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Heterometallic sulphide-bridged transition metal clusters

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ABSTRACT. The literature data on heterometallic clusters with sulphide bridges are described systematically and discussed. The methods for the specific synthesis of clusters and the dependence of their geometry on the electronic structure of their metallic core are examined. The possibilities for the modelling of catalytic systems and materials of the type of magnetic semiconductors and superconductors are discussed.

The bibliography includes 140 references.

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I. Introduction

In recent years, there has been an appreciable growth of interest, both here and abroad, in the study of clusters—polynuclear compounds in which three and more atoms of transition or non-transition elements are linked to one another via metal–metal bonds, bridging ligands, or both.[1] These systems are remarkable because they are shielded by the ligands, throughout the lattice, from cooperative interactions typical of solid state chemistry; clusters are therefore fairly soluble and can be investigated by the usual methods of coordination chemistry. On the other hand, when the number of metal atoms within the cluster is sufficiently large, fragments corresponding to the packing of metallic lattices (triangles, tetrahedra, squares, trigonal bipyramids, octahedra, etc.) arise. All parts of the metallic surface with chemisorbed organic ligands are thus modelled.[2] As a result of the latter factor, clusters became promising starting materials for practical application in the preparation of polymetallic coatings as well as homogeneous and immobilised catalysts.

Among compounds of this kind, heterometallic clusters (HMC) containing several atoms of different metals are especially interesting.[3,4] Sulphide-bridged heterometallic clusters (SHMC) occupy an important place among the HMC. In particular, the active component of the cofactor of the enzyme nitrogenase consists of sulphide-bridged tetrahedra containing iron and molybdenum atoms. Molybdenum atoms fix nitrogen molecules preferentially, while the cluster as a whole, together with the $Fe_4S_4(SR)_4^{4-}$ clusters, ensures electron transfer in the process involving the reduction of nitrogen to ammonia.[5]

Furthermore, the presence in one HMC molecule of atoms of different metals in precisely known (and frequently specified) proportions makes it possible to obtain materials of the type of mixed sulphides with a high degree of homogeneity and the required ratio of the elements. Examples of such practically important systems are provided by the chalcochromites $M^{II}Cr_2X_4$ with a spinel structure, which have the properties of magnetic semiconductors.[6] Superconducting systems, the socalled "Chevrel phases", containing the Mo_6S_8 clusters (an octahedron of molybdenum atoms incorporated in a cubane structure made up of sulphur atoms), which are linked to one another by heterometallic M atoms (Pb, Sn, Cu, Ag, and the lanthanides), also incorporated in cubane structures made up of sulphur atoms have attracted much attention recently.[7]

One of the main problems in the study and application of sulphide-bridged heterometallic clusters is their synthesis, whose principles will be examined in the present review. We may note that the methods for the specific synthesis of various types of HMC,[8–10] including optically active HMC,[10,11] have become available only in the most recent years and so far do not constitute a well constructed system.

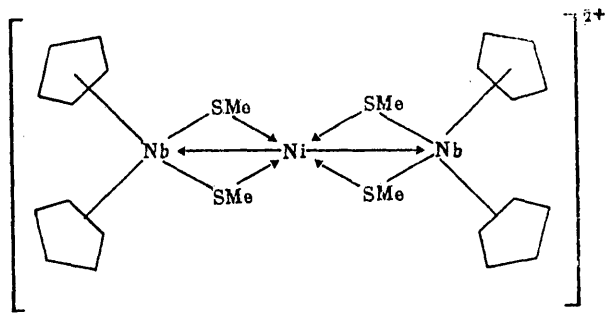
An important aspect of the specific synthesis of SHMC is the "cluster design" principle—the stepwise growth of the cluster core as a result of the employment of mono- and di-nuclear sulphur-containing metal complexes as ligands in relation to other metals (M′). Here one must take into account the electronic characteristics of the "building blocks" such as the presence of unshared electron pairs in the sulphur atoms or the metal atoms participating in the formation of new bonds with M′, the presence of S–S and M–M bonds in which an M′ atom can be inserted, and the presence of unoccupied or semioccupied orbitals of the metal atoms for which new dative bonds with M′ may be formed. Together with steric factors, these factors will be examined in the discussion of the synthesis and structure of clusters, the data being grouped in accordance with the nature of the principal "building blocks" within each Section in order of the arrangement of the heterometals in the Periodic System.

Since the complexity of the composition and geometry of the SHMC imposes special requirements as regards unambiguity in the determination of the structure of the complexes, this review discusses mainly clusters which have been obtained in the form of analytically pure single crystals and have been identified by full X-ray diffraction analysis. Literature data up to 1985 inclusive are incorporated.

II. Sulphide-bridged heterometallic clusters based on sulphur-containing complexes of group VA metals

The mononuclear trianion VS_4^{3-} functions as the central complex-forming agent in reactions with $(Me_4N)_2FeX_4^{2-}$ (X = Cl or SPh) in acetonitrile. This has resulted in the formation[12,13] of the trianions $X_2Fe(S)_2V(S)_2FeX_2^{3-}$ containing the Fe–V–Fe metal chain (for X = Cl, the length of the V–Fe bond is 2.727 Å) with two pairs of sulphide bridges and terminal X groups at the iron atoms. The clusters are paramagnetic (μ_{eff} = 4.96 B.M. for X = Cl and 4.80 B.M. for X = SPh).

The mononuclear sandwich fragments Cp_2M (Cp = C_5H_5), containing the SR groups which are forced to assume a position in the bisector plane between two cyclopenta-dienyl rings using the frontier orbitals with the $1a_1$, b_2, and $2a_1$ symmetries (their energies increase in this sequence) can serve as terminal complex-forming agents.[14] Thus the coordination of the two chelating ligands $Cp_2Nb(SMe)_2$ is observed when the readily displaced water molecules at the Ni(II) ion are substituted. The nickel atoms in the complex $[Cp_2Nb.(SMe)_2Ni(SMe)_2NbCp_2](BF_4)_2$ are linked to the four sulphur atoms of the SMe groups (the Ni–S bond lengths are 2.186–2.206 Å) and form direct Nb–Ni bonds (2.78 Å) via orbitals located in the bisector plane of the angle between the rings:[15,16]



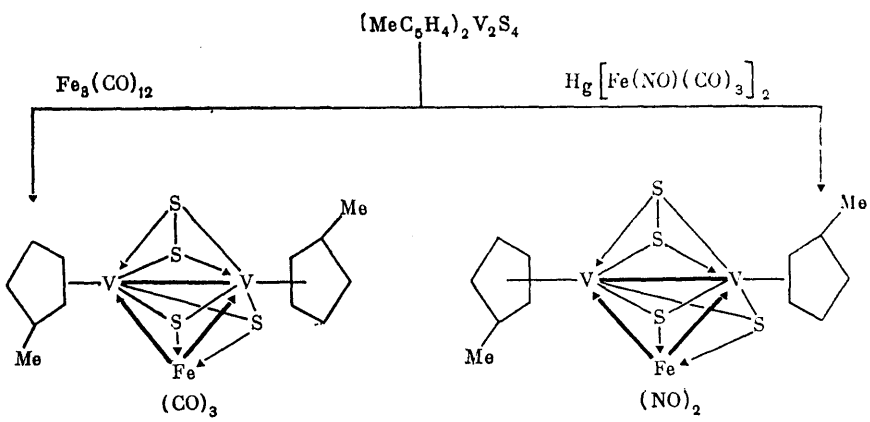
The complexes $(RC_5H_4)_2V_2S_4$,[18] obtained by treating $(RC_5H_4)_2.V_2S_5$ [19] with tributylphosphine, have been used recently as the starting materials for the synthesis of SHMC.[17] According to X-ray diffraction data, the complex $(RC_5H_4)_2V_2S_4$ (where R = iso-Pr) contains two sulphide bridges and the V–S–S–V fragment having a short V–V bond (2.610 Å). As a consequence of the electron deficiency, significant additional $\overline{S-V}$ π-bonding is observed, which shortens the V–S bonds (2.217–2.280 Å). The presence of unoccupied orbitals in $(MeC_5H_4)_2V_2S_4$ in combination with the presence of sulphide groups involved in different types of bonding, ensures a rich chemistry of this complex.

Thus the initial tetrasulphide complex $(MeC_5H_4)_2V_2S_4$ reacts with $IrCl(N_2)(PPh_3)_3$, affording the trinuclear cluster $(MeC_5H_4)_2V_2.(\mu,\eta^2\text{-}S_2)(\mu_3\text{-}S)_2IrCl(PPh_3)$, in which the iridium atom is located in a square planar environment (according to NMR data).[17]

Table 1. The principal geometrical characteristics of the vanadium-containing SHMC.[17,21]

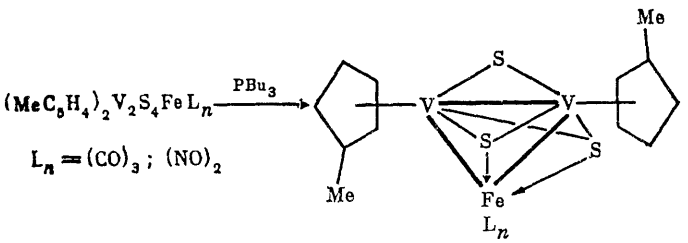
Compound	Bond length, Å (average values)					
	V–V	V–M	V–(μ_3-S)	M–(μ_3-S)	V–(μ,η^2-S)	V–(μ-S)
$(MeC_5H_4)_2V_2S_4Fe(CO)_3$	2.510	2.896	2.318	2.256	2.406	—
$(MeC_5H_4)_2V_2S_4Fe(NO)_2$	2.482	2.849	2.347	2.230	2.398	—
$(MeC_5H_4)_2V_2S_3Fe(CO)_3$	2.506	2.843	2.315	2.266	—	2.235
$(MeC_5H_4)_2V_2S_3Fe_2(NO)_2$	2.957	2.750	2.280	2.241	—	—
$[(MeC_5H_4)_2V_2S_4]_2Ni$	2.484	2.817	2.334	2.193	2.403	—

The addition of the CpCo fragment with formation of the triangular diamagnetic cluster $(MeC_5H_4)_2V_2S_4CoCp$ takes place in the reactions of $(MeC_5H_4)_2V_2S_4$ with $CpCo(C_8H_{12})$, $CpCo(CO)_2$, $[CpCo(CO)]_2$, or with the $CpCo(CO)I_2/Zn$ system (the yield reaches 25% in the last case). The trinuclear cluster $(MeC_5H_4)_2V_2(\mu,\eta^2\text{-}S_2).(\mu_3\text{-}S)_2Fe(CO)_3$ has been obtained by the reaction of $(MeC_5H_4)_2V_2S_4$ with $Fe_3(CO)_{12}$ [17] [or with $Fe(CO)_5$ in the presence of Me_3NO [20]] [$Fe_3S_2(CO)_9$ and $Fe_2S_2(CO)_6$ are formed as side products]:



The nitrosyl cluster $(MeC_5H_4)V_2(\mu,\eta^2\text{-}S_2)(\mu^3\text{-}S)_2Fe(NO)_2$, isoelectronic with the carbonyl-containing cluster, has been obtained by the reaction of $(MeC_5H_4)_2V_2S_4$ and $Hg[Fe(CO)_3(NO)]_2$ in tetrahydrofuran (THF) at 20 °C. The yield rises to 60% when $Fe(CO)_2.(NO)_2$, generated from $(PPh_3)_2N^+.Fe(CO)_3NO^-$ and $NOBF_4$ in the presence of Et_3N,[17,21] is used. When both diamagnetic clusters with the V_2Fe core are formed, the S_2 fragment changes the type of its coordination, being converted from the μ,η^1-bridging fragment (a two-electron donor) to the μ,η^2-bridging fragment (a six-electron donor). This is accompanied by an appreciable lengthening of the V–(μ-S) bond (to 2.318–2.347 Å) and the V–(μ,η^2-S) bond (to 2.406–2.398 Å) (Table 1). Apparently both facts (the rotation of the S_2 group and the lengthening of the V–S bonds) are determined by the decrease in the additional $\overline{V\text{–}S}_{bridge}$ π-bonding, since the unshared electron pairs of the sulphur atoms are used for the formation of the bond with the iron atom. Furthermore, the rotation of the disulphide bridge from the position along the V–V bond to the position at right angles appreciably diminishes (for steric reasons) the length of the V–V bond (2.510 and 2.482 Å respectively) compared with the length of the V–V bond in the initial dimer (V–V = 2.610 Å). The formation of new V–Fe bonds (2.8956 and 2.849 Å) does not interfere with the strengthening of the V–V bond, probably as a consequence of the interaction of the unoccupied orbitals of the vanadium atoms with the occupied orbitals of the iron atom.

When both clusters with the V_2Fe core are treated with tributylphosphine, the S_2 group loses one sulphur atom, affording the trisulphide clusters $(MeC_5H_4)_2V_2(\mu\text{-}S)(\mu_3\text{-}S)_2FeL_n$:[17,20]



In the tricarbonyl cluster, the overall geometry of the $V_2Fe(\mu_3\text{-}S)_2$ fragment [V–V = 2.505 Å, V–Fe = 2.8132 Å, and V–(μ_3-S) = 2.308–2.312 Å] remains the same as in the initial tetrasulphide cluster. However, the V–S bond (2.242 Å) of the V(μ-S)V group is strengthened as a result of the $\overline{V\text{–}S}$ π-bonding, since an electron deficiency arises on the vanadium atom as a consequence of the replacement of the six-electron donating $\mu,\eta^2\text{-}S_2$ group by the formally two-electron-donating bridge μ-S.

