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Cluster Transition Metal Chalcogenide Halides

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The literature data on cluster transition metal chalcogenide halides are described systematically and discussed. The structures of these compounds are examined and compared with those of the analogous cluster metal halides and chalcogenides. The principal preparative methods of synthesis of the cluster chalcogenide halides are discussed and a systematic account is given of the first results obtained in the study of the chemical properties of this class of inorganic compounds.
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I. INTRODUCTION

The principal advances achieved in the chemistry of cluster compounds in recent years are associated primarily with the synthesis and the determination of the structures of numerous low-valence carbonyl clusters of different nuclearity, especially those characteristic of Group VIII metals.[1-4] The formation of metal carbonyl clusters is much less characteristic of the elements at the beginning of the transition series; cluster compounds with "classical" acido-ligands such as halogens and chalcogens have long been known for these metals and have been thoroughly investigated.[5-8] In contrast to the low-valence metal carbonyl clusters, in the cluster compounds with "classical" ligands the metal atom has a higher formal oxidation state and these compounds are therefore classified as high-valence clusters.[4] Although the first representative of transition metal halide clusters was obtained as early as the beginning of the century,[9] vigorous studies on the cluster niobium, tantalum, molybdenum, tungsten, and rhenium halides as well as their complexes with various ligands have been carried out in the last two decades.[5,6,8] The first structural study of cluster compounds was performed in relation to the hexanuclear molybdenum cluster.[10] The structures of the complexes of metals at the beginning of the transition series with halide ligands, in which the number of metal atoms in the cluster group varies from two to six, have now been investigated.

The chemistry of transition metal chalcogenides, in which the metal–metal pair interactions take place or clusters containing three, four, six, nine, and more metal atoms are formed is also being vigorously studied.[7] The interest in compounds of this kind has increased particularly after the discovery of superconductivity in the so called Chevrel phases which are cluster formations.[11]

A polymeric type of structure, in which bridging ligands link the cluster nuclei into infinite chains, layers, or three-dimensional formations are characteristic of cluster transition metal halides and chalcogenides. An extremely interesting feature of certain cluster halides and chalcogenides is the ability of the metallic clusters to link up with one another to produce the so-called condensed clusters.[7] For example, in the structures of binary and ternary phases of the lower transition metal halides and chalcogenides it is possible to differentiate infinite chains consisting of M_6 octahedra linked to one another via common vertices, edges, or faces.[7]

An important class of inorganic compounds consists of transition metal chalcogenide halides in which the metal atoms are coordinated simultaneously to halogens X and chalcogens Y. The chalcogenide halides have long been known,[12] but the most important results in their investigation have been obtained in the last decade.[13-15]

The main efforts of investigators have been directed to the search for reactions leading to the formation of new chalcogenide halides, the optimisation of the conditions of synthesis, and the determination of their structure, while inadequate attention has been devoted to the chemical properties of the chalcogenide halides.

Fig.1 presents the known cluster transition metal chalcogenide halides, i.e. the chalcogenide halides in which the existence of metal–metal bonds has been established on the basis of structural and other data. Evidently the formation of cluster chalcogenide halides is characteristic of metals at the beginning of the transition series, i.e. of metals for which cluster halides and chalcogenides are known.

This review discusses the structure, syntheses, and chemical properties of dinuclear, trinuclear, tetranuclear, and hexanuclear cluster transition metal chalcogenide halides.

II. THE STRUCTURE OF CLUSTER METAL CHALCOGENIDE HALIDES

1. Dinuclear Chalcogenide Halides

(a) The Chalcogenide Halides $NbYX_3$ (Y = Se or Te; X = Cl, Br, or I)

All the niobium chalcogenide halides having the general formula $NbYX_3$ are isostructural and crystallise in the monoclinic system (space group $P/2a$, $Z = 2$).[16] The unit cell parameters of the compounds $NbYX_3$ are presented in Table 1.

The structures of $NbSeBr_3$, $NbTeBr_3$, and $NbTeI_3$ have been determined.[16] The crystal-chemical formula is $[Nb_2(\mu_2\text{-}Y_2)(\mu_2\text{-}X)_2X_2(\mu_2\text{-}X)_{4/2}]_\infty$. The formal oxidation state of the metal is +4. The principal structural motif is illustrated in Fig.2*a*. It is made up of two niobium atoms with Nb = Nb distances of 2.832, 2.875, and 2.932 Å respectively for $NbSeBr_3$, $NbTeBr_3$, and $NbTeI_3$. The dichalcogenide group Y_2 is coordinated asymmetrically to two niobium atoms in relation to the metal–metal bond (rotation of the Y_2 dumbell by 4–5° from the "orthogonal" position towards the metal–metal bond). The distances in the chalcogenide group Y_2, which are 2.305 Å for Se–Se and 2.670–2.685 Å for Te–Te, are close to the length of a single bond (2.34 Å for Se_2 and 2.76 Å for Te_2).[17]

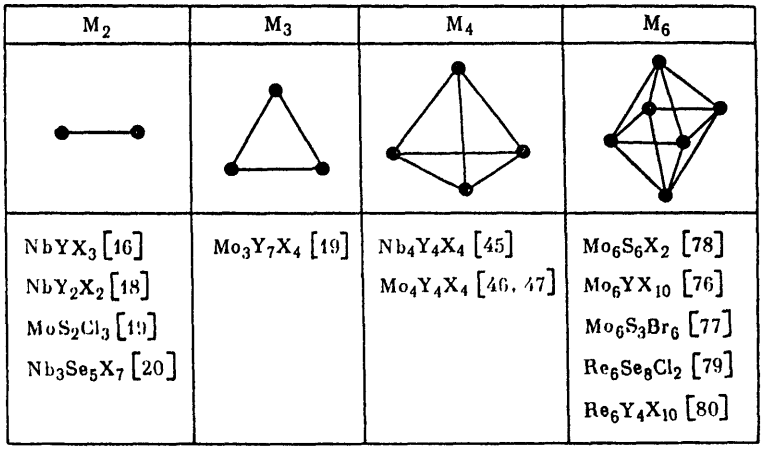


Figure 1. Types of cluster transition metal chalcogenide halides [the numbers in square brackets denote references (Translator)].

Table 1. The unit cell parameters of the cluster chalcogenide halides.

Compound	Unit cell parameters						Density, g cm^{-3}		Refs.
	a, Å	*b*, Å	*c*, Å	α°	β°	γ°	d_{exp}	d_{calc}	
$NbSeCl_3$	11.913	6.714	6.347	—	98.83 (1)	—	—	—	[16]
$NbSeBr_3$	12.540 (12)	6.897 (10)	6.624 (10)	—	98.9 (1)	—	—	4.830	[16]
$NbTeBr_3$	12.597 (13)	7.135 (9)	6.670 (9)	—	97.6 (1)	—	—	5.144	[16]
$NbTeI_3$	13.473 (3)	7.429 (2)	7.141 (2)	—	98.52 (2)	—	—	5.649	[16]
NbS_2Br_2*	6.528 (2)	6.589 (2)	7.254 (1)	67.72 (2)	112.63 (2)	120.05	—	—	[18]
NbS_2I_2*	6.77	6.80	7.23	73.80	102.30	117.4	4.49	4.53	[18]
$NbSe_2Cl_2$*	6.350 (2)	6.538 (3)	7.261 (2)	66.93 (3)	111.35 (3)	119.01 (3)	4.48	4.51	[18]
$NbSe_2Br_2$*	6.667 (2)	6.724 (2)	7.084 (2)	79.40 (2)	111.83 (2)	119.68 (1)	—	—	[18]
$NbSe_2I_2$*	7.060 (1)	7.207 (2)	7.757 (2)	67.59 (2)	113.20 (3)	121.10 (2)	5.48	5.54	[18]
NbS_2Cl_2**	6.27	11.09	6.69	—	111.07	—	3.47	3.49	[18]
NbS_2Br_2**	6.54	11.32	6.91	—	110.54	—	4.30	4.34	[18]
$NbSe_2Cl_2$**	6.64	11.23	6.96	—	108.93	—	—	—	[18]
$NbSe_2Br_2$**	6.76	11.53	7.20	—	113.90	—	5.28	5.32	[18]
$NbSeI_2$**	6.89	12.34—12.46	7.51	—	112.26	—	—	—	[18]
MoS_2Cl_3	6.186	7.244	13.345	—	116.17	—	3.32	3.31	[19]
$Nb_3Se_5Cl_7$	7.599	12.675	8.051	—	106.27	—	4.04	4.110	[20]
$Nb_3Se_5Br_7$	7.621	12.833	8.069	—	106.21	—	—	—	[20]
$Mo_3S_7Cl_4$	9.336	12.185	13.956	—	122.90	—	3.23	3.26	[19]
$Nb_4S_4Br_4$	10.193	—	—	—	—	—	—	—	[45]
$Nb_4S_4I_4$	10.639	—	—	—	—	—	—	—	[45]
$Nb_4Se_4Br_4$	10.368	—	—	—	—	—	—	—	[45]
$Nb_4Se_4I_4$	10.782 (3)	—	—	—	—	—	—	6.332	[45]
$Mo_4S_4Cl_4$	9.68	—	—	—	—	—	—	—	[46, 47]
$Mo_4S_4Br_4$	9.94 (5)	—	—	—	—	—	5.55	5.61	[46, 47]
$Mo_4S_4I_4$	10.33	—	—	—	—	—	—	—	[46, 47]
Mo_6SCl_{10}	9.811 (7)	13.768 (7)	11.821 (9)	—	—	—	3.94	4.00	[76]
Mo_6SeCl_{10}	9.899 (8)	13.783 (11)	11.834 (11)	—	—	—	4.12	4.15	[76]
Mo_6TeCl_{10}	10.078 (9)	13.855 (9)	11.837 (12)	—	—	—	4.20	4.25	[76]
Mo_6SBr_{10}	10.23	14.35	12.24	—	—	—	5.17	5.20	[76]
Mo_6SeBr_{10}	10.28	14.35	12.29	—	—	—	5.26	5.33	[76]
Mo_6TeBr_{10}	10.44	14.35	12.35	—	—	—	5.30	5.39	[76]
Mo_6SeI_{10}	10.86	15.24	13.18	—	—	—	5.84	5.86	[76]
Mo_6TeI_{10}	11.00	15.24	13.20	—	—	—	5.85	5.92	[76]
$Mo_6S_3Br_6$	17.250 (7)	6.600 (4)	11.929 (7)	—	—	—	5.51	5.63	[77]
$Mo_6S_6Br_2$	9.545 (4)	—	10.357 (3)	—	—	—	5.60	5.66	[78]
$Mo_6S_6I_2$	9.639	—	10.437	—	—	—	5.80	6.06	[78]
$Re_6Se_8Cl_2$	6.598	6.640	9.071	100.19	113.52	83.14	—	8.52	[79]
$Re_6Se_4Cl_{10}$	8.898 (5)	8.957 (5)	12.627 (10)	84.20 (4)	84.60 (4)	82.19 (3)	6.05	6.10	[80]

*Low-temperature modification.
**High-temperature modification.

