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Binuclear molybdenum(III) complexes

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ABSTRACT. The methods of synthesis, properties, structure, and electronic structure of binuclear molybdenum(III) complexes are reviewed. Dimers without monatomic bridges and dimers with oxygen, sulphur, and halogen bridging atoms are described. The effect of the bridging ligands on the nature of the M–M bond and the dependence of the distance between the metal atoms in dimeric halomolybdates(III) on the nature of the internal and external coordination spheres are discussed.

The bibliography includes 132 references.

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I. Introduction

Molybdenum has gained a firm reputation as the element which holds the record for the range of cluster systems and compounds with an M–M (metal–metal) bond, including a quadruple bond,[1] formed by it.

A large number of polynuclear complexes in which the M–M bonds differ markedly in length and energy are known for trivalent molybdenum. The diversity of the chemistry of molybdenum(III) clusters is an indication that even for a single electronic configuration, the degree of interaction between metal atoms can vary over wide limits as a function of the ligand environment. In the present review we shall examine binuclear molybdenum(III) complexes, which are the simplest systems in which the Mo–Mo bond can occur.

Dimeric molybdenum(III) complexes can be divided into two groups: 1) complexes whose stability is mainly determined by the Mo–Mo interaction; 2) compounds in which both the Mo–Mo interaction and the ligand bridges make a specific contribution to their stabilisation. To the first group belong dimers without bridging ligands and also complexes which in addition to a strong Mo–Mo bond have bidentate ligands that form polyatomic bridges. The presence of such ligands does not cause any significant change in the structure of the complexes compared to bridgeless dimers. To the second group belong complexes in which the metal atoms are connected by monatomic bridges. The properties and structure of such compounds depend to a considerable extent on the nature of the bridging ligand.

II. Binuclear complexes without monatomic bridges

Molybdenum(III) is capable of forming strong M≡M triple bonds. Such bonds occur in dimers of the type Mo_2L_6 (L = OR^-, R^-, NR_2^-) and their derivatives. A feature of these compounds is the presence of bulky terminal ligands which contain, as a rule, atoms with strong donor properties.[2–7]

Amide, trimethylsilylmethyl, and thiophenol derivatives of the type Mo_2L_6 are obtained by reaction of molybdenum chlorides with LiL. The remaining complexes are synthesised by exchange or addition of ligands or by the insertion of unsaturated molecules into the Mo–L bond in initial Mo_2L_6 dimers in hydrocarbon solvents.[1,5,8–28]

The most commonly occurring structures of the dimers are shown in Fig. 1. Information about the synthesis of the complexes and data on the Mo–Mo interatomic distances are given in Table 1.

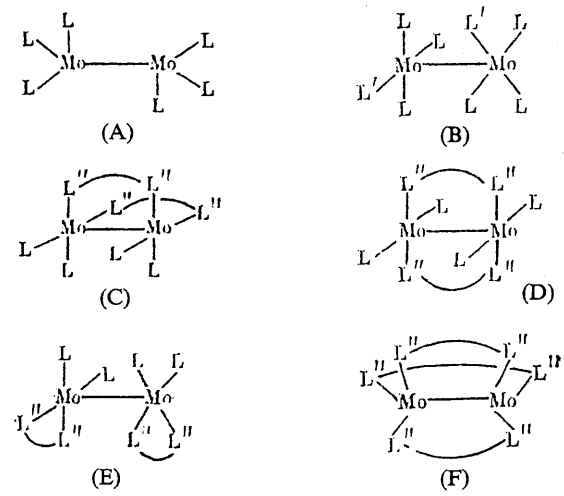


Figure 1. Structures of dimers without monatomic bridges.

Mo_2L_6 molecules have an ethane-like conformation (A). When two ligands are replaced, 1,2-isomers having an *anti* or *gauche* conformation are usually obtained, although 1,1-isomers have also been detected using NMR.[25] For products obtained from the addition of Lewis bases (L′) to Mo_2L_6, a "staggered" configuration of the ligands with an almost planar MoL_3L' square is typical (B). Chelating ligands (L″) can be coordinated in bidentate manner

Table 1. Information on the synthesis and structure of dimers without monatomic bridges.

Initial reactants*	Products*	$R_{M-M'}$ Å	Structural type (Fig.1)	Refs.
$MoCl_5 + LiCH_2SiMe_3$	$Mo_2(CH_2SiMe_3)_6$	2.167	(A)	[1, p.237]
$Mo_2(iso\text{-}OPr)_6 + Mg(CH_2Ph)_2$	$Mo_2(CH_2Ph)_6$	2.175	(A)	[8]
$MoCl_3 + LiNMe_2$	$Mo_2(NMe_2)_6$	2.214	(A)	[1, p.238]
$Mo_2(NMe_2)_6 + HOCH_2Bu\text{-}t$	$Mo_2(OCH_2Bu\text{-}t)$	2.222	(A)	[5]
$Mo_2(t\text{-}BuS)_2(NMe_2)_4 + HSC_6H_2Me_3$**	$Mo_2(SC_6H_2Me_3)_6$	2.239	(A)	[9]
$MoCl_4 + Na + HSC_6H_2(iso\text{-}Pr)_3$	$Mo_2(SC_6H_2(iso\text{-}Pr)_3)_6$	2.228	(A)	[10]
$Mo_2(NMe_2)_6 + Me_3SiCl$	$Mo_2Cl_3(NMe_2)_4$	2.201	(A)	[11]
$Mo_2Cl_3(NMe_2)_4 + LiMe$	$Mo_2Me_3(NMe_2)_4$	2.201	(A)	[12]
$Mo_2Cl_3(NMe_2)_4 + LiP(t\text{-}Bu)_2$	$Mo_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$	2.214	(A)	[13]
$Mo_2Br_3(CH_2SiMe_3)_4 + LiOC_6H_3Me_2$	$Mo_2(OC_6H_3Me_2)_3(CH_2SiMe_3)_4$	2.218	(A)	[14]
$Mo_2(NMe_2)_6 + HOC_6H_3(t\text{-}Bu)Me$	$Mo_2(OC_6H_3(t\text{-}Bu)Me)_2(NMe_2)_4$	2.220	(A)	[15]
$Mo_2(NMe_2)_6 + HOC_6H_3Me_2$	$Mo_2(OC_6H_3Me_2)_4(NMe_2)_2$	2.227	(A)	[16]
$Mo_2(iso\text{-}OPr)_6 + HSC_6H_2Me_3$	$Mo_2(iso\text{-}OPr)_2(SC_6H_2Me_3)_4$	2.230	(A)	[17]
$Mo_2Cl_2(NMe_2)_4 + LiLut$	$Mo_2(NMe_2)_4(Lut)_2$	2.204	(A)	[18]
$Mo_2(NMe_2)_6 + HOSiMe_3$	$Mo_2(OSiMe_3)_6(NHMe_2)_2$	2.241	(B)	[19]
$Mo_4F_4(t\text{-}OBu)_8 + PMe_3$	$Mo_2F_2(t\text{-}OBu)_4(PMe_3)_2$	2.27	(B)	[20]
$Mo_2(t\text{-}OBu)_6 + CO_2$	$Mo_2(t\text{-}OBu)_4(O_2COBu)_2$	2.241	(C)	[5]
$Mo_2(iso\text{-}OPr)_6 + MhpH$	$Mo_2(iso\text{-}OPr)_4(Mhp)_2$	2.206	(C)	[21]
$Mo_2Me_2(NMe_2)_4 + DttaH$	$Mo_2Me_2(NMe_2)_2(Dtta)_2$	2.174	(D)	[22]
$Mo_2(NMe_2)_6 + DttaH$	$Mo_2(NMe_2)_4(Dtta)_2$	2.212	(E)	[23]
$Mo_2(OCH_2Bu\text{-}t)_6 + AcacH$	$Mo_2(OCH_2Bu\text{-}t)_4(Acac)_2$	2.237	(E)	[24]
$Mo_2Cl_2(NMe_2)_4 + LiMeNC_2H_4NHMe$	$Mo_2(MeNC_2H_4NMe)_3$	2.214	(F)	[1, p.251]

*Abbreviations adopted: LutH = 2,6-lutidine; DttaH = ditolyltriazine; MhpH = 2-hydroxy-6-methylpyridine; AcacH = acetylacetone.
**Disubstituted phenols and thiophenols contain substituents at the 2- and 6-positions; trisubstituted products have substituents at the 2-, 4-, and 6-positions.

either with a single molybdenum atom [structure (E)] or they form bridges [structures (C), (D), (F)]. The conformation of complexes with bridging ligands is close to eclipsed.