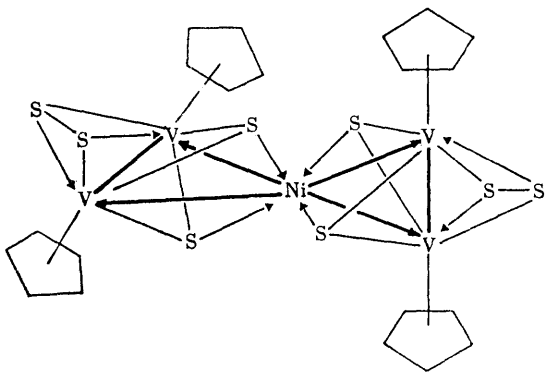
On the other hand, the active disulphide groups are capable of undergoing reactions involving the insertion of new metal atoms. Thus treatment of $(MeC_5H_4)_2V_2S_4Fe(CO)_3$ with $Pt(C_2H_4)L_2$ (L = PPh_3) at 25 °C leads to the insertion of the platinum atom in the S–S bond and the formation of the cluster $(MeC_5H_4)_2V_2.(\mu_3\text{-}S)_4Fe(CO)_3Pt(PPh_3)_2$.[17]

The nitrosyl cluster $(MeC_5H_4)_2V_2S_4Fe(NO)_2$ also contains the active $V_2(\mu,\eta^2\text{-}S_2)$ group, and its reaction with $Hg[Fe(CO)_3(NO)]_2$ or the direct interaction of $(MeC_5H_4)_2V_2S_4$ with $Hg[Fe(CO)_3(NO)]_2$ under severe conditions (in boiling toluene) leads to the addition of two Fe(NO) groups and the formation of the tetranuclear cluster $(MeC_5H_4)_2V_2S_4Fe_2(NO)_2$.[17,21]

The core of the molecule consists of the distorted V_2Fe_2 tetrahedron (V–V = 2.957 Å, V–Fe = 2.750 Å, and Fe–Fe = 2.590 Å), having μ_3-sulphide bridges over each face [$(Fe\text{–}S)_{av}$ = 2.241 Å; $(V\text{–}S)_{av}$ = 2.280 Å] and involving the additional coordination of the π-MeC_5H_4 ring at each vanadium atom and of one nitrosyl group at each iron atom. The cluster contains 58 electrons and its magnetic moment (μ_{eff} = 1.98 B.M. at 27 °C) is reduced compared with the spin-only value of 2.84 B.M. for two unpaired electrons, probably owing to antiferromagnetic exchange interactions. The paramagnetic (2.8 B.M.) 60-electron tetrahedral cluster $(MeC_5H_4)_2V_2S_4Co_2(NO)_2$ is in its turn formed readily (yield up to 95%) in the direct reaction of $(MeC_5H_4)_2V_2S_4$ with $Co(CO)_3(NO)$ in boiling toluene.[21]

The mixed paramagnetic 59-electron cluster $(MeC_5H_4)_2V_2S_4CoFe.(NO)_2$ has been obtained by the transmetallation of the cluster with the V_2Fe_2 core in the reaction with $Co(CO)_3(NO)$ in the presence of Me_3NO.[21] On treatment with metallic zinc and $[CoI(NO)_2]_x$,[17] the trisulphide cluster $(MeC_5H_4)_2V_2S_3Fe(NO)_2$ affords the diamagnetic cluster $(MeC_5H_4)V(\mu_3\text{-}S)_3FeCo_2(NO)_6$, which has 66 electrons and, according to the authors,[17] is constructed similarly to [the anion of] the block Roussin salt $Fe_4S_3(NO)_7^-$.[22]

The attempts to obtain the trinuclear cluster containing the V_2Ni core were unsuccessful and the reactions of $(MeC_5H_4)_2V_2S_4$ with nickel-containing reagents—$Ni(CO)_4$, $(COD)_2Ni$, $[CpNi(CO)]_2$, $Ni(CO)_2(PPh_3)_2$, or $Ni(CO)_2(Ph_2PC_2H_4PPh_2)$—resulted in the formation of the pentanuclear cluster $(MeC_5H_4)_4V_4S_8Ni$ with the V_4Ni metallospiran core:[17]



The peripheral S_2 bridging groups can split off one sulphur atom on treatment with a small excess of PPh_3, giving rise to the cluster $[(MeC_5H_4)_2V_2S_3]_2Ni$ with the V_4NiS_6 core.[17] Finally, insertion in the S–S bond is observed in reactions with one or two moles of $Pt(C_2H_4)(PPh_3)_2$ and leads to the growth of the core as a result of the addition of one or two $Pt(PPh_3)_2$ fragments. The clusters $[(MeC_5H_4)_2V_2S_4]_2Ni[Pt(PPh_3)_2]$ and $[(MeC_5H_4)_2V_2S_4]_2Ni[Pt(PPh_3)_2]_2$ have been identified by chemical analysis and IR and ^1H NMR spectroscopy and probably do not contain Pt–V bonds.[17]

$(MeC_5H_4)_2V_2S_5$, in which the short V–V bond (2.658 Å) is supplemented by the μ-S, $\mu,\eta^1\text{-}S_2$, and $\mu,\eta^2\text{-}S_2$ bridges (i.e. one S_2 fragment is coordinated along the V–V bond and the other is coordinated at right angles to it), can be used directly for the preparation of $(MeC_5H_4)_2V_2S_4$ derivatives.[19] However, the yields of the heterometallic clusters are in this case very low.

III. The synthesis and geometry of sulphide-bridged heterometallic clusters obtained using sulphur-containing group VIA metal complexes as ligands

The dinuclear chromium complexes $(C_5Me_5)_2Cr_2S_5$ [23] and (to an especially large extent) the antiferromagnetic complexes $Cp_2Cr_2.(SCMe_3)_2S$ and $(MeC_5H_4)_2Cr_2(SCMe_3)_2S$ described below are used

for the synthesis of chromium-containing SHMC. The complex $(C_5Me_5)_2Cr_2S_5$ [23] differs from the vanadium complex of analogous composition by the fact that it contains, apart from the μ-S and μ,η^2-S_2 bridges, the unusual S_2 bridge which is linked to two chromium atoms only via one sulphur atom [the second sulphur atom is linked to it by a weakened single bond (2.101 Å) which is probably of the donor–acceptor type]. As a result, this bridge is a two-electron ligand and the chromium atoms have the d^2 electronic configuration. The complex is diamagnetic probably as a result of the strong antiferromagnetic exchange reactions via the direct Cr–Cr bond (2.489 Å). The peripheral sulphur atom is then readily split off on treatment with PPh_3, affording the tetrasulphide complex $(C_5Me_5)_2Cr_2S_4$.[24] The sulphur atom is readily abstracted also in the reaction with $Co_2(CO)_8$, which leads to the formation of the diamagnetic cubane-like cluster $(C_5Me_5)_2Cr_2(\mu_3\text{-}S)_4Co_2(CO)_2$ (I).[25] The cluster is stable in air and contains 60 electrons. When it was treated with PR_3 (R = Ph or OMe), the products of the substitution of one and two CO groups were isolated:[26]

$$\underset{\text{(I)}}{(Me_5C_5)_2Cr_2S_4Co_2(CO)_2} \xrightarrow{PR_3} (Me_5C_5)_2Cr_2S_4Co_2(CO)(PR_3) + \underset{\text{(II)}}{(Me_5C_5)_2Cr_2S_4Co_2(PR_3)_2}$$

$PR_3 = PPh_3,\ P(OMe)_3.$

According to X-ray diffraction data, in the bisphosphine derivative (II) [PR_3 = $P(OMe)_3$] the core of the molecule consists of a distorted Cr_2Co_2 metallotetrahedron (Co–Co = 2.511 Å, Co–Cr = 2.638 to 2.660 Å, and Cr–Cr = 2.872 Å) with tridentate-bridging sulphide ligands over each face (Co–S = 2.155–2.179 Å and Cr–S = 2.256 to 2.278 Å).[26] The 60-electron clusters $Cp_2Cr_2(\mu_3\text{-}S)_4Mo_2(C_5Me_5)_2$ and $(C_5Me_5)_2Cr_2(\mu_3\text{-}S)_4Mo_2Cp_2$ with a pseudocubane core, containing chromium and molybdenum atoms, are formed in the photochemical reaction of $(C_5Me_5)_2M_2S_n$ (M = Cr, n = 5; M = Mo, n = 4) with the dinuclear complexes $Cp_2M'_2(CO)_4$ (M′ = Cr or Mo) containing M′≡M′ triple bonds.[27] On the other hand, if the rings in the dimeric carbonyls also contain methyl groups, then stable paramagnetic trinuclear clusters $(C_5Me_5)_3CrMo_2(\mu_3\text{-}S)(\mu\text{-}S)_3$ are formed.[27]

$Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (III), in which chromium(III) atoms are separated by a short distance (Cr–Cr = 2.689 Å), have been used for the synthesis of a large series of magnetically active SHMC. It is formed in the reaction of chromocene with t-butanethiol and its antiferromagnetic properties are described (μ_{eff} falls from 0.96 B.M. to zero in the temperature range 295–79 K) by the exchange parameter $-2J$ = 430 cm^{-1} for the spins of the Cr(III) ions equal to 3/2.[28,29] The methylated analogue $(MeC_5H_4)_2Cr_2$.$(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (IIIa), which is also antiferromagnetic ($-2J$ = 478 cm^{-1}), was obtained in accordance with the same scheme from $(MeC_5H_4)_2Cr$.[30] From the formal point of view, it means that, after the formation of the Cr–Cr single σ-bond, two half-occupied orbitals, on which the magnetic properties depend, are present at each chromium atom. On the other hand, together with the presence of the unshared electron pairs in the sulphide and thiolate bridges, the presence of the above half-occupied orbitals determines the chemical behaviour of the complexes (III) and (IIIa).

1. Ferromagnetic clusters with the Cr_2Pd core

The complexes (III) and (IIIa) readily react under mild conditions (benzene, 20 °C) with $(PPh_3)_2PdCl_2$, affording the dark-green crystalline complexes $(RC_5H_4)_2Cr_2(SCMe_3)_2(S)(Cl)_2Pd(PPh_3)$ (R = H or Me). The composition of the clusters formally corresponds to 1 : 1 adducts, but, in contrast to the initial dinuclear complexes, the new clusters manifest ferromagnetic exchange interactions [μ_{eff} = 4.11 (296 K)–4.57 (79 K) B.M. and $+2J$ = 28 cm^{-1} for R = H; μ_{eff} = 3.87 (296 K)–4.20 (95 K) B.M. and $+2J$ = 11 cm^{-1} for R = Me).[13] According to X-ray diffraction data for the cluster with R = Me, the preferred rearrangement takes place in the resulting clusters in conformity with Pearson's principle:[32] the Cl atoms (hard Lewis bases) pass from the palladium atom (a soft Lewis base) to the chromium(III) atoms (hard Lewis bases). The $SCMe_3$ groups (soft Lewis bases), which previously served as bridges between the chromium atoms, then becomes bridges between the chromium and palladium atoms. The chelate ligand $(PPh_3)Pd(SCMe)_2$ (Pd–S = 2.350 and 2.381 Å), coordinated to to chromium atoms via thiolate bridges (Cr–S = 2.396 and 2.403 Å; Cr...Pd = 3.230 and 3.380 Å), is ultimately formed. The chromium atoms in this situation are coordinated to the π-MeC_5H_4 rings and the chlorine atoms (Cr–Cl = 2.308 Å) located in the *trans*-positions relative to the Cr_2Pd plane. As a result of such ligand environment of each chromium atom [the MeC_5H_4(centre)–Cr–Cr angle is 124.5° instead of 180° in compound (III)], the effective overlap of the d_{z^2} orbitals, which mainly determines the bonding of the chromium atoms in the dinuclear complexes (III) and (IIIa), becomes impossible. The Cr...Pd distances in the clusters are also large for bonding and, in the absence of M–M bonds, the antiferromagnetic contribution to the exchange interactions diminishes sharply and it is found possible to observe the ferromagnetic exchange via the sulphide bridge (the Cr–S–Cr angle is 121.77°).

2. The $(CpCrSCMe_3)_2S$.ML adducts

The course of the interaction of the complex (III) with metal carbonyls is determined by the coordination number of the corresponding metal [CN(M)]. For CN(M) = 6, any adducts in which the $M(CO)_5$ is linked to the virtually unaltered complex (III) (Cr–Cr = 2.73 Å) via a sulphide bridge (M–S = 2.58 Å for M = Mo or W) are formed for $M(CO)_6$ (M = Cr, Mo, or W) with CN(M) = 6 on UV irradiation. Ultimately the magnetic properties remain unaltered ($-2J$ = 440 cm^{-1}).[33,34] The reaction of compound (III) with $Mn_2(CO)_{10}$ takes place analogously in THF at 10 °C, where the $Mn_2(CO)_9$ fragment is generated under the influence of UV irradiation.[35] It adds to the sulphide bridge in the initial chromium complex (III) in the *cis*-position relative to the Mn–Mn bond. Here CN(M) is also six and the dichromium fragment remains almost unchanged (Cr–Cr = 2.739 Å, Cr–$SCMe_3$ = 2.35 Å, Cr–S = 2.31 Å) like the magnetic properties ($-2J$ = 440 cm^{-1}), although the Mn–S distance is smaller (2.448 Å) than the Mo–S distance in the adducts described above.

Finally, as a result of the photochemical reaction of compound (III) under mild conditions ($h\nu$, 7°C), cyclopentadienylmanganese tricarbonyl $CpMn(CO)_3$ with CN(M) = 6 (the Cp ring occupies three coordination sites) also gives rise to a simple adduct of the initial complex, with $CpMn(CO)_2$ "suspended" under it and linked via a sulphide bridge only, the Mn–S bond being shortened to 2.334 Å. The geometry of the dichromium fragment is virtually unchanged on coordination of the manganese atom (Cr–Cr = 2.704 Å, Cr–$SCMe_3$ = 2.350–2.364 Å, and Cr–S = 2.295 Å).[36] All these adducts have a common geometrical feature involving the coordination of the "suspended group" to an M atom having an octahedral environment (i.e. for a coordination number of 6), the possibility of further interaction of the M atom (Mo, W, or Mn) with the thiolate sulphur atom being sterically blocked by two carbonyl groups.

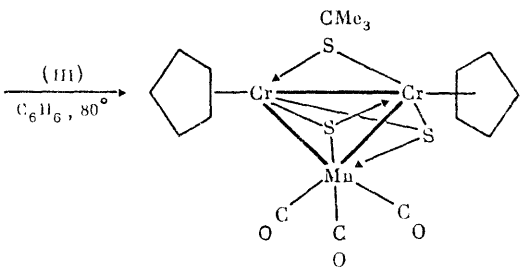
3. Triangular clusters with the Cr_2M core

The reactions involving complexes in which CN(M) is less than 6, i.e. when there is a possibility of the interaction of the orbitals of the M atom with the thiolate sulphur atom in the intermediates, proceed differently.