Two bridging halogen atoms (μ_2-X) are coordinated analogously and they too are located asymmetrically in relation to the Nb–Nb bond. This asymmetry can be accounted for by the van der Waals repulsion of the halogen atoms. Each niobium atom is linked to one terminal halogen atom X; the length of the bond between niobium and the terminal halogen atom is somewhat smaller than the distance between niobium and the bridging halogen atom. The niobium–niobium fragments are linked by the bridging hydrogen atoms into an infinite chain structure.

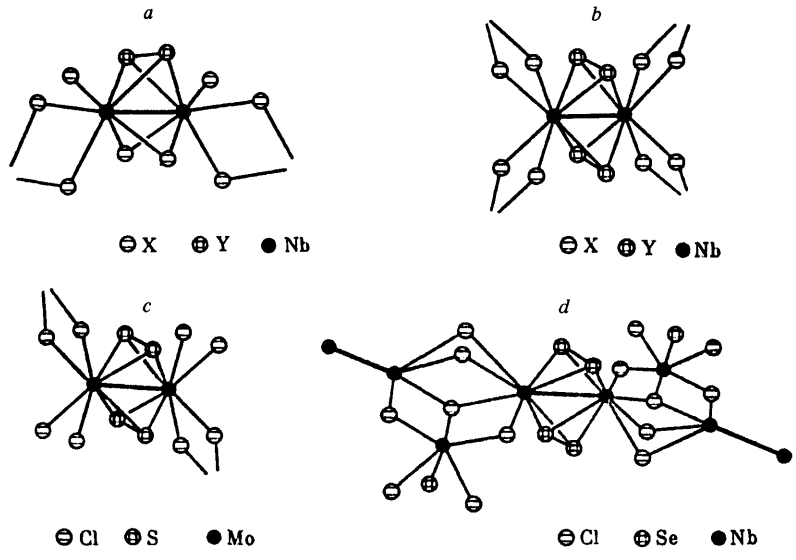


Figure 2. The structure of dinuclear niobium and molybdenum chalcogenide halides: *a*) $NbYX_3$;[16] *b*) NbY_2X_2;[18] *c*) MoS_2Cl_3;[19] *d*) $Nb_3Se_5Cl_7$.[20]

(b) The Chalcogenide Halides NbY_2X_2 (Y = S or Se; X = Cl, Br, or I)

The chalcogenide halides NbY_2X_2 crystallise in the triclinic system under normal conditions (space group $P\bar{1}$, $Z = 2$).[18] The compound NbS_2Cl_2, which has a monoclinic cell at room temperature, is an exception (Table 1). On heating, most of these phases undergo polymorphic transformations (except NbS_2I_2, which does not exhibit polymorphism); there is then a transition from a triclinic to a monoclinic unit cell (space group $C2/m$, $Z = 4$).[18] Table 1 lists the unit cell parameters for the low-temperature and high-temperature modifications of these phases.

The structure of the niobium chalcogenide halides having this composition has been established in relation to the triclinic modification of $NbSe_2Cl_2$ and the monoclinic form of NbS_2Cl_2.[18] The principal structural motif of the given dinuclear complex is presented in Fig. 2*b*. Two niobium atoms are located at the vertices of a distorted Nb_2Y_4 octahedron (D_{2h} symmetry), in which the dichalcogenide groups Y_2, coordinated to the niobium atoms as bridging ligands, make up the equatorial plane. The Nb–Nb distances in these fragments are respectively 2.871 Å in NbS_2Cl_2 and 2.873 Å in $NbSe_2Cl_2$. An interesting crystal-chemical feature of this fragment is the extremely short Y–Y distances in the Y_2 groups, amounting to 1.996 Å for S–S and 2.272 Å for Se–Se. The coplanarity of the S–S bonds in NbS_2Cl_2 indicates the absence of asymmetry in the position of Y_2, noted above in connection with the $NbYX_3$ phases. Admittedly, a slight asymmetry of the orientation of the Se–Se bonds is retained in $NbSe_2Cl_2$. The octahedral Nb_2Y_4 fragments are linked by bridging halogen atoms into layers, i.e. this structure has a layer character.

Thus the crystal-chemical formula of compounds of this type can be represented as follows:

$$[Nb_2(\mu\text{-}Y_2)_2(\mu_2\text{-}X)_{s/2}]_\infty .$$

The formal oxidation state of niobium in such compounds is +4.

(c) The Molybdenum Sulphide Chloride MoS_2Cl_3

The molybdenum sulphide chloride MoS_2Cl_3 crystallises in the monoclinic system (space group $P2_1/c$, $Z = 4$).[19] The unit cell parameters are listed in Table 1.

The MoS_2Cl_3 structure (Fig. 2*c*) can be easily obtained from the NbS_2Cl_2 structure (Fig. 2*b*) by replacing the four bridging chlorine atoms in the *trans*-positions in NbS_2Cl_2 by the terminal atoms. We shall not discuss in detail the structure of MoS_2Cl_3, which is in many respect analogous to NbS_2Cl_2; the Mo–Mo distance is 2.833 Å. In contrast to NbS_2Cl_2, the polymeric motifs in the MoS_2Cl_3 crystals are combined in space in a different manner, namely via the bridging chlorine atoms in the *trans*-positions, which leads to a three-dimensional structure. The oxidation state of molybdenum in this compound is +5.

Among the other crystal-chemical characteristic features of the MoS_2Cl_3 structure, we may mention that the distance between molybdenum and the terminal chlorine atom (2.39 to 2.45 Å) is significantly shorter than the distance between molybdenum and the bridging chlorine atom (2.51–2.56 Å). The short S–S distances (1.98 Å) in the disulphide group S_2 and the absence of asymmetry in their coordination to the two molybdenum atoms are notable.

(d) The Niobium Chalcogenide Halides $Nb_3Se_5X_7$ (X = Cl or Br)

The niobium selenide chloride $Nb_3Se_5Cl_7$ and the niobium selenide bromide $Nb_3Se_5Br_7$ crystallise in the monoclinic system (space group $P2_1/m$, $Z = 2$);[20] the unit cell parameters are presented in Table 1.

A structure of this type has been investigated in relation to $Nb_3Se_5Cl_7$. It can be regarded as derived from the MoS_2Cl_3 structure as a result of the replacement in the latter of each pair of terminal chlorine atoms in the *trans*-positions by the two unusual ligands $NbSeCl_3$ (Fig. 2*d*). The $NbSeCl_3$ ligand

is coordinated to two niobium atoms belonging to neighbouring dinuclear fragments. We may note the short distances between the niobium atom in the $NbSeCl_5$ ligand and the niobium atoms in the neighbouring dinuclear fragments (3.15 Å). Two chlorine atoms in the $NbSeCl_5$ ligand are of the μ_2-bridging type [the Nb–(μ_2-Cl) distances are 2.582 and 2.553 Å], while the third chlorine atom is of the μ_3-bridging type (the distances from μ_3-Cl to the three nearest niobium atoms are 2.629, 2.629, and 2.727 Å). This type of binding of the dinuclear fragment leads to the formation of a chain structure.

The shortest Nb–Nb distance in $Nb_3Se_5Cl_7$ is 2.944 Å. The diselenide groups Se_2 in the central Nb_2Se_4 motif exhibit an appreciable asymmetry in relation to the Nb–Nb bond.

(e) The Nature of the Metal–Metal Chemical Bond in the Dinuclear Chalcogenide Halides

In conclusion of the discussion of the structures of the dinuclear niobium and molybdenum chalcogenide halides, we may mention yet again the common crystal-chemical features of these phases:

1. The dichalcogenide ligands Y_2 (Y = S, Se, or Te), coordinated to both metal atoms, are located in the central dinuclear fragment in all the compounds. The cross-linking of the fragments into chains (for $NbYX_3$ and $Nb_3Se_5Cl_7$) and planar or three-dimensional networks (for NbY_2X_2 and MoS_2Cl_3) is achieved via the bridging halogen atoms.
2. The short metal–metal bonds (2.8–2.9 Å) within the dinuclear fragment alternate with relatively long metal–metal distances (3.9–4.3 Å) between these fragments.

As a result of the efforts of a number of teams of Soviet and foreign specialists, considerable progress has now been achieved in understanding the nature of the metal–metal bond in the dinuclear and polynuclear molecular cluster compounds.[6,21–26] Many properties of the molecular dinuclear compounds can be reasonably explained on the basis of simple theoretical models widely employed at the present time.[5,6,26,27] On the other hand, in the case of polymeric cluster transition metal chalcogenide halides, in the interpretation of the properties of which it is essential to take into account a weaker extended interaction, theoretical models developed in detail are not so far available.

The formation of metal–metal bonds in dinuclear niobium and molybdenum chalcogenide halides can be described qualitatively in approximate terms on the assumption that the metal–ligand bonds are ionic. This approach is widely used in discussing M–M bonds in dinuclear complexes of acido-ligands and has made it possible to account for many properties of these compounds (in particular, magnetic properties). Indeed, bearing in mind the oxidation states of molybdenum and niobium (Mo^{5+} and Nb^{4+}) which obtain in the dinuclear chalcogenide halides as well as the diamagnetism of these compounds, one may conclude that metal–metal bonds are formed. Here one can assume that the valence electrons of the niobium and molybdenum atoms used to form the M–M bonds populate the highest molecular orbital of the σ-type which is largely made up of the *d* orbitals of the metal atoms. This result is in qualitative agreement with the calculation of the molecular orbital diagram for the $[Nb_2(Se_2)_2]^{4+}$ cluster fragment,[28] according to which the highest occupied molecular orbital is of the σ-type, consisting to the extent of 90% of the *d* orbitals of the niobium atom.

The evaluation of the number of valence electrons of the metal atoms in accordance with Sidgwick's rule, the applicability of which to dinuclear molecular complexes has been discussed,[29] may serve as an additional basis for the assumption that the metal–metal bond does or does not exist. According to this rule, the M–M bond is absent if the number of valence electrons in the two metal atoms is 36. The evaluation of the number of valence electrons for the known dinuclear chalcogenide halides with metal–metal bonds shows that the number corresponding to the two metal atoms in the central fragment is less than 36.