The compounds listed in Table 1 are solid, diamagnetic products which are fairly volatile under vacuum; they have colours ranging from yellow to red and are very sensitive to the effect of atmospheric oxygen and moisture.

The lengths of the Mo–Mo bonds in the dimers are about 2.2 Å, which corresponds to the length of an Mo≡Mo triple bond. From a qualitative examination of the orbitals of the metal ions it must be assumed that there is overlap of the d_{z^2} orbitals of the molybdenum atoms to form a σ-bond and overlap of the d_{xz} and d_{yz} orbitals to form two π-bonds. This assumption is confirmed by calculations using the self-consistent field of X_α-scattered waves (SCF-X_α-SW) method (see Ref. 1, p. 443).

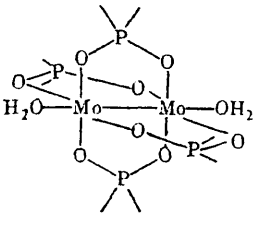


Figure 2. Structure of the $[Mo_2(HPO_4)_4(H_2O)_2]^{2-}$ ion.

The following chemical reactions are typical for complexes of the type Mo_2L_6: a) partial or complete replacement of ligands ($Mo_2L_6^1 \rightarrow Mo_2L_6^2$); b) addition of Lewis bases [$Mo_2(OR)_6 \rightarrow Mo_2(OR)_6L_2$]; c) insertion of unsaturated molecules into Mo–L bonds; d) reductive elimination [$Mo_2R_2(NMe)_4 + CO_2 \rightarrow CO_2 \rightarrow Mo_2^{4+}$ + alkene + alkane]; e) oxidative addition [$Mo_2(OR)_6$ + ROOR → $Mo_2.(OR)_8$]; f) reactions with NO and CO, accompanied by reduction in the bond order of Mo–Mo; g) formation of polynuclear complexes, oligomerisation of $Mo_2(OR)_6$, and replacement of OR^- groups in $Mo_2(OR)_6$ by halide ions to form tetranuclear products.[2,4,6]

Apart from the compounds considered above, a molybdenum(III) phosphate complex—$[Mo_2(HPO_4)_4]^{2-}$—is also known; it was obtained by dissolving $K_4Mo_2Cl_8.2H_2O$ in 2 M H_3PO_4 in air.[29,30] The salts $(PyH)_3[Mo_2(HPO_4)_4Cl]$ and $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$, which are stable to air, have been synthesised (Fig. 2).[29,30]

III. Binuclear complexes with bridging oxygen atoms

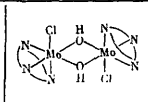
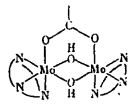
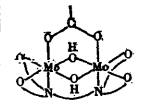
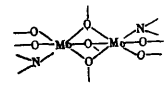
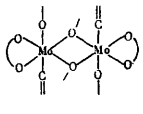
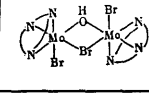
Molybdenum atoms in dimers can be connected by bridging oxygen atoms forming part of hydroxo, alkoxo, or phenoxo groups.

The green ion $[(H_2O)_4Mo(\mu\text{-}OH)_2Mo(H_2O)_4]^{4+}$ occurs in aqueous solutions of Mo(III) in the presence of noncomplexing acids.[31] Reduction of a hydrochloric acid solution of MoO_3 with zinc followed by addition of bis(diphenylphosphino)ethane (DPPE) in 8 M HCl results in the formation of the sky-blue complex $[DPPEH_2]_2[Mo_2(OH)_2Cl_8]$.[32] On hydrolysis of $MoCl_3(C_6H_{15}N_3)$ ($C_6H_{15}N_3$ = triazacyclononane) in the presence of $MeCOO^-$ or HCO_3^-, the green dimers $[Mo_2(OH)_2(MeCOO)(C_6H_{15}N_3)_2]I_3.H_2O$ and $[Mo_2(OH)_2(CO_3)(C_6H_{15}N_3)_2]I_2.H_2O$ are isolated. When the latter is reacted with $MeSO_3H$, HCOOH, and HCl in aqueous solution, $[Mo_2(OH)_2(C_6H_{15}N_3)_2(H_2O)_2]I_4$, $[Mo_2(OH)_2(HCOO)(C_6H_{15}N_3)_2].I_3.2H_2O$, and $[Mo_2(OH)_2(C_6H_{15}N_3)_2Cl_2]I_2$ are synthesised.[33] On reduction of the dimeric molybdenum(V) oxo-complex, $[Mo_2O_4.(C_9H_{21}N_3)_2].[ClO_4]_2.2H_2O$ ($C_9H_{21}N_3$ = 1,5,9-triazacyclododecane), with zinc amalgam in aqueous solutions of HBF_4, RCOOH, HCl followed by the introduction of I^- or ClO_4^-, the complexes [Mo_2.

$.(OH)_2(C_9H_{21}N_3)_2(H_2O)_2]I_4.2H_2O$, $[Mo_2(OH)_2(RCOO)(C_9H_{21}N_3)_2]I_3$, and $[Mo_2(OH)_2(C_9H_{21}N_3)_2Cl_2][ClO_4]_2$ are obtained respectively.[34] Reduction of the ethylenediaminetetraacetate complex $[Mo_2(V).O_4(EDTA)]^{2-}$ in an acetic acid solution gives the di-μ-hydroxo dimers $[Mo_2(OH)_2(Me_3COO)(EDTA)]^-$, $[Mo_2(OH)_2(EDTA)(H_2O)_2]$, and $[Mo_2(OH)_2(EDTA)(SCN)_2]^{2-}$.[35,36] When an aqueous solution of $KMoOCl_2$ and $(NH_4)_2C_2O_4$ is evaporated, $[Mo_2(OH)_2(C_2O_4)_2].6H_2O$ is obtained.[37]

Structural studies of dimers that contain 1,4,7-triazacyclononane or EDTA have shown that geometrically the complexes are distorted octahedra formed by ligand atoms with a common edge of $(\mu\text{-}OH)_2$ (Table 2).[33,35,38] The M–M distances in them are 0.2–0.3 Å longer than in dimers without bridging atoms. A bridging carboxylate ion to all appearances has little effect on the length of the Mo–Mo bond and the weakening of this bond is most probably due to the presence of bridging hydroxo groups.

Table 2. Structure of dimers containing bridging oxygen atoms.

Compound	R_{M-M}, Å	Structure	Refs.
$[Mo_2(OH)_2(C_6H_{15}N_3)_2Cl_2]I_2$	2.501		[33]
$[Mo_2(OH)_2(CH_3COO)(C_6H_{15}N_3)_2]I_3\cdot H_2O$	2.471		[33]
$K[Mo_2(OH)_2(EDTA)(CH_3COO)]$	2.430		[35.38]
$(Me_2NH_2)[Mo_2(OC_6H_4Me)_7(HNMe_2)_2]\cdot C_6H_{14}$	2.601		[39]
$Mo_2(OCH_2Bu\text{-}t)_4(CNBu\text{-}t)_2(Me_2C_3HO_2)_2$	2.508		[40]
$[Mo_2(OH)Br(C_6H_{15}N_3)Br_2]$	2 558		[40]

The formal bond order in di-μ-hydroxo dimers is equal to 3 ($\sigma^2\pi^2\delta^2$).[33] However, the greater M–M distances compared with those in dimers with bridges are due to the lower contribution of a π-interaction.