Thus the photochemical reaction of compound (III) with $Fe(CO)_5$ in THF takes place with the loss of two CO groups and one t-butyl group, the $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Fe(CO)_3$ cluster (IV) being formed.[37] Replacement of the S–CMe_3 σ-bond in it by the Fe–S bond alters little the geometry of the $Cp_2Cr_2S_2(SCMe_3)$ fragment compared with compound (III) (Cr–Cr = 2.707 Å). However, the appearance of the paramagnetic Fe(I) ion with the d^7 electronic configuration leads to the non-equivalence of the Cr–Fe bonds (2.726 and 3.110 Å) and to the magnetic properties being described by three parameters of the antiferromagnetic exchange interactions ($-2J_{Cr-Cr}$ = 380 cm^{-1}, $-2J_{Cr-Fe}$ = 2600 cm^{-1}, and $-2J_{Cr\ldots Fe}$ = 170 cm^{-1}). Apparently the half-occupied and occupied $Fe(CO)_3$ orbitals participate in the interaction with the two half-occupied orbitals in the dichromium fragment, forming a two-electron (single) Fe–Cr bond (2.726 Å) with one of the chromium atoms and a one-electron (bond order 1/2) Fe–Cr bond (3.110 Å) with the other atom.

Although the Mn atom in the above adduct of compound (III) with the $Mn_2(CO)_9$ fragment has CN(M) = 6, on UV irradiation under more severe conditions (boiling benzene or THF) there is a possibility of the dissociation of the Mn–Mn bond with decrease of CN(M) to five:[38]

$$(C_5H_5)_2Cr_2(SCMe_3)_2S\cdot Mn_2(CO)_9 \rightarrow$$



(V)

This results in the formation of the antiferromagnetic metallocyclic cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$, whose composition is analogous to the iron-containing cluster (IV) but which differs in geometry and magnetic properties. Thus both Cr–Mn distances correspond to the presence of M–M′ bonds, although some non-equivalence, induced by the symmetry of the $Mn(CO)_3$ fragment relative to Cr_2S_2, is in fact observed in them (2.716 and 2.828 Å). On passing from the iron- to the manganese-containing cluster, in which the Mu(I) ion has the d^6 electronic configuration, the electron is apparently removed from the antibonding orbital, which leads to a marked stabilisation of the metallic core in compound (V). The Mn(I) ion is diamagnetic and the magnetic properties of the cluster (V) correspond to antiferromagnetic exchange interactions with the parameter $-2J_{Cr-Cr}$ = 670 cm^{-1}, which is much greater than for the $Cp_2Cr_2(SCMe_3)_2SML$ adducts (~440 cm^{-1}). Since the Cr–Cr bond in compound (V) (2.646 Å) has hardly changed compared with compound (III) (2.689 Å), the intensification of the exchange interactions can be evidently explained by the involvement of the bridging manganese atom.

The antiferromagnetic cluster $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2FeCp$ (the iron atom in the cluster has the d^6 electronic configuration), which is formed in the form of dark-brown crystals on prolonged irradiation (17 h) of a boiling solution of compound (III) and $[CpFe(CO)_2]_2$ in THF (reactant ratio 2 : 1), is an isoelectronic analogue of the cluster (V).[39]

In contrast to the Cr, Mo, W, Mn, and Fe carbonyls or the cyclopentadienyl-manganese and -iron carbonyls, whose reactions with $Cp_2Cr_2(SCMe_3)_2S$ require UV irradiation and elevated temperatures, the dinuclear cobalt carbonyl $Co_2(CO)_8$ reacts with the dichromium complexes (III) and (IIIa) even at room temperature. The complex $Co_2(CO)_8$ exists in solutions in the non-bridged form [CN(Co) = 5] with a readily dissociating Co–Co bond (E = 9 kcal mol^{-1} [40] and the coordination with the sulphur atoms and the replacement of the S–CMe_3 bond in compound (III) or (IIIa) by the S–Co bond therefore proceed especially readily. The cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_3$ (A), having a composition analogous to that of the iron-containing cluster (IV) and the manganese-containing cluster (V), should then be formed. However, owing to the d^8 electronic configuration of Co(I), the intermediate (A) must contain two electrons in the antibonding orbital of the metallic core. As a result, both Cr–Co bonds must have a bond order of 0.5 (or one bond is single and the other does not exist). Stabilisation of the intermediate (A) is readily achieved by splitting off of one carbonyl group on evacuation or heating of the reaction mixture, which results in the formation of the cluster $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (VI).[35] According to X-ray diffraction data, compound (VI) has a stable metallic core with short Cr–Co bonds, which are almost equivalent (2.579 and 2.592 Å), since the two CO groups are distributed symmetrically relative to the pairs of chromium and sulphur atoms. The length of the Cr–Cr bond (2.617 Å) is changed relatively little (by 0.07 Å) compared with the initial complex (III). Therefore the increase in the parameter $-2J$ to 530 cm^{-1} is determined by the presence of the diamagnetic bridging cobalt atom.

The cluster $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$, whose structure differs from that of the non-methylated analogue by the appearance of the crossed conformation of the rings instead of the eclipsed conformation, has been obtained analogously. Furthermore, on methylation of the ring, a slight but distinct strengthening of the metallic core compared with compound (VI) is observed (Cr–Cr = 2.590 and 2.617 Å, Cr–Co = 2.530, 2.569, 2.579, and 2.592 Å respectively). The antiferromagnetic exchange interactions are also found to have become more intense ($-2J$ = 578 cm^{-1}).[38]

Thus the introduction of the methyl substituent into the cyclopentadienyl ring strengthens the core and intensifies the exchange interactions, which is apparently associated with the increase in the electron density at the chromium atoms. This agrees with data for the electrochemical oxidation of $(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)Co.(CO)_2$. According to voltametric and microcoulometric data, both clusters give rise to two reversible one-electron oxidation waves in dimethylformamide (DMF) at potentials of 0.63 and 1.47 V (for R = H) and 0.44 and 1.10 V (for R = Me).

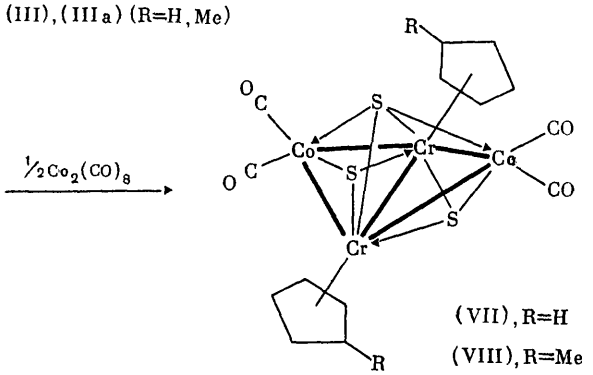
4. "Metallobutterfly" clusters with a Cr_2M_2 core

After the formation of compound (VI) and its methylated analogue, the remaining half-occupied orbitals of the chromium atoms can participate in further Cr–M bonding during the growth of the cluster core as a result of the reaction with an additional amount of $Co_2(CO)_8$, which leads to the formation of diamagnetic clusters having the general composition $(RC_5H_4)_2Cr_2(S)_3Co_2(CO)_4$, where R = H [compound (VII)] or Me [Compound (VIII)] with a metallic

core made up of two chromium atoms and two cobalt atoms.[39] We may note that, together with the replacement of the S–CMe_3 σ-bond in compound (VI) by a new S–Co bond, a μ_4-S bridge is produced by using yet another electron pair at the μ_3-sulphide bridge:

$$(C_5H_4R)_2Cr_2(\mu\text{-}SCMe_3)_2S \xrightarrow{1/2\,Co_2(CO)_8} (RC_5H_4)_2Cr_2(SCMe_3)(\mu\text{-}S)_2Co(CO)_2 \longrightarrow$$

(III), (IIIa) (R=H, Me)



(VII), R=H

(VIII), R=Me

There are no electrons in the antibonding orbitals of the Cr–Co bonds in the 62 electron clusters (VII) and (VIII) with the "metallobutterfly" core and all the Cr–Co bonds are therefore short and virtually equalised [2.617 and 2.622 Å in compound (VII) and 2.614–2.636 Å in compound (VIII)] by virtue of the symmetrical disposition of both $Co(CO)_2$ groups relative to the Cr_2S_2 fragment. The electrons participating in the formation of the Cr–Cr σ-bond are not then involved and the removal of the bulky CMe_3 groups, which hinder the mutual approach of the chromium atoms, shortens the Cr–Cr bonds to 2.544 Å (in both clusters).

The products of the formal replacement of the 13-electron $Co(CO)_2$ fragments in the cluster (VII) are the 15-electron CpNi fragments formed by the reaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (III) with the dinuclear cyclopentadienylnickel carbonyl $[CpNi(CO)]_2$, which, like the isolobal $Co_2(CO)_8$ complex, exists in solution in a non-bridged form [CN(Ni) = 5] and probably readily dissociates at the Ni–Ni bond. Therefore, as for $Co_2(CO)_8$, the reactants interact in equimolar amounts even at room temperature with formation of the 66-electron cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Ni_2Cp_2$ (IX).[41] The cluster has an asymmetric "metallobutterfly" core with Cr–Ni distances non-equivalent in pairs (cf. 2.620 and 2.844 Å) and contains four superfluous electrons compared with $Cp_2Cr_2(S)_3Co_2(CO)_4$ (VII). These electrons are apparently located in the antibonding orbitals of the metallic core and not only the Cr–Ni bonds are lengthened, despite the smaller covalent radius of nickel compared with cobalt, but also the Cr–Cr bond [2.620 instead of 2.544 Å in compound (XVII)]. In addition, this leads to the appearance of antiferromagnetic properties ($-2J$ = 418 cm^{-1}).

5. Heterometallic tetrahedral clusters

The clusters $(\pi\text{-}C_5Me_5)_2Cr_2(S)_4Co_2(PR_3)_2$, containing the tetrahedral Cr_2Co_2 core, were described above.[25] An analogous cluster can be obtained by introducing a fourth sulphur atom instead of two carbonyl groups into the "metallobutterfly" $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2.(CO)_4$ (VII) in the reaction with t-butanethiol:[39]

$$(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4 + Me_3CSH \rightarrow (C_5H_5)_2Cr_2(\mu_3\text{-}S)_4Co_2(CO)_2.$$

A 60-electron diamagnetic cluster with an analogous structure has been obtained by the formal replacement of one Co(CO) fragment by the isoelectronic CpCr fragment. The cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Co.(CO)$ (X) and its methylcyclopentadienyl analogue have been synthesised by treating the metallotriangular clusters $(RC_5H_4)_2Cr_2.(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ of type (VI) (R = H or Me) with diphenylacetylene which leads to the binding of some of the cobalt atoms (probably in the form of stable acetylene complexes).[42] The pseudocubane core is readily loosened on methylation of the Cp rings (the bond lengths in the Cr_3CoS_4 cores with R = H or Me are respectively Cr–Co = 2.650 and 2.692 Å and Cr–Cr = 2.810 and 2.816 Å). The M–S bonds are then found to be extremely short (Co–S = 2.163 and 2.171 Å and Cr–S = 2.244 and 2.263 Å), which indicates the undoubted occurrence of the additional $\overleftarrow{M\text{–}S}$ π-interaction.

The M–M′ bonds are loosened even more after the introduction of additional electrons into the metallic core of new electron-donating ligands, for example, on formation of the cluster $Cp_3Cr_3.(\mu_3\text{-}O)(\mu_3\text{-}S)_3Co(CO)_3HOOCCMe_3$ (XI).[43] It is produced as a result of the treatment with trimethylacetic acid of the reaction mixture of compound (III) and $Co_2(CO)_8$ in benzene [the mixture is obtained without concentration *in vacuo* and without heating, i.e. under conditions where the intermediate containing the $Co(CO)_3$ fragments may be obtained—see above]. As a result of the addition of two carbonyl groups, the metallotetrahedron (XI) is found to have four electrons more than in compound (X). They occupy antibonding orbitals of the metallic core but influence mainly bonds involving the cobalt atom. Not only the Cr–Co bonds (2.875, 3.219, and 3.230 Å), but also the Co–S (2.47 Å) and Co–O (2.16 Å) bonds are found to be greatly lengthened. On the other hand, in the metallotriangle Cp_3Cr_3 the Cr–Cr bond lengths (2.692–2.884 Å) are found to be within the limits characteristic of the trichromium fragment in the metallotetrahedral cluster (X). Trimethylacetic acid is a convenient reagent, binding some of the heterometal atoms occurring in the triangular clusters without the cleavage of the CpCr bond and with retention of the sulphide bridges. Thus treatment of the metallotriangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)Fe(CO)_3$ (IV) with Me_3CCOOH yielded the heterometallotetrahedral cluster $Cp_3Cr_3.(\mu_3\text{-}S)_4Fe(OOCCMe_3)$ (XII), which contains a carboxylate group at the Fe atom linked only via one oxygen atom (Fe–O = 1.896 Å, C–O = 1.32 Å, and C–O = 1.25 Å) and is a structural analogue of the cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (X) with a similar geometry (Fe–Cr = 2.758 Å, Cr–Cr = 2.830 Å, Fe–S = 2.218 Å, and Cr–S = 2.270 Å).[44] However, the replacement of the 11-electron Co(CO) fragment by the 9-electron $Fe(OCOCMe_3)$ fragment renders the cluster (XII) electron-deficient [58 electrons instead of the 60 electrons in compound (X)]. The two upper degenerate orbitals, which are occupied in compound (X), are found to be half-occupied in compound (XII), which is consistent with the observed paramagnetism of the cluster (μ_{eff} = 2.81 B.M.) and is close to the spin-only value for two unpaired electrons and is independent of temperature.

We may note that the reaction of compound (IV) with benzoic acid under the same conditions leads to the loss of the cyclopentadienyl ligands and of the thiolate bridge. All the metal atoms and one μ_3-sulphide bridge are then retained and the complex $Cr_2Fe.(\mu_3\text{-}S)(OOCPh)_6$ is formed.[44] The reactions of benzoic acid with the adducts $Cp_2Cr_2(SCME_2)_2S.ML_n$ [ML_n = $Cr(CO)_5$ or $Mn_2(CO)_9$] led to the analogous complexes in which the iron atom was replaced by the Cr(II) and Mn(II) atoms. The complexes are antiferromagnetic and the exchange parameters $-2J_{Cr...Cr}$ (54, 84, and 60 cm^{-1}

respectively) and $-2J_{Cr...M}$ (6, 36, and 28 cm^{-1})[44] exceed approximately by a factor of 2 the corresponding values for the known μ_3-oxo-bridged analogues.[45] This indicates an appreciable contribution of the exchange via the central bridging atom compared with the exchange via the carboxylate bridges and the small exchange parameters clearly indicate the absence of direct M–M bonds.