The character of the M–M bond can change significantly after the appearance of intracluster bridging ligands of different types (halide and chalcogenide) and also on formation of polymer chains or two-dimensional networks from the dinuclear fragments as a result of their cross-linking by bridging intercluster halide ligands. In the former case the character of the metal–metal bond (in particular, its length) is determined to a large extent by the electronic and geometrical characteristics of the intracluster bridging ligands, while in the second there is a possibility of additional delocalisation of electron density between metal atoms belonging to different dinuclear fragments. In the general case the estimation of each factor separately is a complex experimental and theoretical problem whose solution is simplified when a series of related compounds are considered.[30]

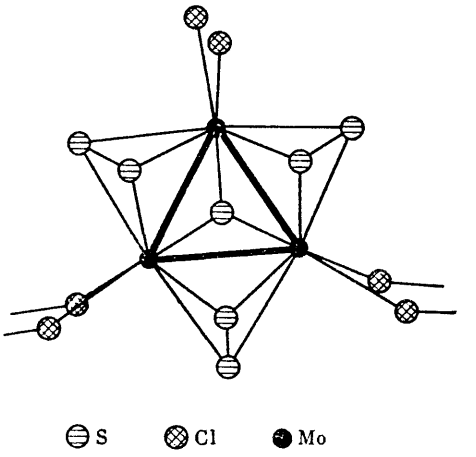


Figure 3. The structure of the trinuclear molybdenum sulphide chloride $Mo_3S_7Cl_4$.[19]

2. The Trinuclear Molybdenum Chalcogenide Halides $Mo_3Y_7X_4$ (Y = S or Se; X = Cl, Br, or I)

Of the six representatives of the trinuclear molybdenum chalcogenide halides $Mo_3Y_7X_4$, a structural study has been carried out for only one phase—the sulphide chloride $Mo_3S_7Cl_4$ (Fig. 3). The compound crystallises in the monoclinic system (space group $P2_1/c$, $Z = 4$;[19] its unit cell parameters are listed in Table 1). The three molybdenum atoms form a virtually equilateral triangle (the Mo–Mo distances are 2.748, 2.741, and 2.747 Å). One sulphur atom (μ_3-S) is located above the centre of the triangle and is linked to the three molybdenum atoms of the cluster. Two chlorine atoms in the molecule are terminal and belong to one molybdenum atom. Two pairs of chlorine atoms at the other two molybdenum atoms function as bridges linking the clusters into an

infinite zig-zag chain. The crystal-chemical formula of the trinuclear molybdenum sulphide chloride can be written thus:

The formal oxidation state of the metal in the trinuclear clusters $Mo_3Y_7X_4$ is +4.

The molybdenum chalcogenide halides $Mo_3S_7Br_4$, $Mo_3Se_7Cl_4$, $Mo_3Se_7Br_4$, $Mo_3S_7I_4$, and $Mo_3Se_7I_4$ were obtained by the same methods as $Mo_3S_7Cl_4$.[89-92] The identical compositions, the common methods of synthesis, and the consistent variation of the thermal properties and infrared spectra in the series of these compounds suggest that their structures are similar.

Within the framework of the ion-covalent model, it is assumed that the three molybdenum atoms in the cluster chalcogenide halide $Mo_3S(S_2)_3.Cl_2Cl_{4/2}$ provide 12 electrons for the formation of bonds with the ligands. Six electrons then remain for the binding of the metal atoms in the triangular Mo_3 cluster and the formal order of the Mo–Mo bond is 1.

On the other hand, evaluation of the number of valence electrons on the assumption of the formation of single Mo–Mo bonds shows that each molybdenum atom then achieves the electronic configuration of the nearest inert gas. This simplest treatment is in good agreement with experimental data: the Mo–Mo distances in the Mo_3 triangle are close to the metal–metal distance in metallic molybdenum.[17]

Speaking of the M–M distances in cluster systems of this kind, one should note in the first place the significant role of the geometrical and electronic properties of the intracluster bridging ligands.[31] To illustrate this, Table 2 presents the Mo–Mo distances in a series of trinuclear molybdenum clusters (structural type—triangle with a single cap). Table 2 shows that in compounds with a μ_3-bridging sulphur atom the Mo–Mo distances are much greater in compounds where oxygen is the μ_3-bridging atom.

Table 2. The metal–metal distances in the trinuclear cluster molybdenum compounds.

Compound	R (Mo–Mo), Å	N_0^*	Refs.
$Mo_3S(S_2)_3Cl_{4/2}Cl_2$	2.75	6	[19]
$[Mo_3S(S_2)_6]^{2-}$	2.72	6	[32]
$[Mo_3S_4(CN)_9]^{5-}$	2.77	6	[33]
$[Mo_3S_4Cp_3]^+$	2.81	6	[34]
$[Mo_3O_4F_9]^{5-}$	2.50	6	[35]
$Zn_2Mo_3O_8$	2.52	6	[36]
$[Mo_3O_4(acac)_3(EtO)_3]$	2.47	6	[37]
$[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$	2.49	6	[38]
$[Mo_3OCl_3(Oac)_3(H_2O)_3]^{2+}$	2.55	8	[39]

*The number of skeletal electrons per Mo_3 cluster.

The most typical intracluster bridging ligands in the dinuclear and polynuclear chalcogenide halides are the dichalcogenide groups $(Y_2)^{2-}$ which in many respects determine the structure of the central motifs. Such groups can be readily identified by spectroscopic methods. For example, the stretching vibrations of the Y–Y bond are manifested in the Raman spectra by a highly intense band.[40,41] Analysis of the kinematic factors established that, for a fairly large difference between the masses of the metal and sulphur atoms, the hypsochromic shift of the $\nu_{(S-S)}$ frequency, due to the kinematic interaction of the S–S and M–S vibrations, is insignificant (~1 cm^{-1}).

The Raman spectra of numerous compounds containing the disulphide fragment S_2 have been investigated and the linear relations between the $\nu_{(S-S)}$ vibration frequency and the S–S bond length has been noted.[40,41] This made it possible to estimate the S–S bond length in the compounds $Mo_3S_7Br_4$ and $Mo_3S_7I_4$. Table 3 lists the S–S bond lengths in the S_2 dichalcogenide fragment obtained from X-ray diffraction data and calculated from Raman spectra.

Table 3. Dependence of the vibration frequency in the Raman spectra on the S–S bond length in the disulphide fragment.[40,100]

Compound	$\nu_{(S-S)}$, cm^{-1}	R (S–S), Å	
		from X-ray diffraction data	from Raman spectroscopic data
NbS_2Cl_2	592	1.996	1.99
$Mo_3S_7Cl_4$	570	2.01	2.01
$Mo_3S_7Br_4$	567	—	2.01
$Mo_3S_7I_4$	554	—	2.02
$[Mo_3S(S_2)_6]^{2-}$	545	2.02	2.03
$[Mo_2(S_2)_6]^{2-}$	530	2.043	2.04
$Mo_2(S_2)(S_2C_2Ph_2)_4$	518	2.04	2.05

3. The Tetranuclear Chalcogenide Halides $M_4Y_4X_4$ (M = Nb or Mo; Y = S or Se; X = Cl, Br, or I)

The tetranuclear cluster chalcogenide halides $M_4Y_4X_4$ have been obtained for niobium and molybdenum.[45-47] All the compounds crystallise in the cubic system (space group $F\bar{4}3/m$; the unit cell parameters are listed in Table 1).

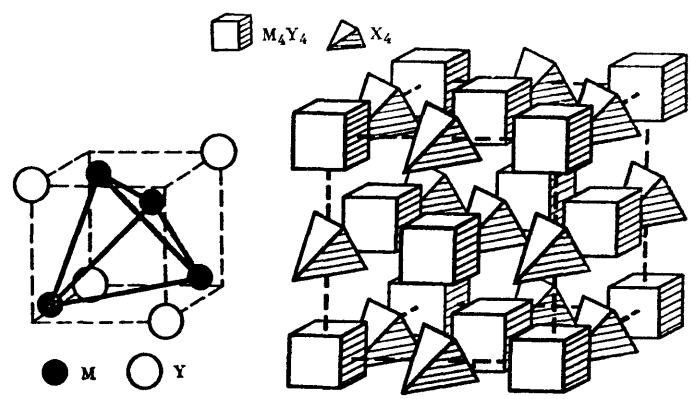


Figure 4. The structure of the tetranuclear niobium and molybdenum chalcogenide halides: *a*) the M_4Y_4 cluster group; *b*) three-dimensional representation of $M_4Y_4X_4$ made up of the M_4Y_4 cluster groups and the X_4 tetrahedra (M = Nb or Mo; Y = S or Se).[45-47]

Their structures have been investigated in relation to niobium selenide iodide $Nb_4Se_4I_4$ and molybdenum sulphide bromide $Mo_4S_4Br_4$. The structure of $Nb_4Se_4I_4$ was determined by the powder method[45] and that of $Mo_4S_4Br_4$ by X-ray diffraction of single crystals.[46,47]

(a) The Structure of $Nb_4Se_4I_4$

Niobium selenide iodide is a tetranuclear cluster containing the Nb_4Se_4 cluster group formed by interpenetrating Nb_4 and Se_4 tetrahedra (Fig. 4*a*).[45] The Nb_4Se_4 groups and the I_4 tetrahedra alternate in the $Nb_4Se_4I_4$ cubic lattice like the sodium and chlorine atoms in the NaCl crystal lattice (Fig. 4*b*). The Nb–Nb distance is 2.96 Å, which appreciably exceeds the Nb–Nb distance in metallic niobium (2.86 Å).[48] Each niobium atom is surrounded by three halogen atoms (the Nb–I distance is 3.02 Å), by three chalcogen atoms (the Nb–Se distance is 2.57 Å), and by three niobium atoms.

(b) The Structure of $Mo_4S_4Br_4$

The compound $Mo_4S_4Br_4$ has the same structure as $Nb_4Se_4I_4$.[46,47] The molybdenum and sulphur atoms occupy the vertices of the Mo_4S_4 pseudocube, the molybdenum atoms being somewhat displaced from its vertices to its centre, so that an Mo_4 tetrahedral cluster is produced. The Mo–Mo distance in the cluster (2.80 Å) is comparable to the metal–metal distance in metallic molybdenum (2.79 Å).[48] The Mo–Br (2.73 Å) and Mo–S (2.34 Å) distances in the octahedral environment of molybdenum are close to those observed in molybdenum bromides and sulphides.[55]

Another approach to the description of the structures of the niobium and molybdenum compounds $M_4Y_4X_4$ is also possible. The structure of these compounds can be represented as of the quasi-spinel type in which the anionic sublattice is made up of X and Y atoms (Fig. 4*b*). The metal atoms occupy half of the octahedral cavities usual for the chalcogenide spinels, are displaced towards the centre of the M_4Y_4 cube, and form the M_4 cluster.

A structure of the quasi-spinel type is known for ternary chalcogenides, for example, $GaMo_4S_8$, $AlMo_4S_8$,[49] and $MMo_2Re_2S_8$.[50] The framework in all these compounds consists of the M_4Y_4 tetrahedral cluster.

In the binary transition metal halides and chalcogenides tetrahedral clusters have not been so far observed, while the "butterfly" and "planar butterfly" structures obtain respectively in the anionic tetranuclear halides $[Mo_4I_{11}]^{2-}$ [51] and $[Nb_4Cl_{11}]^{2-}$.[52]

The niobium and molybdenum chalcogenide halides $M_4Y_4X_4$ are diamagnetic. Assuming an ionic model, one can postulate that the metal atoms give up 12 electrons for the formation of bonds with the ligands Y and X. In the molybdenum compounds the remaining 12 electrons in the Mo_4 cluster are used to form Mo–Mo bonds (two electrons for each edge of the tetrahedron). The formal order of the metal–metal bond in the Mo_4 tetrahedron is 1. In the niobium compound only eight electrons remain for the formation of metal–metal bonds and four electron pairs can participate in the formation of three-centre bonds along the edges of the Nb_4 tetrahedron.

