mo_3S_7(dithiolene/diselenolene)_3$ phases.

| Compound | $\sigma$ (S cm$^{-1}$) | Ref. |
|---|---|---|
| $Mo_3S_7(dmit)_3$ | 1 (pressed pellets)<br>25 (single crystal)<br>50 (crystals at 10 kbar) | [55] |
| $Mo_3S_7(dmid)_3$ | 2 (pressed pellets) | [57] |
| $Mo_3S_7(dsit)_3$ | $9 \times 10^{-2}$ (pressed pellets) | [57] |

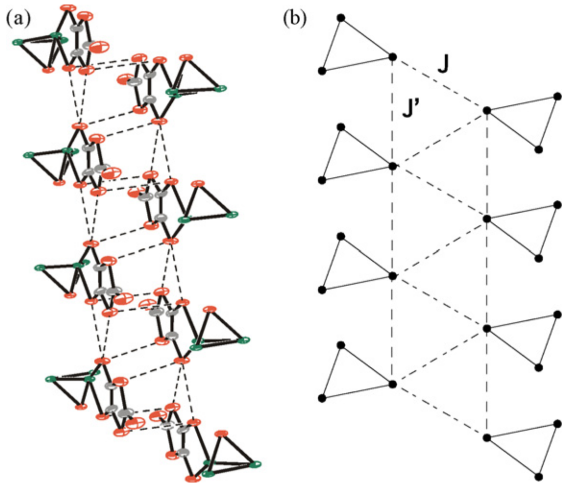


**Fig. 14.** (a) Partial representation of the $Mo_3S_7(dmit)_3$ structure along the *c* axis emphasizing the S···S interactions responsible for the conduction paths. Only two adjacent cluster chains and one dmit ligand per cluster are represented. Bridging disulfides within the cluster core have been omitted for clarity; (b) exchange network of the $Mo_3S_7(dmit)_3$ structure showing the two different exchange parameters *J* and *J*′. Reproduced with permission of the American Chemical Society [55].

Complexes $Mo_3S_7(dmit)_3$, $Mo_3S_7(dmid)_3$, and $Mo_3S_7(dsit)_3$, represent a new family of single-component molecular conductors built by magnetic units. A distinctive feature of these single-component molecular conductors is that the electrons responsible of the conductivity are also of the magnetic properties. In fact, the interactions responsible of the conducting properties have also been used to model the magnetic behavior by considering two competing antiferromagnetic interactions; named as *J* and *J*′ in Fig. 14b. The nearest-neighbor interaction, *J*, corresponds to the exchange pathway through dithiolene ligands belonging to different chains, and the next-nearest-neighbor interaction, *J*′, to the exchange pathway through dithiolenes belonging to the same chain of clusters. In the model each magnetic cluster is in fact a mixed-valence system containing two unpaired electrons delocalized over three sites where the two antiferromagnetic interactions compete to give rise to a spin frustrated network. The hypothetical metallic state for $Mo_3S_7(dmit)_3$ solid was calculated to be only 50 meV/molecule higher in energy that the AFM state. A similar phenomenon was later reported for a mononuclear congener, namely, the anion radical salt (Me-3,5-DIP)$[Ni(dmit)_2]_2$ (Me-3,5-DIP = *N*-methyl-3,5-diiodopyridinium) in which metallic conduction and paramagnetism with AFM interactions derived solely from the molecular π-electrons of $Ni(dmit)_2$ anions [115].