6. Pentanuclear heterometallospiran clusters

The cluster $[(MeC_5H_4)_2V_2S_4)_2Ni$ having the structure of a heterometallospiran with the $V_4(\mu_3\text{-}S)_4Ni$ core was described above.[17] It is the first representative of chromium-containing metallospiran clusters having the cobalt central atom. It arose very unexpectedly in the reaction of the metallotriangle $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (VII) with Me_3CCOOH under severe conditions (xylene, 100 °C). This results in the binding of some of the cobalt atoms in the form $[Co(OOCCMe_3)_2]_n$ and the formation of the brown crystals of the antiferromagnetic cluster $[Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Co$ (XIII) [μ_{eff} falls from 3.26 (292 K) to 2.19 (81 K) B.M.].[43] According to the results of full X-ray diffraction analysis, the two metallotriangular Cr_2Co fragments in the spiran core are arranged at an angle of 94.6° and are joined by the common cobalt atom. On the one hand, the geometry of each triangular fragment is similar to that observed in the initial triangle (VI). The dichromium fragments $Cp_2Cr_2(\mu\text{-}SCMe_3)(S)_2$ (designated henceforth by Q) remain almost unchanged under these conditions (Cr–Cr = 2.679 and 2.665 Å) (Table 2). On the other hand, pronounced loosening and asymmetry of the lengths of the Cr–Co heterometallic bonds are observed (2.766 and 2.744 Å in one triangle and 2.809 and 2.959 Å in the other).

If the dinuclear five-electron fragment Q is regarded as an unusual antiferromagnetic chelate ligand, then the cluster (XIII) is a formal product of the substitution of two CO groups in the initial compound (VI) by the fragment Q, the sulphur atoms occupying the places of the CO groups. As a result of such bonding, a 19 electron environment arises at the cobalt atom, the one superfluous electron loosening the Co–Cr and Co–S bonds [the Co–S bonds in compound (XIII) are lengthened on average by 0.075 Å compared with the initial compound (VI)]. We may note that, as in the metallotriangular cluster (IV) with the Cr_2Fe core, this occurs despite the general electron deficiency of the cluster (one half-occupied orbital remains in each chromium atom as before, which ensures the antiferromagnetic properties of the cluster).

The removal of an electron from the antibonding orbitals takes place on formal replacement of the central Co(II) ion by the Fe(II) ion. Such a cluster, $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Fe$ (XIV), has been obtained by the reaction of two moles of compound (III) with one mole of $Fe(CO)_5$ on prolonged UV irradiation in boiling THF, the reaction proceeding (according to IR spectroscopic data) via the intermediate formation of the triangular cluster $Cp_2Cr_2(SCMe_3).(\mu_3\text{-}S)_2Fe(CO)_3$ (IV) described above.[39] The cluster (XVI) was isolated in the form of fine black-green prisms, stable in air, by recrystallisation from a THF–heptane mixture; the composition of the cluster was established by elemental analysis, its IR spectrum being virtually identical with that of the cluster (XIII). The cluster (XIV) is antiferromagnetic and its μ_{eff} diminishes from 3.32 to 2.37 B.M. in the temperature range 290–80 K. Unfortunately, the crystals of the cluster (XIV) proved to be unsuitable for X-ray diffraction study.

The methylcyclopentadienyl analogue $[(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3).(\mu_3\text{-}S)_2]_2Fe$ (XV) was obtained by the prolonged reaction of compound (IIIa) with $[CpFe(CO)_2]_2$ for a 4 : 1 reactant ratio in boiling toluene.[46] In this case the geometry of the metallic core of the cluster is determined to an appreciable extent by the steric effects

Table 2. Comparison of the principal geometrical parameters of the metallospiran clusters $[(RC_5H_4)_2Cr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2M$.

Parameter	Central metal atom M in metallospiran				
	Cr(R=H)	Mn(R=H)	Mn(R=Me)	Fe(R=Me)	Co(R=H)
Cr–Cr (distance in peripheral fragments), Å	2.665	2.690	2.726; 2.657	2.693; 2.658	2.679; 2.665
Cr–M, Å	2.933; 2.889	2.947; 2.936	2.839–3.104	2.736–2.982	2.774–2.959
Cr–$SCMe_3$, Å	2.361–2.354	2.388–2.356	2.302–2.414	2.392–2.313	2.341–2.353
Cr–(μ_3-S), Å	2.302–2.327	2.307–2.323	2.250–2.372	2.275–2.329	2.248–2.270
M–(μ_3-S), Å	2.328–2.337	2.393–2.383	2.318–2.502	2.167–2.234	2.243–2.275
CrSRCr, deg	68.82	69.90	69.2–69.9	68.39–69.89	69.44–69.49
CrSCr, deg	70.02–70.62	71.00	70.9–72.1	71.92–70.08	71.08–71.23
CrSM, deg	76.6–78.1	77.6–77.7	73.6–82.0	73.75–81.03	75.25–80.42
Angle between Cr_2M planes, deg	90	90	109.60	113.80	94.60

of the MeC_5H_4...S repulsion (2.9–3.1 Å), leading to a marked change of the angle between the Cr_2Fe triangles (to 113.8°). This effect probably determines the non-equivalence of the Fe–Cr and Fe–S distances in the spiran core: Fe–Cr = 2.749 and 2.827 Å and Fe–S = 2.166 and 2.242 Å in one triangle and Fe–Cr = 2.910 and 2.969 Å and Fe–S = 2.293 and 2.368 Å in the other. Bearing in mind the difference between the covalent radii of iron and cobalt (1.34 and 1.29 Å), the Fe–Cr distances in compound (XV) indicate some stabilisation of the heterometallic bonds in the core compared with compound (XIII), i.e. on removal of an electron from the antibonding orbitals of the metallic core. The geometry of the $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(S)_2$ = Q′ fragments (especially the middle distance Cr–Cr = 2.675 Å) then remains very close to that found in compound (III). The cluster (XV) exhibits antiferromagnetic properties.

The same steric effects of the methyl groups in the rings are observed in the analogous cluster $[(MeC_5H_4)_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Mn$ (XVI) containing the central Mn(II) ion. The cluster (XVI) was obtained by the reaction of compound (IIIa) in boiling toluene with manganocene Cp_2Mn, which readily loses the Cp ligands.[46] Owing to the short MeC_5H_4...S contacts (2.95–3.12 Å), the planes of the Cr_2Mn triangle are rotated by an angle of 109.6°. Not only do the Mn–Cr bonds differ under these conditions but also the lengths of the Cr–Cr bonds are not the same, a shorter Cr–Cr bond (2.657 Å) corresponding to the greatly lengthened Mn–Cr bonds (3.104 and 3.019 Å). The opposite picture is observed for the other triangle: a lengthened Cr–Cr bond (2.726 Å) corresponds to the shortened Mn–Cr bonds (2.839 and 2.967 Å). It is notable that all the Mn–Cr and Mn–S bonds (2.318–2.502 Å) are significantly lengthened compared with the corresponding bonds in the trinuclear cluster $QMn(CO)_3$. This is apparently due to the greater amount of ionic character in the bonds with a high-spin Mn(II) ion (d^5 electronic configuration). This idea agrees with the magnetic properties: μ_{eff} diminishes from 2.51 to 1.26 B.M. in the temperature range 295–80 K, which is described by the antiferromagnetic exchange parameters $-2J_{Cr-Cr}$ = 668 cm^{-1} and $-2J_{Cr-Mn}$ = 418 cm^{-1} for the spins of the Cr(III) and Mn(II) ions of 3/2 and 5/2 respectively.

The steric nature of the distortions in the geometries of the clusters (XV) and (XVI) is demonstrated by the removal of these distortions on passing to the non-methylated cluster $[Cp_2Cr_2.$ $.(SCMe_3).(S)_2]_2Mn$ (XVIII), which has been obtained by the reaction of two moles of compound (III) with one mole of $CpMn(CO)_3$ under severe conditions (on UV irradiation in boiling toluene).[47] The adduct $Cp_2Cr_2(SCMe_3)_2S.MnCp(CO)_2$ is formed as an intermediate and reacts with a second molecule of compound (III), affording the cluster (XVII) in the form of dark-green prisms. In compound (XVII), the angle between the Cr_2Mn planes is 90° and the geometry of the fragments Q remains unchanged (Cr–Cr = 2.690 Å and Cr–S = 2.307–2.324 Å), but, owing to the increased amount of ionic character, the Cr–Mn (2.947 and 2.936 Å) and Mn–S (2.393 and 2.324 Å) bonds are found to be lengthened compared with the triangular cluster $QMn(CO)_3$ (V).

The homonuclear cluster $[Cp_2Cr_2(SCMe_3)(S)_2]_2Cr$, containing the central Cr(II) ion (d^4 electronic configuration), which has been obtained by the reaction of compound (III) with C_6H_6 $Cr(CO)_3$ in THF on UV irradiation (not only the carbonyl groups but also the photolabile arene ligand are then substituted), has virtually the same geometry.[48] The peripheral Cr–Cr bonds are extremely short (2.665 Å) compared with the Cr_{periph}–Cr_{centr} bonds (2.933 and 2.889 Å). However, when account is taken of the difference between the covalent radii of Cr and Mn (1.46 and 1.34 Å respectively), the latter bonds are strengthened compared with Cr–Mn in compound (XVII). This can apparently be explained by the decrease in the amount of ionic character in the bonds on passing from d^5 to d^4.

We may note that the metallospiran clusters Q_2M (M = Cr, Mn, Fe, or Co) represent a new class of complex with chelate antiferromagnetic ligands Q, the character of the bonding of which to the central metal depends on the electronic configuration of M and the steric effect of the methyl substituents in the cyclopentadienyl ligands at the chromium atom.

The series of the structurally characterised clusters with the Cr_4Co, Cr_4Fe, Cr_4Mn, and Cr_4Cr cores presented here is supplemented by the clusters with the Cr_4V and Cr_4Ni cores. The vanadium-containing cluster has been obtained by the reaction of $V(BH_4)_2$ with compound (III) in the presence of Et_3N:[39]

$$2\,(C_5H_5)_2Cr_2(SCMe_3)_2S \xrightarrow[Et_3N]{V(BH_4)_2} [(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2V.$$
(III)

The brown antiferromagnetic crystals have been characterised by elemental analysis and by IR spectra, which are identical with the spectra of the clusters Q_2M with M = Co, Fe, Mn, or Cr.

Finally, the reactions of compounds (III) and (IIIa) with the nickel complexes [Ni], which readily lose their ligands [$Ni(CO)_4$, $Ni(COD)_2$, and $(MeC_5H_4)_2Ni$] have been used to synthesise the clusters $[(RC_5H_4)_2Cr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Ni$ (R = H or Me):[39]

$$2\,(RC_5H_4)_2Cr_2(SCMe_3)_2S \xrightarrow{[Ni]} [(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Ni.$$

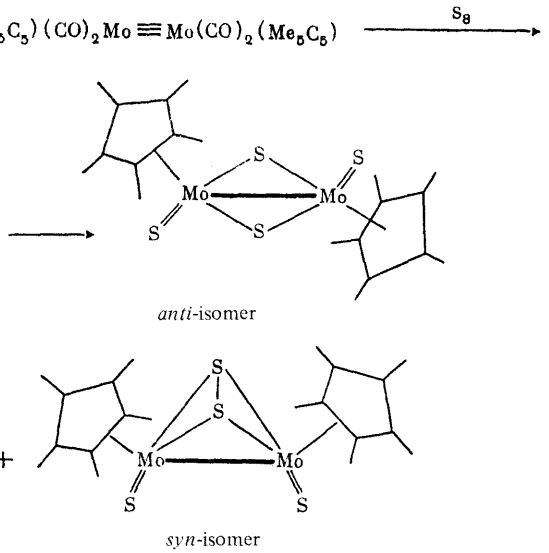
Both antiferromagnetic clusters have been isolated in the form of dark-green crystals and have been characterised by elemental analysis and IR spectra.

7. Sulphide-bridged heterometallic clusters based on $(C_5R_5)_2Mo_2S_4$ and $(C_5R_5)_2Mo_2(SH)_2(S)_2$

Dinuclear molybdenum tetrasulphide complexes exist in the form of three isomers, whose formation depends on the duration of the reaction of $(C_5Me_5)_2Mo_2(CO)_4$ with elemental sulphur. Thus the isomer $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ arises in hot toluene in the course of 17 h. It contains, apart from two sulphide bridges, the S_2 fragment coordinated at right angles to the short Mo–Mo bond (2.599 Å).[49] The analogous complex $(MeC_5H_4)_2Mo_2$ $(\mu\text{-}S)_2(\mu\text{-}S_2)$ has been described.[50] The diamagnetism of both molybdenum complexes probably indicates the presence of the Mo=Mo double bond and some shortening of the Mo–S bonds is evidence for an appreciable contribution by the additional Mo–S π-interaction.

If the reaction of $(C_5Me_5)_2Mo_2(CO)_4$ with S_8 is carried out over a period of three days, then the tetrasulphide complex described above is converted into two isomers with terminal sulphur atoms, which involves the dissociation of either the S–S bond or of the Mo–S bridge bonds. In the former case, the isomer contains Mo(V) atoms and, according to X-ray diffraction data,[51] only two sulphide bridges are present in the complex (Mo–S = 2.297 Å), while the other two sulphur atoms are terminal (Mo=S = 2.144 Å). The Mo(V) atoms then form a single Mo–Mo bond (2.905 Å). The complex has the *anti*-configuration as regards the Mo=S bonds and the C_5Me_5 rings.

