DALTON
PERSPECTIVE

Rhenium sulfide cluster chemistry †

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Rhenium sulfides are still very rare except for octahedral cluster compounds. The chemistry of trinuclear, tetranuclear and octahedral cluster compounds is reviewed in comparison with that of molybdenum sulfide clusters and in the light of the relationships between molecular and solid state cluster compounds. A promising outlook is expected.

1 Introduction

Rhenium is one of the rarest elements on the earth and its concentration in the earth's crust is only 0.0004 ppm.[1] No ore deposit containing rhenium as the main metal component is known and rhenium is produced as a by-product in the metallurgy of other metals, especially of molybdenum. A pure rhenium mineral with a composition between ReS_2 and Re_2S_3 was discovered recently from a volcano in the Kuril islands.[2] This is claimed to be the first natural mineral with Re as the only cation and the first example of macroscopic Re mineralization.

There are two known rhenium sulfides. One is the disulfide ReS_2 and the correct structure was determined recently by single crystal X-ray analysis.[3,4] The other is the heptasulfide Re_2S_7 which has been obtained only in amorphous forms and the structure is still unknown.[5] Both solid state and molecular sulfide cluster compounds are less abundant than those of molybdenum which otherwise is in many ways similar to rhenium.[6,7] Because of the paucity of good starting compounds, the chemistry of the sulfide cluster compounds of rhenium is still in a very early stage of development. There is, however, good reason to expect that the chemistry of the rhenium sulfide clusters and their congeners of selenium and tellurium will be as rich as that of molybdenum. The present article focuses on the characteristics of this chemistry compared with those of the early or late transition metals, molybdenum in particular,[8] and on the relationship between the molecular and solid state clusters.[9]

Table 1 Trinuclear and tetranuclear rhenium sulfide cluster compounds

Compound	MCE	Ref.
$[Re_3S_7Cl_6]Cl$	6	10
$[Re_3S_7Cl_6]AlCl_4$	6	11
$[Re_3S_7Br_6]Br$	6	11
$[PEt_3H][Re_3S_4Cl_6(PEt_3)_3]$	8	14
$[Re_3S_4Cl_4(PEt_3)_3]$	9	20
$[Re_3S_4Br_3(PEt_3)_4]$	10	20
$[Et_4N][Re_3S_3(SO_2)Cl_6(PEt_3)_3]$	8	22
$[NH_4]_4[Re_4S_{22}]$	12	26
$[Ph_4P]_4[Re_4S_4(CN)_{12}]$	12	28
$[Cs_2K_2][Re_4S_4(CN)_{12}]$	12	30
$[Re_4S_4Cl_8(TeCl_2)_4]$	12	31
$R_4S_4Te_4$	12	34
$K_8[Re_4S_2(SO_2)_4(CN)_{10}]$	14	24
ReS_2	12	3, 40

2 Position of rhenium in the periodic table

Rhenium being a Group 7 element located between the early and late transition metals, forms compounds having properties intermediate between those expected for these extremes. The ground state electronic configuration is $[Xe]4f^{14}5d^{5}6s^{2}$ which allows for the formation of rhenium compounds in oxidation states from −III to +VII (d^{10} to d^{0}).[1] The number of valence electrons in the same oxidation states is larger by one than that of molybdenum which is located in a diagonal position to the upper left. If the isoelectronic analogy holds, we can expect compounds of rhenium in an oxidation state one electron higher than those of molybdenum. In cluster compounds with a metal nuclearity of *n* and with the same number of anionic ligands, the isoelectronic relationship can be realized by changing *n* monovalent anions to *n* divalent anions, or by introducing counter anions X^{n-}. The replacement of halogens by chalcogens has proved very fruitful in the preparation of new rhenium compounds with similar cluster frameworks to those of molybdenum. This has been the case especially for the octahedral cluster compounds. The number and variety of the rhenium sulfide clusters are still limited as seen in Table 1 which lists the reported trinuclear and tetranuclear cluster compounds.

3 Triangular clusters

The first halogen–sulfur mixed anion clusters were reported by

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† Dedicated to Professor Warren Roper on the occasion of his 60th birthday.

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Taro Saito

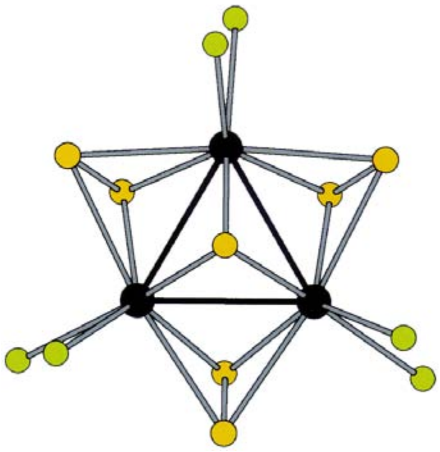

Fig. 1 Structure of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_6]^+$ in **1** (Re black, S yellow, Cl light green).

Timoshchenko *et al.*[10,11] $Re_3S_7Cl_7$ **1** (Fig. 1) was prepared by the reaction of $ReOCl_4$ with sulfur in a solution in S_2Cl_2 at 200 °C. The product is a black crystalline compound and relatively stable in air. It is insoluble in S_2Cl_2, CCl_4, CS_2, hydrocarbons, and acetonitrile, but soluble in pyridine, DMSO, and DMF. The yield was 80% based on $ReOCl_4$ and the reaction equation is considered to be

$$6\ ReOCl_4 + 27\ S \longrightarrow 2\ Re_3S_7Cl_7 + 3\ SO_2 + 5\ S_2Cl_2$$

Similar compounds $Re_3S_7Br_7$ and $Re_3S_7Cl_6AlCl_4$ were prepared by the reaction of Re_2O_7 with S_2Br_2, and with a solution of $AlCl_3$ and S_2Cl_2, respectively.

The structures of these compounds comprise a triangular rhenium framework, a capping sulfur and three edge-bridging S_2, and six terminal halogen ligands. Thus the structures are formulated as $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_6]X$. The counter anion has weak "secondary" bonding with the S_2 ligands. The whole structures are very like those of the molybdenum analogue $[Et_4N]_2[Mo_3S_7Cl_6]$,[12] which is isoelectronic with the rhenium cluster. The oxidation state of rhenium is +V (d^2), while that of molybdenum +IV (d^2). The Re–Re distances (2.698 Å for **1**) are somewhat shorter than the Mo–Mo distances (2.758 Å) reflecting the higher oxidation state. The molybdenum cluster has been prepared from a chain cluster compound $Mo_3S_7Cl_2Cl_{4/2}$[13] by the scission of the bridging chlorine with concomitant introduction of two terminal chlorine ligands. In order to keep the isoelectronic relationship, the pentavalent rhenium atoms require three extra halogens and the result is the formation of the ionic cluster compounds instead of the bridged chain compound.

