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DISULFUR COMPLEXES

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A. INTRODUCTION

(i) Background

Metal complexes of diatomic species are of academic, biological and catalytic interest. Complexes of stable diatomic ions and molecules (e.g. O_2, N_2, CO, NO, CN^-) are well known and have been extensively studied. Much less is known about metal complexes containing Se_2 [1–6], Te_2 [7], P_2 [8], As_2 [9] and S_2 [10], the subject of this review. In recent years a number of metal complexes containing one or more coordinated S_2 units have been prepared and rigorously characterized by X-ray structure determination, vibrational spectroscopy and other physical methods. It is now clear that metal complexes with S_2 units can be formed for many metals under a variety of conditions and that coordinated S_2 ligands exhibit a rich chemistry.

This review provides the first comprehensive summary of this relatively novel but rapidly growing area of chemistry. The emphasis is on molecular complexes. Solid-state structures with S_2 moieties have been described elsewhere [10a], and only new results and those which provide additional understanding of disulfur ligands will be considered here. Complexes of other $S_x (x \geqslant 3)$ units are also outside the scope of this review. The chemistry and bonding in such complexes is considerably different from that in disulfur complexes [11].

It is hoped that this review of disulfur complexes will be pedagogically useful, will stimulate further research and provide a framework for assessing the possible significance of such complexes in biochemistry and in catalytic reactions of industrial importance such as the desulfurization of oil and coal.

(ii) Biochemical implications

There is as yet no definitive evidence for the presence of disulfur complexes in biological systems. However, it has been suggested that the reaction of xanthine oxidase with cyanide to yield thiocyanate and the inactive desulfo form of the enzyme involves abstraction of a sulfur atom from a disulfur complex [12] or from a persulfido group [13]. Another biochemical reaction which may involve disulfur complexes is the oxidation of sulfhydryl (SH) groups to a disulfur (S–S) group; this oxidation is still poorly understood [14]. The widespread occurrence of metal—sulfur clusters in electron transfer proteins and the growing number of known disulfur compounds have led Vergamini and Kubas to suggest that disulfur units may occur in some natural metal–sulfur clusters. Such units would not be easily detected from analytical data because of the difficulty in obtaining accurate metal: sulfur ratios for proteins [15].

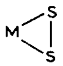
(iii) Nomenclature

A variety of names has been used for the S_2 unit when coordinated to metals, including: persulfido, disulfido and disulfur. Persulfido implies an S_2^{2-} unit and emphasizes the similarity to peroxide complexes. Disulfido is the recommended name for the S_2^{2-} ligand. However, this name is also frequently used for complexes which contain two sulfido groups but no S–S bond. The name disulfur clearly implies an S–S bond and is consistent with the recommended nomenclature for diatomic molecules (e.g. N_2 and O_2) coordinated to transition metals. The name disulfur is used throughout this review to indicate an S_2 unit coordinated to transition metals. The name does not imply any particular charge distribution or formal oxidation state for the ligand. The probable charge on the disulfur ligand in complexes is discussed in subsequent sections.

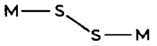
B. STRUCTURAL CHEMISTRY

(i) Structural variety

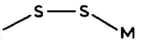
The known disulfur complexes show an astonishing variety of structures. This variety results from extension of the fundamental structures Ia (side-on coordination) and IIa and IIb (*cis* and *trans* end-on bridging coordination) which are known for dioxygen complexes [16,17] by using the remaining lone pairs of electrons on sulfur to coordinate additional metal atoms.



Ia



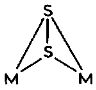
IIa(*trans*)



IIb (*cis*)

Such coordination of additional metal atoms occurs for all three fundamental structural types (Ia, IIa and IIb), and representative examples of all of the known structures are summarized in Table 1. In contrast to dioxygen, end-on coordination of a disulfur ligand to a single metal atom to give a terminal MS_2 moiety is unknown.

Another type of structural unit found in many disulfur–metal cluster compounds is III, in which both sulfur atoms of the disulfur ligand are bonded to each of two metal atoms.

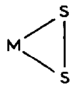
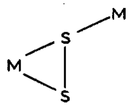
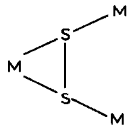
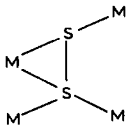
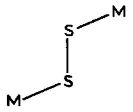
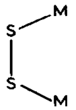
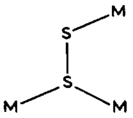
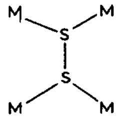
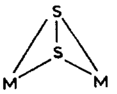
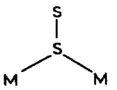


III

The S–S bond is orientated approximately normal to the metal–metal vector.

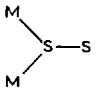
TABLE 1

Typical geometries of disulfur complexes

Structural type	Example	d(S–S) (pm)	Ref.
Ia 	$[\mathrm{Ir(dppe)_2(S_2)}]^+$	207	3, 18
Ib 	$[\mathrm{Mo_4(NO)_4(S_2)_5S_3}]^{4-}$	205	19
Ic 	$\mathrm{Mn_4(S_2)_2(CO)_{15}}$	207	20, 21
Id 	$\mathrm{Mn_4(S_2)_2(CO)_{15}}$	209	20, 21
IIa 	$[\mathrm{(NH_3)_5Ru(S_2)Ru(NH_3)_5}]^{4+}$	201	22, 23
IIb 	$\mathrm{Cp_2Fe_2(S_2)(SEt)_2}$	202	24, 25
IIc 	$\mathrm{Cp_4Co_4(S_2)_2S_2}$	201	26
IId 	$\{\mathrm{SCo_3(CO)_7}\}_2\mathrm{(S_2)}$	204	27, 28
III 	$[\mathrm{Mo_2(S_2)_6}]^{2-}$	204	29, 30
IV 	$\mathrm{Cp'_2Cr_2(S_2)_2S}$[a]	210	31

[a] Cp′ = $\mathrm{Me_5Cp}$.

Very recently a new type of bridging disulfur ligand was discovered in which two metal atoms are attached to the same sulfur atom of the ligand (structure type IV).



IV

(ii) *Complexes with type I structures*

Complexes with type I structures are listed in Table 2 along with their S–S distances and S–S vibrational frequencies. The most common mode of coordination of disulfur is structure type Ia in which the disulfur ligand occupies two coordination sites of the metal atom. One example of this type of binding is the structurally characterized complex $[Ir(dppe)_2(S_2)]Cl$ (**1**)

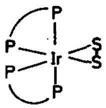
TABLE 2

Disulfur complexes with side-on coordinated ligands (type I)

Complex	Type	*d*(S–S) [a] (pm)	*ν*(S–S) [a] (cm^{-1})	Color	Ref.
$[Ir(dppe)_2(S_2)]^+$	Ia	207	528 [g]	Orange	3, 18
$[Rh(dmpe)_2(S_2)]^+$	Ia	–	525	Orange	3
$RhL1(S_2)Cl$ [b]	Ia	–	546	Orange	32, 33
$Os(CO)_2(PPh_3)_2(S_2)$	Ia	–	–	Orange	4, 34
$[Rh(vdiars)_2(S_2)]^+$ [c]	Ia	–	554	Red-brown	35
$[Rh(L2)_2(S_2)]^+$ [d]	Ia	–	–	Brown	36
$[MoO(S_2)_2(mtox)]^{2-}$ [e]	Ia	201	530	Dark red	37, 38
$MoO(S_2)(dtc)_2$ [f]	Ia	202	558	Blue	39, 40
$Cp_2Mo(S_2)$	Ia	–	536	Red	41
$Cp_2Nb(S_2)Cl$	Ia	–	540	Red	42
$Cp_2Nb(S_2)Me$	Ia	201	540	Orange	43, 44
$[Mo_2O_2S_2(S_2)_2]^{2-}$	Ia	208	510	Red-orange	45, 46, 47
$[Mo_2S_4(S_2)(S_4)]^{2-}$	Ia	207	–	Red-violet	48
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	Ia	204	536 [g]	Red	19
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	Ib	205	550 [g]	Red	19
$Cp_2Fe_2(S_2)_2CO$	Ib	199	–	Green	49
$Mn_4(S_2)_2(CO)_{15}$	Ic	207	–	Red	20, 21
$Mn_4(S_2)_2(CO)_{15}$	Id	209	–	Red	20, 21

[a] Mean value. [b] $L1 = PPh(CH_2CH_2CH_2PPh_2)_2$. [c] $vdiars = Ph_2AsCHCHAsPh_2$. [d] $L2 = R_2PNHPR_2$. [e] $mtox = O_2CCOS^{2-}$. [f] $dtc = S_2CNPr_2^-$. [g] Ref. 50.