## 7. Summary and outlook

Both the synthetic, electronic and structural characteristics of $C_3$-symmetrized $Mo_3S_7$/dithiolene clusters are comprehensively reviewed, emphasizing the versatility of these $Mo_3S_7$/dithiolene systems for the design of two-component or single-component molecular conductors. Until now, remarkable findings in the field of magnetic conductors based on cluster units coordinated to dithiolene ligands, have been accomplished using a limited number of sulfur-rich $Mo_3$ cluster units, most of them described above. It is noteworthy the synthesis of radical cation salts made of TTF-based donors and the octanuclear copper complex $[Cu_8(i\text{-}mnt)_6]^{4-}$ featuring 1,1-bis-dithiolene ligands [116]. However, as a result of continuous efforts of cluster chemists, a wide spectrum of cluster topologies as well as improved synthetic strategies are now available, although only prospective work has been done in the field of molecular conductors, where the first steps are being currently established. A relevant example is that of introducing heavier chalcogen atoms in the $Mo_3S_7$ cluster core to afford $Mo_3Q_7$/dithiolene (Q = S, Se, Te), an approach that has been widely utilized for the preparation of closely related selenium-rich molecular conductors. This is mainly motivated because their electronic states are quite sensitive to molecular arrangement and orientation, and this may be controlled by increasing the dimensionality via Se···Se short contacts. This has been illustrated recently for a family of all-sulfur, all-selenium and mixed S/Se heterocyclic thia/selenazyl radical conductors for which Se···Se interactions in the solid significantly affects the transport and magnetic properties [117], or for some single-component Ni and Au conductors incorporating Se in the extended TTF backbone [118]. Very interesting perspectives emerges for the series of $Mo_3S_7(dmit)_3$ and dmit isologues since their structural analysis reveal segregation of columns of the $Mo_3S_7(dmit)_3$ molecules by means of $\mu_3$-S···$\mu_2$-$S_2$ interactions. In order to separately unravel the individual contributions of each type of interaction into the conductivity path, ways of preparation of the mixed-chalcogen $[Mo_3(\mu_3\text{-}Q)(\mu\text{-}Q_2)_3]^{4+}$ (Q = S, Se, Te) clusters with two different chalcogen atoms represent a promising alternative. Examples of $Mo_3Se_7$, $Mo_3Te_7$ as well as mixed chalcogen $Mo_3S_{7-x}Se_x$, $Mo_3S_{7-x}Te_x$ and $Mo_3Se_{7-x}Te_x$ ($x$ = 0–7) with cyanide ligands have been identified [119], well-defined isomers of $Mo_3S_4Se_3$ [120,121], and $Mo_3SSe_6$ with bromine ligands [122] or $Mo_3Se_4S_3$ and $Mo_3Te_7$ clusters with dithiophosphate ligands [123–126], are also known, although their coordination to 1,2-dithiolene ligands remains unknown.

It is also appealing, the search of new cluster topologies for dithiolene-based ligand coordination. A topologically related $C_{3v}$-symmetrized family of clusters is that comprising a $V_3S_7$ cluster core from which only a limited number of bidentate ligands have been coordinated such a bipyridines or dithiocarbamates of general formula $[V_3S_7(bipy)_3]^+$ and $[V_3S_7(dtc)_3]^-$ [127,128]. Other $C_3$-symmetrized sulfur-rich clusters are known [129], such as several $V_3S_4$ [130], $Nb_3SO_3$ (because of the O/S exchange, it is not strictly $C_3$-symmetrized) cluster core [131]. However, in all cases, formation of these clusters cores remains less rationalized and typically involves self-assembly reactions starting from low nuclearity compounds. Even less developed is the substitutional lability of terminal ligands in these $V_3S_7$, $V_3S_4$ or $Nb_3SO_3$ cluster units so that coordination of 1,2-bis-dithiolene ligands has not been reported. This is in part due to the lack of starting precursor of $V_3S_7$, $V_3S_4$ or other trinuclear units featuring dihalide ligands in a cis disposition amenable to enter dithiolene substitution reaction. This cis disposition has proved to be very suitable to enter ligand substitution reactions, not only for the $Mo_3S_7$ clusters reviewed herein but also for transition metal cyclopentadienyl complexes of general formula CpM(dithiolene) [132]. In this context, several families of sulfur-rich clusters are very attractive, such as those comprising the tetranuclear $Ta_4S_9Br_8$ and $Ta_4Se_9I_8$ clusters which are prepared from the elements where each Ta atom has two terminal bromine atoms in a cis orientation (see Fig. 15) [133,134]. A topologically related complex is $V_4S_9Br_8$, also obtained from the elements, whose molecular structure displays a polymeric form. The compound can be described by the crystallochemical formula $[V_4S_9Br_{8/2}]_n$ where each V atom has two bridged bromine atom-bonded cluster fragments in a layered polymeric structure.

While compounds $Ta_4S_9Br_8$ and $Ta_4Se_9I_8$ are diamagnetic, compound $[V_4S_9Br_{8/2}]_n$ is paramagnetic at room temperature displaying an AFM-type ordering at low temperatures. These tetranuclear $Ta_4S_7Br_8$, $Ta_4Se_9I_8$ and $V_4S_7Br_8$ clusters holds much promise for the straightforward access to dithiolene coordination since these clusters features halide ligands coordinated to each metal site in a cis configuration. We believe that exploration of these new cluster units will provide additional examples of synergy between cluster entities and dithiolene ligands.

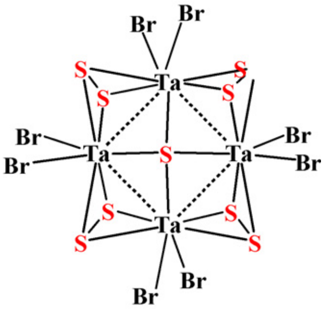


**Fig. 15.** Schematic representation of the cluster $Ta_4S_9Br_8$ also applicable to the repeating unit in the polymer $[V_4S_9Br_{8/2}]_n$.

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