Trinuclear rhenium sulfide cluster complexes with triethylphosphine ligands have been prepared by the reaction of $Re_3S_7Cl_7$ with triethylphosphine in benzene. One of the sulfur atoms in the S_2 bridging ligands is removed as triethylphosphine sulfide and the vacant coordination sites are occupied by triethylphosphine ligands. Two cluster complexes have been isolated from these reactions.

The first one, crystallized from a benzene solution, is $[PPh_3H][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]$ **2** which has a triangular rhenium core capped and bridged by sulfur ligands.[14] Each rhenium is coordinated by a triethylphosphine and two chlorine ligands. All the triethylphosphine ligands are directed below the Re_3 plane capped by the μ_3-S atom and the chlorine ligands are above the plane (Fig. 2). The Re–Re distances are 2.715 Å, 2.716 Å, and 2.725 Å and the Re–Re–Re angles range from 59.87° to 60.23°. Therefore the cluster core distorts slightly from a regular triangle. The cluster part is a monovalent anion with 8 MCE (metal cluster electron) and the rhenium atoms are in the mixed valence oxidation state of 2 × Re(IV) and Re(V)

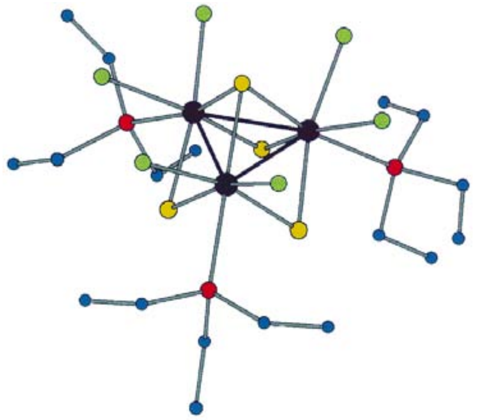

Fig. 2 Structure of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$ in **2** (Re black, S yellow, Cl light green, P red, C blue).

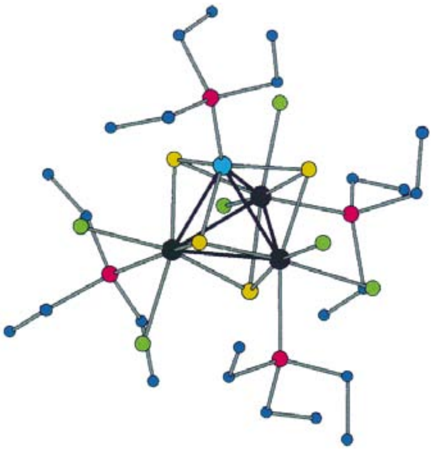

Fig. 3 Structure of $[Re_3Ni(\mu_3\text{-}S)_4Cl_6(PEt_3)_4]$ **3** (Re black, Ni light blue, S yellow, Cl light green, P red).

(= +13/3). The Re–Re distances are slightly longer than those in the starting 6-electron compound (2.701 Å),[10] reflecting the lower oxidation states of rhenium atoms. The Re–Re distances are shorter than those of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(MeOH)_2]$ (Mo–Mo 2.738–2.780 Å)[15] and may be explained by the smaller Re metallic radius (1.29 Å *vs.* 1.31 Å for Mo).[16] The two cluster complexes differ in the number of MCE, and are not isoelectronic. The reason why an 8-electron cluster complex forms preferentially from the 6-electron cluster compound $Re_3S_7Cl_7$ is not clear. Probably the reducing conditions with excess triethylphosphine are responsible for the formation of the more reduced cluster.

The cluster core is very similar to the molybdenum analogues[8] which have proved useful for the construction of larger cluster compounds.[17] For example $[Mo_3Ni(\mu_3\text{-}S)_4(H_2O)_{10}]^{4+}$ has been prepared by the condensation of $[Mo_3S_4(H_2O)_9]^{4+}$ with metallic nickel.[18] The reaction of the rhenium cluster **2** with $Ni(cod)_2$ formed a mixed metal tetrahedral cluster complex $[Re_3Ni(\mu_3\text{-}S)_4Cl_6(PEt_3)_4]$ **3** (Fig. 3).[19]

The other trinuclear cluster complex formed under similar reaction conditions, but crystallized from acetone, is $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Cl)Cl_3(PEt_3)_3]$ **4**.[20] (Fig. 4). The cluster core consists of three rhenium atoms with two capping sulfur, two bridging sulfur and a bridging chlorine atom. A chlorine atom is located in the bridging position by comparison of the structure with that of an analogous 10-electron cluster complex $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Br)Br_2(PEt_3)_4]$.[20] The Re–Re distances are 2.628–2.677 Å (mean 2.653 Å) and the Re–Re bond with the bridging chlorine is the longest one. The distances are considerably shorter than the mono-capped triangular rhenium cluster. Each rhenium is coordinated by a terminal chlorine and a triethylphosphine ligand. This complex has 9 MCE with 3 Re(IV)

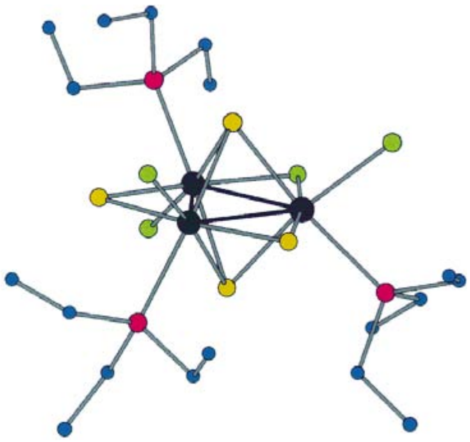

Fig. 4 Structure of $[Re_3(\mu_3\text{-}S)_2(\mu\text{-}S)_2(\mu\text{-}Cl)Cl_3(PEt_3)_3]$ **4** (Re black, S yellow, Cl light green, P red, C blue).

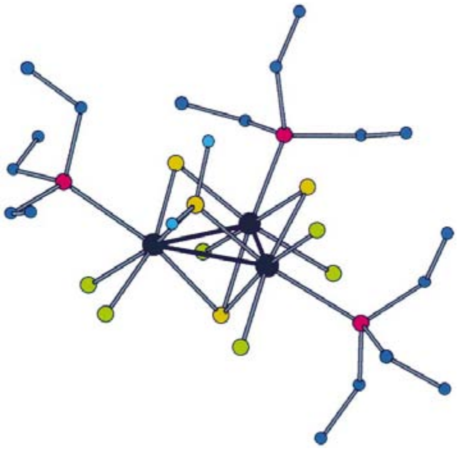

Fig. 5 Structure of $[Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]^-$ in **5** (Re black, S yellow, Cl light green, P red, C blue).