Dimeric complexes containing EDTA[36] and 1,5,9-triazacyclododecane[34] are diamagnetic. The complex $[Mo_2(OH)_2(C_2O_4)_2].6H_2O$ is characterised by a small paramagnetism, which indicates the weakening of the bond between the metal atoms.[37]

Reaction of $Mo_2(NMe_2)_6$ with 4-methylphenol in hexane gives a dimer with three bridging phenolate ions $(Me_2NH_2)[Mo_2(OC_6H_4Me)_7.(HNMe_2)_2].C_6H_{14}$ (Table 2) in which the overlying paramagnetic states become thermally populated as a result of the increase in the Mo–Mo distance to 2.601 Å.[39]

Dimeric Mo complexes with two alcoxide bridges containing μ-OH and μ-Br ligands are known (Table 2).[40]

The oxychloride $Mo_2O_2Cl_2(H_2O)_6$ has been isolated from a hydrochloric acid solution of molybdenum(III) and acetone;[41–43] its dimeric structure and the oxo bridges present in it have been established hypothetically from an analysis of its magnetic properties and IR spectra. A number of derivatives of this dimer with acetylacetone, carboxylic acids, and *S*-donor ligands (LH) of the type $Mo_2OL_4(H_2O)_x$ and Mo_2OClL_3 have been obtained.[41–44] Reaction of $Mo(OH)_3$ with oxalic acid in an aqueous acetone solution gives $Mo_2O(C_2O_4)_2.6H_2O$.[45] $Mo_2OF_4(H_2O)_6$, which hypothetically contains an Mo–O–Mo fragment, is synthesised by electrolysis of a solution of molybdenum(VI) in 1 M HF.[46]

IV. Binuclear complexes with bridging sulphur atoms

Structural data on dimers containing bridging sulphur atoms are given in Table 3. The Mo–Mo distance in them is even greater than in complexes with bridging oxygen atoms.

Reaction of $(NH_4)_5Mo_2Cl_9.H_2O$ with RSSR in the presence of dithiaoctane (DTO), dithiadecane (DTD), and bis(dimethylphosphino)ethane (DMPE) (LL) results in formation of the dimer $Mo_2(SR)_2Cl_4(LL)_2$.[47] Cotton et al[48] studied the magnetic properties of such dimers and carried out calculations of the electronic structures of hypothetical molecules using the Fenske–Hall and

Table 3. Structure of dimers containing bridging sulphur atoms.

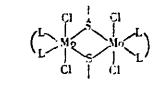
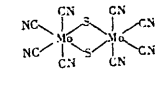
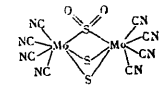
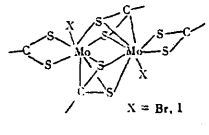
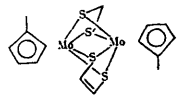
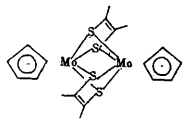
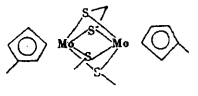
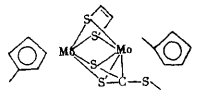
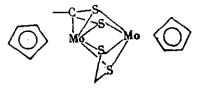
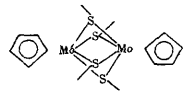
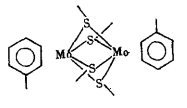
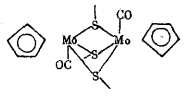
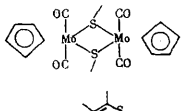
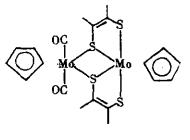
Compound	R_{M-M}, Å	Structure*	Refs.
$Mo_2(SEt)_2Cl_4(DTO)_2$ $Mo_2(SEt)_2Cl_4(DMFE)_2$	2.682 2.712		[47. 48]
$Ba_3[Mo_2S_2(CN)_8]$	2.644		[49–51]
$(Ph_4P)_4[Mo_2S_2(SO_2)(CN)_8]$ $K_4[Mo_2S_2(SO_2)(CN)_8]$	2.730 2.691		[52] [53]
$Mo_2(EtOCS_2)_4Br_2$ $Mo_2(EtOCS_2)_4I_2$	2.723 2.717	 X = Br, I	[54]
$Cp'_2Mo_2(S_2CH_2)(SC_2H_5S)$	2.601		[55]

Table 3 (contd.)

Compound	R_{M-M}, Å	Structure*	Refs.
$Cp_2Mo_2[S_2C_2(CF_3)_2]_2$	2.584		[56]
$Cp'_2Mo_2(S_2CH_2)(SMe)_2$	2.596		[55]
$[Cp'_2Mo_2(SC_2H_2S)(S_2CSMe)]I$	2.623		[57]
$Cp_2Mo_2(S_2CH_2)(S_2CMe)]Br\cdot{}^1/_2EtOH$	2.635		[58]
$Cp_2Mo_2(SMe)_4$	2.603		[59]
$[(PhMe)_2Mo_2(SMe)_4][BPh_4]_2$	2.614		[60]
$[Cp_2Mo_2(SMe)_2(CO)_2]Br\cdot H_2O$	2.785		[61]
$[Cp_2Mo_2(SBu\text{-}t)_2(CO)_4]\cdot[BF_4]_2$	3.008		[62]
$Cp_2Mo_2[S_2C_2(CF_3)_2]_2(CO)_2$	3.256		[56]

*For the sake of simplicity, hydrocarbon substituents are not shown.

Reaction of $Mo_2(MeCOO)_4$ with $K(EtOCS_2)$ in ethanol followed by oxidation of the product with a free halogen in a dichloroethane solution led to the synthesis of the ethyl xanthate complex $Mo_2(EtOCS_2)_4X_2$ (X = Cl, Br), containing four bridging sulphur atoms from two xanthate ions.[54]

A large number of diamagnetic cyclopentadienyl molybdenum(III) dimers with four bridging sulphur atoms have been reported.[55–60,63–65] On reacting $CpMoH(CO)_3$ or $[CpMo(CO_3)_3]_2$ (Cp = cyclopentadienyl) with thioepoxides in tetrahydrofuran, $Cp_2Mo_2(SC_nH_{2n}S)_2$ complexes, where n = 2 or 3, were isolated, from which Cp_2Mo_2. .$(SCHRCHRS)_2$ and $Cp_2Mo_2(SCRCRS)_2$ complexes were obtained by reaction with alkenes and alkynes.[64] As a result of treating $[CpMo(CO)_3]_2$ with dimethyl disulphide, $Cp_2Mo_2(SMe)_4$ was isolated.[59] Reaction of $Cp'_2Mo_2S_2(S_2CR_2)$ (Cp′ = methylcyclopentadienyl) with the same alkenes and alkynes results in the formation of the dithiol and dithiolene derivatives Cp'_2Mo_2. .$(S_2CR_2)(SC_2H_4S)$ and $Cp'_2Mo_2(S_2CR_2)(SC_2H_2S)$, while with LiMe the complex $Cp'_2Mo_2(S_2CH_2)(SMe)_2$ is formed.[55] The dimers $Cp'_2Mo_2(SC_2H_2S)(S_2CS)$, $[Cp'_2Mo_2SC_2H_2S)(S_2CSMe)]I$,[57] $[Cp_2Mo_2(S_2CH_2)(S_2CMe)]Br.\frac{1}{2}EtOH$,[58] $Cp_2Mo_2(S_2CNR)_2$, and $[Cp_2Mo_2(S_2CNRR')_2]X_2$ have also been synthesised.[63]

On reacting $[(PhR)MoPy_3][PF_6]$ (R = H, Me) with an excess of an aqueous solution of MeSH and MeOH followed by extraction with HPF_6 in acetone, orange complexes $[(PhR)_2Mo_2(SMe)_4][PF_6]_2$ were isolated; as a result of anion exchange $[(PhMe)_2Mo_2(SMe)_4]$. .$[BPh_4]_2$ was obtained.[60] Reduction of these compounds with zinc amalgam in the presence of 1-methylimidazole (MeIM) in acetonitrile, oxidation with oxygen, and extraction with HPF_6 in acetone gives the green paramagnetic (μ_{eff} = 1.45 B.M.) complex $[Mo_2(SMe)_3(MeIm)_6][PF_6]_3$ in which there are hypothetically three bridging thiolate ligands.