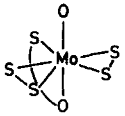
[3,18] whose dioxygen analogue exhibits a similar structure [51]. The Ir atom is in a distorted octahedral environment, as would be expected for a six-coordinate metal with a d^6 electron configuration. Structurally similar



(1)

complexes are formed by other Group VIII metals, e.g. $[Rh(dmpe)_2(S_2)]Cl$ [3], $RhL(S_2)Cl$ [$L = PPh(CH_2CH_2CH_2PPh_2)_2$] [32,33], $Os(CO)_2(PPh_3)_2(S_2)$ and $Ru(CO)_2(PPh_3)_2(S_2)$ [4,34], $[Rh(vdiars)_2(S_2)]X$ (vdiars = $Ph_2AsCHCHAsPh_2$; $X = Cl, PF_6$) [35] and $[Rh(R_2PNHPR_2)_2(S_2)]X$ ($X = Cl, PF_6$) [36].

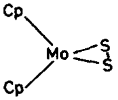
Higher coordination numbers are found for complexes of the early transition elements. In $Cs_2[MoO(S_2)_2(C_2O_3S)]$ (**2**) the Mo atom adopts a pentagonal bipyramidal coordination geometry with the S atoms of the disulfur ligand and of the thiooxalate ligand in the pentagonal plane [37,38].



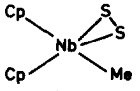
(2)

Pentagonal bipyramidal coordination of the Mo atom also occurs in $MoO(S_2)(dtc)_2$ [39,40]. Again the disulfur ligand is found in the equatorial plane.

High coordination numbers of the central metal atom often occur for type I disulfur complexes. For example, the complex $Cp_2Mo(S_2)$ (**3**) [41] has an effective formal coordination number of eight for the Mo atom and is the disulfur analogue of the well known molybdocene dichloride Cp_2MoCl_2. In $Cp_2Nb(S_2)Cl$ [42] the Nb atom has a formal coordination number of nine. The unusually short S–S distance of 170 pm originally reported for this complex is an artifact of disorder in the crystal structure. Redetermination of the structure gives a longer S–S distance [38]. An X-ray structure determination for the related compound $Cp_2Nb(S_2)Me$ (**4**) [43,44] shows an S–S distance of 201 pm.



(3)



(4)

Several binuclear Mo(V) complexes contain type Ia disulfur ligands. Fig. 1

shows the structure [45,46] of the anion in $(NMe_4)_2[Mo_2O_2S_2(S_2)_2]$. The central $\{MoO(\eta^2\text{-}S)_2MoO\}^{2+}$ structural unit has the Mo=O groups in *syn* stereochemistry [52], as is common with bidentate ligands [53]. There is a metal–metal bond between the Mo atoms [d(Mo–Mo) = 283 pm] [46,54]. It is interesting to note that with NMe_4^+ as the cation both of the S_2 ligands are asymmetrically bonded to the Mo atoms (Mo–S = 242.4, 243.2, 238.3, 239.0 pm) [45,46], whereas with NEt_4^+ as the cation the bonding of the S_2 ligands is much more symmetric (Mo–S = 238.1–240.9 pm) [47]. Replacement of the Mo=O group by the Mo=S group yields structurally similar complexes [48,55] which contain one S_2 ligand and one S_4 ligand [48]. The corresponding complex with two S_4 ligands also exists [55].

Disulfur ligands of structure type Ib are formed in the interesting compound $(NH_4)_4[Mo_4(NO)_4(S_2)_5S_3] \cdot 2\,H_2O$ (Fig. 2) [19] which contains sulfur atoms in five different bonding situations. Four of the five disulfur ligands unsymmetrically bridge pairs of Mo atoms (structure type Ib) and one disulfur ligand is side-on coordinated to a single Mo atom (structure type Ia). The complex also contains three sulfido ligands. Two sulfido ligands bridge groups of three Mo atoms, while one sulfido ligand is coordinated to all four Mo atoms. The complex contains no metal–metal bonds. Similar unsymmetrical type Ib coordination of disulfur occurs in $Cp_2Fe_2(S_2)_2(CO)$ [49].

Structure types Ic and Id (Table 1) in which the disulfur ligand is coordinated to three and four metal atoms, respectively, both occur in $Mn_4(S_2)_2(CO)_{15}$ (**5**) [20,21]. Neither the S–S distances nor the Mn–S dis-

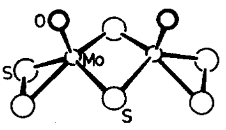


Fig. 1. Structure of the $[Mo_2O_2S_2(S_2)_2]^{2-}$ ion.

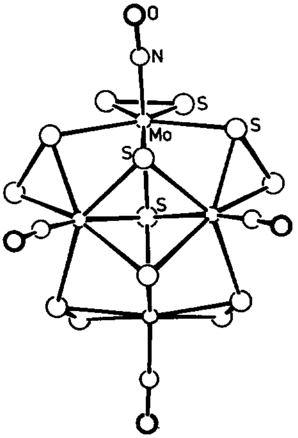
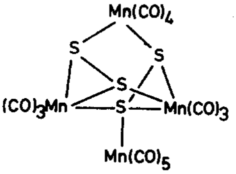


Fig. 2. Structure of the $[Mo_4(NO)_4(S_2)_5S_3]^{4-}$ ion.

tances show any significant variations for the two kinds of disulfur ligands. There are no unusual steric interactions, and the carbonyl ligands are coordinated so that each Mn atom has nearly octahedral geometry. This highly unsymmetrical structure has no metal–metal bonds.

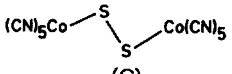


(5)

(iii) Complexes with type II structures

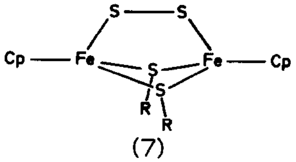
Many diatomic ligands including N_2, CO, CS, CN^- and NO favor end-on coordination to a single metal atom. This mode of coordination is also known for several O_2 complexes, although bridging end-on coordination (structural types IIa and IIb) is more common [16]. For the disulfur ligand only type IIa and type IIb structures are known. This may be due to the greater "softness" of sulfur compared to oxygen. Complexes with type II structures are listed in Table 3 along with their S–S distances and S–S vibrational frequencies.

There are several examples of disulfur complexes of structure type IIa (planar *trans* end-on bridging coordination). Vibrational spectroscopy indicates that this structure occurs in $[(CN)_5Co(S_2)Co(CN)_5]^{6-}$ (6) [5] and that the central $\{Co(S_2)Co\}^{4+}$ unit should be planar as in the analogous dioxygen complex [64]. A *trans* arrangement of the metal atoms (structure type IIa) has been proven by X-ray structure determination for $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]Cl_4$ [22,23], $Cp(CO)_2Mn(S_2)MnCp(CO)_2$ [56] and for $K_2Re_3S_6$ [57–59] $[\{(Re_6S_8)S_{4/2}(S_2)^{4-}_{2/2}\}_n]$. The latter compound contains a polymeric anion in which the S_2 ligands and sulfido ligands bridge Re_6S_8 clusters. Structure type IIa is also likely for the $\{Cr(S_2)Cr\}^{4+}$ unit [65].



(6)

Structure type IIb, *cis* end-on bridging coordination, is found in $Cp_2Fe_2(S_2)(SEt)_2$ (7) where it is dictated by the two bridging SEt groups [24,25]. The Fe(S_2)Fe group is planar in (7) just as with type IIa structures.