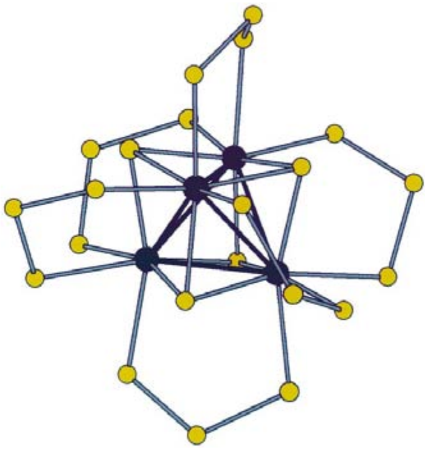

Fig. 6 Structure of $[Re_4(\mu_3\text{-}S)_4(\mu\text{-}S_3)_6]^{4-}$ in **6** (Re black, S yellow).

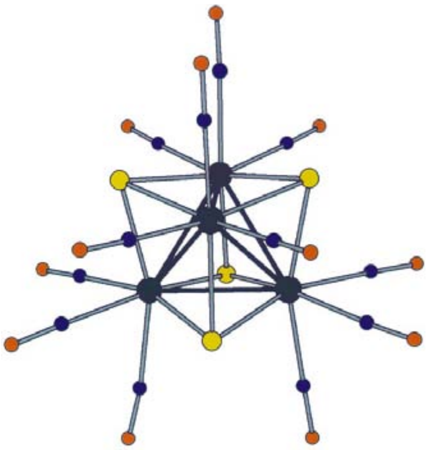

Fig. 7 Structure of $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$ in **7** (Re black, S yellow, C blue, N orange).

centers in contrast with the mono-capped cluster **2** and is paramagnetic.

The bi-capped triangular cluster of rhenium resembles the molybdenum cluster $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ with 8 MCE.[21] The Mo–Mo distance is 2.714 Å and is longer than the Re–Re distances. In the bi-capped molybdenum and rhenium clusters, the number of MCE is larger than necessary for 3 M–M 2c–2e bonds (6 electrons) and the excess electrons are considered to enter the a_1'' orbital for the molybdenum cluster and e' orbital for the rhenium cluster. The molybdenum cluster has a regular triangular core and the rhenium cluster has an isosceles triangle one.

The reaction of $Re_3S_7Cl_7$ with PEt_3 in benzene at room temperature under a nitrogen atmosphere for 1 week and with addition of Et_4NCl to the reaction solution formed large black crystals of a compound with the formula $[Et_4N][Re_3(\mu_3\text{-}S)(\mu\text{-}SO_2)(\mu\text{-}S)_2Cl_6(PEt_3)_3]\cdot 2Me_2CO$ **5**.[22] The Re atoms form a monocapped triangle and are bridged by two S and one SO_2 ligands (Fig. 5). The Re–Re distances are significantly longer (mean 2.81 Å) than in any of previously observed triangular Re–S clusters, the shortest one is bridged by SO_2 (2.79 Å). Examples of SO_2 bridged Re–Re bonds are also found in binuclear $[Re_2(SO_2)_2(CN)_8]^{6-}$ (2.636 Å)[23] and rhombic $[Re_4(\mu_3\text{-}S)_2(\mu\text{-}SO_2)_4(CN)_{10}]^{8-}$ (2.837 Å).[24] Another feature is the very short distances between the Re and the μ-S atoms. At 2.24–2.26 Å, this is considerably shorter than those in other compounds having Re–S–Re bridges (average value is about 2.30 Å).[14] Thus the incomplete cubane framework Re_3S_4 has a high degree of distortion in **5**.

The S=O distance (1.47 Å) is slightly shorter than that found in both the above mentioned rhenium clusters with bridging SO_2 (1.49 Å). Only two of the three PEt_3 ligands are found in positions *trans* to the capping sulfur, the third phosphine ligand being *cis* to μ_3-S and *trans* to μ-SO_2. It is assumed that the SO_2 ligand is acting as a 4-electron donor, SO_2^{2-}. It is likely that the cluster $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$ forms first and then is oxidized by oxygen to give **5**. In the electron-rich 8-electron $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]^-$, the two extra electrons in the $Re_3S_4^{5+}$ core are delocalized over the $Re_3(\mu\text{-}S)_3$ ring, given the closeness of energy of Re 5d and S 3p AO as shown in the MO calculations for analogously built incomplete $Mo_3S_4^{4+}$ cubes.[25] This delocalization enhances negative partial charge on bridging sulfur atoms and facilitates attack by an electrophilic agent (O_2) to give SO_2.

4 Tetrahedral clusters

The first tetrahedral cluster of rhenium $[NH_4]_4[Re_4(\mu_3\text{-}S)_4(\mu\text{-}S_3)_6]$ **6** was synthesized by Müller *et al.* upon heating a solution of $[NH_4][ReO_4]$ with an aqueous ammonium polysulfide solution.[26,27] The cluster core consists of a Re_4 tetrahedron capped by a sulfur atom on each face and bridged by a S_3 ligand on each of the six edges (Fig. 6). The Re–Re distances are 2.763 Å and the Re–μ_3-S distances are 2.319 Å. The S_3 ligands bridge the rhenium atoms in envelope shapes with S–S distances of 2.140 Å. The compound is diamagnetic with 4 Re(IV) and 12 MCE to be assigned to the 6 Re–Re bonds.

Griffith *et al.* obtained $[Re_4Q_4(CN)_{12}]^{4-}$ **7** in attempts to repeat the preparation of the salts of $[Re(CN)_6]^-$ from $K_2[ReCl_6]$, KSCN and excess KCN.[28] The structures of the tetraphenylphosphonium salts turned out to be tetrahedral clusters $[Ph_4P]_4[Re_4Q_4(CN)_{12}]\cdot 3H_2O$ (Q = S, Se) (Fig. 7). The sulfide anion contains a tetrahedron of bonded rhenium atoms

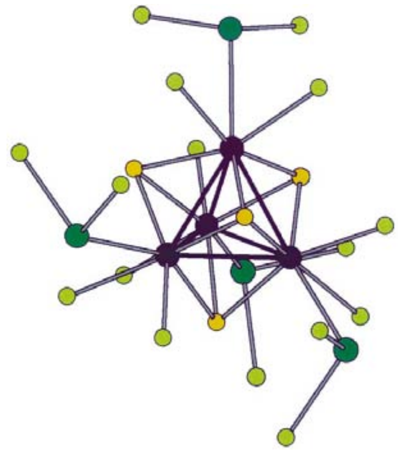

Fig. 8 Structure of $[Re_4(\mu_3\text{-}S)_4Cl_8(TeCl_2)_4]$ **8** (Re black, S yellow, Cl light green, Te green).