4. The Hexanuclear Cluster Chalcogenide Halides

Ternary compounds of molybdenum and rhenium of the following composition belong to the hexanuclear chalcogenide halides: $Mo_6Y_{8-x}X_x$ (Y = Se, Te; X = Br, I); $Mo_6S_6X_2$ (X = Br, I); Mo_6YX_{10} (Y = S, Se, Te; X = Cl, Br, I); $Mo_6S_3Br_6$; $Re_6Se_8Cl_2$; $Re_6Y_4X_{10}$ (Y = Se, Te; X = Cl, Br). In the hexanuclear chalcogenide halides the metallic clusters constitute as a rule M_6 octahedra distorted to some extent.

For a deeper understanding of the crystal-chemical features and the somewhat unusual stoichiometry of the hexanuclear metal chalcogenide halides, it is useful to compare these phases with, on the one hand, the halide complexes and, on the other, the chalcogenide systems in which similar cluster fragments are produced.

We shall consider briefly the structures of the octahedral clusters of the above three types.

(a) Octahedral Clusters in Halide Systems

In the crystal chemistry of the lower molybdenum and tungsten halides (binary and ternary phases), the cluster group $[M_6X_8]$, which consists of six metal atoms forming the M_6 octahedron and eight halogen atoms located at the vertices of the X_8 cube (Fig. 5*a*), is well known. The M_6 octahedron is inscribed into the X_8 cube in such a way that the X atoms are located above the triangular faces of the octahedron, i.e. behave as μ_3-ligands.

In the halide systems of refractory metals the cluster groups carry a positive charge, namely $[M_6X_8]^{n+}$.[5] Each metal atom in such a group is capable of coordinating one additional ligand with formation of fragments of the type $[M_6X_8]L_6$, where L can be the same atom as X or a ligand of another kind (Fig. 5*b*). Such fragments are the main structural motif in virtually all compounds containing the $[M_6X_8]$ cluster group. Numerous binary and complex molybdenum(II) and tungsten(II) halides as well as the lower niobium iodide Nb_6I_{11} and its derivatives belong to this class of compounds.[5,53–55]

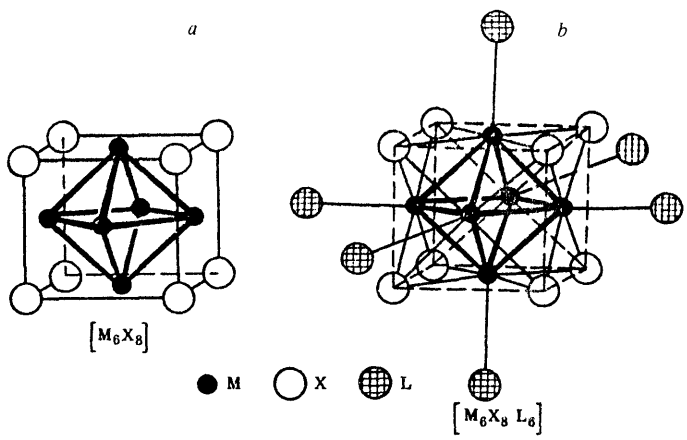


Figure 5. The cluster structure of the octahedral halide complexes: *a*) the $[M_6X_8]$ cluster group; *b*) the $[M_6X_8]L_6$ octahedral complex.

The complexes $[M_6X_8]L_6$ can be formed not only from the given molecules "own" atoms, which is observed in complexes of the type $M'_n[M_6X_8]L_6$, but also in compounds where the total number of ligands per M_6 cluster is less than 14. In these cases the coordination takes place via ligands belonging to other fragments, i.e. the ligands L become μ_2-bridging and belong simultaneously to two neighbouring cluster groups (intercluster bridges). Structures with two bridges, i.e. $[M_6X_8]L_4L_{2/2}$, four bridges, i.e. $[M_6X_8]L_2L_{4/2}$, or six bridges, i.e. $[M_6X_8]L_{6/2}$, are known. For example, certain lower niobium and molybdenum halides can be represented by the following crystal-chemical formulae: $[Nb_6I_8]I_{6/2}$;[56]

$[Mo_6Cl_8]Cl_2Cl_{4/2}$;[57] $[Mo_6Br_8]Br_4.2H_2O$.[58] The formula $[Nb_6I_8]I_{6/2}$ means that all the cluster groups $[Nb_6I_8]$ in the compound Nb_6I_{11} are linked to one another by six intercluster bridging iodine atoms in three different directions; the $[Mo_6Cl_8]$ fragments in molybdenum dichloride are joined by four intercluster bridging chlorine atoms in two directions, so that layers of interlinked cluster groups with two terminal chlorine atoms are formed; finally, a structure with isolated molecular fragments, where, in contrast to the first two examples, all the ligands L are terminal, obtains in molybdenum dibromide dihydrate, so that there are no bridge bonds at all between the cluster groups $[Mo_6Br_8]$ in the $[Mo_6Br_8]Br_4.2H_2O$ crystal.

Instances of more complex bridges linking cluster groups are also encountered. Thus the $[W_6Br_8]Br_6$ cluster complexes in crystals of the tungsten bromide W_6Br_{16} are linked into chains by additional Br_2 bridging groups,[59] while in W_6Br_{18} such complexes are linked by Br_2 bridging groups in two directions, which leads to the formation of layers[60] (Fig.6).

Table 4. Coordination of the ligands L to the metal atoms of the $[M_6X_8]$ cluster group.[5]

Compound	$[M_4X_4]L_4$	Total number of ligands in molecules	Number of intercluster bridging μ_2-ligands
$Mo_6Br_{12}.2H_2O$	$[Mo_6Br_8]Br_4(H_2O)_2$	14	0
$Cs_2Mo_6Br_{14}$	$[Mo_6Br_8]Br_6$	14	0
$CsMo_6Br_{13}$	$[Mo_6Br_8]Br_4Br_{2/2}$	13	2
Mo_6Br_{12}	$[Mo_6Br_8]Br_2Br_{4/2}$	12	4
Nb_6I_{11}	$[Nb_6I_8]I_{6/2}$	11	6

Depending on the type of ligand, their number, charge, and the character of the bonding (terminal or bridging), the complexes $[M_6X_8]L_6$ can be either negatively charged species (behaving as anions in compounds of involved composition) or uncharged.

The change to structures with bridging ligands following a decrease in the number of ligands per M_6 cluster is illustrated in Table 4. The limiting composition of a cluster compound with six simple μ_2-bridging intercluster L ligands is described by the formula $[M_6X_8]L_{6/2}$. The lower niobium iodide Nb_6I_{11}, for example, has this composition.

(b) Octahedral Clusters in Chalcogenide Systems

Octahedral cluster groups are characteristic also of binary and ternary molybdenum chalcogenides.[61,62] For example, in the lower molybdenum selenide and telluride having the analytical formula Mo_3Y_4 the main structural fragment is the $[Mo_6Y_8]$ cluster group. In the Mo_3Se_4 structure the $[Mo_6Se_8]$ cluster fragments are arranged in such a way that the molybdenum atoms of one cluster group interact with the selenium atoms of the neighbouring groups (Fig.7*a*).[63] If this case is then treated in terms of the idea that complexes of the type $[M_6Y_8]L_6$ are formed, then the Mo_6Se_8 binary phase can be described by the crystal-chemical formula $[Mo_6Se_2Se_{6/2}]Se_{6/2}$, which implies that six Y ligands in the $[M_6Y_8]$ cluster fragments function at the same time as the ligands L for other neighbouring cluster groups, i.e. behave simultaneously as intercluster bridges. This example demonstrates significant differences between the hexanuclear halide and chalcogenide clusters.

In the crystals of compounds belonging to the Mo_6Se_8 structural type the interaction of the Mo_6 metallic clusters with one another via direct metal–metal bonds is also observed (Fig.6*a*). Such interaction leads to the metallic character of the conductivity of these compounds and even to superconducting properties (MO_6Se_8 is a superconductor with T_c = 6.25 K).[11]

Another important feature of the Mo_6Se_8 structure is the existence of free channels between the cluster groups. When these channels are filled by atoms of various metals, it is possible to obtain a whole series of ternary chalcogenides having the general formula $M_xMo_6Y_8$ (Y = S or Se).[61] Such ternary chalcogenides, which have extremely interesting superconducting properties, have come to be called the Chevrel phases after one of the first investigators of substances of this class who still continues to work vigorously in the field of the chemistry of cluster compounds.[62]

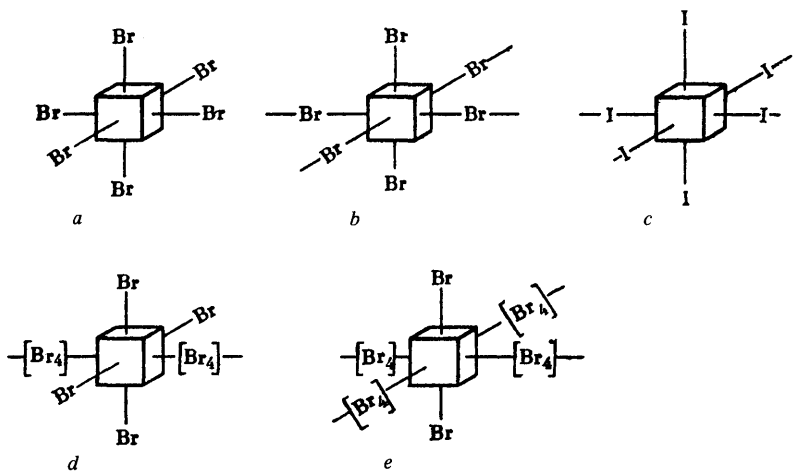


Figure 6. The intercluster bridging ligands in the octahedral transition metal halide complexes:[5] *a*) W_6Br_{14}; *b*) W_6Br_{12}; *c*) Nb_6I_{11}; *d*) W_6Br_{16}; *e*) W_6Br_{18}.

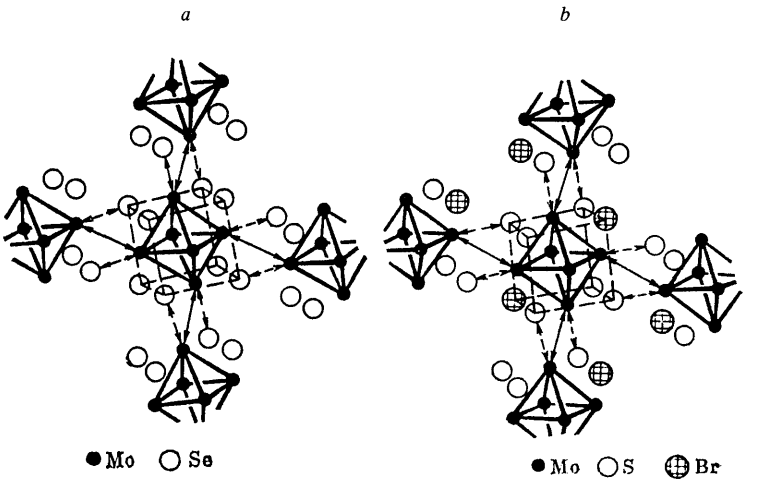


Figure 7. The structure of octahedral clusters: *a*) Mo_6Se_3;[63] *b*) $Mo_6S_6Br_2$.[78]

The chalcogenide cluster groups $[Mo_6Y_8]$, which are so characteristic of molybdenum compounds, have been unknown for other transition metals for a long time. Thus no mention whatever is made of octahedral clusters in a recently published review[64] devoted to the crystal chemistry of rhenium compounds with metal–metal bonds.