(7)

TABLE 3

Disulfur complexes with end-on coordinated ligands (type II)

Complex	Type	d(S–S) [a] (pm)	ν(S–S) [a] (cm^{-1})	Color	Ref.
$[(CN)_5Co(S_2)Co(CN)_5]^{6-}$	IIa	–	490	Red-brown	5
$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	IIa	201	514	Green	22, 23
$Cp(CO)_2Mn(S_2)MnCp(CO)_2$	IIa	201	–	Dark green	56
$\{(Re_6S_8)S_{4/2}(S_2)^{4-}_{2/2}\}_n$	IIa	209	–	Dark red	57–59
$Cp_2Fe_2(S_2)(SEt)_2$	IIb	202	507	Dark green	24, 25, 60
$[Mo_4(NO)_4(S_2)_6O]^{2-}$	IIb	208	480	Violet	61
$Cp'_2Mo_2(S_2)_5$ [c]	IIb [b]	204	–	Black	62
$Cp_4Co_4(S_2)_2S_2$	IIc	201	–	Black	26
$Cp_4Fe_4(S_2)_2S_2$	IIc	204	503	Black	15, 60
$\{SCo_3(CO)_7\}_2(S_2)$	IId	204	–	Black	27, 28
$\{CpMn(NO)(S_2)\}_n$	IId	–	491(?)	Red-brown	63
$[(Cp_4Fe_4(S_2)_2S_2)_2Ag]^+$	IId	205	478	Black	15, 60

[a] Mean value. [b] Mo–S–S–Mo torsion angle = ~59.7°. [c] $Cp' = Me_5Cp$.

The same kind of disulfur bridging occurs in $[Mo_4(NO)_4(S_2)_6O]^{2-}$ (Fig. 3) [61]. This complex consists of a distorted tetrahedral cage of Mo atoms with an interstitial four-coordinate oxygen atom. Two non-adjacent edges of the

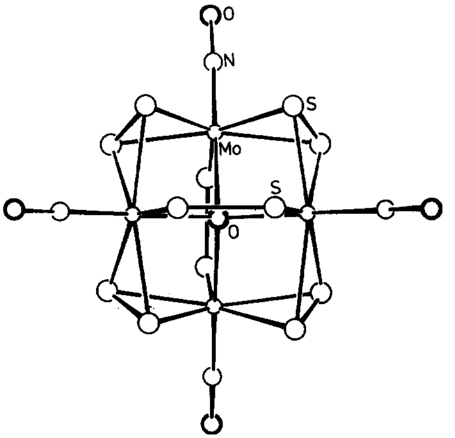
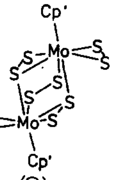


Fig. 3. Structure of the $[Mo_4(NO)_4(S_2)_6O]^{2-}$ ion.

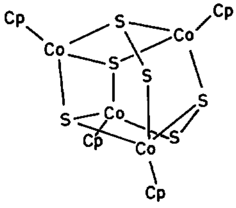
the tetragonal bisphenoid are bridged by type IIb disulfur ligands. The remaining four edges are bridged by disulfur ligands of structure type III [see Section B(iv)]. Each Mo atom has approximate pentagonal bipyramidal coordination geometry with the sulfur atoms in the equatorial plane.



(8)

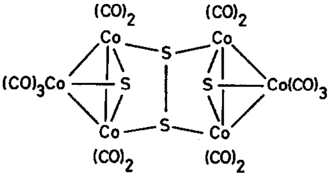
The compound $(Me_5Cp)_2Mo_2(S_2)_5$ (**8**) contains three different kinds of disulfur ligands [62]. The most unusual feature is a non-planar type II disulfur ligand with a Mo–S–S–Mo torsion angle of 59.7°. The two Mo atoms are also bridged by two type Ib disulfur ligands and each Mo contains one type Ia terminal disulfur ligand [62]. Expansion of structures IIa and IIb through coordination of additional metal atoms to the disulfur ligand destroys the planarity of the central $\{M(S_2)M\}$ unit.

The complex $Cp_4Co_4(S_2)_2S_2$ (**9**) [26] has a cage structure with two disulfur ligands, each of which bridges three Co atoms. The complex also has two bridging sulfido ligands. Each Co atom achieves the rare gas electron configuration without forming metal–metal bonds. In contrast the analogous iron complex, $Cp_4Fe_4(S_2)_2S_2$ requires a metal–metal bond for each Fe atom in order to satisfy the 18-electron rule [15].



(9)

A few complexes have been structurally characterized in which a disulfur ligand bridges four metal atoms (structure type IId, Table 1). In the cluster compound $\{SCo_3(CO)_7\}_2(S_2)$ (**10**) the disulfur ligand is bonded to one edge of each of two Co_3 triangles [27,28]. The resulting structure consists of two Co_3S_2 planes which have a common S_2 edge. The dihedral angle between these planes is ca. 120°. A similar mode of coordination for disulfur may occur in $\{CpMn(NO)(S_2)\}_n$ [63]. The cation $[\{Cp_4Fe_4(S_2)_2S_2\}_2Ag]^+$ which is prepared from $Cp_4Fe_4(S_2)_2S_2$, also contains disulfur ligands coordinated to four metal atoms [15,60]. In this case the coordination is very asymmetric and there are no planar $M_2(S_2)$ fragments.



(10)

(iv) Complexes with type III structures

Another class of complexes containing bridging disulfur ligands are those with structure type III in which the S–S bond is oriented approximately perpendicularly to the metal–metal vector so that each sulfur atom is bonded to both metal atoms. These complexes are listed in Table 4. Of particular interest are the cluster anions which contain only molybdenum and sulfur. The unusual binuclear cluster $(NH_4)_2[Mo_2(S_2)_6] \cdot 2\,H_2O$ (Fig. 4) contains only disulfur ligands [29,30]. Two of the S_2 ligands bridge the two Mo atoms (type III) and four of the S_2 ligands are bonded to a single Mo atom [type Ia structure, see Section B(ii)]. An unusual feature of the crystal structure is the orientation of the two independent $[Mo_2(S_2)_6]^{2-}$ anions relative to the crystallographic C_2 axes. One anion has a C_2 axis along the Mo–Mo vector; the other has a C_2 axis perpendicular to the Mo–Mo vector. The idealized symmetry for each anion is D_2. The coordination geometry about each Mo atom is a distorted dodecahedron, similar to that found for

TABLE 4

Disulfur complexes with side-on bridging ligands (type III)

Complex	d(S–S)[a] (pm)	ν(S–S)[a] (cm^{-1})	Color	Ref.
$[Mo_2(S_2)_6]^{2-}$	204	550[c]	Green-black	29, 30
$\{Mo_2(S_2)_2Cl_4Cl_{4/2}\}_n$	198	561[c]	Dark brown	66
$Nb_2(S_2)_2Cl_4$	203	588	Brown	6, 67, 68
$[Mo_3S(S_2)_6]^{2-}$	202	545[c]	Red	69, 70
$Mo_3S(S_2)_3Cl_4$	203	562[c]	Red	66
$Fe_2(S_2)(CO)_6$	201	555	Red	71–73
$Ta_2(S_2)_2(PS_4)_2$	205	–	Grey	74
$Mo_2(n\text{-}BuCp)_2(S_2)Cl_4$	202	–	Black	75, 76
$Mo_2(S_2)(S_2C_2Ph_2)_4$	204	518	Green-black	77
$Nb_2S(S_2)Br_4(tht)_4$[b]	201	–	Green	78
$[Mo_2(S_2)(SO_2)(CN)_8]^{4-}$	200	520	Violet	79

[a] Mean value. [b] tht = Tetrahydrothiophene. [c] Ref. 50.

the $[Mo(O_2)_4]^{2-}$ [80] and the $[Cr(O_2)_4]^{3-}$ anions [81] which contain two perpendicular $M(O_2)_2$ units. The coordination of the individual O_2 and S_2 ligands in these complexes is slightly asymmetric [see Section B(v)]. Although $[Cr(O_2)_4]^{3-}$ exists as a mononuclear Cr(V) complex with a single unpaired electron in an orbital which is primarily Cr 3*d*, the hypothetical isoelectronic $[Mo(S_2)_4]^{3-}$ ion "dimerizes" to form $[Mo_2(S_2)_6]^{2-}$ which has a metal–metal bond and bridging S_2 ligands. The presence of the metal–metal bond is indicated by the short Mo–Mo distance (283 pm), magnetic measurements, and by EH-SCCC calculations [82].

An interesting feature of the type III bridging S_2 ligands is the asymmetric bonding of the S_2 ligand to the Mo atoms. The averages of the pairs of

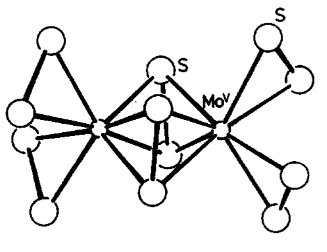


Fig. 4. Structure of the $[Mo_2(S_2)_6]^{2-}$ ion.