(mean Re–Re 2.755 Å) with one sulfur atom per face of the tetrahedron, equally bonded to each rhenium atom (mean Re–S 2.34 Å). Three CN groups are attached to each Re atom making the coordination number of the rhenium atom 9 including the Re–Re bonds. The cluster compound is diamagnetic and the number of MCE is 12 for the tetravalent rhenium atoms (d^3) consistent with 6 metal–metal single bonds. In the isoelectronic and isostructural molybdenum cluster $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$,[29] the Mo–S distances (2.38 Å) are almost the same but the metal–metal distances are much longer (2.854 Å) reflecting not only a larger ionic radius of Mo(III) than that of Re(IV) but also probably a weaker metal–metal bonding interaction.

Recently, a high-yield synthesis of the $[Re_4S_4(CN)_{12}]^{4-}$ anion has been attained by the reaction of an aqueous solution of $Re_3S_7Br_7$[11] and KCN at room temperature for 60 min.[30] The addition of CsCl formed $Cs_2K_2[Re_4S_4(CN)_{12}]\cdot 2H_2O$ in 78% yield. The reaction is believed to proceed *via* trinuclear $[Re^{V}{}_3S_4]^{7+}$ and binuclear $[Re^{VI}{}_2S_4]^{4+}$ yielding the $[Re^{IV}{}_4S_4]^{8+}$ compound.

A new series of tetrahedral rhenium chalcogenide cluster compounds with novel $TeCl_2$ ligands has recently been reported.[31] The sulfide (**8**) among $[Re_4(\mu_3\text{-}Q)_4Cl_8(TeCl_2)_4]$ (Q = S, Se, Te) is prepared by the reaction of $ReCl_5$, elemental sulfur, and elemental tellurium at 400 °C for 48 h in 93% yield. The Re–Re (2.706–2.742 Å) and Re–S (2.332–2.349 Å) distances are near those of the other Re_4 clusters mentioned above and the most prominent feature is the presence of the coordinated $TeCl_2$ ligand (Fig. 8) (Re–Te 2.725 Å, Te–Cl 2.328 Å, and Cl–Te–Cl 96.5°). The $TeCl_2$ is stabilized upon bonding to the rhenium cluster core. The cluster compound is insoluble in organic solvents and water but reacts slowly with DMF to form $[Re_4(\mu_3\text{-}S)_4Cl_8(DMF)_4]$ and with KCN in water to form $K_4[Re_4(\mu_3\text{-}S)_4(CN)_{12}]$. A rhenium telluride $[Re_4(\mu_3\text{-}Te)_4Br_8(TeBr_2)_4]$ having a similar tetrahedral Re_4 cluster core and $TeBr_2$ ligands has also been reported.[32]

The tetrahedral rhenium cluster $Re_4S_4Te_4$ **9** was synthesized by Fedorov *et al.*[33] and characterized by a single crystal study as well as by powder X-ray diffraction.[34] The compound was obtained from the reaction of rhenium metal, elemental sulfur and tellurium in the ratio of 1 : 1 : 6 at 900 °C for 3 weeks. The Re_4 cluster core is a tetrahedron capped by a sulfur atom on each face forming a distorted cube of Re_4S_4. The Re–Re distance is 2.785 Å and the Re–S distance is 2.337 Å. Each rhenium atom is further coordinated by three bridging tellurium atoms at a distance of 2.790Å (Fig. 9). The short Re–Re distance results from the tetravalent rhenium atoms which leave 12 MCE for the 6 metal–metal single bonds. The structure is of the type found in those of the chalcogeno halides of niobium and molybdenum $M_4Q_4X_4$ (M = Nb, Mo; Q = S, Se; X = Cl, Br, I)[35,36] which have been described as an NaCl-type arrangement of M_4Q_4 clusters and tetrahedral X_4 fragments. The rhenium analogue can also be regarded as a NaCl-type or zinc-blende-type arrangement of Re_4S_4 clusters and Te_4 tetrahedra, or a distorted spinel in which the octahedral cavities formed by sulfur and tellurium atoms are occupied by rhenium atoms and the tetrahedral cavities are vacant. The NaCl type (Te–Te 3.60 Å) and zinc-blende type (Te–Te 3.49 Å) are different in the assumed tetrahedra of tellurium atoms. X-Ray emission and X-ray photoelectron studies of $Re_4S_4Te_4$ have been reported.[37]

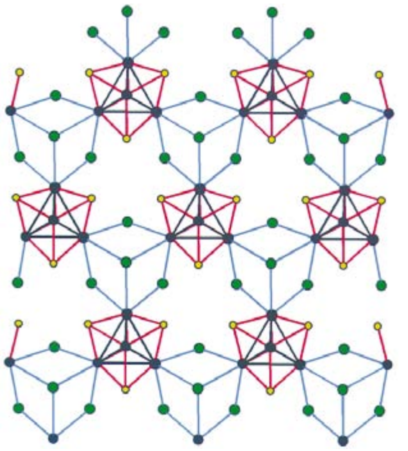

Fig. 9 Connectivity in $Re_4S_4Te_4$ **9** (Re black, S yellow, Te green).

5 Rhomboidal clusters

The reaction of amorphous Re_2S_7 with aqueous CN^- solution at 85 °C formed a crystalline cluster compound $[Re_4(\mu_3\text{-}S)_2(\mu\text{-}SO_2)_4(CN)_{10}]^{8-}$ **10** together with $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$.[24] The cluster anion has a rhomboidal Re_4 framework capped by two μ_3-S atoms. The four edges are bridged by SO_2 ligands which are considered to be formed by the oxidation of the μ-S ligands in the intermediate product '$[Re_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(CN)_{10}]^{8-}$'. The oxidation states of the rhenium atoms are III and IV and the number of MCE is 14. As 5 Re–Re bonds require only 10 electrons, Müller claims that the localization of negative charge on the central Re(III) atoms leads to the formation of considerable double-bond character in the transannular Re–Re bond.[24]

Rhomboidal molybdenum sulfide clusters $[Mo_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4X_2(PMe_3)_6]$ (X = SH, Cl, Br, I, SCN) have been reported.[38,39] The molybdenum atoms are in mixed valence states represented by $Mo(IV)_2Mo(III)_2$. The number of MCE is 10 corresponding to an electron-precise cluster core with 5 Mo–Mo bonds (2.817–2.828 Å) for the Cl derivative. The transannular Mo–Mo distance (2.817 Å) is considerably longer than the transannular Re–Re distance (2.740 Å) reflecting the single bond nature. The DV-Xα MO calculations on the model compound $[Mo_4S_6Cl_2(PH_3)_6]$ have shown that the Mo–Mo bonding orbitals are strongly mixed with Mo–S orbitals and the HOMO–LUMO gap is 1.55 eV. The gap is larger than that in the $[Re_4S_2(SO_2)_4]^{2+}$ fragment (1.3 eV) obtained by EH-SCCC MO calculations.[24]