The reaction via the second pathway affords a low yield of the *syn*-isomer, containing the disulphide group:



The *anti*-isomers of $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2(S)_2$ are formed in a low yield even in the reactions of $(Me_nC_5H_{5-n})_2Mo_2(CO)_6$, where n = 0, 1, or 5, with S_8, but the main products are found to be the insoluble polymeric complexes $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_4$.[51]

The geometry of the Mo_2S_2 cores of the cyclopentadienyl[52] and methylcyclopentadienyl[51] complexes hardly differs form the geometry of the core in the pentamethylcyclodienyl analogue. The molybdenum atoms in these systems have a 16-electron environment (when account is taken of the Mo–Mo bond), which lead to a sharp shortening of the bonds with bridging sulphur atoms (to 2.297 Å) in conformity with the significant contribution of the additional Mo–S π-bonding.

The tetrahedral clusters $(C_5R_5)Mo_2(\mu_3\text{-}S)_4(Cr_2(C_5R'_5)_2$ (R = H, R′ = Me or R = Me, R′ = H), obtained by the reactions of the *anti*-isomers of $(C_5R_5)_2Mo_2S_4$ with $(C_5R'_5)_2Cr_2(CO)_4$, were described above.[27] If all the rings are methylated, then the interaction of $(C_5Me_5)_2Mo_2S_4$ with $(C_5Me_5)_2M'_2(CO)_4$ (M′ = Cr or W) gives rise to the stable paramagnetic trinuclear clusters $(C_5Me_5)_3Mo_2M'(\mu_3\text{-}S).(\mu\text{-}S)_3$.[27]

A 60-electron tetrahedral cluster, in which the (C_5R_5)Cr groups have been replaced by the isoelectronic Fe(NO) groups, is formed in the reaction of $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ with $(Ph_3PNPPh_3)^+Fe.(CO)_3(NO)^-$.[53] On the other hand, the reaction of $(C_5Me_5)_2Mo_2.(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ with $Fe_2(CO)_9$ at 25 °C in THF or with $Fe(CO)_5$ on UV irradiation gives rise to the tetranuclear cluster $(C_5Me_5)_2Mo_2.(\mu_3\text{-}S)_4Fe_2(CO)_4$ containing two $Fe(CO)_2$ fragments.[54] The cluster therefore has 62 electrons and the metal atoms form a "butterfly" structure with the Mo–Mo "abdomen" (2.761 Å) and the Mo_2Fe "wings" (Mo–Fe = 2.792–2.832 Å) and a non-bonded Fe...Fe distance of 3.334 Å. In addition, the trinuclear clusters $(C_5Me_5)_2.Mo_2(\mu,\eta^2\text{-}S_2)(\mu_3\text{-}S)_2Fe(CO)_2$ and $(C_5Me_5)_2Mo_2\{\mu\text{-}SC(O)S\}(\mu_3\text{-}S)_2Fe.(CO)_5$, containing the metallotriangular Mo_2Fe fragment (Mo–Mo = 2.592 and 2.574 Å and Mo–Fe = 2.777 and 2.826 Å respectively in the first and second triangular clusters) are formed. A distinctive feature of the second cluster is the insertion of the CO molecule in the disulphide bridge present in the initial dimer and in the first triangle (S–S = 2.071 Å).

The formation of the trinuclear cluster $(C_5Me_5)_2Mo_2S_4Mn(CO)_2Cp$ in the reaction of $(C_5Me_5)_2Mo_2S_4$ and $CpMn(CO)_2$.THF has been briefly reported. It probably has the structure of an adduct with the coordination of the $CpMn(CO)_2$ fragment via one sulphide bridge, although the authors do not rule out a structure with the insertion of the Mn atom in the S–S bond.[24]

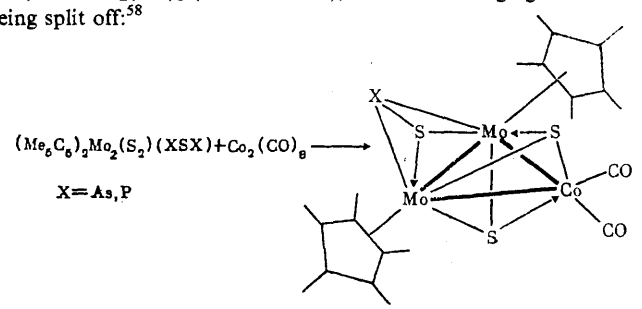
All the isomers of $(Me_nC_5H_{5-n})_2Mo_2S_4$ (n = 0, 1, or 5), including also the insoluble polymers, are converted on treatment with H_2 into the dinuclear tetrabridged complexes $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2.(\mu\text{-}SH)_2$. These complexes are of interest because they contain two types of functional groups: MoSMo with unshared pairs in the sulphur atoms and Mo(SH)Mo with the thiol group SH.[55] The thiol groups in these complexes are readily substituted on treatment with HSR, affording $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2$ (R = Me, Et, Pr^i, or Ph). Accorinng to X-ray diffraction data, the sulphide bridges in the methyl analogue (Mo–S = 2.352 Å) alternate with the mercaptide bridges (Mo–SMe = 2.479 Å), while the Mo(IV) atoms (d^2 electronic configuration) with a 16-electron environment form the Mo=Mo double bond (2.582 Å).

The complex $(MeC_5H_4)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ reacts with $Fe(CO)_5$ in the presence of Me_3NO, combining with two $Fe(CO)_3$ fragments. The cluster $(MeC_5H_4)_2\ Mo_2(\mu_3\text{-}S)_4Fe_2(CO)_6$, which has 66 electrons and the corresponding planar metallic core with a diagonal Mo–Mo bond (2.853 Å) and only two Mo–Fe bonds (2.826 Å) (the sulphide bridges are located over each Mo_2Fe fragment), is obtained. As a result, the metallic core acquires the "metallozigzag" Fe–Mo–Mo–Fe configuration[56] in contrast to the "metallobutterfly" obtained for the C_5Me_5 derivative.

The influence of the nature of the cyclopentadienyl ligands at the Mo atom is also manifested in reactions with $Co_2(CO)_8$. In the case of the $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ isomer, a 60-electron tetrahedral cluster $(C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4Co_2(CO)_2$ is formed.[25] On the other hand, if one begins with $Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$, then the 62-electron cluster $Cp_2Mo_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$, with a "metallobutterfly" core and containing only three sulphur atoms, is formed. As in the $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ cluster described above, one of the sulphur atoms is tetradentate and is located between the Mo_2Co_2 wings (Mo–Mo = 2.646 Å and Mo–Co = 2.640 Å). The other two sulphur atoms are tridentate and are located under the Mo_2Co wings. Each cobalt atom is linked to two CO groups and each Mo atom is linked to the Cp ring.[57]

The $Cp_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2$ cluster, containing four tridentate sulphide bridges and two Ni(CO) fragments, is also of the 62-electron type. It is formed in the reaction of $Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ with $Ni(CO)_2$ and has the "metallobutterfly" Mo_2Ni_2 core (Mo–Mo = 2.829 Å and Mo–Ni = 2.772 Å) with a non-bonded Ni...Ni distance of 2.962 Å.[57]

The insertion of the $Co(CO)_2$ fragment in the S–S bond is observed in the reaction of $(C_5Me_5)_2Mo_2(\mu,\eta^2\text{-}S_2)(\mu\text{-}XSX)$ (X = As or P) with $Co_2(CO)_8$ (toluene 25 °C), one of the bridging X atoms being split off:[58]



According to X-ray diffraction data for the As-containing derivative, the cluster has the Mo_2Co metallotriangular core (Mo–Mo = 2.610 Å and Mo–Co = 2.722–2.725 Å) with tridentate sulphide bridges located above and under the metallotriangle. The AsS μ,η^2-bridging group (As–S = 2.237 Å), which is a 5-electron donor, is located along the periphery of the cluster between the molybdenum atoms. In this situation, the cluster with the Mo_2Co core is an isoelectronic analogue of the $(C_5Me_5)_2Mo_2S_4Fe(CO)_2$ complex described above,[54] containing the 6-electron group μ,η^2-S_2 in combination with the $Fe(CO)_2$ groups having one electron less than the $Co(CO)_2$ fragment.

Among other cyclopentadienyl-containing SHMC with Group VIA metals, we may mention $\{[Cp_2Mo(SMe)_2]_2Ni\}^{2+}(BF_4^-)_2$, obtained from $Cp_2Mo(SMe)_2$ and $Ni(BF_4)_2$.[17] In contrast to the analogous niobium(IV) complex described above (d^1 electronic configuration), in the given molybdenum(IV) complex (d^2 electronic configuration) there are two electrons more. They are apparently found in the antibonding orbitals, which leads to a marked lengthening of the Mo–Ni bonds to 3.39 Å (bond order 0.5).

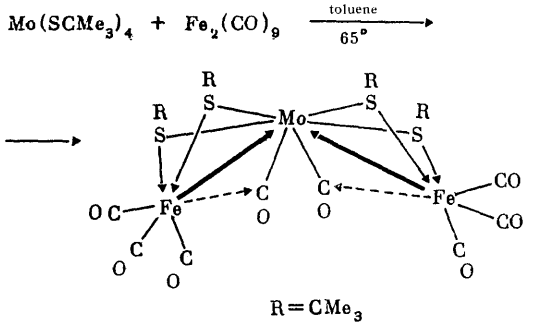
Finally, the cubane-like clusters with the $M_2Co_2(\mu_3\text{-}S)_4$ core (M = Mo or W) (Mo–Mo = 2.788 Å, Co–Co = 2.533 Å, and Mo–Co = 2.680 and 2.672 Å) have been obtained in reactions of the dinuclear molybdenum or tungsten diethyldithiocarbamate sulphides with cobalt carbonyl:[59]

$$(Et_2NCS_2)_2M_2S_4 + Co_2(CO)_8 \xrightarrow{MeCN} [(Et_2NCS_2)(MeCN)M]_2[Co(CO)]_2(\mu_3\text{-}S)_4$$
$$M = Mo, W.$$

In such a 60-electron cluster, the chelating Et_2NCS_2 group and the MeCN molecule occupy three orbitals at the M atom, donating five electrons, i.e. the entire system is similar to the $(CpMo)_2Co_2(CO)_2.(\mu_3\text{-}S)_4$ clusters described above. It has been noted that the MeCN molecule is not coordinated to the initial Mo or W dimers owing to the additional π-bonding to the sulphur atoms (the Mo–S bond length increases from 2.09 to 2.312 Å).

8. Sulphide-bridged heterometallic clusters based on $Mo(SCMe_3)_4$

The trimetallic complex $Mo(\mu\text{-}SCMe_3)_4(\mu\text{-}CO)_2Fe_2(CO)_6$ is formed in the reaction of $Mo(SCMe_3)_4$ with an excess of $Fe_2(CO)_9$. The reaction can be regarded as the addition of two $Fe(CO)_3$ fragments to pairs of SR groups at the Mo(IV) atom with an additional dative Fe–Mo interaction and the incomplete transfer of two CO groups to the molybdenum atom.[60] The molecular core is the almost linear Fe–Mo–Fe metal chain (Mo–Fe = 2.757 Å with an FeMoFe angle of 160.43°) having two bridging $SCMe_3$ groups above each Mo–Fe bond, the FeS_2Mo fragments having the "butterfly" configuration:

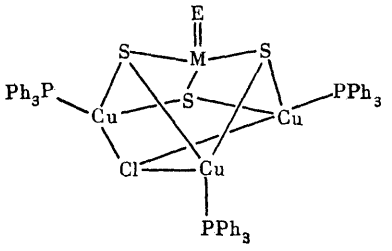


Treatment of $Fe_4S_4(SPh)_4^{2-}$ with $Mo(SCMe_3)_4$ results in transmetallation probably as a consequence of the greater strength of the Mo–Fe bonds compared with Fe–Fe. The $(Me_3CS)MoFe_3S_4.(SPh_2)^{2-}$ dianion was isolated under these conditions. It is reduced by sodium acenaphthenide in the presence of $(NBu_4)Br$ to the salt $(NBu_4)_3[(Me_3CS)MoFe_3S_4(SPh)_3]$ containing a trianion.[61] These cubane-like clusters model the active MoFeS centre of the cofactor of nitrogenase.

9. Sulphide-bridged heterometallic clusters based on the thiometallates MS_4^{2-} (M = Mo or W)

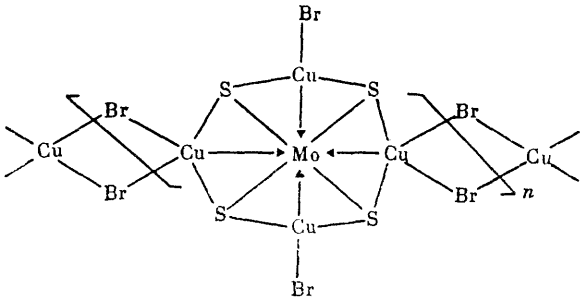
The readily available thiometallate complexes comprising Group VI transition metals, namely MS_4^{2-} (in the main, M = Mo or W), which are isolated as a rule in the form of ammonium or phosphonium salts, are extremely common starting materials for the synthesis of SHMC. Such monomeric anions contain the tetrhedral MS_4 fragment (Mo=S = 2.175 Å [62]). The highly electron-deficient character of M(VI) (d^0 electronic configuration) promotes the formation of dative M ← M′ bonds with the salts of other metals (in their absence, MS_3 and the sulphide of the heterometal are formed readily). Several reviews[63–65] have been devoted to their reactions and here we shall consider only examples of Cu- and Fe-containing complexes whose structure has been confirmed by X-ray diffraction data.