In dimers with four bridging sulphur atoms the Mo–Mo distance varies from 2.60 to 2.72 Å (Table 3). Calculation using the extended Hückel method (EHM) gives the electronic configuration a_{1g} (σ-Mo–Mo), b_{1u} (δ*-Mo–Mo), b_{2g}(δ-Mo–Mo) or $\sigma^2\delta^{*2}\delta^2$, which virtually corresponds to a single Mo–Mo bond.

Carbonyl-containing molybdenum dimers with μ-*S*-ligands are known: $Cp_2Mo_2[S_2C_2(CF_3)_2]_2(CO)_2$,[56] $[Cp_2Mo_2(SMe)_3(CO)_2]$. .$Br.H_2O$,[61] and $[Cp_2Mo_2(SBu\text{-}t)_2(CO)_4][BF_4]_2$.[62] In the first of these the molybdenum atoms are at a distance of 3.256 Å and there is apparently no Mo–Mo bond.

The synthesis of dimeric complexes with N-, O-, and S-containing thiols of the type $Mo_2Cl_6L_m$, m = 2, 3, has been reported.[66] The values of the effective magnetic moments of these complexes is lower than the pure spin values. The existence of sulphide bridges in these complexes has been proposed.

SCF-X_α-SW methods. The effective multiplicity of the Mo–Mo bond proved to be close to 2 ($\sigma^2\pi^2$), while the δ-interaction was very weak. On the assumption that $^1A_{1g}$ ($\sigma^2\pi^2\delta^2$) is the ground state of the dimers, the energies of the thermally populated states $^3B_{1u}$, $^1B_{1u}$, and $^1A^*_{1g}$, corresponding to filling with electrons from the δ^* orbital, were calculated from magnetic data.

The complexes $K_6[Mo_2S_2(CN)_8]$ and $Ba_3[Mo_2S_2(CN)_8]$, each containing two sulphide bridges, have been obtained.[49–51] Oxidation of the complex anion $[Mo_2S_2(CN)_8]^{6-}$ with atmospheric oxygen results in the formation of $[Mo_2S_2(SO_2)(CN)_8]^{4-}$, in which the molybdenum atoms are connected by a disulphide ion and an SO_2 molecule coordinated via its sulphur atom.[52,53]

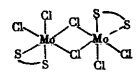
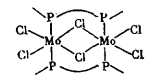
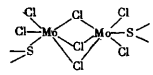
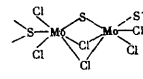
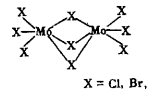
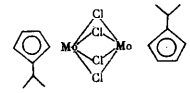
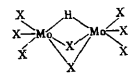
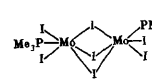
V. Binuclear complexes with halide bridges

In dimeric molybdenum(III) complexes with halide bridges (Cl, Br, I) the Mo–Mo bonds are of approximately the same length as in dimers containing bridging sulphur atoms (Table 4).

When a dichloromethane solution of $Mo_2Cl_4(DTO)_2$ is kept under a layer of hexane, crystals of $Mo_2Cl_6(DTO)_2$ are formed. The $Mo_2Cl_6(DTO)_2$ complex consists of two octahedra connected by a Cl–Cl edge.[67] $Mo_2Cl_6(Ph_2PCH_2PPh_2)_2$, obtained by the reaction of $K_2Mo_2Cl_8$ with $HC(PPh_2)_3$, has a similar structure.

Reduction of $MoCl_4(Me_2S)_2$ using EtSiH in dichloromethane leads to the synthesis of $Mo_2Cl_6(Me_2S)_3$, from which the complex $Ph_4P[Mo_2Cl_7(Me_2S)_2$ is obtained by exchanging an Me_2S group for Cl^-.[68] The NMR data indicate that there is thermal population of the electronic states of the latter complex with spins $S \neq 0$. A similar structure (with three halide bridges) occurs for $Mo_2X_9^{3-}$ ions (X = Cl, Br, I), which will be examined in Section VI.

Table 4. Structure of dimers with halide bridges.

Compound	R_{M-M}, Å	Structure*	Refs.
$Mo_2Cl_6(DTO)_2$	2.735		[67]
$Mo_2Cl_6(Ph_2PCH_2PPh_2)_2$	2.789		[40]
$(Ph_4P)[Mo_2Cl_7(Me_2S)_2]$	2.746		[68]
$Mo_2Cl_6(Me_2S)_3$	2.462		[68]
$Cs_3Mo_2Cl_9$ $Cs_3Mo_2Br_9$ $Cs_3Mo_2I_9$	2.655 2.516 3.07*	 X = Cl, Br, I	[69] [69] [70]
$Mo_2[C_5H_4(iso\text{-}Pr)]_2Cl_4$	2.607		[71]
$Rb_3Mo_2Cl_8H$ $(PyH)_3Mo_2Cl_8H$ $(Me_4N)_3Mo_2Cl_8H$ $(Et_4N)_2(H_3O_2)Mo_2Cl_8H$ $(Et_4N)_3(H_3O_2)[Mo_2Cl_8H][MoOCl_4(H_2O)]$ $(Me_4N)_2(H_7O_3)Mo_2Br_8H$ $(Et_4N)_2(H_7O_3)Mo_2I_8H$	2.38 2.371 2.374 2.384 2.375 2.384 2.408		[72] [73] [74] [75] [76] [77] [77]
$[PHMe_3][Mo_2I_7(PMe_3)_2]$ $[AsPh_4][Mo_2I_7(PMe_3)_2]$	3.021 3.022		[78] [78]

*According to X-ray powder diffraction analysis.

Molybdenum(III) complexes of the type $Mo_2(C_5H_4-R)_2Cl_4$ (R = iso-Pr), which contain four bridging chlorine atoms, have been obtained by treatment of $Mo(C_6H_6)(C_5H_4-R)$ with hydrogen chloride in toluene.[71]

The complexes $[PHMe_3][Mo_2I_7(PMe_3)_2]$ and $[AsPh_4][Mo_2I_7.(PMe_3)_2]$, each containing three iodide bridges, have been synthesised by reaction of $MoI_3(THF)_3$ with PMe_3, NMe_4I and $AsPh_4I$.[78]

Association of $MoCl_3(THF)_3$ in CH_2Cl_2 solution results in the formation of the dimeric $Mo_2Cl_6(THF)_3$, and reaction of $MoCl_5$ with MeCN gives $Mo_2Cl_6(MeCN)_3$.[79] By replacing the organic ligands in such complexes with tertiary phosphines, pyridine, and nitriles, products of the type $Mo_2Cl_6L_3$ can be obtained.[79,80] Thermolysis of monomeric halomolybdates(III) results in the formation of compounds that contain $Mo_2Cl_{10}^{4-}$ ions.[81] Thermal decomposition of $(oxineH_2)_3Mo_2Cl_9.3H_2O$ gives $Mo_2Cl_6(oxineH)_3$ (oxineH = 8-hydroxyquinoline).[82] Similar tri-μ-chloride complexes with thiourea[83] and bis(diphenylphosphino)ethane[84] derivatives are known.

Diamagnetic halogen-hydrido bridge complexes of the type $A_3Mo_2X_8H$ (X = Cl, Br, I; A is a single-charged cation) have been studied in detail (Table 4). They were synthesised by dissolving $Mo_2(MeCOO)_4$ in a concentrated acid HX at 60 °C and precipitating out the resulting $Mo_2X_8H^{3-}$ with a suitable cation.[72–77,85] Complexes of this type are readily converted to Mo(III) ($Mo_2X_9^{3-}$, MoX_3Py_3) or Mo(II) ($Mo_2Cl_4Py_4$) compounds.[86] Introduction of the hydride bridge reduces the Mo–Mo distance by ~0.4 Å compared to that in purely chloride-bridged dimers. This is due to the small size of the hydride ion compared to halide ions, which prevent the molybdenum atoms converging.[85] As can be seen from Table 4, the ligand environment has little effect on the length of the Mo–Mo bond in the $Mo_2X_8H^{3-}$ ion, which is an indication of the high rigidity of the Mo(μ-H)(μ-X_2)Mo group, the geometry of which is determined to a large extent by the presence of the hydride ion.