According to Müller, the greater number of valence electrons for the rhenium compound results in stronger M–M bonding, which is further strengthened because of the larger 5d–5d overlap than the 4d–4d overlap. Also it is suggested from the comparison of the rhenium and molybdenum cluster compounds that the rhomboidal rhenium cluster framework is stable in the presence of 4 excess MCE. However, whether these electrons enter the "transannular π* orbital" forming a Re–Re double-bond does not seem very clear, since the transannular metal–metal distances in $[Mo_4S_6Cl_2(PMe_3)_6]$ (10-electron, electron-precise), ReS_2 (12-electron, electron-precise) and $[Re_4S_2(SO_2)_4(CN)_{10}]^{8-}$ (14-electron, excess electron) are always the shortest ones. Therefore the shortness may be due to a steric

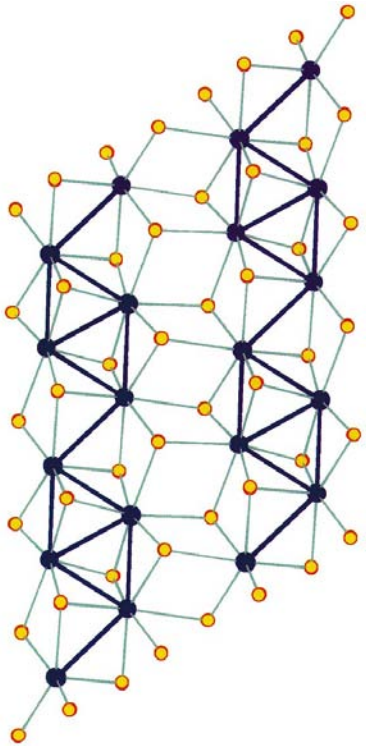

Fig. 10 Connectivity in ReS_2 (Re black, S yellow).

constraint in the cluster framework composed of amalgamation of two $M_3(\mu_3\text{-}S)$ triangular units.

Rhenium disulfide had been considered to be isostructural with $ReSe_2$ before the single-crystal X-ray diffraction study of Murray *et al.*[3] Layers of nearly hcp arrays of sulfur atoms stack along the *a* axis and are nearly parallel to the *bc* plane of the unit cell. The Re atoms occupy the octahedral sites between every other pair of the hcp layers of sulfur atoms. Each rhenium atom is coordinated by six sulfur atoms which in turn have trigonal pyramidal coordination to three rhenium atoms. Consequently, rhenium layers are sandwiched between two sulfide layers forming a distorted $CdCl_2$-type structure. The distances between the rhenium atoms are close enough to invoke Re–Re bonds and rhenium atoms form Re_4 parallelograms with Re–Re distances 2.790 Å and 2.824 Å and the shorter distance between the apexes is 2.695 Å (Fig. 10). The study has indicated that the crystal is not isostructural with the selenide in the sense that the fractional coordinates of corresponding atoms in different structures are similar. However, more recent comparative studies of $ReSe_2$ and ReS_2 have suggested that Murray *et al.* overlooked the doubling of the *c* axis in their structure description.[40] The new crystallographic study has indicated that the corresponding Re–Re distances in the Re_4 cluster are 2.805 Å, 2.800 Å, and 2.693 Å. A scanning probe microscopy study of ReS_2 has been reported.[4]

The rhomboidal rhenium cluster framework is the characteristic feature of the tetravalent d^3 rhenium disulfide and differs from molybdenum disulfide in which each molybdenum atom is in a trigonal prismatic coordination site and no apparent Mo–Mo bonds exist.[41] It is considered that metal–metal bonding is more favourable for rhenium than for molybdenum because of the larger 5d–5d overlap than the 4d–4d overlap.[24] The number of MCE for the Re_4S_8 unit is 12 resulting in 5 intracluster Re–Re bonds and 1 intercluster Re–Re bond. The molybdenum is in the tetravalent d^2 state and has one less electron for each metal. Therefore if a triangular molybdenum cluster forms Mo_3S_6 (=MoS_2) can use 6 MCE with 3 Mo–Mo bonds. This form of molybdenum disulfide may have $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu_3\text{-}S)_{6/3}$.[42]

Re_2S_7 has been obtained only in amorphous phases. The structure of the compound has been studied by a radial distribution analysis using experimental intensities from the powder patterns.[5] The study shows that it contains a Re_4 cluster framework similar to that of ReS_2. The Re–Re distances range from 2.6 to 2.9 Å and the shortest Re–S distance is 2.38 Å. The formal oxidation state of rhenium is heptavalent but Müller and his co-workers consider that the compound contains tetrahedral and rhomboidal Re_4 cluster units linked irregularly through S_x^{2-} ligands.[24] Thus the actual oxidation state of rhenium is lower than tetravalent and the compound can be considered a "quasi-solid" solution of clusters in S_x^{2-} solvent. The intramolecular oxidation of x S^{2-} into S_x^{2-} by 2 x electrons with the concomitant reduction of Re^{VII} into lower oxidation states is the reason for the presence of reduced metal cluster moieties. Also the presence of different kinds of metal clusters and S_x^{2-} anions with different chain lengths may be responsible for the failure of crystallization of Re_2S_7. The reaction of the compound with a CN^- solution forms two kinds of discrete cluster compounds, $[Re^{IV}_4S_4(CN)_{12}]^{4-}$ and $[Re_4S_2(SO_2)_4(CN)_{10}]^{8-}$.[24]

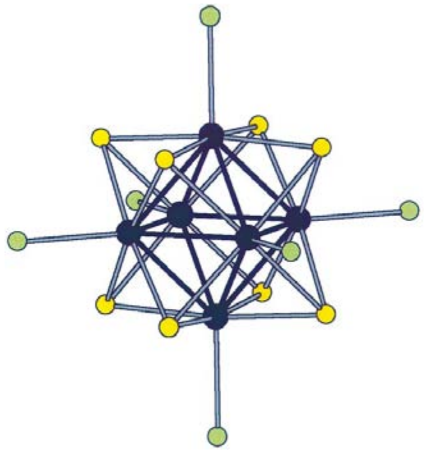

Fig. 11 Structure of $[Re_6(\mu_3\text{-}S)_8Cl_6]^{4-}$ (Re black, S yellow, Cl light green).

6 Octahedral clusters

Octahedral rhenium cluster compounds with 3-D to 0-D dimensionality have been prepared by solid state synthesis. Neutral ligands are not contained in these cluster compounds. Halogen bridges in the 1-D or 2-D compounds can sometimes be split by either MX or neutral ligands to form 0-D clusters (Fig. 11). No solution methods to prepare discrete octahedral cluster compounds by condensation have been reported. Condensation of octahedral molecular clusters is a possible route to the solid state clusters of higher dimensionality.