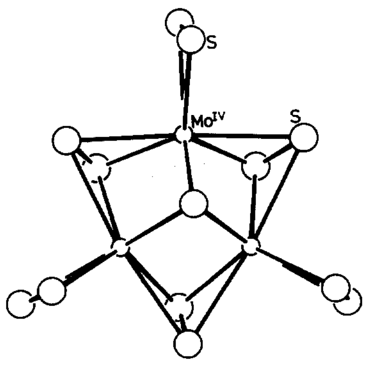


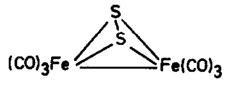
Fig. 5. Structure of the $[Mo_3S(S_2)_6]^{2-}$ ion.

crystallographically independent Mo–S distances show differences of ca. 10 pm (249.4 and 239.4 pm). Asymmetric Mo–S distances appear to be a common feature of disulfur complexes of structure type III (vide infra).

Another cluster anion with type III disulfur ligands and which contains only molybdenum and sulfur atoms occurs in $(NH_4)_2[Mo_3S(S_2)_6] \cdot nH_2O$ ($n = 0$–2; with variable non-stoichiometric amounts of water, which are disordered in the crystal lattice [83]) (Fig. 5) [69,70,84,85]. Each edge of the triangle of Mo atoms is bridged by an S_2 ligand. In addition a type Ia S_2 ligand is coordinated to each Mo atom. Again the Mo–S distances for the type III disulfur ligands fall into two groups (249 and 242 pm) (an additional discussion of the structure and its similarity to that of $[Mo_2(S_2)_6]^{2-}$ may be found in ref. 85).

Type III disulfur ligands also occur in several polymeric solid-state structures. These include: $Mo_2(S_2)_2Cl_6[\{Mo_2(S_2)_2Cl_4Cl_{4/2}\}_n]$ [66]; $Nb_2(S_2)_2Cl_4$ $[\{Nb_2(S_2)_2Cl_{8/2}\}_n]$ [6,7]; $Ta_2(S_2)_2(PS_4)_2$ $[\{Ta_2(S_2)_2(PS_4)_2\}_n]$ [74] and $Mo_3S(S_2)_3Cl_4$ $[\{Mo_3S(S_2)_3Cl_2Cl_{4/2}\}_n]$ [66]. The latter compound can be formally derived from $[Mo_3S(S_2)_6]^{2-}$ [69,70,84,85] by replacement of each of the type Ia disulfur ligands by two Cl atoms.

Other binuclear compounds with type III disulfur ligands as the only bridging ligands include $Fe_2(S_2)(CO)_6$ (**11**) [71,72] and $Mo_2(n\text{-BuCp})_2(S_2)Cl_4$ [75,76]. The latter compound shows slight asymmetry in the bonding of the S_2 ligand [242.6(2) and 239.3(2) pm].



(11)

Type III disulfur ligands have been established by X-ray structure determination for binuclear complexes which also contain other bridging ligands. These include: $Mo_2(S_2)(S_2C_2Ph_2)_4$, with bridging SR groups [77] (Fig. 6); $Nb_2S(S_2)Br_4(tht)_4$ [78]; $(PPh_4)_4[Mo_2(S_2)(SO_2)(CN)_8] \cdot 6\,H_2O$, with

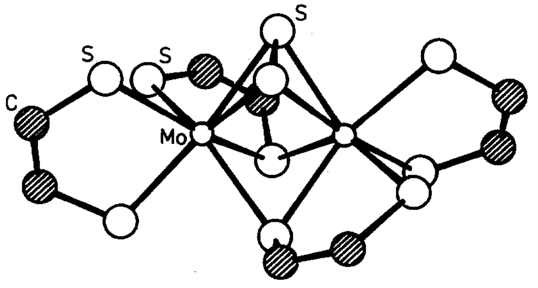
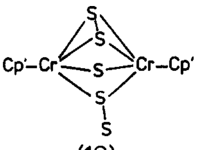


Fig. 6. Structure of $Mo_2(S_2)(S_2C_2Ph_2)_4$; phenyl groups omitted for clarity.

bridging SO_2 [79]. Type III bridging has been inferred from vibrational spectroscopy and/or other physical measurements for $Cp_2Mo_2(S_2)_2$ [86,87], $\{Mn(CO)_2(PMe_3)\}_2(S_2)(CO)$ [21], $Mn_2(S_2)(CO)_8$ [88] and $Mo_2S_5X_3$ (X = halogen) [68,89].

In $Cp'_2Cr_2S(S_2)_2$ the two Cr atoms are bridged by a type III disulfur ligand, by a sulfido group and by a type IV disulfur ligand (**12**). This compound is the first example of a type IV disulfur ligand. Both the type III and IV S–S distances are unusually long, 215 and 210 pm, respectively [31].



(12)

(v) General structural features of disulfur complexes

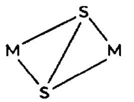
Several common features of the structures of disulfur complexes can be noted.

(a) Structural diversity is exhibited by disulfur complexes through the utilization of the non-bonded pairs of electrons on the S_2 ligand to coordinate additional metal atoms. This feature is common to both type I and type II structures.

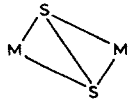
(b) S–S distances of known complexes range from 198 to 215 pm, with standard deviations of 0.2 pm or larger for individual determinations. Most S–S distances are intermediate between the distance of 189 pm for $S_2(^3\Sigma_g^-)$ [90,91] and 213 pm for $S_2^{2-}(^1\Sigma_g^+)$ in Na_2S_2 [92]. The mean S–S distances show no systematic trend with structural type: type Ia, 204(3) pm (seven compounds, Table 2); types IIa and IIb, 204(4) pm (six compounds, Table 3); type III, 202(3) pm (11 compounds, Table 4).

However, average S–S distances for a wide variety of compounds could easily conceal small systematic variations in S–S distances as a function of structure type. Consequently, it is more useful to compare different structure types in the same compound so that all of the S_2 ligands are bound to the same metal in the same oxidation state. The data collected in Tables 2–4 enable three such comparisons to be made among type Ia, type IIb and type III ligands.

The average type Ia S–S distances for $[Mo_2(S_2)_6]^{2-}$ [29,30,82] and $[Mo_3S(S_2)_6]^{2-}$ [69,70,84,85] are slightly longer than the average type III S–S distances (0.6–4.0 pm, 1–3σ). The data for $[Mo_4(NO)_4(S_2)_6O]^{2-}$ [61] indicate that type IIb S–S distances may be slightly longer than type III S–S distances (1.8 pm, 3–6σ). Caution must be exercised in interpreting these trends because of the known tendency for type III ligands to be slightly asymmetrically bound to the metal (see below).



(13)

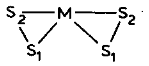


(14)

Partial disorder of an asymmetrically bound type III disulfur ligand between structures (**13**) and (**14**) will be manifest as a slightly shorter S–S distance. But a slightly shorter S–S distance for type III ligands is also consistent with vibrational spectra (see Section E).

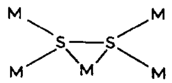
(c) High coordination numbers of the metal atom are favored for type I and type III structures by the small coordination angle of the bidentate disulfur ligand. In $[Mo_2(S_2)_6]^{2-}$ each Mo atom is coordinated to eight S atoms. High coordination numbers also protect the metal center from nucleophilic attack, an important factor in stabilizing metal–metal bonds.

(d) M–S distances are similar to those for metal complexes of other simple sulfur-containing ligands. Several complexes with structure types Ia and III ligands exhibit slightly asymmetric M–S distances. This inequality is usually 3–4 pm [45,46], however, it can be as large as 6–8 pm in complexes which contain structural units such as (**15**) in which the sulfur atoms from two different disulfur ligands are approximately *trans* to one another [37,38]. Similar asymmetries are found for some O_2 complexes in which the ligand is coordinated side-on to the metal [82,85].

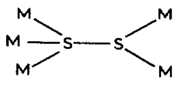


(15)

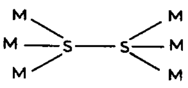
(e) Other coordination types for disulfur complexes can be envisaged in addition to those of Table 1. If the disulfur ligand is formally regarded as S_2^{2-} then, in principle, six electron pairs are available to coordinate to metals. This suggests that complexes with units such as Ie, IIe and IIf might be accessible under appropriate conditions.