However, the most recent studies have shown that rhenium is also capable of forming octahedral cluster systems. Compounds having the composition $Mo_{6-x}Re_xY_8$ (Y = S or Se) and $Mo_4Re_2Te_8$, belonging to the Mo_6Se_8 structural type in which $Mo_{1.5}Re_{4.5}$ and Mo_4Re_2 heterometallic octahedral clusters are produced, were obtained in 1978.[65,66] Solid solutions having the composition $Mo_2Re_4S_{8-x}Se_x$ ($0 \leq x \leq 8$) and $Mo_2Re_4Se_{8-x}Te_x$ ($0 \leq x \leq 1.2$) have also been synthesised.[65]

On the other hand, octahedral rhenium clusters have been observed in the ternary sulphides $Cs_4Re_6S_{13}$,[67] $K_4Re_6S_{12}$, $Na_4Re_6S_{12}$,[68,69] $Li_4Re_6S_{11}$,[70] and finally $Sr_2Re_6S_{11}$ and $Ba_2Re_6S_{11}$.[71] The structure of ternary rhenium sulphides in which the $[Re_6S_8]$ cluster groups are linked to one another by μ_2-S and μ_2-S_2 bridging ligands (Figs.8*a* and 8*b*) are described by the following crystal-chemical formulae: $[Re_6S_8SS_{2/2}(S_2)_{3/2}]^{4-}$ (in $Cs_4Re_6S_{13}$), $[Re_6S_8S_{4/4}(S_2)_{2/2}]^{4-}$ (in $K_4Re_6S_{12}$ and $Na_4Re_6S_{12}$), and $[Re_6S_8S_{6/2}]^{4-}$ (in $Li_4Re_6S_{11}$).

The octahedral cluster is the principal structural fragment of the binary rhenium telluride which had been assumed to be a ditelluride for a long time. However, it has been shown convincingly[72] that the composition of this phase corresponds to the analytical formula Re_2Te_5. The crystal structure of rhenium telluride was determined by ourselves together with N.V.Podberezskaya and by Liu et al.;[73] the $[Re_6Te_8]Te_6$ cluster groups in the Re_2Te_5 structure are linked to one another by tellurium atoms (Fig.8*c*).

The first carbonyl compound containing an octahedral rhenium cluster with an incorporated carbon atom, i.e. $[Re_6(\mu_3\text{-}H)_2C(CO)_{18}]^{2-}$, has been obtained recently.[74]

Consequently the formation of hexanuclear cluster groups is characteristic of all the metals considered. However, niobium, tantalum, and tungsten compounds containing the $[M_6Y_8]$ (Y = S, Se, or Te) cluster groups are at present unknown; rhenium compounds where all the X atoms are halogens in the $[Re_6X_8]$ cluster groups have not been so far obtained either.

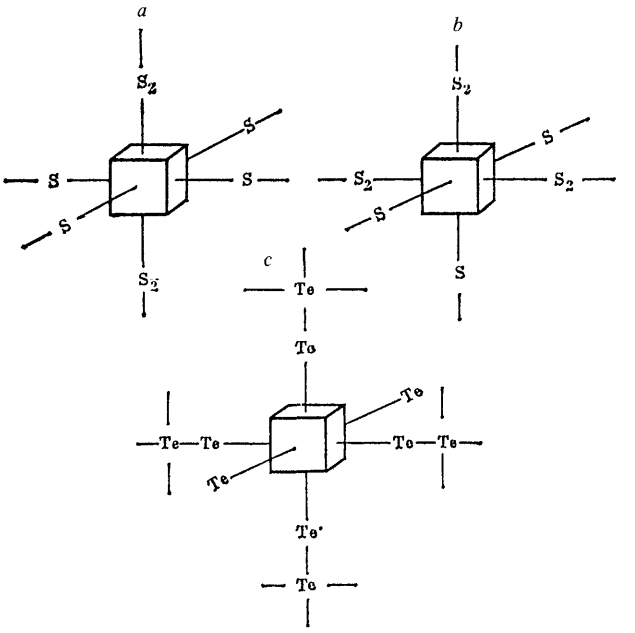


Figure 8. The intercluster bridging ligands in the octahedral rhenium chalcogenide clusters: *a*) $Na_4Re_6S_{12}$;[69] *b*) $Cs_4Re_6S_{13}$;[67] *c*) Re_6Te_{15}.[73]

Since the $[M_6X_8]$ and $[M_6Y_8]$ halide and chalcogenide cluster groups have virtually identical structures, the possibility of the formation of similar groups with mixed ligands, i.e. chalcogenide halides, is indicated; such groups in the cubane $X_{8-n}Y_n$ would contain halogen and chalcogen atoms simultaneously. The similarity of the crystal-chemical characteristics of the halogen and chalcogen atoms makes it possible to replace one ligand by another without a significant alteration in the structure of the cluster groups. Naturally, one must

bear in mind that the halogen and chalcogen atoms have different electron-accepting capacities; the electron density on the M_6 cluster therefore changes significantly following an alteration of the ligand environment of this kind, which should lead to a change of many properties of the compounds considered.

(c) Cluster Octahedral Molybdenum Chalcogenide Halides

The molybdenum chalcogenide halides Mo_6YX_{10} (Y = S, Se, or Te; X = Cl, Br, or I) belong to the Nb_6I_{11} structural type (space group P_{ccn}, orthorhombic system, $Z = 4$).[75,76] The unit cell parameters of these compounds are presented in Table 1.

The structure of the compounds has been established by the X-ray diffraction of Mo_6SeCl_{10} single crystals.[76] The crystal-chemical formula of the compounds Mo_6SeCl_{10} is $[Mo_6SeCl_7]Cl_{4/2}Cl_{2/2}$. The $[Mo_6SeCl_7]$ cluster groups are linked by four bridging chlorine atoms: two other bridging chlorine atoms link the layers to one another. The selenium atom enters into the composition of the $[Mo_6Y'_8]^+$ cluster fragment (Fig. 9*a*). The non-equivalence of the μ_3-ligands in $[Mo_6SeCl_7]$ results in the C_i symmetry of the Mo_6 cluster in Mo_6SeCl_{10}; this is the lowest symmetry among all the known octahedral clusters present in other phases with $[Mo_6Y_8]$ groups. The Mo–Mo distances in the Mo_6 cluster are in the range 2.598–2.626 Å.

As was to be expected, the Mo–Y′ distances (2.468–2.516 Å) in the $[Mo_6Y'_8]$ cluster group are somewhat greater than the average Mo–(μ_3-Cl) distance (amounting to approximately 2.46 Å) in the $[Mo_6Cl_8]$ cluster group of the corresponding chloride complexes[55] and are appreciably less than the Mo–(μ_3-Se) distances (2.52–2.58 Å) in Mo_6Se_8, which can be attributed to a different oxidation state of selenium in Mo_6SeCl_{10} than in Mo_6Se_8.

The distances between the molybdenum atoms and the six bridging chlorine atoms linking the $[Mo_6Y'_8]$ cluster groups with one another are in the range 2.494–2.534 Å, which is close to the analogous distance in molybdenum dichloride (2.49 Å).[57] Each molybdenum atom in the $[Mo_6Y'_8]$ group is at a distance of 0.09 Å from the corresponding face of the Y'_8 pseudocube (the plane passing through the four Y′ atoms); this results in the formation of a greatly flattened square pyramid.

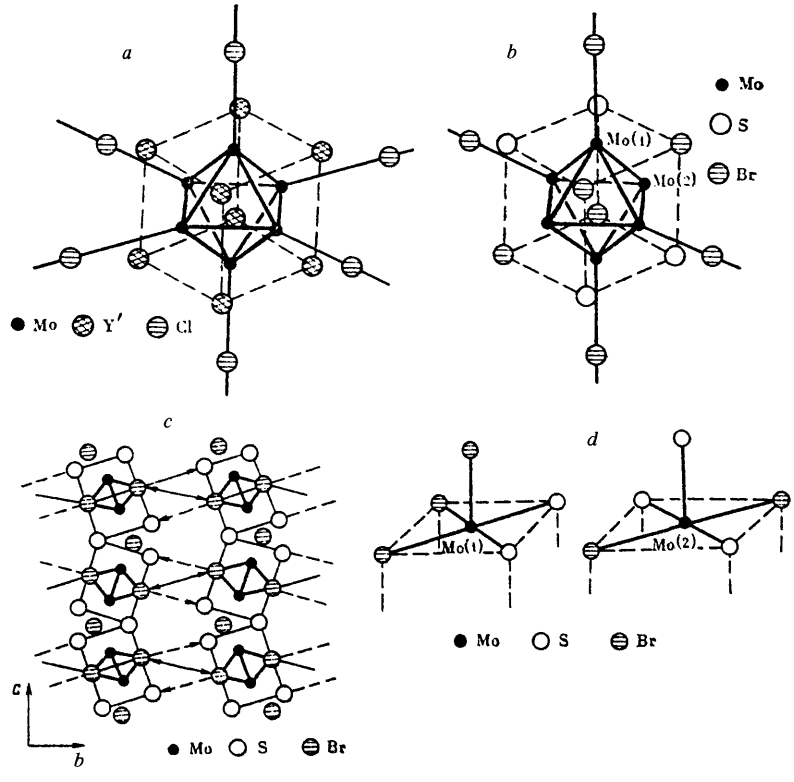


Figure 9. The structure of the hexanuclear molybdenum chalcogenide halides: *a*) a fragment of the Mo_6SeCl_{10} structure;[76] *b*) a fragment of the $Mo_6S_3Br_6$ structure;[77] *c*) three-dimensional packing of $Mo_6S_3Br_6$;[77] *d*) the difference between the coordinations of the molybdenum atoms in $Mo_6S_3Br_6$.[77]

†In this complex sevel Cl atoms and one Se atom are distributed statistically among the eight Y′ poistions of the Mo_6 coordination sphere.

The sulphide bromide $Mo_6S_3Br_6$ crystallises in the orthorhombic system (space group *Cmcm*, $Z = 4$; the unit cell parameters are presented in Table 1).[77] $Mo_6S_3Br_6$ has a layer structure, which represents a new structural type of cluster compounds containing the $[Mo_6Y'_8]$ group.

The principal structural motif of $Mo_6S_3Br_6$ is the $[Mo_6S_4Br_4]$ cluster group in which the sulphur and bromine atoms are ordered and are arranged in pairs along the diagonally opposite edges of the Y'_8 pseudocubane (Fig. 9*b*). All the bromine atoms in $[Mo_6S_4Br_4]$ belong to one cluster group and constitute μ_3-ligands usual for such structures. However, the sulphur atoms in $[Mo_6S_4Br_4]$ are non-equivalent. The two sulphur atoms located on one spatial diagonal are μ_4-ligands: they are linked to three molybdenum atoms in the given cluster group and in addition react with the molybdenum atom of the neighbouring cluster group in the direction of the *b* axis. The other two sulphur atoms are μ_6-ligands, linking two Mo_6 clusters of two neighbouring $[Mo_6S_4Br_4]$ cluster groups, which are thus linked to one another via a common sulphur atom. Consequently the principal structural motif of $Mo_6S_3Br_6$ can be described by the crystal-chemical formula $[Mo_6S_{2/2}S_{2/2}Br_4]$.