VI. Nonahalodimolybdates(III)

$Mo_2X_9^{3-}$ anions (X = Cl, Br) are of considerable interest as interaction between the *d* electrons of the two molybdenum atoms results in the formation of a relatively weak Mo–Mo, with the result that the ligand environment and even the outer coordination sphere of the complex appreciably affect the bonding of the molybdenum atoms.

A single iodide complex $Cs_3Mo_2I_9$ is known. Its IR spectra have been studied,[87] and the Mo–Mo distance in the dimer has been determined by X-ray powder photography.[70] Information is also available on the synthesis of $K_3Mo_2F_9.2H_2O$ (see Ref. 88, p. 111).

Nonachloro- and nonabromo-dimolybdates(III) can be obtained by the following methods: a) disproportionation of MoX_6^{2-} in liquid ammonia;[89] b) oxidation of Mo(II) and Mo(II, III)[90–92] dimers or electrolytic oxidation of the $Mo_2X_8H^{3-}$ ion in concentrated HX;[72] c) fusing metal halides ($2MoX_3 + 3CsX$) are 800 °C;[93] d) coproportionating Mo(0) and Mo(II) carbonyl complexes with Mo(IV) and Mo(V) halides;[94–96] e) precipitation of Mo(III) with a suitable cation in hydrochloric acid;[97] f) replacement of ligands in Mo(III) dimers by halide ions;[90,98] g) electrolytic reduction of MoO_3 in concentrated hydrochloric acid, evaporation of an Mo(III) solution in concentrated hydrochloric or hydrobromic acid and precipitation of nonahalomolybdate(III) with a suitable cation.[82,99–105]

The latter synthetic method is the most convenient. It is based on the reaction between MoX_6^{3-} and $[MoX_5(H_2O)]^{2-}$ ions that occurs when the concentration of molybdenum(III) in hydrohalic acid is increased, leading to the formation of the $Mo_2X_9^{3-}$ ion.[99,104] If the Mo(III) solution is evaporated in a mixture of HCl and HBr, the mixed-ligand anions $Mo_2Cl_3Br_6^{3-}$ and $Mo_2Cl_6Br_3^{3-}$ can be obtained.[102]

The dimerisation of halomolybdate(III) ions takes place according to the following scheme:

$$2\,MoX_6^{3-} + 3\,H_3O^+ \rightarrow Mo_2X_9^{3-} + 3H_2O\uparrow + 3HX\uparrow.$$

A similar reaction takes place on thermolysis of the "acid" halomolybdates(III) $(PimH_2)(H_5O_2)MoX_6$ (Pim = 2-amino-4,6-dihydroxypyrimidine) and $(oxineH_2)_2H[MoBr_6].3H_2O$, from which $(PimH)_3Mo_2X_9$ and $(oxineH_2)_3Mo_2Br_9$ are obtained by isothermal decomposition.[82,105]

The monoethanolammonium (MeaH) salts $(MeaH)_3Mo_2X_9$, which are readily soluble in HX, have proved to be convenient reagents for the synthesis of nonachloro- and nonabromo-dimolybdates(III) with organic cations. A number of compounds, including both cation and anion mixed salts, have been synthesised from these reagents by cation exchange.[106–108]

The chloro- and bromo-complexes are solid compounds, red and brown in colour. They are more or less stable towards atmospheric oxygen and moisture; in solution they are slowly oxidised by air. In hydrohalic acid solutions a slow decomposition of the $Mo_2X_9^{3-}$ dimer occurs, giving MoX_6^{3-} and $[MoX_5(H_2O)]^{2-}$ ions (at room temperature over a period of several hours).[102,109] However, in the presence of 4,4′-dipyridyl in a mixture of concentrated HCl and ethanol, $Mo_2Cl_9^{3-}$ very rapidly decomposes to monomeric complexes.[108] Reaction of $Cs_3Mo_2X_9$ with pyridine at 200 °C results in the formation of *trans*-MoX_3Py_3.[86] In contrast to monomeric halomolybdates(III), the $Mo_2Cl_9^{3-}$ ion is readily reduced by zinc amalgam to Mo(II) dimers.[110]

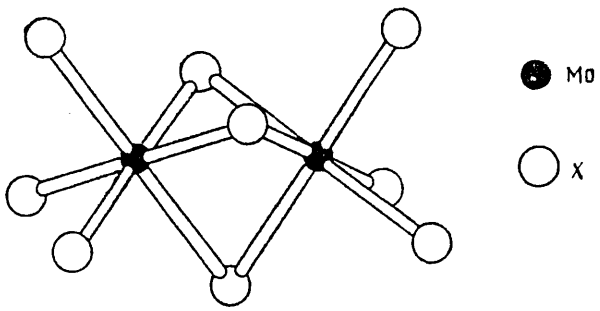


Figure 3. Structure of the $Mo_2X_9^{3-}$ ion (X = Cl, Br).[69]

The complete X-ray diffraction analysis of $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ which was carried out for the first time by Saillant et al[69] made it possible to establish the structure of the anion, which is shown in Fig. 3. By comparing the geometric characteristics of $M_2X_9^{3-}$ ions, where M = Cr, Mo, W; X = Cl, Br (Table 5) it was possible to identify interesting structural features of molybdenum dimers. In $Cr_2X_9^{3-}$ ions the Cr atoms are displaced from the octahedral centres towards the outer halogen atoms and there is no Cr–Cr bond. This is confirmed by the presence of three unpaired electrons in each Cr^{3+} ion according to the results of magnetic measurements.[111] In the $W_2Cl_9^{3-}$ ion the W–W distance is ~0.7 Å shorter than the Cr–Cr distance in $Cr_2Cl_9^{3-}$. The tungsten atoms are very considerably displaced from the octahedral centres towards each other, forming a W–W bond. As a result of this, $K_3W_2Cl_9$ has only a temperature-independent paramagnetism. In $Mo_2X_9^{3-}$ the Mo atoms are displaced from the octahedral centres towards each other to a lesser degree than in $W_2Cl_9^{3-}$. The Mo–Mo bond is weaker than the W–W bond, so compounds $A_3Mo_2X_9$ display a weak paramagnetism, the temperature dependence of which indicates that there is a considerable antiferromagnetic coupling between the molybdenum atoms in such dimers. In systems where direct exchange takes place between the molybdenum atoms, the antiferromagnetic interaction energy can characterise the strength of the Mo–Mo bond (see Ref. 113, p. 125).

Table 5. Structural characteristics of $M_2X_9^{3-}$ ions (M = Cr, Mo, W).[69]

Compound	R_{M-M}, Å	Angle of X_B-M-X_B, deg.*
$Cs_3Cr_2Cl_9$	3.12	85.8
$Cs_3Cr_2Br_9$	3.31	83.0
$Cs_3Mo_2Cl_9$	2.66	94.2
$Cs_3Mo_2Br_9$	2.82	93.9
$K_3W_2Cl_9$	2.41	98.4

* X_B is bridging halogen atom.