The former are of interest from the standpoint of the antagonism between copper and molybdenum in biological systems, throwing light on the nature of the Cu–Mo–S interaction.[66] The dianions MS_4^{2-} (M = Mo or W) reduce copper to Cu^+ on interaction with Cu^{2+}, forming polymers having the composition $\{[NH_4][Cu(MoS_4]\}_n$[67] or $\{[NH_4][Cu(WS_4)]\}_n$.[68] Discrete molecules with Cu and M (Mo or W) atoms can be obtained by treating $(CN)_nCu_n(MS_4)^{m-}$ with KSPh in acetonitrile. $[PhSCu(S)_2Mo(S)_2]^{2-}$ and $[PhSCu(S)_2Mo(S)_2CuSPh]^{2-}$ were isolated under these conditions. In both cases the molybdenum atoms have a tetrahedral environment and the copper atoms have a planar trigonal environment. Furthermore, Mo ← Cu dative bonds (2.636 Å) are formed.[69] The metal chain in $Et_3PAu(S)_2.Mo(S)_2AuPEt_3$ is constructed analogously (the Mo ← Au bond length is 2.815 Å).[70] The interaction of MS_4^{2-} (or MoS_3^{2-}) with $CuCl_3$ in the presence of PPh_3 in CH_2Cl_2 results in the formation of clusters with a distorted pseudocubane core $(PPh_3)_3Cu_3S_3ClM(E)$ (M = Mo or W; E = S or O):[71]

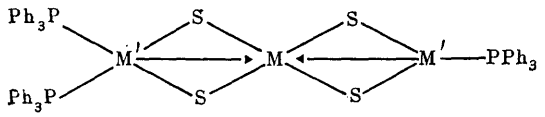


A cluster with the ratio Cu : Mo = 3 : 1 is also formed in the reaction of stoichiometric amounts of CuCl and $(Ph_4P)_2(MoS_4)$. In $(ClCu)_3.MoS_4^{2-}$, two sulphur atoms are bidentate and two are tridentate.[72,73] There is a possibility of the situation where all four sulphur atoms become tridentate. This happens in the cluster $(CuBr)_4MoS_4^{2-}$, which is a one-dimensional polymer.[74] In this polymeric cluster, two *trans*-Cu atoms have a planar-trigonal environment and two

others have a tetrahedral environment (all the metal atoms are then located in a single plane):

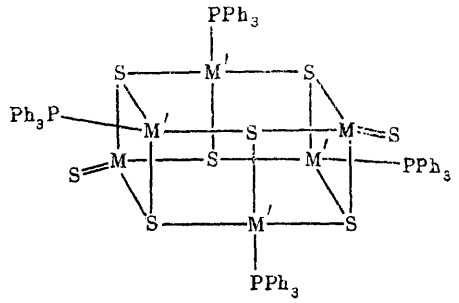


Partial cleavage of the Cu-S-M bridges has been observed[75] when the $[Cu(MS_4)]_n$ and $[Cu_2(MS_4)]_n$ polymers are treated with PPh_3. Complexes with a non-equivalent environment of the copper atoms are then formed. A cluster containing silver atoms of an analogous type has been isolated after the reaction of MS_4^{2-} with $AgNO_3$ in the presence of PPh_3 in CH_2Cl_2:[71]



M=Mo, W M′=Cu(I), Ag(I)

Finally, the bonding of each MS_4 group to other metals occurs in the complexes $(Ph_3P)_4M'_4(MS_4)_2$ (M = Mo or W; M′ = Cu or Ag):[76]

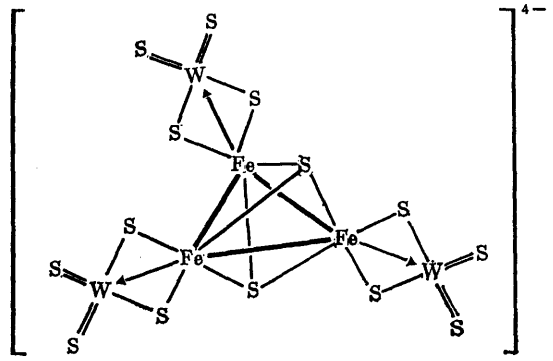


The core of this cluster is a complex polyhedron produced by the binding of two $MS_2M'_2S$ fragments.

The composition of the iron-containing complexes depends on the reactant ratio. For the MS_4^{2-}:$[M']^{2+}$ = 1:1 or 1:2 reactant ratio, the complexes $MoS_4FeCl_2^{2-}$ or $Cl_2FeS_2MoS_2FeCl_2^{2-}$, for example, were isolated,[64] in which the MoS_2 fragment chelates are the iron atom. Reactions of MS_4^{2-} (M = Mo or W) with iron carboxylates[77] and thiolates[78] take place analogously:

$$Fe(OOCMe)_2 + (Et_4N)_2(MS_4) \xrightarrow{MeCN} (MeCOO)_2FeS_2MS_2^{2-},$$
$$Fe(SPh)_4^{2-} + MS_4^{2-} \rightarrow (PhS)_2FeS_2MS_2^{2-}.$$

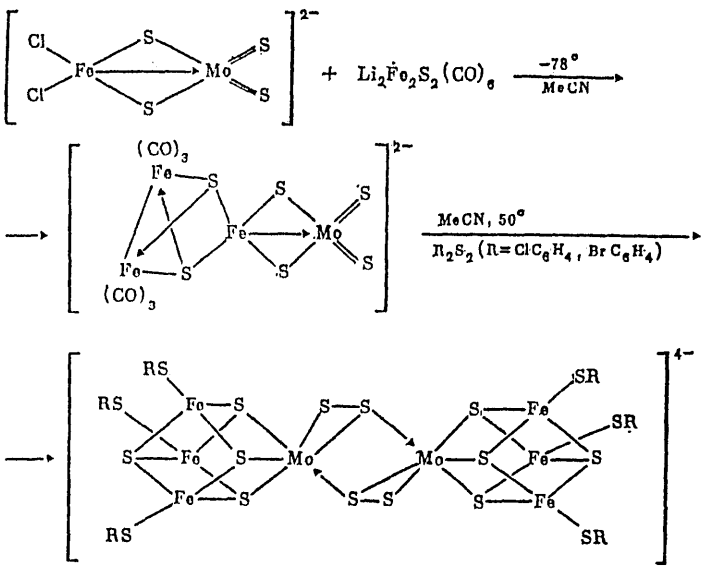
On the other hand, an excess of MS_4^{2-} reacts with various transition metal $[M']^{2+}$ salts, affording the anionic complexes $M'(MS_4)_2^{2-}$ [in particular, $TcO(MoS_4)_2^{2-}$, $(Ph_3P)_2Tc(MoS_4)_2$,[79] $Fe(MoS_4)_2^{2-}$,[80] $(FeMoS_4)_2^{3-}$,[81] $Co(MoS_4)_2^{3-}$,[82] $Co(WS_4)_2^{2-}$, $Fe(WS_4)_2^{2-}$, $Fe(WS_4)_2^{3-}$,[83] and $Fe(WS_4)_2^{4-}$], in which all the metal atoms have a tetrahedral environment made up of sulphur atoms. In the presence of an excess of PPh_4^+ and Et_4N^+ cations, the complex $Fe(WS_4)_2^{2-}$ is converted into the more stable cluster anion $Fe_3W_3S_{14}^{4-}$ with loss of some of the tungsten sulphide fragments.[84,85]



The cluster contains the triangular $Fe_3(\mu_3\text{-}S)_2$ core in which the iron atoms are linked by chelate bonds to three WS_4 fragments via sulphide bridges and have direct dative Fe → W bonds (2.774 Å).[84]

10. MoFe-containing sulphide-bridged heterometallic clusters modelling the active centre of the cofactor of nitrogenase

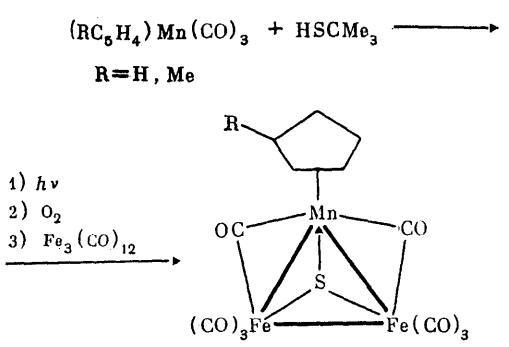
Thiometallate anions are good starting materials for the synthesis of the main types of the Mo–Fe–S clusters modelling the iron-molybdenum centre of the nitrogenase cofactor.[86-88] Such systems are obtained as a rule by the single-stage interaction of simple reactants ($FeCl_3$, NaSR, and MoS_4^{2-}) in methanol. Depending on the reaction conditions and the reactant ratio, three main types of complexes are formed: $Mo_2Fe_6S_8(\mu\text{-}S)(\mu\text{-}SR)_2(SR)_6^{3-}$, $Mo_2Fe_6S_8.(\mu\text{-}SR)_3(SR)_6^{3-}$, and $Mo_2Fe_7S_8(\mu\text{-}SR)_6(SR)_6^{n-}$ (n = 3, 4).[89-96] All these clusters have the structure of two Fe_3MoS_4 cubane-like moieties connected by bridging ligands. The mechanism of the formation of Mo–Fe–S clusters of this type is so far obscure, but it has been possible to achieve a multistage synthesis of compounds of this type from $Cl_2FeMoS_2^{2-}$ and iron carbonyl complexes:[97]



In the intermediate cluster $MoFe_3S_6(CO)_6^{3-}$, the diiron disulphide fragment (Fe–Fe = 2.491 Å) adds to the Fe atom of the initial complex via μ_3-S bridges [Fe–(μ-S) = 2.288 Å, Mo–Fe = 2.762 Å, Mo=S = 2.156 Å, and Mo–(μ-S) = 2.263 Å]. Further treatment of this cluster with the disulphide $(XC_6H_4S)_2$ (X = Cl or Br) affords a cluster with a double cubane-like core in which the molybdenum atoms are linked by two S_2 bridging groups (Mo...Mo = 3.97 Å). This cluster has also been obtained by specific synthesis in accordance with the traditional mechanism from MoS_4^{2-}, $FeCl_2$, Na_2S_2, $(XC_6H_4S)_2$, and NaOMe in methanol.

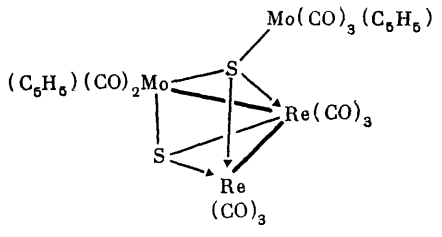
IV. Sulphur-containing group VIIA metal complexes as ligands and the clusters based on them

There are very few sulphur-containing complexes of Group VIIA metals used as cluster-forming agents. One of them is the paramagnetic complex $(C_5R_5)Mn(CO)_2SCMe_3$ (R = H or Me), which has been characterised by X-ray diffraction (for R = Me, the Mn–SR bond length is 2.187 Å).[98] It is probably in fact the cluster-forming agent in the photochemical reaction of $(RC_5H_4)Mn(CO)_3$ with $HSCMe_3$ and subsequent treatment with O_2 and $Fe_3(CO)_{12}$, which resulted in the formation of the cluster $(RC_5H_4)Mn(\mu_3\text{-}S).(\mu\text{-}CO)_2Fe_2(CO)_6$ (R = H or Me):[99]



In this metallotriangular cluster (Mn–Fe = 2.660 and 2.689 Å and Fe–Fe = 2.609 Å), the sulphur atom is located above the plane of the Fe_2Mn triangle (Fe–S = 2.176 Å and Mn–S = 2.206 Å) and the sides of the triangle are linked additionally by bridging CO groups.

Another starting material for the formation of SHMC is the complex $[(CO)_4Re(\mu\text{-}SSnMe_3)]_2$.[100] Its reaction with $CpMo(CO)_3Cl$ in benzene results in the elimination of two moles of $ClSnMe_3$ and three moles of CO and the formation of a tetranuclear cluster in which the initially planar Re_2S_2 fragment is converted into a "butterfly", the electron deficiency in the partially decarbonylated rhenium atoms being compensated by the Mo–Re and Re–Re bonding:



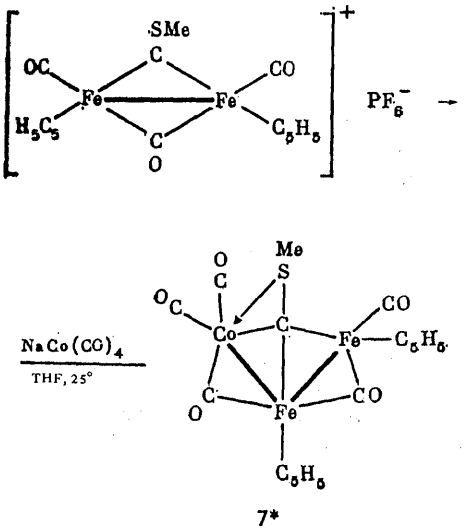
This results in the formation of the Mo–Re–Re "metal chain" (Mo–Re = 2.909 Å and Re–Re = 2.985 Å), above and under the plane of which are located tri- and tetra-dentate bridging sulphur atoms [the latter forms a σ-bond with the $Mo(CO)_3Cp$ group[101]].

A cluster containing three different metal atoms can be obtained by using $M(SAsMe_3)(CO)_3(PMe_3)_2$ (M = Mn or Re) as ligands in relation to $FeCo(\mu\text{-}AsMe_2)(CO)_7$.[102] This leads to the formation of the trinuclear cluster $(PMe_3)_2(CO)_3M(\mu\text{-}SAsMe_2)Co(CO)_3(\mu\text{-}AsMe_2).Fe(CO)_4$ containing the M–Co–Fe (M = Mn or Re) metal chain.[103]

V. Clusters based on sulphur-containing group VIII metal complexes

Among these compounds, the greatest number of SHMC have been obtained from sulphur-containing iron complexes. For example, it has been shown[104] that treatment of 1/2 of a mole of $Rh_2(CO)_4Cl_2$ with $CpFe(CO)_2SR$ leads to the formation of the trinuclear linear cluster $[Cp(CO)_2Fe]_2(\mu\text{-}SR)_2Rh^+$.

A cluster with two iron atoms and a cobalt atom is formed in the reaction of the ionic complex $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CSMe)Fe(CO)Cp^+$ with $NaCo(CO)_4$ in THF at 25 °C:[105]



7*

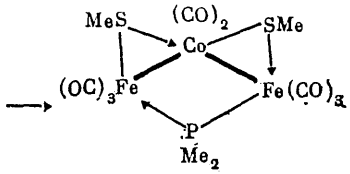
The cluster has a core consisting of a non-linear metal chain with short Fe–Co (2.500 Å) and Fe–Fe (2.537 Å) distances. The sulphur atom in this compound plays the role of a stabilising agent, building up the coordination sphere of the cobalt atom (Co–S = 2.313 Å) to an 18-electron shell.