In each such group the four molybdenum atoms lying in one plane are coordinated to four bridging bromine atoms, which connect the $M_6Y'_8$] fragments in pairs. As a result, an infinite molecular chain of the $[M_6Y'_8]$ cluster groups joined by the common vertices of the pseudocubanes Y'_8 is formed in a direction parallel to the *c* axis. It can be described by the crystal-chemical formula $[Mo_6S_{2/2}S_{2/2}Br_4]Br_{4/2}S_{2/2}$.

The molecular chains extended along the *c* axis interact with one another in the direction of the *b* axis via the Mo–S bonds 2.503 Å long and Mo–Mo bonds 3.536 Å long. This results in the formation of layers parallel to the *bc* plane with a weak interaction also along the *a* axis. The Br...Br distances between the layers are in the range 3.634–3.742 Å and are close to the usual length of the van der Waals contacts between bromine atoms (Fig. 9*c*).[17]

The molybdenum atoms in $Mo_6S_3Br_6$ are crystal-chemically non-equivalent (Fig. 9*d*). The Mo(1) atoms are coordinated to three bromine atoms and two sulphur atoms via the vertices of a tetragonal pyramid, while the Mo(2) atoms are coordinated via two bromine atoms and three sulphur atoms, the sulphur atoms located at the vertex of the pyramid belonging to a neighbouring $[Mo_6S_4Br_4]$ fragment.

The Mo_6 cluster in $Mo_6S_3Br_6$ has the C_{2h} symmetry and the Mo–Mo distances are in the range 2.63–2.68 Å. These distances are intermediate between those observed in the Mo_6Se_8 and $Mo_6Br_{12}.2H_2O$ crystals.

Each molybdenum atom is located over the corresponding face of the S_4Br_4 pseudocubane, so that a flattened tetragonal pyramid with the molybdenum atom at the apex is formed. The Mo(1) atoms is at a distance of 0.10 Å from the S_2Br_2 plane, while the Mo(2) atom is virtually in the plane [the distance from the S_2Br_2 plane to Mo(2) is only 0.02 Å].

The molybdenum sulphide halides $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ crystallise in the orthorhombic system (Mo_6Se_8 structural type; space group $\bar{R}3$, $Z = 1$; the unit cell parameters of these compounds are listed in Table 1).[78]

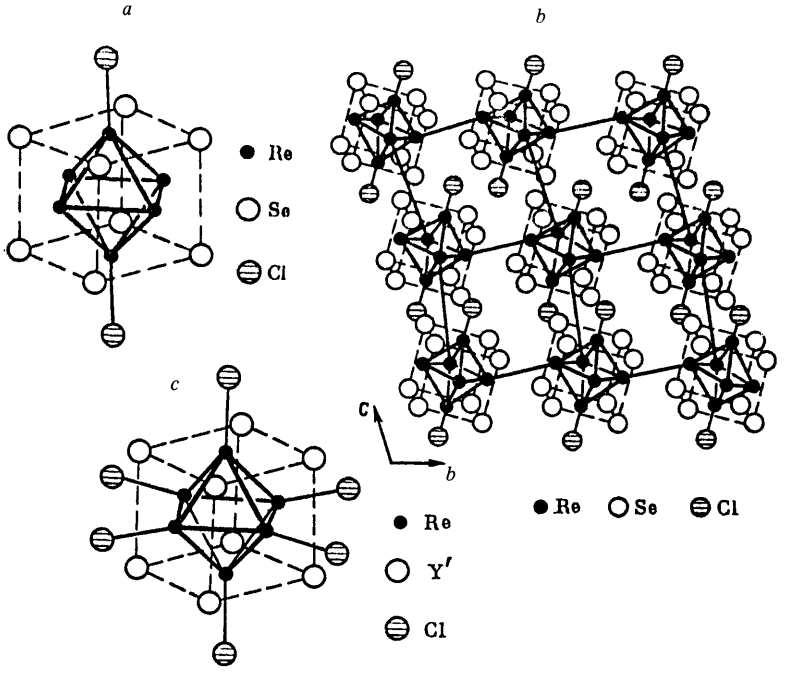


Figure 10. The structure of the hexanuclear rhenium chalcogenide halides: *a*) a fragment of the $Re_6Se_8Cl_2$ structure;[79] *b*) three-dimensional packing of $Re_6Se_8Cl_2$;[79] *c*) a fragment of the $Re_6Se_4Cl_{10}$ structure.[80]

The structure of the molybdenum sulphide bromide $Mo_6S_6Br_2$ resembles that of Mo_6Se_8.[78] An octahedron made up of molybdenum atoms is inscribed in the somewhat distorted pseudocubane S_6Br_2, the opposite two vertices of which are occupied by bromine atoms in such a way that each molybdenum atom is located above the centre of the face outside the cube at a distance of 0.18 Å. The Mo_6 octahedral cluster with D_{3h} symmetry is characterised by two independent Mo–Mo distances of 2.719 and 2.732 Å. While the Mo_6 octahedron in $Mo_6S_6Br_2$ is close to ideality, the S_6Br_2 pseudocubane in this structure is highly distorted (Fig. 7*b*).

The most important feature of the $Mo_6S_6Br_2$ structure is the fact that the halogen atoms in the cluster group are ordered and occupy two *c* positions in the direction of the threefold rhombohedral axis. This factor in fact leads to the formation of compounds with the given stoichiometry.

The interaction of the $[Mo_6Y_8]'$ motifs in the crystal takes place via the bonds between the molybdenum atoms and the sulphur atoms in other cluster groups; the length of such bonds is 2.485 Å (Fig. 7*b*). Thus the molybdenum sulphide bromide $Mo_6S_6Br_2$ has the crystal-chemical formula $[Mo_6S_{6/2}Br_2]S_{6/2}$.

Molybdenum sulphide halides have high temperatures corresponding to the transition to the superconducting state (T_c = 13.8 K for $Mo_6S_6Br_2$ and T_c = 14.0 K for $Mo_6S_6I_2$). It has been suggested that[61] the appearance of superconductivity is associated with the interaction of the molybdenum atoms belonging to neighbouring octahedral clusters and located at a distance of 3.225 Å from one another.

(d) Octahedral Cluster Rhenium Chalcogenide Halides

The rhenium selendie chloride $Re_6Se_8Cl_2$ crystallises in the triclinic system (space group $P\bar{1}$, $Z = 1$; the unit cell parameters are listed in Table 1).[79] The crystal structure of $Re_6Se_8Cl_2$ (Fig. 10) can be described as one made up of $[Re_6Se_8]Cl_2$ motifs.[79] These motifs consist of Re_6Se_8 cluster groups, which are coordinated above and below to two terminal chlorine atoms via bonds with two rehnium atoms located on the opposite faces of the Se_8 cube (the Re–Cl distance is 2.37 Å).

The $[Re_6Se_8]Cl_2$ fragments in the crystal are arranged in layers parallel to the *ab* plane. The interaction of the cluster groups in such layers takes place via the Re–Se bonds. Four rhenium atoms in each $[Re_6Se_8]$ cluster group are linked to the selenium atoms belonging to four neighbouring $[Re_6Se_8]$ fragments. The lengths of these Re–Se bonds is 2.65 Å, which differs little from that observed in $[Re_6Se_8]$, which is 2.5–2.6 Å. This arrangement is described by the crystal-chemical formula $[Re_6Se_4Se_{4/2}]Cl_2Se_{4/2}$. The Re...Re distances between neighbouring clusters within the layer are 3.41 and 3.44 Å (the Re–Re distances in the Re_6 cluster are in the range 2.62–2.66 Å).

The interaction of the $Re_6Se_8Cl_2$ molecular layers in the direction of the *c* axis is insignificant and takes place via the Se...Cl bonds over distances of 3.17 and 3.45 Å. This character of the interaction of the layers determines the quasi-two-dimensional properties of the crystal structure $Re_6Se_8Cl_2$.

The rhenium chalcogenide halides $Re_6Y_4X_{10}$ (Y = Se or Te; X = Cl or Br) crystallise in the triclinic system (space group $P\bar{1}$, $Z = 2$). The crystal structure has been determined for $Re_6Se_4Cl_{10}$ single crystals[80] (Fig. 10*c*). The rhenium selenide chloride consists of molecular crystals and the Re_6 octahedral clusters in the structure are not linked by intercluster bridging ligands, so that the crystal-chemical formula is $[Re_6Se_4Cl_4]Cl_6$. Two independent cluster fragments are located at the centres of inversion. The Re–Re distances in the octahedral Re_6 cluster are 2.601–2.618 Å. An interesting feature of this structure is the fact that the Se and Cl atoms behave as μ_3-ligands in the $[Re_6Se_4Cl_4]$ cluster group. Although an unambiguous determination of their positions is difficult, the variant where the Se_4Cl_4 pseudocubane is made up of two interpenetrating Se_4 and Cl_4 tetrahedra is the most likely. The model with the X and Y atoms at the opposite vertices of the cubane is well correlated with the spectroscopic properties of the compounds.[80]

(e) The Crystal-chemical Features of the Octahedral Cluster Molybdenum and Rhenium Chalcogenide Halides

In discussing the crystal-chemical features of the structures of the octahedral cluster chalcogenide halides, it is essential in the first place to note, as a general feature, the tendency of the $[M_6Y_8']$ cluster groups to form complexes of the type $[M_6Y_8']L_6$. If the total number of ligands (Y′ + L) is 14 per M_6 cluster, then structures with isolated $[M_6Y_8']L_6$ complexes are formed as in the halide systems. This is clearly seen in relation to the rhenium chalcogenides $[Re_6Y_4X_4].X_6$ as an example, which are characterised by a molecular type of structure. With decrease of the number of ligands, the complexes $[M_6Y_8']L_6$ are formed as a result of the coordination at the L site of atoms belonging to other cluster groups. However, in contrast to the halide system discussed above, where ligands of type L constitute common intercluster bridges, in the chalcogenide halides this function is fulfilled by the Y′ atoms, i.e. the atoms which form part of the $[M_6Y_8']$ cluster group. The same simple behaviour is observed in this instance too: with decrease of the number of ligands per M_6 cluster, the number of atoms common to two neighbouring cluster groups increases and the Y′ begin to assume the function of intercluster bridges. This rule is well illustrated by the data in Table 5: a steady variation of the character of the coordination is seen on passing from isolated molecular chalcogenide halides of the type $[Re_6Y_4X_4]X_6$ (14 ligands per cluster) to the $[Me_6S_{6/2}Br_2]S_{6/2}$ structure (eight ligands per cluster). Depending on the atoms in the Y_8' cubane through which the cluster groups are linked to one another, structures of different size can be produced.