As long ago as the late 1960's it was found that the magnitude of the antiferromagnetic exchange coupling in the nonahalodimolybdate(III) ion depended to a considerable extent on the nature of the cation, and at the time attempts were made to relate this phenomenon to the change in Mo–Mo distance in the dimer.[103,104,114]

Grey and Smith[114] studied the dependence of the exchange integral on the Mo–Mo distance in a number of nonachlorodimolybdates with different cations. However, these distances were known only for the compounds $K_3Mo_2Cl_9$ and $Cs_3Mo_2Cl_9$, and as it subsequently transpired, the correlation found proved to be incorrect. A relationship between the stretching vibrational frequencies of the bridging chloride atoms and the size of the cation was established by Grey and Smith.[103] By making a combined analysis of the IR spectra and structural characteristics of $Cs_3Cr_2Cl_9$ and $Cs_3Mo_2Cl_9$ it could be assumed that on increasing the $Cl_B-Mo-Cl_B$ angle (Cl_B is bridging chlorine atom), namely, by axial compression of the dimer, the difference between the vibrational frequencies of a_2'' and e' of the Mo–Cl_B bond will also increase. The $Cl_B-Mo-Cl_B$ angle increases on going from $K_3Mo_2Cl_9$ to $Cs_3Mo_2Cl_9$, but the $Cl_T-Mo-Cl_T$ angle (Cl_T is terminal chlorine atom) changes only slightly.[69,103] Consequently, the difference between the vibrational frequencies of a_2'' and e' of the Mo–Cl_T bond will be small, but it will be considerable for the Mo–Cl_B bond. This assumption is also confirmed by IR spectroscopic analysis.[103] What is more, as the size of the cation increases the difference between the frequencies of a_2'' and e' of the Mo–Cl_B bond decreases, in other words, the $Cl_B-Mo-Cl_B$ angle decreases, hence (if the change in distance of Mo–Cl_B is ignored) in the cation series K^+, NH_4^+, Cs^+, Me_4N^+, Et_4N^+ the dimer becomes more and more "extended" axially.[103]

The dependence of the chemical shift (ΔE) of the L_{α_1,α_2} line in the X-ray emission spectra of $K_3Mo_2Cl_9$, $Cs_3Mo_2Cl_9$, $MoCl_3$, K_3MoCl_6 on the Mo—Mo distance has been studied.[115] As the Mo—Mo distance decreases ΔE increases, which corresponds to an increase in the degree of bonding between the *d* electrons of the molybdenum atoms.

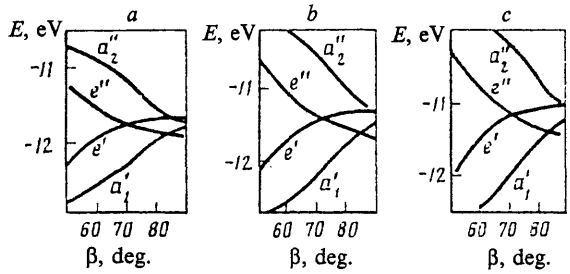


Figure 4. Dependence of the energy of the electron levels in the $M_2Cl_9^{3-}$ ion on the magnitude of the M—Cl_B—M angle, where M = Cr (*a*), Mo (*b*), W (*c*).[118]

The first calculations of the electronic structure of the $Mo_2Cl_9^{3-}$ ion were carried out using the RMK[116] and Fenske—Hall methods. An examination was subsequently made of the dependence of the energies of the orbitals responsible for the M—M bonding on the degree of axial distortion of the dimeric $M_2Cl_9^{3-}$ anion (M = Cr, Mo, W) (Fig. 4).[118] The M—Cl_B—M angle was taken as a parameter for the magnitude of distortion, in accordance with the method suggested by Cotton and Ucko[119] for studying such dimers. As can be seen from Fig. 4, on reducing the M—Cl_B—M angle (this corresponds to a convergence of the metal atoms for a fixed length of the M—Cl_B bond), there is a reduction in energy of the $a_1'(\sigma)$ and $e'(\pi)$ bonding orbitals of M—M and an increase in energy of the $a_2''(\sigma^*)$ and $e''(\pi^*)$ antibonding orbitals. In the series M = Cr, Mo, W, the gap between the bonding and antibonding orbitals in the dimer increases, with the strengthening of the bond between the metal atoms assisting the compression of the dioctahedron despite the repulsion between the terminal and bridging chlorine atoms and the rigidity of the M—Cl_B—M angle.[118]

More rigorous calculations of the electronic structure of the $Mo_2Cl_9^{3-}$ ion in the salts $Cs_3Mo_2Cl_9$ and $K_3Mo_2Cl_9$ were carried out by Ginsberg[120] using the SCF-X_α-SW method. The energies of the antiferromagnetic exchange coupling were determined theoretically and correlated with the experimental data. The data on the structure of the upper molecular orbitals of $Cs_2Mo_2Cl_9$ salt are given in Table 6. The successively grouped $21a_1'$, $22e'$, $17e''$, and $18a_2''$ orbitals retain the nature of 4*d* orbitals of Mo to the extent of 64—81% and constitute respectively the following orbitals of the Mo—Mo bond: σ, $2(1/3\pi + 2/3\delta)$, $2(1/3\pi^* + 2/3\delta^*)$, and σ^*. The electronic configuration of the ground state $\sigma^2(1/3\pi + 2/3\delta)^4$ formally corresponds to the formation of an Mo≡Mo triple bond. However, whereas the $\sigma-\sigma^*$ separation is quite large (~2 eV), the difference between the energy of the $22e'$ and $17e''$ orbitals is ten times less, in other words, the bond between the molybdenum atoms is essentially a single bond.

In order to determine the contribution of superexchange interactions through the bridging chlorine atoms to the total exchange coupling, the electronic structure of the dimeric anion in $K_3Mo_2Cl_9$ was calculated when the Mo—Cl_B distance was reduced by 0.06 Å.[120] The change in the magnitude of exchange integral in this case was less than 1%. Such a result was to be expected since the Mo—Mo bonding orbitals, although overlapping with the orbitals of the bridging chlorine atoms, are nonbonding in relation to them and hence they do not make a substantial contribution to the Mo—Mo coupling.[120]

In the electronic spectra of $Mo_2X_9^{3-}$ ions there are usually four absorption bands.[91,93–95,99–101,121] The appearance of bands at ~13000 and ~15000 cm^{-1} is due to the formation of the Mo—Mo bond.[91] By studying the absorption spectra, circular dichroism, and

Table 6. Energy levels of the $Mo_2Cl_9^{3-}$ ion in $Cs_3Mo_2Cl_9$. (Calculation using the SCF—X_α—SW method[120]).

Energy level	Energy, a.u.	Charge distribution, %					Spherical harmonics	Description
		2Mo	$6Cl_T$	$3Cl_B$	int	out		
$22a_1'$	—0.124	1	3	3	59	35	—	—
$23e'$	—0.180	54	8	16	17	5	d_{xz}, d_{yz}	Mo—Cl antibonding
$18e''$	—0.209	68	12	8	10	2	$d_{x^2-y^2}$, d_{xy}	Mo—Cl antibonding
$18a_2''$	—0.278	78	2	10	10	0	d_{z^2}	σ^*-Mo-Mo; Mo, Cl nonbonding
$17e''$	—0.384	81	2	7	10	0	d_{xz}, d_{yz}	$(\pi+\delta)^*$-Mo-Mo; Mo, Cl nonbonding
$22e'$	—0.403	64	0	21	14	0	$d_{x^2-y^2}$, d_{xy}	$(\pi+\delta)$-Mo—Mo; Mo, Cl nonbonding
$21a_1'$	—0.485	69	7	13	11	0	d_{z^2}	σ-Mo—Mo; Mo, Cl nonbonding

Table 7. Average geometric parameters of $Mo_2Cl_9^{3-}$ ions.[123]

Compound	Chemical formula	Geometric parameters					
		Mo—Mo, Å	Mo—Cl_B, Å	Mo—Cl_T, Å	Mo—Cl_B—Mo, deg.	Cl_B—Mo—Cl_B, deg.	Cl_T—Mo—Cl_T, deg.
(I)	$(Bu_4N)_4[Mo_2^{III}Cl_9][Mo^{V}OCl_4(H_2O)]$	2.815 (3)	2.465 (6)	2.418 (7)	69.7 (2)	90.6 (2)	91.0 (2)
(II)	$(Et_4N)_2(H_7O_3)Mo_2Cl_9$	2.743 (3)	2.459 (6)	2.415 (6)	67.8 (1)	91 9 (2)	90 2 (2)
(III)	$(PipeH)_3Mo_2Cl_9$	2.734 (1)	2 447 (2)	2,409 (2)	67.9 (1)	91.8 (1)	89.3 (1)
(IV)	β-(4-MePyH)$_3Mo_2Cl_9$	2.719 (5)	2.45 (1)	2.41 (1)	67.3 (3)	92 2 (4)	90.0 (4)
(V)	$(PyH)_3Mo_2Cl_9$	2.685 (1)	2.460 (1)	2.409 (1)	66.15 (5)	93.0 (1)	90.1 (1)
(VI)	$Cs_3Mo_2Cl_9$	2.655 (11)	2.487 (12)	2,384 (6)	64.5 (1)	94.2 (1)	91.0 (3)
(VII)	α-(4-MePyH)$_3Mo_2Cl_9$	2.634 (2)	2,465 (3)	2,411 (4)	64.6 (1)	94 1 (1)	91.6 (1)
(VIII)	(4,4′-DipyH$_2$)(MeaH)Mo_2Cl_9	2.619 (1)	2,470 (2)	2,417 (2)	64.03 (5)	94.5 (1)	91.5 (1)
(IX)	(4-NH_3PyH)(MeaH)Mo_2Cl_9	2.610 (2)	2.465 (5)	2,410 (5)	63.9 (1)	94.6 (2)	91.0 (2)
(X)	$(EmH_2)_2[Mo_2Cl_9]Cl$	2.585 (3)	2.460 (7)	2,404 (8)	63.4 (2)	94.9 (3)	90.7 (3)
(XI)	$(NH_4)_3Mo_2Cl_9$	2.569 (4)	2,462 (6)	2,397 (6)	62.9 (1)	95.3 (2)	90.5 (2)