Table 2 lists the known and possible types of 0-D octahedral sulfide clusters with the combination of cations, monoanions, and neutral ligands. The MCE is fixed to 24-electron, because other oxidation states are rarely encountered. There is also the possibility of geometrical isomers such as *cis*, *trans*, *mer*, *fac* or isomerism due to the positions of the μ_3 ligands. It is easily seen that by elaborate combination of cations, divalent chalcogens, monovalent halogens, or neutral ligands, the total MCE remains 24-electron. As is evident from the small number of known examples, these combinations of ligands are not always easy to realize.

The correspondence of the Werner type octahedral complexes and octahedral cluster complexes has been noted[43] and some geometrical isomers of the octahedral molybdenum,[44] tungsten,[45] and rhenium,[46,47] cluster complexes have been isolated. The syntheses of several geometrical isomers of the octahedral rhenium cluster compounds coordinated by triethylphosphine ligands are remarkable.[47] Some of the geometrical isomers have been intended for use as precursors in

Table 2 Types of zero-dimensional octahedral rhenium sulfide clusters and reported examples

Type	Example	Ref.
$M_4[(Re_6S_8)X_6]$	$KCs_3[(Re_6S_8)(CN)_6]$	68
$M_3[(Re_6S_8)LX_5]$		
$M_2[(Re_6S_8)L_2X_4]$	$[Bu_4N]_2[\textit{cis}\text{-}\{(Re_6S_8)(PEt_3)_2Br_4\}]$	47
$M[(Re_6S_8)L_3X_3]$	$[Bu_4N][\textit{mer}\text{-}\{(Re_6S_8)(PEt_3)_3Br_3\}]$	47
$[(Re_6S_8)L_4X_2]$	$\textit{cis}\text{-}[(Re_6S_8)(PEt_3)_4Br_2]$	47
$[(Re_6S_8)L_5X]X$	$[(Re_6S_8)(PEt_3)_5Br]Br$	47
$[(Re_6S_8)L_6]X_2$	$[(Re_6S_8)(PEt_3)_6]Br_2$	47
$M_3[(Re_6S_7X)X_6]$	$[Bu_4N]_3[(Re_6S_7Cl)Cl_6]$	71
$M_2[(Re_6S_7X)LX_5]$		
$M[(Re_6S_7X)L_2X_4]$		
$[(Re_6S_7X)L_3X_3]$		
$[(Re_6S_7X)L_4X_2]X$		
$[(Re_6S_7X)L_5X]X_2$		
$[(Re_6S_7X)L_6]X_3$		
$M_2[(Re_6S_6X_2)X_6]$	$K_2[(Re_6S_6Br_2)Br_6]$	70
$[(Re_6S_6X_2)L_2X_4]$		
$[(Re_6S_6X_2)L_3X_3]X$		
$[(Re_6S_6X_2)L_4X_2]X_2$		
$[(Re_6S_6X_2)L_5X]X_3$		
$[(Re_6S_6X_2)L_6]X_4$		
$M[(Re_6S_5X_3)X_6]$	$K[(Re_6S_5Br_3)Br_6]$	67
$[(Re_6S_5X_3)LX_5]$		
$[(Re_6S_5X_3)L_2X_4]X$		
$[(Re_6S_5X_3)L_3X_3]X_2$		
$[(Re_6S_5X_3)L_4X_2]X_3$		
$[(Re_6S_5X_3)L_5X]X_4$		
$[(Re_6S_4X_4)X_6]$	$[(Re_6S_4Cl_4)Cl_6]$	71
$[(Re_6S_4X_4)LX_5]X$		
$[(Re_6S_4X_4)L_2X_4]X_2$		
$[(Re_6S_4X_4)L_3X_3]X_3$		
$[(Re_6S_4X_4)L_4X_2]X_4$		
$[(Re_6S_3X_5)X_6]X$		
$[(Re_6S_3X_5)LX_5]X_2$		
$[(Re_6S_3X_5)L_2X_4]X_3$		
$[(Re_6S_3X_5)L_3X_3]X_4$		
$[(Re_6S_2X_6)X_6]X_2$		
$[(Re_6S_2X_6)LX_5]X_3$		
$[(Re_6S_2X_6)L_2X_4]X_4$		
$[(Re_6SX_7)X_6]X_3$		
$[(Re_6SX_7)LX_5]X_4$		

M = Monocation or M_2 = dication; X = monoanion; L = neutral ligands.

Table 3 Connectivity and dimensionality of octahedral rhenium chalcogenide clusters

Compound	Connectivity	Dimensionality	Ref.
$Rb_4Re_6S_{13}$	$[Re_6(\mu_3\text{-}S)_8S_{2/2}(S_2)_{4/2}]^{4-}$	3-D	89
$Rb_4Re_6S_{12}$	$[Re_6(\mu_3\text{-}S)_8S_{4/2}(S_2)_{2/2}]^{4-}$	3-D	81
$Ba_2Re_6S_{11}$	$[Re_6(\mu_3\text{-}S)_8S_{6/2}]^{4-}$	3-D	75
$Re_6S_8Br_2$	$Re_6(\mu_3\text{-}S_6)(\mu_4\text{-}S)_{2/2}Br_{4/2}S_{2/2}$	3-D	97
$Re_6S_7Br_4$	$Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_{6/2}$	3-D	66
$Cs_6Re_6Se_{15}$	$[Re_6(\mu_3\text{-}Se)_8(Se_2)_{6/2}]^{4-}$	3-D	82
$Re_6Se_8Te_7$	$Re_6(\mu_3\text{-}Se)_8(Te_7)_{6/6}$	3-D	106
Re_6S_{12}	$Re_6(\mu_3\text{-}S)_8S_{4/2}S_2$	2-D	90
$Re_6Se_6Cl_6$	$Re_6(\mu_3\text{-}Se)_6(\mu_3\text{-}Cl)_2Cl_2Cl_{4/2}$	2-D	66
$Re_6Se_8Cl_2$	$Re_6(\mu_3\text{-}Se)_4(\mu_4\text{-}Se)_{4/2}Cl_2Se_{4/2}$	2-D	63
$TlRe_6Se_8Cl_3$	$[Re_6(\mu_3\text{-}Se)_5(\mu_4\text{-}Se)_{3/2}Cl_3Se_{3/2}]^-$	2-D	92
$CsRe_6Se_8I_3$	$[Re_6(\mu_3\text{-}Se)_6(\mu_4\text{-}Se)_{2/2}I_2I_{2/2}Se_{2/2}]^-$	2-D	83
$Re_6S_5Cl_8$	$Re_6(\mu_3\text{-}S)_5(\mu_3\text{-}Cl)_3Cl_4Cl_{2/2}$	1-D	71
$Cs_2Re_6Se_8Br_4$	$[Re_6(\mu_3\text{-}Se)_6(\mu_4\text{-}Se)_{2/2}Br_4Se_{2/2}]^{2-}$	1-D	83