Ie



IIe



IIf

C. SYNTHESES

Disulfur complexes have been prepared by various methods, in contrast to dioxygen complexes which can only be prepared by two principal routes, namely oxidative addition of O_2 to a low-valent metal complex, and reaction of a metal complex with H_2O_2 [16]. The preparative routes to disulfur complexes can be grouped into five classes.

(i) Reactions of low-valent metal complexes with elemental sulfur

Oxidative addition of elemental sulfur to an electron-rich metal which is coordinatively unsaturated is a convenient method for preparing disulfur complexes. Reaction (1)

$$ML_4 + S_8 \rightarrow ML_4(S_2) \qquad (1)$$

has a high yield for metal atoms with d^8 electron configurations such as Ir^I, Rh^I, Ru^0 and Os^0 [3,4,32–36]. The additional ligands (L) are π-acceptor ligands such as CO and PPh_3. Upon addition of disulfur the coordination of the central metal atom changes from square planar to distorted octahedral.

However, not all reactions of low-valent metal complexes with elemental sulfur proceed in such a straightforward manner. Many reactions produce mixtures of various metal–sulfur complexes, often in low yield [26–28,40,43,49,62,63,93].

(ii) High-temperature reactions of metals or metal halides with S_8 and/or S_2Cl_2

Several compounds with network structures which contain disulfur units can be prepared by high-temperature (250–700°C) reactions. Examples are $Mo_2(S_2)_2Cl_6$, $Mo_3S(S_2)_3Cl_4$, $Nb_2(S_2)_2Cl_4$ and $Na_4Re_6S_{12}$ (see Section B) [6,57–59,66,68,74,78,89]. The sulfur-containing reagent is S_2Cl_2 or a mixture of S_8 and S_2Cl_2. The metal is reacted in elemental form or as a low-valent chloride. For S_2Cl_2, the reaction involves the reduction of the formally positively charged S_2^{2+} unit [see eqn. (2)] [6].

$$Nb + S_2Cl_2 \rightarrow Nb_2(S_2)_2Cl_4 \qquad (2)$$

An example of a reaction of a metal halide with sulfur and S_2Cl_2 is [66]

$$MoCl_3 + S_8/S_2Cl_2 \rightarrow Mo_3S(S_2)_3Cl_4 + Mo_2(S_2)_2Cl_6 \qquad (3)$$

The conditions under which these S_2-containing cluster compounds are formed illustrate their high stability.

(iii) Reactions of metal complexes with S_x^{2-}

One method for directly introducing the disulfur ligand is by substitution of S_2^{2-} for other ligands. For this purpose Na_2S_2 [41] [eqn. (4)]

$$Cp_2MoCl_2 + Na_2S_2 \rightarrow Cp_2Mo(S_2) + 2NaCl \tag{4}$$

or a polysulfide solution [94,95] can be used [eqns. (5) and (6)].

$$[Mo_3S_4(CN)_9]^{5-} + S_x^{2-} \rightarrow [Mo_3S(S_2)_6]^{2-} \tag{5}$$

$$Mo_3S(S_2)_3Cl_4 + S_x^{2-} \rightarrow [Mo_3S(S_2)_6]^{2-} \tag{6}$$

Aqueous polysulfide solutions are especially useful reagents for the synthesis of disulfur complexes [5,19,29,37,38,61,69,96–98]. The solutions are prepared by saturating an aqueous solution of ammonia after addition of sulfur with H_2S. The Raman spectra of such solutions show that S_2^{2-} is a major component of the solutions [99].

With MoO_4^{2-} the Mo(VI) is reduced and the products obtained depend upon the sulfur content of the polysulfide solutions. From polysulfide solutions of 6 g S per 500 ml H_2O the Mo(IV) cluster $(NH_4)_2[Mo_3S(S_2)_6] \cdot n\,H_2O$ ($n = 0$–2) (Fig. 5) is precipitated at 90°C. The Mo(V) complex $(NH_4)_2[Mo(S_2)_6] \cdot 2\,H_2O$ (Fig. 4) is obtained from the corresponding filtrate at lower temperatures [96]. The tetranuclear complex $[Mo_4(NO)_4(S_2)_5S_3]^{4-}$ can also be obtained from this solution in presence of NH_2OH [98]. If a more concentrated polysulfide solution is used (90 g S per 500 ml H_2O) then a nearly quantitative yield of $(NH_4)_2[Mo_3S(S_2)_6] \cdot nH_2O$ is obtained [98]. However, $(NH_4)_2[Mo_2(S_2)_6] \cdot 2\,H_2O$ can also be obtained from this reaction by heating up to 70°C for only a few minutes [100]. The compound $(PPh_4)_2[Mo_2(S_2)_6]$ can be prepared directly in non-aqueous media by heating $(PPh_4)_2MoS_4$ in DMSO with methanolic polysulfide solution [100].

(iv) Oxidation of sulfur-containing ligands

An interesting way of forming disulfur ligands is by the oxidation of two SR ligands. One example is [65,87] eqn. (7).

$$Fe(CO)_4(SH)_2 \xrightarrow{ox} Fe_2(S_2)(CO)_6 \tag{7}$$

Such a reaction also proceeds when R is a good leaving group, e.g. $SnMe_3$ [21].

Intramolecular redox reactions within metal–sulfido moieties are another important route to disulfur complexes. An example is the formation of $[Mo_2O_2S_2(S_2)_2]^{2-}$ from $[MoO_2S_2]^{2-}$ [45,47] where the following redox processes might be involved

$$\mathrm{Mo^{VI}} \overset{\text{red}}{\rightarrow} \mathrm{Mo^{IV}} \tag{8}$$

$$(\mathrm{Mo^{IV}} + \mathrm{Mo^{VI}} \rightarrow 2\ \mathrm{Mo^{V}}) \tag{9}$$

$$2\ \mathrm{S^{2-}} \overset{\text{ox}}{\rightarrow} \mathrm{S_2^{2-}} \tag{10}$$

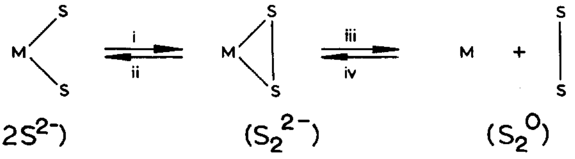
(v) Reactions with other sulfur-containing reagents

The formation of S_2 complexes by other sulfur-containing reagents such as H_2S [22,39,42], P_4S_{10} [40], COS [22,56], Na_2S_4 or Na_2S [5], R_2S_x [15,22,24,86,87] and Na_2SO_3 [28] has also been reported. Here, however, it is not possible to make a clear statement about the mechanism.

D. REACTIONS

(i) Electron transfer and intramolecular redox reactions

The redox behavior of S_2 complexes is of particular interest because it can probably provide a foundation for understanding the course of reactions in enzymes and catalysts (especially desulfurization catalysts). Oxidation and reduction reactions related to type Ia disulfur ligands can be summarized by reaction scheme (11)

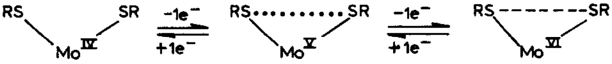


(11)

Examples of reaction (i) of (11) are provided by the oxidations of =S and –SR groups described in Section C(iv) [21,45,46,65,101]. Reaction (ii) of (11) involves reduction of the S–S bond to form two sulfido groups [102,103].

The reduction of a disulfur complex can follow reaction paths other than (ii). For example, electrochemical reduction of $[Ir(dppe)_2(S_2)]^+$ results in dissociation of S_2^- from the complex [104].

Reaction sequence (12) proposed by Stiefel et al. [105] for molybdenum enzymes is directly related to reactions (i) and (ii) of (11). In this context it is interesting to note that organic disulfides as well as disulfur complexes undergo reactions with low-valent metal complexes to form complexes with two sulfido ligands [102,103] or trinuclear sulfido-bridged complexes [102,106–108].



(12)

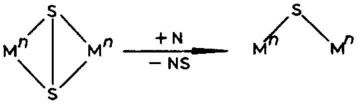
Reaction sequences (i) and (ii) of (11) and the proposal of Stiefel et al. (12) also give new importance to the methylation reactions of S_2 complexes in which the S–S bond remains intact [4,34,42,109]. An example of reaction (iii) of (11) is the thermal decomposition of $Cs_2[Mo_2(S_2)_6] \cdot n\ H_2O$ to give S_2 as the main gaseous product [see Section D(iv)].