The dinuclear thiolatoiron carbonyl complexes $Fe_2(\mu\text{-}SR)_2(CO)_6$, which have already been known for about 30 years, have themselves proved to be inert in relation to other metal carbonyls [for example, $Fe_2(\mu\text{-}SMe)_2(CO)_6$ does not react with $Co_2(CO)_8$ even under severe conditions].[106] However, after preliminary treatment with $HPMe_2$,

the subsequent reaction with $Co_2(CO)_8$ proceeds in accordance with the scheme[107]

$$Fe_2(SMe)_2(CO)_6 \xrightarrow{PMe_2H} Fe_2(SMe)_2(CO)_5(PMe_2H) \xrightarrow{Co_2(CO)_8}$$

$$\longrightarrow (CO)_3Fe(\mu\text{-}SMe)_2Fe(CO)_2(\mu\text{-}PMe_2)Co(CO)_3 \longrightarrow$$

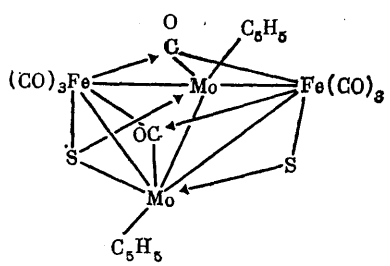


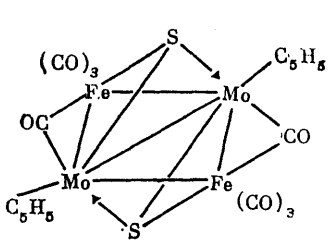
The same product has been obtained in the reaction of $Fe_2(SMe)_2.(CO)_6$ with $(C_3H_5)Co(CO)_3$ in the presence of PMe_2H.[108]

The commonest starting material for the synthesis of iron-containing SHMC is the complex $S_2Fe_2(CO)_6$, first synthesised by Hieber and Gruber.[109] According to X-ray diffraction data,[110] the two iron atoms in this complex are separated by a short distance of 2.552 Å and form together with the disulphide fragment (S–S = 2.007 Å) a distorted Fe_2S_2 tetrahedron in which the angle between the planes of the Fe_2S triangles is 54°, the three Co groups at each iron atom being directed away from the S_2 group. The latter group is the site of attack by the metal-containing $M'L_n$ reagent, which donates electrons to the LUMO antibonding in relation to the S–S bond.[111,112]

On interaction of $S_2Fe_2(CO)_6$ with $[CpCr(CO)_3]_2$, the cluster $Cp_2Cr_2Fe_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$ with the "metallobutterfly" Cr_2Fe_2 core was isolated. When the cluster is produced, the Fe–Fe bond is ruptured and the CO group at each Cr atom acquires tridentate-bridging character and is bound to two iron atoms.[113]

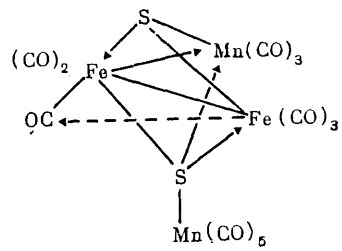
A "butterfly" cluster of analogous composition, containing molybdenum atoms, has been obtained by the reaction of $S_2Fe_2.(CO)_6$ with $Cp_2Mo_2(CO)_4$.[114] Later it proved possible to isolate this isomer with a planar disposition of the four metal atoms and the bridging CO groups between the iron and molybdenum atoms:[115]





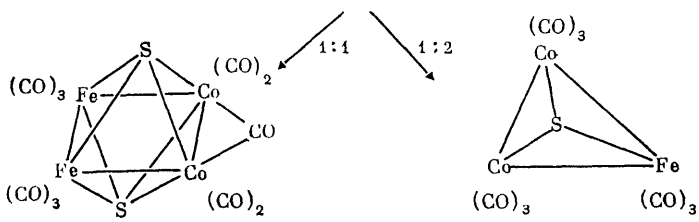
The tetranuclear clusters $Mn_2Fe_2S_2(CO)_{14}$, having a complex structure, is formed in the reaction of $S_2Fe_2(CO)_6$ with $Mn_2(CO)_{10}$. It is possible to identify in it the MnFeFe metal chain with a semibridging CO group between the iron atoms. The tetradentate bridging sulphur atom, located above the $MnFe_2$ plane, is σ-bonded to the manganese atom of the $Mn(CO)_5$ group:[116]

$$S_2Fe_2(CO)_6 + Mn_2(CO)_{10} \xrightarrow[h\nu]{THF}$$



The reaction of $S_2Fe_2(CO)_6$ with $Co_2(CO)_8$ is equimolar amounts at 20 °C gives rise to the cluster $Fe_2Co_2(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_{10}$ with a square planar metallic core. The "capping" sulphur atoms in the cluster are involved in a tetradentate coordination and the cobalt atoms are linked in addition to the CO group.[117] The reaction of $S_2Fe_2(CO)_6$ with an excess of $Co_2(CO)_8$ at room temperature takes place with the dissociation of the S–S and Fe–Fe bonds, giving rise to the trinuclear cluster $FeCo_2(\mu_3\text{-}S)(CO)_9$.[118] The yield of the cluster increases on UV irradiation.[106] According to X-ray diffraction data, this diamagnetic 48-electron cluster has the Co_2Fe triangular metallic core with equalised M–M distances (2.550 to 2.556 Å) over which is located the tridentate sulphur atom (M–S = 2.152–2.164 Å):[118]

$$S_2Fe_2(CO)_6 + Co_2(CO)_8$$



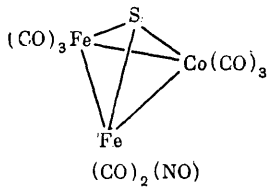
The dissociation of $S_2Fe_2(CO)_6$ into two fragments is also observed in the reaction with $[CpNi(CO)]_2$, which is isolobal in relation to $Co_2(CO)_8$. This entails the formation of the metallotriangular cluster $Cp_2Ni_2Fe(CO)_3(\mu_3\text{-}S)$.[119] According to Bogan et al.,[120] the formation of clusters with the Fe_2M_2 core is a common stage in the reactions of the dinuclear metal complexes with $S_2Fe_2(CO)_6$, which is followed by processes involving the elimination and addition of the ML or S fragments, ensuring the isolation of a wide variety of structures.

The $CpRh(\mu_3\text{-}S)_2Fe_2(CO)_6$ cluster has been obtained in the form of two isomers (a metal chain with a central or terminal rhodium atom) by treating $S_2Fe_2(CO)_6$ with $CpRh(CO)_2$ in boiling hexane.[121] Finally, trinuclear clusters without Fe–M bonds have been obtained by the reaction of $S_2Fe_2(CO)_6$ with $L_2M(C_2H_4)$ (L = PPh_3; M = Pt

or Pd).[122] The structure of the sulphide-bridged clusters $(PPh_3)_2$.$M(\mu_3\text{-}S)_2Fe_2(CO)_6$ (M = Pt or Pd) has been proposed on the basis of X-ray diffraction data for the selenium-containing analogue $(PPh_3)_2Pt(\mu_3Se)_2Fe_2(CO)_6$ (Fe–Fe = 2.533 Å and Pt–Fe = 3.45 Å).[122] A palladium-containing complex is also obtained in the reaction of $S_2Fe_2(CO)_6$ with $Pd(PPh_3)_4$ via a transmethylation reaction–the substitution of the $Fe(CO)_3$ fragment in $Fe_3(CO)_9(S)_2$ on treatment with $(PPh_3)_2PdCl_2$ and elimination of $PdCl_2$. The cluster contains no Fe...Pd bonds and the Pd atom has a square planar environment made up of phosphorus atoms (Pd–PO = 2.313 and 2.348 Å) and sulphur atoms (Pd–S = 2.305 and 2.326 Å). The PdS_2 plane is perpendicular to the Fe–Fe bond (2.504 Å).[123]

1. Reactions of iron-containing sulphide-bridged heterometallic clusters

In the reaction with $THF.Cr(CO)_5$, the $FeCo_2S(CO)_9$ cluster is capable of coordinating an additional $Cr(CO)_5$ fragment via a μ_4-sulphide bridge.[124] The mixed-ligand clusters $Fe_3(\mu_3\text{-}S)(\mu_3\text{-}ER)$.$(CO)_9$ (R = alkyl or aryl and E = P or As) react analogously with $(THF)M(CO)_5$ at 0 °C.[125] It has been shown by X-ray diffraction that the $Fe_3S(ER)$ core with ER = $PCMe_3$ remains unchanged compared with the initial cluster and the $Cr(CO)_5$ or $W(CO)_5$ fragment remains on the periphery of the molecule, adding on via a fairly long S → M bond (Cr–S = 2.428 Å and W–S = 2.547 Å).[126] The syntheses of chiral iron-containing SHMC are of special interest. Thus $Fe_2Co(CO)_9(\mu\text{-}S)^-$ has been isolated in the form of the salt with the NEt_4^+ anion on reaction of $Co_2(CO)_8$ and $Fe_3(CO)_9S^{2-}$ in CH_2Cl_2. The anion has a triangular metallic core with a "capping" sulphur atom and is converted into a neutral form on nitrosylation as a result of acidification in the presence of the nitrite ion:[127]

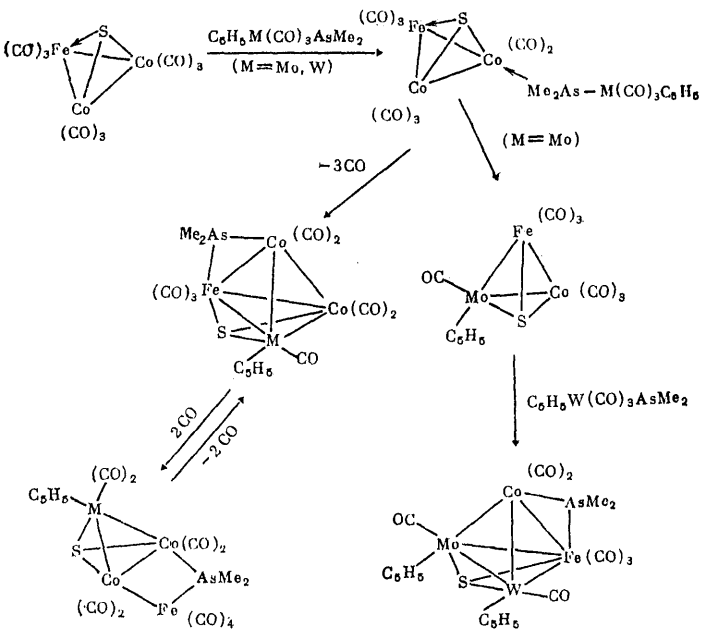


A second pathway leading to the synthesis of chiral clusters involves the formation of tetrahedra with sulphide groups at the vertices, at the base of which there is a triangle with three different metal atoms. Such clusters were first obtained[128] in 1978 by the specially developed "transmethylation" reaction of cobalt-containing clusters on treatment with dimethyl arsenide complexes of molybdenum, tungsten, and iron.[128] The cluster $CpMo(CO)_2(\mu_3\text{-}S)FeCo$.$(CO)_6$ was synthesised in this way. The substitution of one CO group at the Co atom in this cluster by the chiral ligand (*R*)-PMePrPh affords the diastereoisomers of the cluster $CpMo(CO)_2Co(CO)_2$(PMePrPh) $(\mu_3\text{-}S)Fe(CO)_3$, which were separated by crystallisation [the (–)-(*R*)-isomer with m.p. 119 °C is less soluble, while the (+)-(*S*)-isomer with m.p. 133 °C is readily soluble]. The corresponding enantiomers were then obtained by treatment with CO under conditions where phosphine was bound by methyl iodide.[129]

After transmethylation, intermediates were also isolated in which the $AsMe_2$ fragment is present as a bridging group, for example, $FeCo_2S(CO)_8$–$AsMe_2$–$MCp(CO)_3$ (M = Mo or W). The subsequent elimination of CO leads to the metallotetrahedral clusters $FeCo_2M(\mu_3\text{-}S)(\mu\text{-}AsMe_2)Cp(CO)_8$, which can in their turn combine irreversibly with two molecules of CO, the process being accompanied by the dissociation of two bonds, Fe–M and Fe–Co, whereupon the new system $CpMFeCo_2(\mu\text{-}AsMe_2)(\mu_3\text{-}S)(CO)_{10}$ (M = Mo or W) is generated.[130]

On the other hand, a cluster with four atoms of different metals was obtained for the first time with the aid of analogous reaction from the $FeCoMo(\mu_3\text{-}S)Cp(CO)_8$ cluster described above[131] (see below).