Table 5. Variation of the intercluster metal–metal distances as a function of the type of bridging ligands.

Compound	$[M_4Y_8']L_6$	N_L^*	$\frac{R}{(M...M)}$, Å	Character of structure	Refs.
$Re_6Se_4Cl_{10}$	$[Re_6Se_4Cl_4]Cl_6$	14	3.69	molecular	[80]
Mo_6SeCl_{10}	$[Mo_6SeCl_7]Cl_{6/2}$	11	3.687	polymeric (three-dimensional)	[76]
$Re_6Se_6Cl_2$	$[Re_6Se_4Se_{4/2}]Cl_2Se_{4/2}$	10	3.42	polymeric (layer)	[79]
$Mo_6S_3Br_6$	$[Mo_6S_{2/2}S_{2/2}Br_4]Br_{4/2}S_{2/2}$	9	3.536	polymeric (layer)	[77]
$Mo_6S_6Br_2$	$[Mo_6S_{6/2}Br_2]S_{6/2}$	8	3.225	polymeric (three-dimensional)	[78]
Mo_6S_8	$[Mo_6S_{6/2}S_2]S_{6/2}$	8	3.086	polymeric (three-dimensional)	[61]

*The number of ligands per cluster in the molecule.

It is also of interest ot note that the coordination of the ligands Y_8' changes on formation of such intercluster bridges: on formation of additional bonds, the μ_3-ligands beome μ_4-ligands and even μ_6-ligands (as has been observed in $Mo_6S_3Br_6$).

The character of the chemical bonds in octahedral cluster chalcogenide halides can apparently be described within the framework of the ionic-covalent model, where it is assumed that there is a covalent interaction between the metal atoms in the M_6 octahedron, while the bonds between the metal and the ligands are ionic. Calculations of the electronic structure of the hexanuclear metal halides and chalcogenides have convincingly confirmed the validity of this treatment.[22,61] An important feature of these systems consists in the fact that two groups of molecular orbitals are formed by the atomic *d* orbitals of the metal; 12 bonding MO (which describe 12 two-centre M–M bonds oriented along the edges of the octahedral M_6 cluster) are separated from the higher antibonding unoccupied MO.[81,82]

Consequently the formation of 12 simple two-electron M–M bonds in the M_6 cluster requires 24 valence electrons. This situation obtains in halide systems with the $[Mo_6X_8]^{4+}$ cluster group and also in the chalcogenide halides Mo_6YX_{10} and $Mo_6S_3Br_6$ (Table 6). However, in the $Mo_6S_6Y_2$ and also Mo_6S_8 chalcogenide halides the Mo_6 cluster is electron-deficient, which implies that the bonding MO, characterising the M–M interaction in the octahedral cluster, are only partly occupied. Consequently the Mo–Mo bond order should decrease in the series of compounds $Mo_6S_3Br_6 \rightarrow Mo_6S_6Br_2 \rightarrow Mo_6S_8$. A decrease of the number of valence electrons in the Mo_6 cluster entails an increase of the Mo–Mo distances (Table 6). Indeed the molybdenum sulphide Mo_6S_8, which has only 20 electrons per cluster, is thermodynamically unstable and cannot be obtained by direct synthesis from the elements. The addition of electrons to the electron-deficient cluster system stabilises the phases, which is clearly demonstrated by chalcogenide halides of the type of $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ (22 electrons per cluster), and also by the $M_xMo_6S_8$ Chevrel phases, which can contain 21–24 electrons per cluster depending on the nature of the metal M. It has been shown convincingly for a large number of Chevrel phases that the interatomic Mo–Mo distances in the Mo_6 cluster depend on the number of valence electrons localised on the cluster.[61]

Table 6. Dependence of the Mo–Mo interatomic distances in the Mo_6 cluster on the number of valence electrons localised on the cluster.

Compound	R (Mo–Mo), Å	N_e^*	Refs.
$[Mo_6Cl_8]Cl_2Cl_{4/2}$	2.61	24	[59]
$Cs_2[Mo_6Cl_8]Br_6$	2.61	24	[76]
$Hg[Mo_6Cl_8]Cl_6$	2.62	24	[76]
$[Mo_6SeCl_7]Cl_{6/3}$	2.62	24	[76]
$[Mo_6Br_6]Br_4 \cdot 2H_2O$	2.64	24	[60]
$Mo_6S_3Br_6$	2.66	24	[77]
$Mo_6S_6Br_2$	2.73	22	[78]
Mo_6S_8	2.78	20	[61]

*The number of electrons per Mo_6 cluster.

Thus shorter distances between the molybdenum atoms in the Mo_6 cluster are observed in those compounds where the number of electrons per cluster approaches 24. The size of the Mo_6 octahedron can serve as a measure of the degree of occupation of the conductivity band. In the most highly contracted octahedron all the bonding states are occupied and the number of electrons per cluster is 24.

An interesting aspect of the crystal chemistry of the octahedral cluster chalcogenide halides is the variation of the shortest metal–metal distances between the clusters (Table 5). With increase of the number of bridging cross-links between the cluster groups, conditions arise for closer direct contacts between the metal atoms of neighbouring clusters. Thus the Mo–Mo distances between neighbouring clusters decrease steadily in the series of molybdenum chalcogenide halides Mo_6SeCl_{10}, $Mo_6S_3Br_6$, and $Mo_6S_6Br_2$: 3.687, 3.536, and 3.225 Å respectively.

The conducting properties of the binary and ternary chalcogenide containing the $[M_6Y_8]$ cluster groups are extemely interesting. The unique superconducting properties of the Chevrel phases are widely known.[11,62] They are determined mainly by the 4*d* electrons of molybdenum occupying the conductivity band. If the conductivity band is incompletely filled, favourable conditions arise for the appearance of superconductivity in such phases. The Mo–Mo distances between neighbouring clusters are then also significant.[61]

From this point of view, among the chalcogenide halides considered here the $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ phases are of the greatest interest (22 electrons) per cluster. They are conductors and undergo a transition to the superconducting state at 13.8 and 14.0 K respectively.[78]

If the conductivity band is fully occupied, the compounds exhibit semiconducting or dielectric properties. For example, $Mo_6S_3Br_6$ and $Re_6Se_4Cl_{10}$, in which there are 24 valence electrons per cluster, can be included among such phases.

III. METHODS OF SYNTHESIS

The cluster niobium, molybdenum, and rhenium chalcogenide halides are usually obtained by the high-temperature synthesis involving prolonged heating of mixtures of different composition in evacuated sealed tubes: (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. The initial substances are usually taken in proportions corresponding to the stoichiometry of the substance to be synthesised.

A general preparative method of synthesis of transition metal chalcogenide halides at high temperatures is that of gas-transport chemical reactions. A characteristic feature of these reactions, whereby it is possible to obtain high quality crystals, is mass transfer under the conditions of a temperature gradient with segregation of the solid phase in the cold zone; phases separated in space from the initial reaction mixture are then produced.[84]

(a) The Synthesis and Properties of Dinuclear Chalcogenide Halides

All the compounds having the composition $NbYX_3$ (Y = Se or Te; X = Cl, Br, or I) have been obtained by the high-temperature sealed tube synthesis from the elements. A stepwise increase of temperature with a final treatment at 800 °C for 3–4 days has been used. When a temperature difference is created at the ends of the sealed tube, mass transport and growth of acicular single crystals are observed.[16]

The chalcogenide halides $NbYX_3$ are stable in air; they form grey single crystals with metallic lustre. The thermal properties of these substances have been investigated.[16] The final product of the thermal decomposition of $NbTeI_3$ *in vacuo* is Nb_3Te_4.

Compounds having the analytical formula MYX_3 have been obtained also for other metals (M = Ta, Mo, or Re) by the interaction of the corresponding metal pentahalides with Sb_2Y_3 (Y = S or Se) in solution in CS_2.[85] However, the structure of these phases is unknown and at the present time

there are no grounds for assigning them to dinuclear compounds.

Compounds having the composition NbY_2X_2 (Y = S or Se; X = Cl, Br, or I) have been obtained by the sealed tube method in the 480–530 °C temperature gradient. The starting materials were metallic niobium, the elemental chalcogen, and niobium tetrahalides. The single crystals of niobium chalcogenide halides were grown in the cold zone of the sealed tube in the form of plates. The transport time was 3–4 weeks.[18] The compounds NbS_2Cl_2 and NbS_2Br_2 can be obtained on heating the metal in S_2Cl_2 and S_2Br_2 vapours.[86]

The compounds NbY_2X_2 are stable in air and are insoluble in the majority of solvents. On heating, they undergo polymorphic transformations (Table 1). The thermal decomposition of the compounds proceeds in different ways depending on the composition. For example, the compounds NbY_2X_2 (X = Cl or Br) decompose in accordance with the scheme

$$3NbY_2X_2\,(\text{solid}) \rightarrow NbY_2\,(\text{solid}) + X_2\,(\text{gas}) + 2NbYX_3\,(\text{gas}).$$

The chalcogenide iodides NbY_2I_2 dissociate via the reaction

$$NbY_2I_2 \rightarrow NbY_2\,(\text{solid}) + I_2\,(\text{gas}).$$

The compounds are diamagnetic and are semiconductors.[86]

Single crystals of the black sulphide chloride MoS_2Cl_3 have been obtained on heating to 450 °C a 1 : 10 mixture of $MoCl_3$ and S in S_2Cl_2.[19] A yellow-brown sulphide chloride of the same composition has been obtained on heating molybdenum pentachloride in S_2Cl_2 at 250 °C.[87] The structure of the black MoS_2Cl_3 has been established by X-ray diffraction[19] and the yellow-brown molybdenum sulphide chloride has been characterised only by infrared and Raman spectra.

Single crystals of the brown selenide chloride $Nb_3Se_5Cl_7$ have been obtained accidentally in a study of the transport of $NbSe_2Cl_2$ in the presence of $NbCl_4$ in a temperature gradient (at 535–525 °C). The transport time was 2–3 weeks.[20] The dark-blue bromide analogue $Nb_3Se_5Br_7$ has been obtained in the form of single crystals on heating a reaction mixture comprising $NbSe_2Br_2$ and $NbSeBr_3$. The authors noted a poor reproducibility of this syntheses.[20]

(b) The Synthesis and Properties of Trinuclear Chalcogenide Halides

The trinuclear chalcogenide halides $Mo_3Y_7X_4$ have been obtained in quantitative yields on heating the lower molybdenum halides MoX_2 and MoX_3 (X = Cl, Br, or I) in a sulphur or selenium melt at temperatures in the range 350–450 °C:[89–92]

$$6MoCl_3 + 24S \rightarrow 2Mo_3S_7Cl_4 + 5S_2Cl_2\,.$$

The excess chalcogen and the Y_2X_2 formed as a result of the reaction are removed by heating *in vacuo* or are washed out with CS_2.[89] Another convenient method of synthesis of the trinuclear molybdenum chalcogenide halides involves the conversion of the chalcogenide halide MoY_4X_2 (Y = S or Se; X = Br or I) on heating in sealed tubes:[93]

$$3MoS_4I_2 \rightarrow Mo_3S_7I_4 + 5S + I_2\,.$$

The cluster compounds $Mo_3Y_7X_4$ are insoluble in organic solvents and do not sublime *in vacuo*, which hinders their further purification.