Zeeman splitting for $Cs_3Mo_2Cl_9$ monocrystals,[122] it was possible to detect and interpret the fine structure of the absorption bands due to the Mo—Mo interaction. The absorption bands were attributed to the following transitions: $^1A_1' \rightarrow {}^3E$ (7800 cm^{-1}), $^1A_1' \rightarrow {}^3A_1''$ (~11600 cm^{-1}), $^1A_1' \rightarrow {}^1A_1'$, $^1A_1''$ (12600 → 14000 cm^{-1}), $^1A_1' \rightarrow {}^1E'$ (~15300 cm^{-1}). On the basis of the theoretical calculations it was concluded that there was a very weak Mo—Mo π-interaction when the strength of the Mo—Mo σ-bond was high.

The geometry and magnetic properties of the $Mo_2Cl_9^{3-}$ ion in relation to the crystal environment were studied in detail and the structures of ten nonachlorodimolybdates(III) with different organic cations and ammonia were determined.[109,123–127] In the crystal lattice of each compound this ion undergoes low-symmetry distortions. The average geometric parameters determined when it was assumed that the dimeric anion has D_{3h} symmetry are given in Table 7.

The $Mo_2Cl_9^{3-}$ anion has the following characteristics. The Mo—Cl_B—Mo angle in all cases is less than 70.5° (for a true dioctahedron) and the molybdenum atoms have converged as a result of Mo—Mo bonding. The dimeric anion is slightly distorted along the Mo—Mo axis from the effect of the crystal environment. The distance between the metal atoms in the dimer varies from 2.815 Å in the tetrabutylammonium salt (I) to 2.569 Å in the simple ammonium salt (XI). As the Mo—Mo distance decreases, the Mo—Cl_B—Mo angle also decreases, but the lengths of the Mo—Cl_B and Mo—Cl_T bonds and the Cl_T—Mo—Cl_T angle show little variation. It follows from this that in essence only the bridging $Mo(Cl_B)_3Mo$ fragment is distorted.

The geometry of the dimeric anion is determined by two forces acting in opposition: 1) the mutual attraction of the molybdenum atoms, leading to compression of the dimer; and 2) the effect of "pushing apart" from the bridging chlorine atoms, which is due to the increase in overlap of atomic orbitals in the system Mo—Cl_B—Mo and at the same time the mutual repulsion of the bridging and terminal chlorine atoms. The balance of forces probably leads to the energy curve near the minimum on the z coordinate (the axis passes along the Mo—Mo bond) having a small bend, and hence even with a significant change in Mo—Mo distance the energy of the $Mo_2Cl_9^{3-}$ ion varies only slightly.

In an $Mo_2Cl_9^{3-}$ ion free from external effects the repulsion between the chlorine atoms assists the extension of the dimer along the Mo—Mo axis. In the crystal lattice the interligand repulsion is weakened by the effect of the positive charges of the cations; this together with the Mo—Mo interaction leads to compression of the $Mo(Cl_B)_3Mo$ fragment and a reduction in Mo—Mo distance.

Cations that form hydrogen bonds have the most marked effect. Thus, in $(Bu_4N)_4[Mo_2(III)Cl_9][Mo(V)OCl_4(H_2O)]$ the positive cation centres are at a considerable distance from the chlorine atoms, the effect of the cations is small, and the Mo—Mo distance is the greatest (see Table 7). In the structure of $(Et_4N)_2(H_7O_3)Mo_2Cl_9$ only one of the cations, namely, the hydrated proton, has any appreciable effect on the geometry of the dimer as a result of the formation of hydrogen bonds; the Mo—Mo distance is 2.743 Å. In the crystal lattices of compounds (III)—(VI) all cations have their positive centres directed towards the chlorine atoms, so N—H...Cl hydrogen bonds are formed and the Mo—Mo distance is reduced. In the structures of nonachlorodimolybdates(III) containing doubly charged cations, a further compression of the bridging group occurs. These structures display a trimeric network of hydrogen bonds joining all cations and anions. The ammonium cation has the maximum effect on the Mo—Mo distance; it is lowest in $(NH_4)_3Mo_2Cl_9$. It is worth noting that in compounds (VII)—(X) (Table 7), which contain organic cations that are much larger than in $Cs_3Mo_2Cl_9$, the length of the Mo—Mo bond is less than in the caesium salt. This demonstrates the strong effect of hydrogen bonding on the geometry of the dimeric group.

It may be assumed that the minimum effect of the cations and correspondingly the maximum Mo—Mo distance in the $Mo_2Cl_9^{3-}$ ion in the crystal lattice will occur when there are bulky low-polarity cations present. If cations, even those of large volume, can form strong hydrogen bonds with the anion, the Mo—Mo distance in nonahalodimolybdates(III) will be relatively short.

The values of the exchange integrals for structurally determined nonachlorodimolybdates(III) have been calculated from magnetic susceptibility data [for compounds (I)—(V) and (VII)—(XI), see the study by Kazin;[109] for $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$, see the study by Grey and Smith.[104]]

To all appearances a direct Mo—Mo exchange coupling mainly occurs in $Mo_2Cl_9^{3-}$ ions.[120] The dependence of the exchange integral ($-2J$) on the Mo—Mo distance in a dimer is shown in Fig. 5. As the relative change in parameters is low, this dependence approximates to a linear function.[109] The tendency for the exchange coupling to increase as the Mo—Mo distance decreases is apparent, but deviations from a linear dependence are considerable.

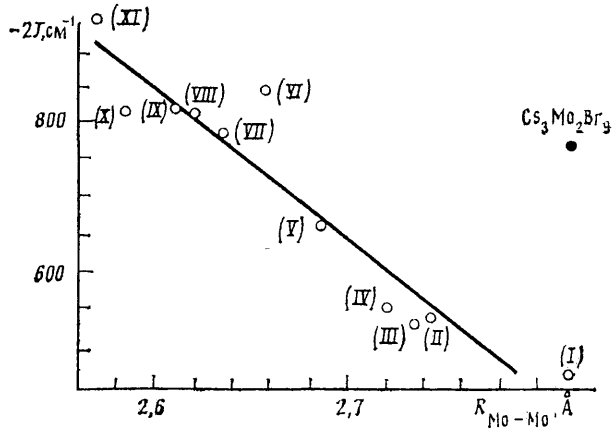


Figure 5. Dependence of the exchange integrals on the Mo—Mo distance in $Mo_2Cl_9^{3-}$ ions.[109] For the numbering of the compounds, see Table 7.

For a more accurate representation of the exchange interaction, the values of the exchange integrals were expressed as a two-parameter function of R and α (the geometry of the bridging fragment $Mo(Cl_B)_3Mo$ in D_{3h} symmetry is determined by these two parameters).[109] The derived dependences of the antiferromagnetic interaction energy on the geometric parameters of the $Mo_2Cl_9^{3-}$ ion can prove useful for predicting the structure of similar dimers from their magnetic properties.