Examples of reaction (iv) of (11) are provided by the syntheses of disulfur complexes from reactions employing elemental sulfur [see Section C(i)].

The electrochemical one-electron oxidation of $Cp_2Fe_2(S_2)(SEt)_2$ (7) results in the formation of a metal–metal bond rather than in extrusion of sulfur [reaction (iii) of (11)] or the coupling of the two SEt groups [sequence (12)]. The chemical two-electron oxidation of (7) in MeCN results in the elimination of disulfur and the formation of $[Cp_2Fe_2(MeCN)_2(SEt)_2]^{2+}$ [15,60,110].

(ii) Reactions with nucleophiles (abstraction of S^0)

A characteristic reaction of disulfur ligands is the abstraction of a sulfur atom by nucleophiles (N) such as PPh_3, SO_3^{2-}, SR^-, CN^- and OH^-, e.g. reaction (13) for type III ligands [15,109,111–115]

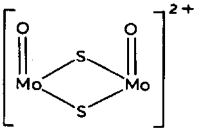


(13)

The reaction involves loss of a neutral sulfur atom from the complex with no change in the formal oxidation state of the metal atoms. This reaction occurs especially in disulfur complexes in which there is a substantial transfer of electron density from the ligand to the metal so that the population of the ligand π^* level is decreased [15,109,111] [see Section F].

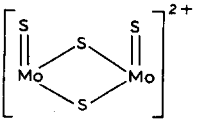
In this regard the reaction of $[Mo_3S(S_2)_6]^{2-}$ with CN^- is particularly interesting as a possible model for the inhibition of xanthine oxidase by CN^- with the concomitant formation of SCN^- [12,13]. The bridging disulfur ligands are converted to bridging sulfido ligands and the terminal S_2 ligands are replaced by CN^- groups [111].

Reactions of $[Mo_2(S_2)_6]^{2-}$ with nucleophiles also convert the bridging S_2 ligands to bridging sulfido ligands. With weak nucleophiles the units



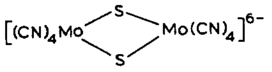
[114]

(for example, the interesting species $[Mo_2O_2S_2(S_2)_2]^{2-}$ with aqueous ammonia, Fig. 1) and



[48,113,115]

are formed. With the strong nucleophile CN^- the final product is



[114]

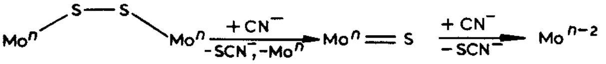
and the molybdenum atoms have been reduced from oxidation state V to III (discussion in ref. 114). Clearly, $[Mo_2(S_2)_6]^{2-}$ is a useful starting material for the generation of other molybdenum–sulfur compounds.

In $[Mo_4(NO)_4(S_2)_4(S_2)'_2O]^{2-}$ both the end-on bridging S_2 ligands of type IIb and the type III bridging S_2 ligands react with CN^- to produce a strongly distorted $\{Mo_4S_4\}$ cube (14) [112]

$$[Mo_4(NO)_4(S_2)_4(S_2)'_2O]^{2-} + CN^- \rightarrow [Mo_4S_4(NO)_4(CN)_8]^{8-} + SCN^- \quad (14)$$

The cube results from abstraction of a sulfur atom from each of the four type III ligands by reaction (13).

A reasonable mechanism for the reaction of the two type IIb disulfur ligands is the stepwise sequence (15)



(15)

where a pair of two-electron reductions occurs forming two metal–metal bonds within the $\{Mo_4S_4\}$ cube [112].

Type III bridging S_2 ligands are more susceptible to nucleophilic attack with extrusion of a neutral sulfur atom than are type Ia disulfur ligands. This is consistent with a generally lower electron density on the S atoms of type III disulfur ligands (bonded to two metal atoms) than of the type Ia ligands (bonded to one metal atom; see Section F for additional discussion).

(iii) Oxidation of the ligand by external agents

In $Ir(dppe)_2(S_2)Cl$ the disulfur ligand can be oxidized stepwise on the metal to form S_2O and S_2O_2 complexes [116,117]. A complex with a bridging S_2O ligand is also known [40]. The reaction of $Os(S_2)(PPh_3)_2(CO)_2$ with I_2 to form elemental sulfur and $OsI_2(PPh_3)_2(CO)_2$ provides chemical evidence for a negatively charged disulfur ligand [4].

(iv) Thermal decomposition of disulfur complexes (generation of S_2)

The main gaseous product of thermal decomposition at rather low temperatures (100–200°C) of $Cs_2[Mo_2(S_2)_6] \cdot nH_2O$ is the S_2 molecule, which results from a reductive elimination process. This has been proven by mass spectroscopy and matrix isolation Raman, UV/VIS and IR spectroscopy [118] (Fig. 7). (The IR intensity of the fundamental is induced by intermolecular interactions in the matrix [119].) The solid residue contains $Cs_2[Mo_3S(S_2)_6]$ at 270°C [50]. Other S_x species ($x = 4, 6$) in addition to S_2 can be seen in the matrix spectra and probably result from S_2. In the thermal decomposition of $(NH_4)_2[Mo_2(S_2)_6] \cdot 2\,H_2O$ the NH_4^+ cations are also involved, and NH_3 and H_2S are produced in addition to S_2. The final product is MoS_2 at 380°C [50].

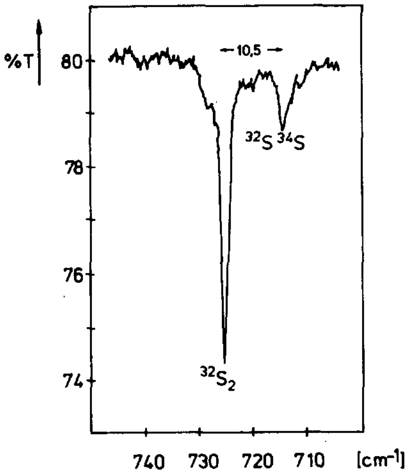


Fig. 7. Induced IR absorption band of S_2 in an argon matrix at 15 K ($Ar/S_2 \approx 200$).

The thermal decomposition of $(NH_4)_2[Mo_3S(S_2)_6] \cdot n\,H_2O$ ($n = 0$–2, with variable non-stoichiometric amounts of water) at 270°C produces initially one mole of NH_3 and half a mole of H_2S per mole of trinuclear complex [83]. The persistence of trinuclear Mo–S clusters in the intermediate amorphous product is strongly suggested by its IR spectrum [83] and by the formation of $[Mo_3S_4(CN)_9]^{5-}$ upon reaction of it with CN^- [100].

E. PHYSICAL MEASUREMENTS

(i) Vibrational spectra

In disulfur complexes the ν(S–S) frequencies range from ca. 480 to 600 cm^{-1}. Comparison of the ν(S–S) values for the discrete diatomic sulfur

TABLE 5

Frequencies for ν(S–S) and ν(M–S) vibrations of disulfur complexes

Complex	Type	ν(S–S) [a] (cm^{-1})	ν(M–S) [a] (cm^{-1})	Ref.
$[Mo_2O_2S_2(S_2)_2]^{2-}$	Ia	516(0), 508(0)	357(7.0), 321(4.0)	124
$[Ir(dppe)_2(S_2)]^+$	Ia	528	369, 350	3, 50
$MoO(S_2)(dtc)_2$	Ia	556	374, 350	39, 50
$Cp_2Mo(S_2)$	Ia	530	386, 351	41, 50
$Mo_3S(S_2)_3Cl_4$	III	562	405, 395, 366, 333, 295, 285 [b]	50
$[Mo_3S(S_2)_6]^{2-}$	III, Ia	544(1.0), 510(0), 504	386(7.0), 361(8.5), 331(3.0), 298(3), 283(1.0)	50, 123
$[Mo_2(S_2)_6]^{2-}$	III, Ia	550(2.0), 541, 530(2.0), 524	382 [b], 361, 354(7.0), 341(6.0), 300(1.0), 272	50
$Nb_2(S_2)_2Cl_4$	III	588	377, 362, 336 [b], 323, 317 [b] 252 [b]	125, 126
$\{Zr_2S_2(S_2)_2\}_n$	III	529	365, 326 [b]	125, 127
$Fe_2(S_2)(CO)_6$	III	555	332, 310	73, 128

[a] IR bands unless otherwise noted; values in parentheses are $\Delta\nu(^{92}Mo/^{100}Mo)$ (cm^{-1}). [b] Raman bands.

species $S_2(^3\Sigma_g^-$: 725 cm^{-1}) [118,120], $S_2^-(^2\Pi_g$: 589 cm^{-1}) [121,122] and $S_2^{2-}(^1\Sigma_g^+$: 446 cm^{-1}) [50] leads to the conclusion that the approximate charge distribution in disulfur complexes is somewhere between that for S_2^- and that for S_2^{2-}. However, in this comparison the strong coupling of the ν(S–S) vibration with the ν(M–S) vibrations which lead to higher ν(S–S) values must also be considered. This coupling is indicated by the shift of 1–2 cm^{-1} in ν(S–S) upon substitution of ^{92}Mo by ^{100}Mo in $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$ [82,84,123].