$Mo_3S_4Cl_4$ single crystals have been obtained on heating molybdenum trichloride and sulphur at 450 °C in a sealed tube in the presence of S_2Cl_2.[19]

The thermal properties of the trinuclear molybdenum chalcogenide halides have been investigated. Heating of $Mo_3Y_7X_4$ *in vacuo* or in an inert atmosphere results in the formation of their corresponding dichalcogenides.[89–92]

The process has a stepwise character in an atmosphere of hydrogen; the final reduction products at model temperatures are also dichalcogenides.[89–92]

(c) The Synthesis and Properties of Tetranuclear Chalcogenide Halides

The tetranuclear chalcogenide halides $M_4Y_4X_4$ (M = Nb or Mo; Y = S or Se; X = Cl, Br, or I) have been obtained by high-temperature annealing in evacuated quartz tubes, the reaction mixture consisting of the metal, the chalcogen, and a lower metal halide.

The niobium chalcogenide halides $Nb_4Y_4X_4$ have been obtained from Nb_3X_8, metallic niobium, and the chalcogen in a two-zone furnace with a temperature gradient of 700–800 °C.[45] The molybdenum sulphide halides $Mo_4S_4X_4$ have been synthesised at 1100 °C and the reaction mixture consisted of the corresponding dihalide, molybdenum, and sulphur.[46,47]

The tetranuclear niobium and molybdenum chalcogenide halides are stable in air and are insoluble in the usual organic solvents.

(d) The Synthesis and Properties of Hexanuclear Chalcogenide Halides

Practically all chalcogenide halides of this type are obtained via solid-phase synthesis reactions using high temperatures. The only exception is $Re_6Te_4Br_{10}$, which can be obtained by the reaction of rhenium telluride with bromine even at room temperature. The reason why the reaction proceeds under such mild conditions is apparently that the initial rhenium telluride Re_6Te_{15} already contains the octahedral Re_6 cluster in its structure. The lower halides, the chalcogen, and the metal in stoichiometric amounts are used as the starting reactants for the synthesis of compounds with a high metal content.

The compounds Mo_6YX_{10} (Y = S, Se, or Te; X = Cl or Br) have been obtained by the sealed tube method, the stoichiometric amounts of $MoX_2(MoX_3)$, Mo, and Y being sintered at temperatures in the range 1000–1150 °C for 24 h with subsequent reannealing under the same conditions.[76] Single crystals suitable for X-ray diffraction studies grow during the synthesis. The colour of the single crystals of the chalcogenide halides Mo_6YX_{10} varies from red to dark-brown depending on the composition. The compounds are stable in air, are diamagnetic, and are dielectrics.

The molybdenum sulphide bromide $Mo_6S_3Br_6$ has been obtained by the sealed tube synthesis, in which stoichiometric amounts of the $3MoBr_2$ + 3Mo + 3S powders, pressed into discs, are heated at 1200 °C for 24 h. The preparation of single-phase specimens requires reannealing under the same conditions after mixing the reaction products. $Mo_6S_3Br_6$ single crystals in the form of black lustrous plates grew at 1250 °C.[77]

The chalcogenide halides $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ have been obtained by the sealed tube method. Stoichiometric amounts of powdered MoX_2, molybdenum, and sulphur were pressed into discs and the reaction was carried out at 1050 °C for 24 h. After mixing the reaction products, the latter were reannelaed under the same conditions.[78] The possible admixtures in this method of synthesis of the sulphide halides $Mo_6S_6X_2$ can be the Mo_2S_3 and $Mo_4Y_4X_4$ phases. In the synthesis of $Mo_6S_6I_2$ one can also begin with a mixture of stoichiometric amounts of the elements.[94] The attempts to obtain molybdenum sulphide chlorides having the same composition were unsuccessful.

The compounds are weakly paramagnetic and exhibit metallic conductivity. On decrease of temperature, they pass to the superconducting state, the width of the transitional region amounting to 1–2 K. The critical temperatures are 13.8 K for $Mo_6S_6Br_2$ and 14.0 K for $Mo_6S_6I_2$.[78]

The interaction of $Mo_6S_6I_2$ with copper has been investigated.[94] It has been established that single-phase products having the composition $Cu_xMo_6S_6I_2$, where $0 < x < 1.2$, which are isostructural with $Mo_6S_6I_2$, can be obtained at 470 °C. With increase of the amount of copper in the $Cu_xMo_6S_6I_2$ phases, the size of the unit cell increases somewhat but the temperature of the transition to the superconducting state decreases.

The rhenium selenide chloride $Re_6Se_8Cl_2$ has been obtained by the sealed tube method at 1000 °C from a mixture of $ReCl_5$, Re, and Se.[79] The compounds $Re_6Se_4Cl_{10}$ and $Re_6Se_4Br_{10}$ are obtained by the sealed tube method in which the $ReSe_2 + 2ReX_5$ (X = Cl or Br) reaction mixture is heated at 700–750 °C for 10–15 h (the rhenium trihalide is taken in a slight excess). The reaction products are separated by vacuum-thermal distillation.[95] The rhenium selenide bromide $Re_6Se_4Br_{10}$ is also obtained by brominating $ReSe_2$ at 650–700 °C.[96]

The compound $Re_6Te_4Br_{10}$ is obtained by brominating the rhenium telluride Re_6Te_{15} with liquid bromine. The reaction proceeds even at room temperature, but the temperature is raised to 50–60 °C to achieve a more rapid completion of the process.[96]

IV. CHEMICAL PROPERTIES

As shown in the previous sections of the review, molecular structures with a metal–metal bond are not characteristic of the chalcogenide halides—the M_n cluster nuclei are linked into infinite chains, layers, or give rise to three-dimensional structures. Such polymeric structure of the cluster chalcogenide halides is manifested in their properties: their volatility is low and they are insoluble in organic solvents, which greatly hinders the study of their chemical properties. These compounds are as a rule stable in air and their reactivity is low.

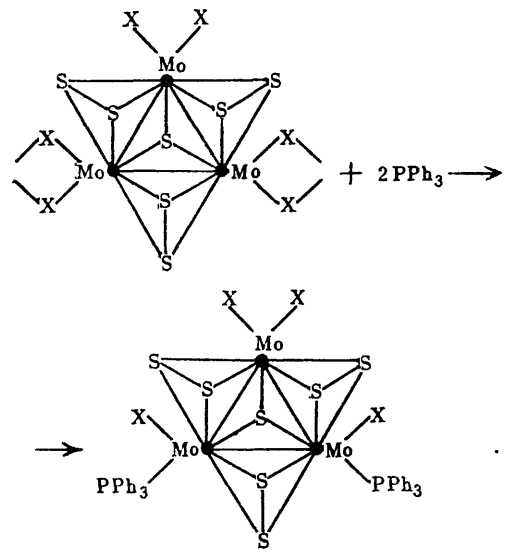
Related structural motifs arise in the cluster transition metal halides, chalcogenides, and chalcogenide halides. The chalcogenide halides occupy an intermediate position between the metal halides and chalcogenides. The cluster metal chalcogenides are frequently soluble in organic solvents, undergo complex formation reactions, and, as shown recently in relation to rhenium trihalides,[97] they enter into organometallic synthesis reactions. The cluster chalcogenides are chemically inert and decompose on treatment with strong oxidants or reductants under severe conditions.

We shall consider what synthetic approaches are possible in the study of the chemical properties of cluster chalcogenide halides. In our view, it is initially necessary to find ways of dissolving the cluster chalcogenide halides. The synthetic methods of the chemistry of complex and organometallic compounds are applicable to clusters soluble in organic solvents. In order to achieve the dissolution of the compounds, it is necessary to find reagents in the presence of which one-, two-, or three-dimensional structures are disrupted, but the main cluster fragments should persist. Monomeric structures in the cluster chalcogenide halides are usually formed with the aid of bridging halogen and chalcogen atoms or via the metal–metal intercluster interaction. The ways used to disrupt such different structures should apparently also be different.

We shall now turn to analogies from the chemistry of cluster metal halides. The reactions of hexanuclear cluster niobium, tantalum, molybdenum, and tungsten halides as well as the trinuclear rhenium halides with oxygen, sulphur-, nitrogen-, and phosphorus-containing ligands are well known. As a result of such reactions, the polymeric structures are broken up and molecular cluster complexes of metal halides with various ligands are formed, for example:[5,98]

$$Mo_6Cl_{12} + 2Et_3N \rightarrow Mo_6Cl_{12} \cdot 2Et_3N \ ;$$
$$Re_3Cl_9 + 3PPhEt_2 \rightarrow Re_3Cl_9 \cdot 3PPhEt_2 \ .$$

It has been shown recently[99] that the polymeric cluster sulphide halides $Mo_3S_7Cl_4$ and $Mo_3S_7Br_4$ interact with triphenylphosphine on heating in acetonitrile or benzonitrile, giving rise to molecular trinuclear complexes soluble in organic solvents:



The reaction of molybdenum sulphide chloride with PPh_3 in proportions of 1 : 5 produces a molecular complex having a different composition:

$$Mo_3S_7Cl_4 + 5PPh_3 \rightarrow 3S{=}PPh_3 + Mo_3S_4Cl_4 \cdot 2PPh_3 \ .$$

The formation of the triphenylphosphine sulphide can be accounted for by the elimination of sulphur atoms from the disulphide group. Reactions leading to the elimination of a chalcogen atom from the dichalcogenide group on treatment with various nucleophiles are convenient models for the understanding of many biochemical processes.[100]

Reactions involving the nucleophilic substitution of halogen atoms are of independent interest. Such reactions have been known for a long time for the cluster transition metal halides. For example, it has been shown for rhenium trihalides that the intercluster halogen atoms are the first to be involved in the substitution reaction with nucleophiles.[101] The first instance of the nucleophilic substitution of the halogen has been found for the cluster chalcogenide halides. The sulphide chloride $Mo_3S_7Cl_4$ interacts with sodium polysulphide with retention of the trinuclear cluster framework:[102]

$$Mo_3S(S_2)_3Cl_4 \xrightarrow[s_2^n]{} [Mo_3S(S_2)_6]^{2-} \ .$$

Thus the first examples of the conversion of polymeric molybdenum chalcogenide halides into molecular clusters soluble in organic solvents have been found, which leads to wide possibilities for the investigation of the properties of compounds of this class.

In conclusion we may note that the study of the chemical properties of cluster transition metal chalcogenide halides may promote the solution of one of the most interesting problems in modern chemistry: Cotton has pointed out[4] the necessity for

the mutual approach of two fields of the chemistry of cluster compounds which have been largely developing independently, namely those concerned with the study of high valence clusters (the clusters with acido-ligands) and low-valence clusters (organometallic clusters). It may be that the cluster transition metal chalcogenide halides discussed in this review will prove important starting compounds for organometallic synthesis reactions, including reactions involving reactive cyclopentadienyl compounds of metals.

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