Clusters in which the iron atom has been replaced by a ruthenium atom, for example, $RuCo_2(CO)_9(\mu_3\text{-}S)$ obtained by the reaction of $Co_2(CO)_8$ with $Ru_3(CO)_{12}$ in the presence of EtSH with the reactant ratios 3 : 1 : 3.5 in an autoclave under a pressure of H_2 and CO (60 and 140 atm respectively), react similarly.[132] Treatment with the organometallic arsines $Me_3AsM(CO)_3Cp(L)$ leads to the formation of the clusters $RuCo_2(\mu_3\text{-}S)(CO)_{9-n}AsMe_2M(CO)_3Cp_n$ (M = Cr, Mo, or W; n = 1, 2), which in the case where n = 1 exists in the form of two isomers in which the ligand L is linked either to the cobalt atom or to the ruthenium atom. On heating the first isomer in cyclohexane in a CO atmosphere (T = 75–85 °C), the $Co(CO)_3$.$AsMe_2$ fragment is split off and the chiral clusters $(\mu_3\text{-}S)RuCoMCp$.$(CO)_8$ are formed. They have also been obtained by direct transmethylation in the reaction of $SRuCo_2(CO)_9$ with $[CpM(CO)_3]_2$ (M = Cr, Mo, or W).[132] The replacement of one CO group by optically active phosphines (L') yielded the corresponding diastereoisomers $CpMoRuCo(\mu_3\text{-}S)(CO)_7L'$, in which L' is linked to the cobalt atom:[132]

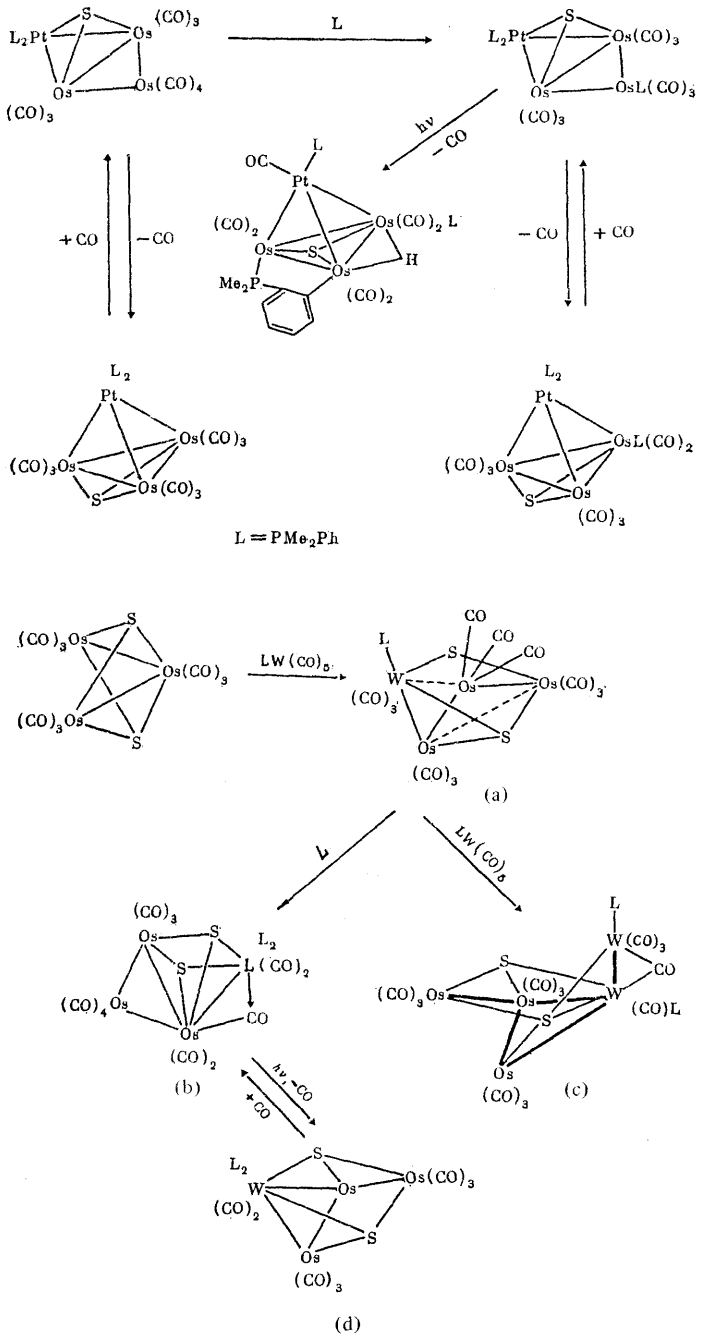


2. Sulphide-bridged heterometallic clusters based on trinuclear osmium clusters

The use of the trinuclear osmium cluster $Os_3(\mu_3\text{-}S)(CO)_{10}$ as a metal-containing ligand in the photochemical reaction with $W(CO)_6$ in hexane, affording the cluster $(CO)_9Os_3(\mu_4\text{-}S)W(CO)_5$, has been described.[133] The $W(CO)_5$ group is then located on the periphery of the molecule (W–S = 2.550 Å) and the structure of the Os_3S core hardly changes compared with the initial cluster (Os–Os = 2.804

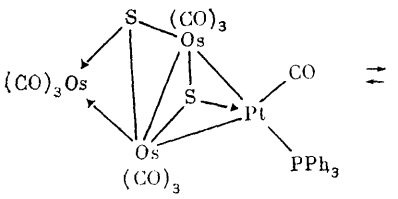
and 2.895 Å respectively). The cluster $Os_3(CO)_{10}(\mu_3\text{-}S)$ reacts readily with $Pt(C_2H_4)(PMe_2Ph)_2$ at 20 °C, forming four clusters: $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$, $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$, $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$, and $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$.[134] The first and second clusters with a planar metallic $PtOs_3$ core (Pt–Os = 2.768 and 2.838 Å and Os–Os = 2.869 and 2.833–2.907 Å respectively) are isoelectronic and have similar geometries, the first cluster being converted into the second on treatment with phosphine. They are readily decarbonylated, affording the third and fourth isoelectronic clusters, which contain the metallotetrahedral $PtOs_3$ core (Pt–Os = 2.740, 2.766, and 2.853 Å and Os–Os = 2.770, 2.896, and 3.064 Å) with a tridentate sulphur atom under the Os_3 triangle.

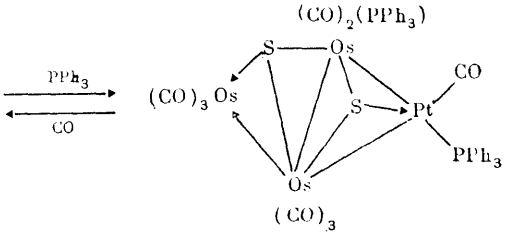
Prolonged photolysis of the second cluster leads to the formation of a cluster having a bridging hydride atom over the Os_3 triangular base of the cluster (Pt–Os = 2.684, 2.806, and 2.816 Å and Os–Os = 2.837, 2.930, and 2.972 Å). One of the phosphine ligands then becomes a bridge between two osmium atoms as a result of the formation of the Os-P and Os–C_6H_4 bonds.[134] The cluster $Os_3(CO)_9(\mu_3\text{-}S)_2$, containing two sulphide bridges, gives rise to four clusters in the formally analogous reaction with the phosphine-tungsten carbonyl complex $W(CO)_5L$ (L = PMe_2Ph); $LWOs_3(\mu_3\text{-}S)_2(CO)_{12}$ (a), $L_2WOs_3(\mu_3\text{-}S)_2(CO)_{12}$ (b), $L_2WOs_3(\mu_3\text{-}S)_2(CO)_{11}$ (c), and $(LW)_2Os_3(\mu_3\text{-}S)(\mu_4\text{-}S)(\mu\text{-}CO)(CO)_{13}$ (d):[135]



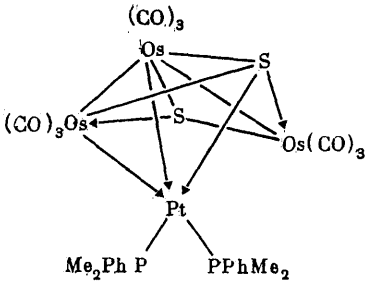
In three of them, namely (a), (c), and (d), Os_3W "metallobutterfly" core is produced to some extent with the axial Os–Os distances of 2.963, 2.923, and 2.924 Å respectively for (a), (c), and (d) and with tridentate bridging sulphur atoms located between the Os_3 and Os_2W "wings". In the 64 electron cluster (a), the two opposite M–M bonds in the "wings" are loosened under these conditions (M–Os = 3.050 and 3.054 Å). In the isoelectronic cluster (c), one WOs_2 wing contains non-equivalent W–Os bonds (2.814 and 3.016 Å), while in the second wing one Os–Os bond is missing (2.829 and 3.813 Å). Finally, in the cluster (d) the overall geometry of the "butterfly" core is close to that in (c), but the W atom is the bound to the second tungsten atom via a short bond (2.711 Å) supported by the bridging CO group, while one of the bridging sulphur atoms becomes tetradentate. In this situation, the Os–W distance (in the Os_2W wing) is shortened to 2.703 Å (the second distnce is 2.991 Å). On the basis of the analysis of the geometry of NMR data, the authors postulate the existence of the cluster (d) in two isomeric forms with short W=W and Os=W bonds. The fourth cluster (b) has a planar geometry of the rhombic Os_3W metallic core with short Os–Os (2.895 and 2.887 Å) and Os–W (3.044 Å) bonds and a long W...Os distance (3.612 Å). In this case, the sulphur atoms, remaining tridentate, bind two osmium atoms and a tungsten atom.[135]

The disulphide cluster $Os_3(CO)_9(\mu_3\text{-}S)_2$ also reacts with $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$, forming the isoelectronic clusters $PtOs_3(CO)_{11-n}\cdot(PPh_3)_nX_2$ (n = 1,2), which are interconverted on treatment with phosphine or Co respectively:[136]





Both clusters contains the planar Os_3Pt metallic core with a metallotriangular Os_2Pt fragment (Os–Pt = 2.858–2.905 and 2.868–2.904 Å and Os–Os = 2.990 and 2.998 Å respectively) and one Os atom bound to Os_2Pt via a single direct Os–Os bond and one Os–S bond (Os–Os = 2.826 and 2.819 Å and Os–S = 2.399 and 2.403 Å respectively).[136] If PPh_3 in the platinum complex is replaced by PMe_2Ph, then both phosphine ligands in the Os–Pt-containing cluster $(PMe_2Ph)_2PtOs_3(\mu_3\text{-}S)(\mu_4\text{-}S)(CO)_9$ are bound to the Pt atom, and are non-equivalent:[137]



Although the platinum atom forms strong bonds only with the two neighbouring Os atoms (Os–Pt = 2.789 and 2.936 Å), the migration of Pt over all Os atoms is observed (according to NMR data) and the Pt–(μ_4-S) bond is always retained.[137]

3. Sulphide-bridged heterometallic clusters based on platinum-containing complexes

The "butterfly" Pt_2S_2 core is produced in the complex $(S)_2Pt_2L_4$ (L = PPh_3),[138] but here there are neither S–S (S...S = 3.1 Å) nor Pt–Pt bonds.[139] The platinum(II) atoms then have the traditional square planar environment made up of two sulphur atoms and two phosphorus atoms. As a result, the phosphine ligands are directed away from the sulphide bridges and do not prevent the coordination of the metal atoms to the latter.

Chelate coordination solely via the sulphide bridges without the formation of new M–M bonds has been observed when $L_4Pt_2(\mu\text{-}S)_2$ was used as the metal-containing ligand. The complex reacts with various mononuclear palladium compounds and affords, depending on the reaction conditions, SHMC containing between 3 and 6 nuclei.[139] The Scheme overleaf also indicates the products of the reactions of $L_4Pt_2(\mu\text{-}S)_2$ with mecury[139] and silver[140] compounds. According to X-ray diffraction data, the pentanuclear cluster $L_8Pt_4(\mu_3S)_4Pd^{2+}$ (L = PPh_3) contains no M–M bonds (M...M is greater than 3.15 Å). The palladium atom then has a square planar environment made up of four sulphur atoms (Pd–S = 2.348 Å and Pt–S = 2.344–2.351 Å, as a result of which all five metal atoms are located in the same plane (the average deviation is ±0.088 Å):[139]

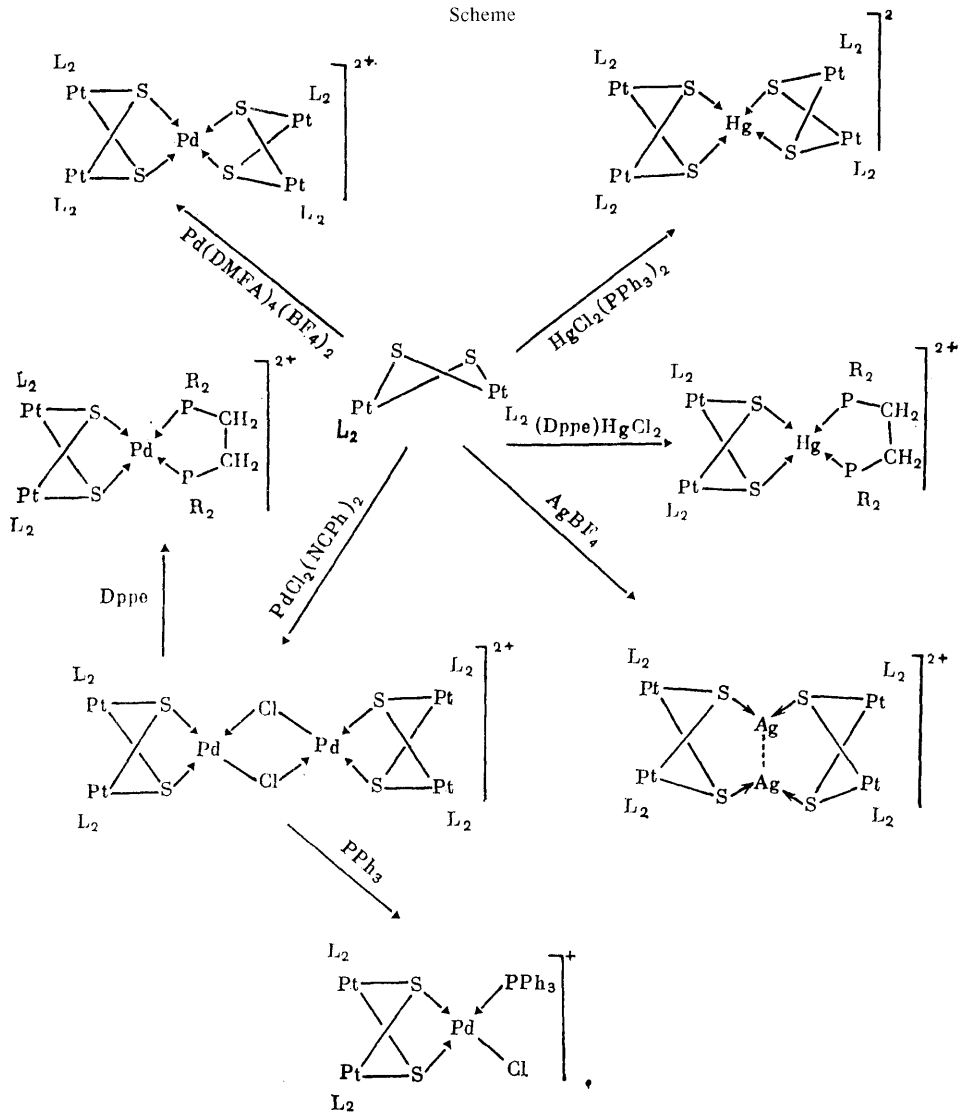
In the hexanuclear $Ag_2Pt_4(\mu_3\text{-}S)_4L_8^{2+}$, the two $L_4Pt_2S_2$ fragments (Pt...Pt = 3.278 and 3.350 Å) fragments are linked by two silver atoms (in a quare-trigonal environment made up of sulphur atoms) (Ag–S = 2.381–2.399 Å and Pt–S = 2.350–2.374 Å), which are separated by a fairly short distance (2.815 Å). The Ag...Pt distances of 3.450–3.905 Å imply the absence of bonds between these atoms.[140]

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Scheme



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