The frequencies of the type III bridging disulfur ligands are generally higher than those for type I structures (Table 5). This is illustrated by comparison of the spectra of $Mo_3S(S_2)_6Cl_4$ and $[Mo_3S(S_2)_6]^{2-}$ (Fig. 8). Both clusters contain the same central $Mo_3S(S_2)_3$ unit [see Section B(iv) and Fig. 5] with type III disulfur ligands. Since $Mo_3S(S_2)_6Cl_4$ contains only type III disulfur ligands the vibration at 562 cm^{-1} is due to ν(S–S) of the type III ligand. For $[Mo_3S(S_2)_6]^{2-}$ the vibration at 544 cm^{-1} can then be assigned to the type III ligands and the bands at 504 and 510 cm^{-1} to the type I disulfur ligands. The higher frequencies found for type III disulfur ligands are consistent with the slightly shorter S–S distances for this structure type [see Section B(v)].

The intensities of the ν(S–S) bands of type III ligands are normally high in the IR as well as in the Raman spectra. The type Ia ligands show intense ν(S–S) bands in the IR, but in the Raman spectrum these bands are usually weak (Fig. 9) [50].

The ν(M–S) bands in the known complexes are observed between 250 and 420 cm^{-1} (Table 5).

For type Ia structures the symmetric M–S stretching vibration of the

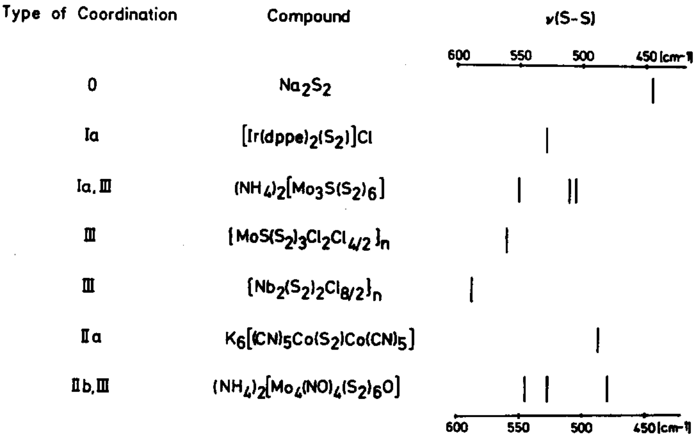


Fig. 8. ν(S–S) frequencies for disulfur ligands of various structural types.

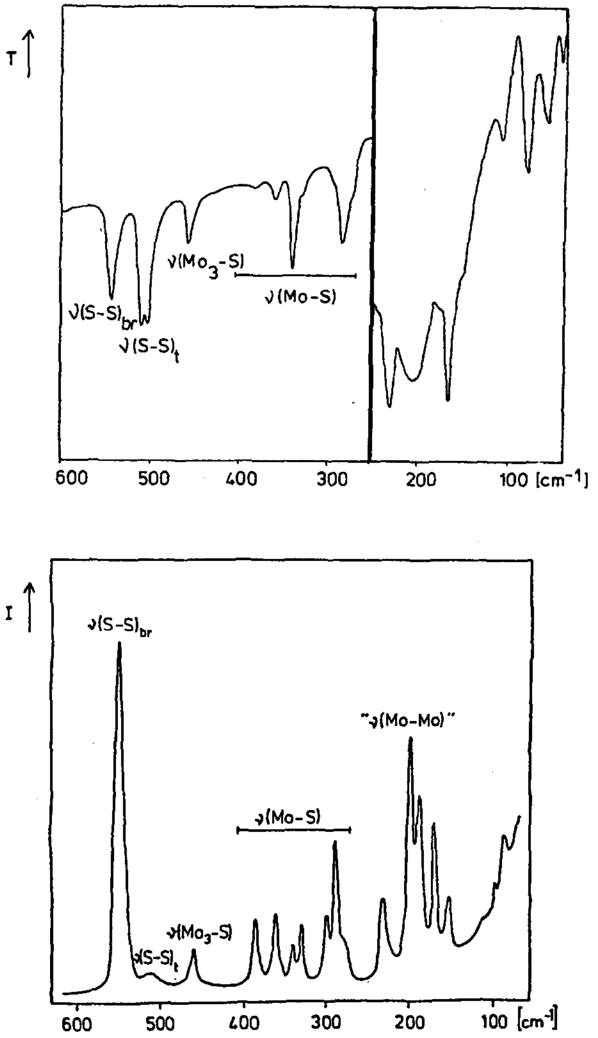
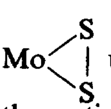


Fig. 9. IR (top) and Raman (bottom) spectra of the $[\mathrm{Mo_3S(S_2)_6}]^{2-}$ ion ($\mathrm{NH_4^+}$ salt; IR in polyethylene).

 $\mathrm{Mo}{<}\begin{smallmatrix}\mathrm{S}\\|\\\mathrm{S}\end{smallmatrix}$ unit shows a larger isotope shift ($^{92}\mathrm{Mo}/^{100}\mathrm{Mo} \approx 7\,\mathrm{cm}^{-1}$) than does the antisymmetric one ($^{92}\mathrm{Mo}/^{100}\mathrm{Mo} \approx 2\,\mathrm{cm}^{-1}$). The symmetric stretching vibration also has a higher frequency ($> 350\ \mathrm{cm}^{-1}$) [50].

For structure type IIa ligands both the ν(S–S) and the totally symmetric ν(M–S) vibrations are practically forbidden in the IR spectrum, but the corresponding bands (very intense and strongly polarized) can easily be observed in the Raman spectrum [61].

TABLE 6

Approximate stretching force constants for S–S and M–S bonds in disulfur complexes

Complex	$f_{(S\text{-}S)}$(mdyn Å^{-1})	$f_{(M\text{-}S)}$(mdyn Å^{-1})	Ref.
$Fe_2(S_2)(CO)_6$	2.5	1.6	128
$Nb_2(S_2)_2Cl_4$	2.5	1.2	126
$[Mo_3S(S_2)_6]^{2-}$	2.0	1.5	123
$[Mo_2O_2S_2(S_2)_2]^{2-}$	2.0	1.4	124
S_2	5.0	–	[a]
S_2^-	3.3	–	[a]
S_2^{2-}	1.9	–	[a]

[a] Calculated from the frequencies of S_2(725 cm^{-1} [118]), S_2^-(589 cm^{-1} [121,122]) and S_2^{2-}(446 cm^{-1} [50]).

Approximate normal coordinate analyses have been carried out for several disulfur complexes. Comparison of the force constants of the S–S bond with those of S_2^{n-} ($n = 0$–2) species confirms the conclusion drawn from the S–S frequencies, that is, the S–S bond strength in disulfur complexes lies between that for S_2^- (bond order = 1.5) and that for S_2^{2-} (bond order = 1.0) (Table 6).

(ii) XP spectra

The X-ray photoelectron spectra of disulfur complexes have been measured in order to obtain additional information about the effective charge on

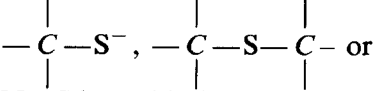
TABLE 7

Binding energies of sulfur in disulfur complexes (calibrated to C 1*s* = 285.0 eV) [50]

Complex	S 2*p* E_B (eV)	S 2*s* E_B (eV)
$Nb_2(S_2)_2Cl_4$	164.1	228.1
$Nb_2(S_2)_2Br_4$	163.2	227.0
$(NH_4)_2[Mo_2(S_2)_6]$	163.9	228.2
$(NH_4)_2[Mo_3S(S_2)_6]$	163.5	228.8(?) [a]
$Mo_3S(S_2)_3Cl_4$	164.4	228.3(?) [a]
$Cp_2Mo(S_2)$	163.2	–
$MoO(S_2)(dtc)_2$	163.2	227.1
$(NMe_4)_2[Mo_2O_2S_2(S_2)_2]$	163.2	227.4
$(NH_4)K[Mo_4(NO)_4(S_2)_6O]$	162.9	227.7
$(NH_4)_4[Mo_4(NO)_4(S_2)_5S_3]$	163.6	227.6

[a] Not clearly resolved.

the sulfur atoms in these ligands. The results are summarized in Table 7.