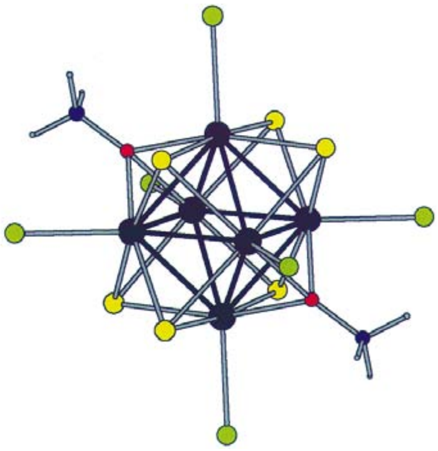

Fig. 12 Structure of $[Re_6(\mu_3\text{-}S)_5(\mu_3\text{-}NMe)(\mu_3\text{-}Cl)_2Cl_6]^{2-}$. The μ_3-NMe group is disordered onto two opposite faces of the Re_6 octahedron (Re black, S yellow, N orange, C blue, Cl light green).

bridged assemblies such as $[Re_{12}Se_{16}(PEt_3)_{10}][SbF_6]_2$ or $[(PEt_3)_5Re_6Se_8(4,4'\text{-bipy})Re_6Se_8(PEt_3)_5]$.[46–48] Similar dodecanuclear cluster complexes of cobalt,[49] chromium,[50] and molybdenum[51] have been reported. Another type of bridged twin cluster $[Bu_4N]_4[(Re_6S_5OCl_7)_2O]$ has been obtained by the reaction of rhenium metal, $ReCl_5$, KCl and sulfur in the presence of a controlled amount of water at 850 °C for 4 days.[52] In the structure of this compound, two identical $[Re_6S_5OCl_7]^{2-}$ cores are linked by an apical oxygen ligand.

Ligand substitutions are very general reactions used to prepare various kinds of complexes in Werner type or organometallic transition metal chemistry. These reactions have as yet been little explored for the early transition metal clusters with π-donor ligands.[53] The conversion of terminal chlorine ligands in the octahedral chloride clusters of molybdenum and tungsten into alkyls offers one of the rare examples.[44,45,54] In this respect, the preparation of $[Re_6Q_5(NR)Cl_8]^{2-}$ (R = methyl, benzyl) (Fig. 12) and $[Re_6Q_5(NSiMe_3)Cl_8]^{2-}$ (Q = S, Se) and the nucleophilic conversion of the $NSiMe_3$ group into NH by Bu_4F are important as new synthetic methods to prepare inorganic–organic hybrid compounds starting from cluster compounds prepared by high-temperature solid state synthesis.[55] One of the face-capping chlorines in $[Bu_4N][Re_6Q_5Cl_9]$ can be transformed also into divalent anions to form $[Bu_4N]_2[Re_6Q_5ECl_8]$ (E = O, S, Se, Te) by means of $(Me_3Si)_2E$.[55]

In solid state chemistry, a number of octahedral rhenium chalcogenide clusters have been reported by Fedorov,[56–62] Perrin,[63–70] Batail,[71,72] Bronger,[73–82] Holm,[46,83] Ibers[84,85] and others.[86,87] They are prepared by high-temperature solid state synthesis in evacuated sealed tubes from the combinations of (a) metal + halogen + chalcogen, (b) metal chalcogenide + halogen, (c) metal halide + chalcogen, (d) metal halide + metal + chalcogen, (e) metal chalcogenide + metal halide, (f) metal + chalcogen halide, (g) metal + hydrogen sulfide, (h) metal + chalcogen + hydrogen, and the chemical compositions depend on the ratio of the reactants and heating conditions.[82,88,89] Recently the octahedral clusters $Re_6Q_4Br_{10}$ and $Re_6Q_8Br_2$ (Q = S, Se, Te) have been prepared by condensation from triangular rhenium bromide Re_3Br_9 and PbQ or CdQ.[62] It is considered that the choice of lead and cadmium chalcogenides is very important to promote the reaction by thermodynamic control of the formation of lead or cadmium bromides. This kind of formal condensation of trinuclear rhenium clusters was once suggested by Perrin and Sergent.[6] Some of the $A_4Re_6Q_{12}$ type compounds have been prepared by an ion exchange method from $Tl_4Re_6Q_{12}$.[86,87] Topotactic oxidation of $Na_4Re_6S_{12}$ at ambient temperature forms Re_6S_{12}.[90]

The octahedral rhenium chalcogenide clusters invariably have 6 Re(III) (d^4) atoms (24 MCE) with 8 capping and 6 terminal ligands [$Re_6(\mu_3\text{-}L)_8L'_6$ type]. Depending on the ratio of chalcogen to halogen ligands, the connectivity of the Re_6 cluster units changes to become molecular or 1-, 2- and 3-D cluster compounds. Replacement of two halogen atoms by a chalcogen atom or introduction of counter ions can make the oxidation state of the rhenium atoms the same (trivalent). The connectivity of the Re_6 cluster frameworks is determined by the sum of the halogen and chalcogen atoms. Smaller numbers lead to higher connectivity. Table 3 lists the representative higher

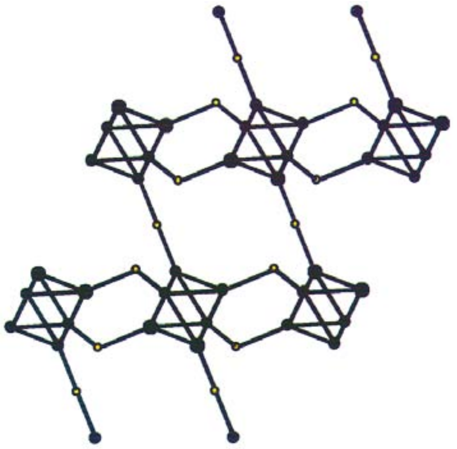

Fig. 13 Three-dimensional connectivity in $Ba_2[Re_6|S_8|S_{6/2}]$ (Re black, S yellow).

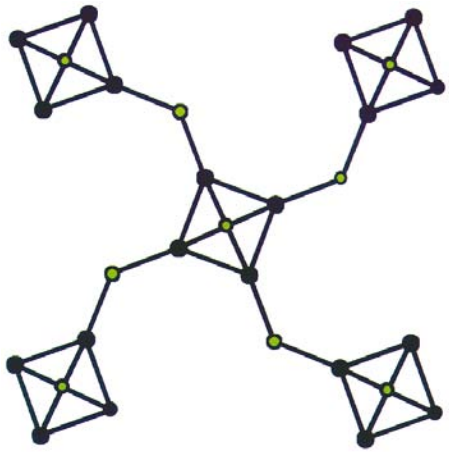

Fig. 14 Two-dimensional connectivity in $Re_6|Se_6Cl_2|Cl_2Cl_{4/2}$ (Re black, Cl light green, Se omitted).

dimensional clusters. As sulfides do not cover all the known types of compounds, selenides are included. In cases where the sulfides and selenides have equivalent compositions, they usually have equivalent structures. Therefore it is very likely that pairs of compounds should exist even if one of the pair has not yet been synthesized.