The value of $-2J$ for the structurally determined compound $Cs_3Mo_2Br_9$ is substantially higher than that which should occur if the linear dependence of $-2J$ on R_{Mo-Mo} obtained for $Mo_2Cl_9^{3-}$ ions were applied to it (Fig. 5). The most probable reason for the increase in the exchange coupling is the lesser electronegativity of bromine compared to chlorine. Consequently, the effective positive charge on the molybdenum atoms in the bromide complex is less, giving rise to a greater diffuseness of the $4d$ orbitals of the metal atoms and correspondingly a greater overlap of the orbitals in the direction of the Mo—Mo bond than in the chloride dimer at the same distance between the molybdenum atoms.

For isomorphous nonabromodimolybdates(III) the values of $-2J$ are usually less than their chloride analogues.[104,109] Evidently the decrease in exchange resulting from the increase in Mo—Mo distance in bromo-complexes exceeds the increase caused by the greater diffuseness of the $4d$ orbitals of the molybdenum atoms.

Reaction of $(Bu_4N)_3Mo_2Cl_8H$ with I_2 in dichloroethane solution followed by addition of diethyl ether led to the synthesis of $(Bu_4N)_3$. Mo_2Cl_8I, and $(NH_4)_3Mo_2Cl_8I$ was isolated by exchanging cations in methanol. The dimeric anions contain bridging iodine atoms in addition to chlorine atoms.[128] The values of $-2J$, calculated from the magnetic susceptibility of the ammonium and tetrabutylammonium salts differ substantially. The nature of the cation probably has a similar strong effect on the geometry of the $Mo_2Cl_8I^{3-}$ ion as on the structure of nonachloro- and nonabromodimolybdate(III) ions.

Compounds containing $[Mo_2Cl_8.(H_2O)]^{2-}$ and $Mo_2X_8^{2-}$ (X = Cl, Br) ions have been obtained by thermal decomposition of "acidic" nonahalodimolybdates(III) in the solid state.[129–132] A study of the temperature dependence of magnetic susceptibility showed that exchange couplings in such compounds are localised within the dimers.[109] To all appearances the bridging $Mo(X_B)_3Mo$ group is preserved in the crystal lattice.

The values of the exchange integrals for an $(Et_4N)_3Mo_2X_9$ complex, the initial "acidic" tetraethylammonium salts, and their thermolysis products are given below.

Compound	$-2J$, cm^{-1}	Compound	$-2J$, cm^{-1}
$(Et_4N)_3Mo_2Cl_9$	480±13	$(Et_4N)_3Mo_2Br_9$	430±10
$(Et_4N)_2(H_9O_4)Mo_2Cl_9$	540±15	$(Et_4N)_2(H_9O_4)Mo_2Br_9$	490±15
$(Et_4N)_2(H_5O_2)Mo_2Cl_9$	600±15	$(Et_4N)_2(H_5O_2)Mo_2Br_9$	555±15
$(Et_4N)_2[Mo_2Cl_8(H_2O)]$	580±15	$(Et_4N)_2Mo_2Br_8$	515±15
$(Et_4N)_2Mo_2Cl_8$	575±15		

On replacing a single Et_4N^+ cation in $(Et_4N)_3Mo_2Cl_9$ by the proton tetrahydrate $H_9O_4^+$ cation in $(Et_4N)_3Mo_2Cl_9$ by the proton tetrahydrate $H_9O_4^+$, which forms hydrogen bonds with anions and thus assists in compressing the dimer, the exchange coupling increases. In the complex $(Et_4N)_2(H_5O_2)Mo_2Cl_9$, which contains a proton dihydrate, a further increase in the exchange coupling occurs, which may be due to the strengthening of the hydrogen bonds between the hydroxonium ion and the complex anion. The values of $-2J$ for $(Et_4N)_2[Mo_2Cl_8(H_2O)]$ and $(Et_4N)_2Mo_2Cl_8$ occur within the limits of the exchange integral values for the previous two compounds. The same pattern occurs for tetraethylammonium bromo-complexes. Consequently, replacement of the terminal ligands in the $Mo_2X_9^{3-}$ ion leads to a change in exchange coupling to about the same extent as replacing one of the cations; and the effect of the ligand environment on the magnetic properties and geometry of the $Mo(X_B)_3Mo$ fragment is comparable with the effect of exterior cations.

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An analysis of the literature data shows that molybdenum(III) in binuclear complexes can form strong Mo≡Mo triple bonds. However, such a situation occurs only in dimers without bridges and in complexes containing polyatomic bridges. The occurrence of monatomic bridges results in a considerable weakening of the Mo—Mo bond. What are the main reasons for this?

Calculations of the electronic structure of dimers without bridges indicate that the Mo—Mo bond is formed by being filled with electrons in σ and 2π orbitals. The dimers with monatomic bridges have the following electronic configuration: with two bridges—$\sigma^2\pi^2\delta^2$; with three bridges—$\sigma^2(1/3\pi + 2/3\delta)^4$; with four bridges—$\sigma^2\delta^{*2}\delta^2$. Thus, the bridging ligands use some of the $4d$ orbitals of the metal atoms to form Mo—L—Mo bonds. In this case the Mo—Mo σ bond remains unchanged while as the number of bridges increases the Mo—Mo π bonds are gradually replaced by the much less effective δ bonds. At the same time the Mo—Mo bond order decreases, so that in a four-bridged dimer it reduces to 1. However, as follows from Tables 2—4, there are no clear correlations between the length of the Mo—Mo bond and the number of monatomic bridges, but on the other hand the dimensions of the

bridging atoms have a marked effect. The literature data on the Mo—Mo distances in molybdenum(III) dimers are correlated in Table 8.

Table 8. Mo—Mo distances in molybdenum(III) dimers with different bridging ligands.

Bridging fragment	Range of Mo—Mo distances, Å	Number of known compounds	Refs.
Without bridging ligands	2,17—2,27	16	[4,7—20, 23, 24]
Polyatomic bridges	2,17—2,24	4	[4,7, 21, 22]
Monatomic bridges			
(μ-H) + 2(μ-X), X = Cl, Br, I	2,37—2,41	7	[72—77]
2(μ-O), 3(μ-O)	2,43—2.60	4	[33, 35, 38, 39]
(μ-S) + 2(μ-Cl)	2,46	1	[68]
2(μ-S), 3(μ-S), 4(μ-S)	2.60—2.79 3.01; 3,26	15	[47—62]
2(μ-Cl), 3(μ-Cl), 4(μ-Cl)	2,57—2,82	16	[67—71, 123]
3(μ-Br)	2.82	1	[69]
3(μ-I)	3.02—3.07	3	[70, 78]

Mo—Mo bonds are shortest in length in dimers without bridges and in complexes with polyatomic bridges. In $Mo_2X_8H^{3-}$ complexes, whose geometry is determined by the hydride ion, the Mo—Mo distances are 0.2 Å greater on average than in dimers without bridges. In binuclear complexes with oxygen bridges the lengths of the Mo—Mo bonds are slightly greater than in complexes with hydride bridges. A further increase in Mo—Mo distance is characteristic of dimers that have bridging sulphur or chlorine atoms.

In $Cs_3Mo_2Br_9$ the Mo—Mo distance is at the upper limit of the range of these distances for chloride-bridged dimer. If the lengths of the Mo—Mo bonds in the isomorphous salts $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ (2.655 and 2.815 Å respectively) are compared, it may be assumed that the Mo—Mo distance in bromide dimers will on average be 0.15 Å greater.

In complexes with iodide bridges the Mo—Mo distances exceed 3 Å, which results form the large size of the iodide ion.

Thus, although monatomic bridges weaken the Mo—Mo interaction in dimers by involving the 4*d* orbitals of the molybdenum atoms in the formation of the Mo—L bond, in all probability the main result of their presence in the molecule is their influence on the geometric structure of the dimers, resulting in a considerable extension of the Mo—Mo bond. The weakening of this bond in turn is accompanied by a decrease in the rigidity of the bridging group. In this case, as studies on dimeric halomolybdates(III) have shown, the effect of the internal and external coordination spheres on the characteristics of Mo—Mo bonds must be considered in totality.

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