The dimensionality and connectivity of the octahedral rhenium chalcogenide clusters have been described thoroughly before,[6,7,46,83,91] and the possible and realized structures are given in these references.[83] Consequently, it may be sufficient to summarize the connectivity in Table 3 and present figures (Fig. 13–15) of representative types of compounds.

One of the most important features of octahedral cluster chemistry is that it offers the general concept of the relationships between the solid state and molecular inorganic compounds.[9,91] One aspect is the so-called dimensionality reduction[83,92] and the other one is the condensation of molecular cluster compounds to form larger clusters.[46,48,50,51] We can envisage the relation better in cluster compounds than in ionic compounds without apparent metal–metal bonding. The constraint imposed by the cluster frameworks and the limitation of the bridging modes may simplify the possible packing schemes compared with more flexible packings in "mononuclear" ionic compounds. However, the relationship between the preparative conditions and the structure of the product is not always clear. Replacement of chalcogens [*e.g.* $Re_6S_8Cl_2$ (3-D) and $Re_6Se_8Cl_2$ (2-D)] or halogens [*e.g.* $Re_6Se_8Cl_2$ (2-D) and $Re_6Se_6Br_2$ (3-D)] changes the connectivity. Although the varieties of oxidation states in $[Mo_6Q_8]^{n-}$ (Q = S, Se, Te; $n = 0$ to ≈4) have been realized,[93] only 24-electron clusters have been well characterized in rhenium chemistry. The cluster Re_6S_{12} (20-electron) prepared by topotactic oxidation of $Na_4Re_6S_{12}$ appears to be the sole exception.[90] Chevrel phase type 3-D compounds have not yet been reported. The mixed metal cluster $Mo_4Re_2Te_8$ (22-electron) has a similar intercluster linkage to those of the Chevrel phases and is a superconducting material.[94]

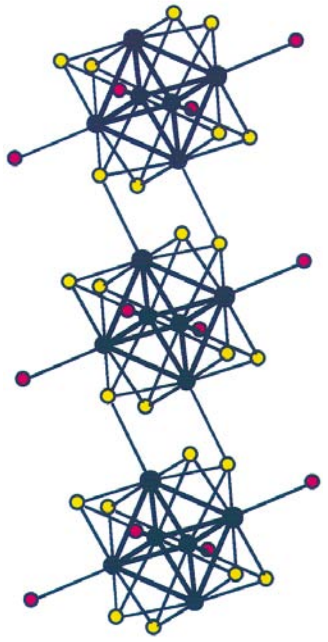

Fig. 15 One-dimensional connectivity in $Cs_2[Re_6|Se_6Se_{2/2}|Br_4Se_{2/2}]$ (Re black, Se yellow, Br pink).

7 Physical properties and catalysis

Despite the structural diversity of the octahedral rhenium cluster chalcogenides, the electronic structure remains the same (24-electron) and most of them are either insulators or semiconducting. The temperature dependence of the resistivity of $A_4Re_6Q_{12}$ (A = Tl, Na, K, Rb, Cs; Q = Se, S) phases has been measured.[86,87] The 2-D clusters $Re_6Q_8Cl_2$ are n-type semiconductors with band gaps of 1.42 eV (Q = S)[95] and 0.83 eV (Q = Se).[96] The p-type behaviour of $Re_6Q_8Br_2$ (Q = S, Se) was characterized photoelectrochemically and the photocurrent action spectra indicated band gaps of 1.65 eV and 0.84 eV for the sulfide and selenide, respectively.[97] Another 3-D cluster $Re_6Se_7Br_4$ also behaves as a p-type semiconductor and the band gap is about 1.78 eV.[98] Photoelectric properties of ReS_2 and $ReSe_2$ single crystals have also been reported.[99]

The attempts to prepare conductive complexes using electron donors have met with considerable success and Batail *et al.* have synthesized a metallic complex by the combination of electron donors and 0-D soluble selenide clusters, $[BEDT\text{-}TTF]_4[Re_6Se_5Cl_9]$[guest] [BEDT-TTF = 3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene; guest = DMF, THF, dioxane].[100] Conducting organic cation radical slabs are sandwiched by inorganic cluster monoanion layers in these cluster complexes. They are metallic at room temperature and their electrical conductivity at low temperatures depends on the size, shape, and symmetry of the neutral guest molecules. Especially in the case of dioxane, the metallic regime is sustained down to 4.5 K.

Stiefel has reviewed catalysis by transition metal sulfides in industrial reactions.[101] Major reactions are hydrodesulfurization (HDS), hydrodenitrogenation, hydrodeoxygenation and hydrodemetallation in the petrochemical industries. It was reported that Re_2S_7 and ReS_2 are more active than MoS_2 or CoS_x as liquid-phase hydrogenation catalysts.[102] The activity and selectivity of Re_2S_7 in the hydrogenation of nitric oxide to nitrous oxide or dinitrogen and sulfur dioxide to hydrogen sulfide was reported.[103] Comparative studies on the hydrodesulfurization of dibenzothiophene by various transition metal sulfides indicated that the activity of ReS_2 is higher than those of the early transition metal sulfides but lower than Ru, Rh, Os, or Ir sulfides.[104] Although the rhenium chalcogenide cluster compounds described above may be active for HDS reactions, few reports are available at present. The influence of d-state density on catalytic electrochemical dihydrogen evolution and dioxygen reduction in acid medium was studied using a mixed metal octahedral cluster $Mo_2Re_4Se_8$.[105]

8 Perspectives of rhenium sulfide clusters

The solid state and discrete chalcogenide cluster compounds of rhenium so far synthesized have triangular, tetrahedral, rhomboidal and octahedral cluster frameworks. The frameworks are essentially determined by the number of MCE, and reported triangular clusters have 6–10, tetrahedral 12, rhomboidal 14 and octahedral 24 electrons. The tetrahedral and octahedral clusters are electron-precise having 6 and 12 Re–Re single bonds, respectively. The connectivity of the cluster units depends on the number of anionic ligands. Also, the presence of S_x^{2-} polysulfide units modifies the situation. The coordination of neutral ligands is favourable for the formation of molecular clusters. It seems that there are a number of possible cluster compounds of various sizes by the appropriate combination of anionic and neutral ligands as well as cations. These potential clusters will be prepared by the discovery of appropriate reaction conditions in the case of the solid state compounds, and mainly by ligand substitution and condensation reactions for the molecular clusters. Little of the chemical and physical properties of the known rhenium cluster compounds have been studied so far and they will provide us with good opportunities for interesting studies of cluster compounds. The location of rhenium in the Periodic Table and the ability of the element to take a wide range of oxidation states are the basis for the exploitation of the properties of the rhenium chalcogenide clusters.

9 Acknowledgements

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