The sulfur $2p$ binding energies lie between 162.9 and 164.4 eV, indicating that the sulfur atoms are generally more negatively charged than in neutral sulfur [$E_B(2p)$ for S_8 is 164.2 eV] [129]. The corresponding binding energy for sulfur in complexes with reduced sulfur-containing ligands such as S^{2-},  $-\overset{|}{\underset{|}{C}}-S^-$, $-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-$ or $>C{=}S$ are in the range 161.5–163.5 eV [130]. Na_2S has a binding energy of 162.0 eV [129] and thiometallates have binding energies of 162.2–163.4 eV [131]. Thus, the S $2p$ binding energies for disulfur complexes are consistent with the conclusion drawn from S–S bond distances and from vibrational spectroscopy, i.e. the effective charge on the sulfur atoms in the disulfur ligand in metal complexes is between 0 and −2.

The sulfur binding energies depend upon the electronegativity of the other ligands attached to the metal. This is illustrated by the higher sulfur binding energy for $Nb_2(S_2)_2Cl_4$ compared to $Nb_2(S_2)_2Br_4$ and for $Mo_3S(S_2)_3Cl_4$ compared to $[Mo_3S(S_2)_6]^{2-}$ (Table 7). For each pair the metal binding energy is nearly identical (Table 8). Taken together the metal and sulfur

TABLE 8

Comparison of the electron binding energies in molybdenum compounds[c] (calibrated to C $1s$ = 285.0 eV)

Compound	Oxidation state	Mo $3p_{3/2}$ E_B (eV)	Mo $3d_{5/2}$ E_B (eV)	Ref.
MoO_3	+6	–	232.5	132
$(NH_4)_2MoO_4$	+6	–	232.1	132
Cs_2MoS_4	+6	–	231.7	131
$MoO(S_2)(dtc)_2$	+6	396.9	231.3	50
$MoCl_5$	+5	–	231.0	132
$Mo_2(S_2)_2Cl_6$	+5	397.3	231.3	50
$(NH_4)_2[Mo_2(S_2)_6]$	+5	397.1	230.3	50
$(NMe_4)_2[Mo_2O_2S_2(S_2)_2]$	+5	397.2	230.6	50
MoO_2	+4	–	230.9	132
$(NH_4)_2[Mo_3S(S_2)_6]$	+4	395.3	230.8(?)[a]	50
$Mo_3S(S_2)_3Cl_4$	+4	395.6	230.1(?)	50
$(NH_4)K[Mo_4(NO)_4(S_2)_6O]$	+4[b]	395.6	229.7(?)[a]	50
$(NH_4)_4[Mo_4(NO)_4(S_2)_5S_3]$	+4[b]	395.9	230.1	50
$K_8[Mo_4S_4(CN)_{12}]$	+3	395.1	229.0	133
Mo	0	–	226.1	132
$Mo(CO)_6$	0	–	226.6	132

[a] Not clearly resolved. [b] Taking NO as NO^-, which seems reasonable. [c] No water of crystallization given in any of the Tables.

binding energies indicate that the disulfur ligand is an effective electron donor to the metal, and that donation from the disulfur ligand increases as the electronegativity of the other ligands increases.

Additional evidence about the oxidation state of the sulfur can be obtained by comparison of the metal binding energies in disulfur complexes to the metal binding energies in complexes in known oxidation states. Table 8 summarizes the metal binding energy data for a series of molybdenum complexes. In particular it is clear that the Mo binding energies of $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$ can be understood if the disulfur ligands are formulated as $(S_2)^{2-}$ units rather than neutral S_2 fragments [84] (Fig. 10). Similar results are found for the metal binding energies of Ir and Os complexes of disulfur ligands [4,134].

In summary both the sulfur and metal XPS results are consistent with the disulfur ligand having an effective negative charge of about −2. However, neither the sulfur nor the metal XPS data are sufficiently sensitive to distinguish among the various modes of coordination of the S_2 ligand summarized in Section B. A recent XPS survey of several molybdenum complexes with a variety of sulfur ligands showed that the range of S 2*p* binding energies for sulfide and thiolate ligands is only ~ 1 eV [135].

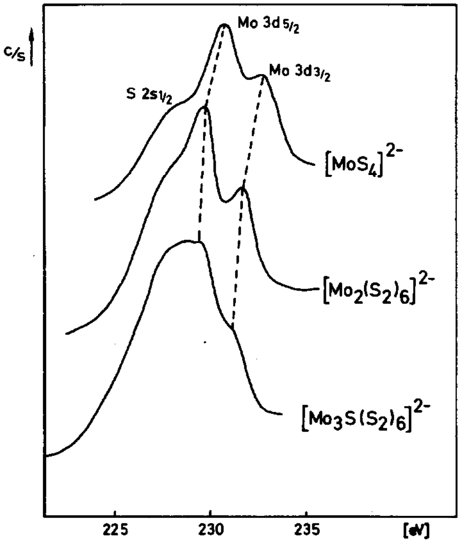


Fig. 10. XP spectra of $[MoS_4]^{2-}$, $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$ in the region of the Mo 3*d* binding energies (NH_4^+ salts). The decrease in the metal binding energies in this series is consistent with a change in oxidation state from VI to IV.

TABLE 9

Electronic absorption bands in disulfur complexes

Complex	Type	Color	Band maxima (10^3 cm^{-1}) [a]	Ref.
$Cp_2Nb(S_2)Cl$	Ia	Red	20.7(0.9) [b], 27.2(0.9), 36.8(7.8)	42
$Cp_2Nb(S_2)Br$	Ia	Dark red	21.1(1.1) [b], 26.9(1.2), 35(83(?))	42
$Cp_2Nb(S_2)I$	Ia	Violet	21.3(0.8) [b], 26.9(3.1), 34.5(6.8)	42
$MoO(S_2)(dtc)_2$	Ia	Blue	17.2(1.3) [b], 25.4(3.8)	93
$[Mo_2O_2S_2(S_2)_2]^{2-}$ [c]	Ia	Red-orange	21.6(2.0) [b], 27, 32.8(10.6), 36.0(11.3)	50
$Mo_2(S_2)_2Cl_6$ [d]	III	Dark brown	13.1, 21.1, 27.4	50
$[Mo_2(S_2)_6]^{2-}$ [e]	III, Ia	Black-green	13, 16, 20, 24, 28, 32	50
$Mo_3S(S_2)_3Cl_4$ [d]	III	Red	20, 27	50
$[Mo_3S(S_2)_6]^{2-}$ [e]	III, Ia	Red	18.5(1.1), 21.5(3.6), 27, 30	50, 84
$Nb_2(S_2)_2Cl_4$ [d]	III	Brown	15, 18, 22, 26, 29, 37, 43	50
$Nb_2(S_2)_2Br_4$ [d]	III	Red-brown	18, 22, 26, 29, 43	50
$Fe_2(S_2)(CO)_6$	III	Red	21, 30(11.9), 36	136
$[Mo_4(NO)_4(S_2)_6O]^{2-}$ [c]	III, IIb	Violet	14, 17, 18.8(2.6), 22	50
$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	IIa	Green	14.2(14.6), 24.3(1.4), 35.1(5.1), 45.2(19.8)	22
$\{Cr(S_2)Cr\}^{4+}$	IIa	Yellow-brown	25(2.7), 33(3.6)	65
$[(CN)_5Co(S_2)Co(CN)_5]^{6-}$	IIa	Red-brown	15.5, 19.0(0.7), 27.0, 32.0(8.7), 38.7(8.7)	5
$Cp_2Fe_2(S_2)(SEt)_2$	IIb	Dark green	11.9(4.4), 16.7(2.1), 20.9(28), 32.4(12), 42.9(28)	60

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[a] Extinction coefficients are given in parentheses (10^3 M^{-1} cm^{-1}). [b] $\pi_v^*(S) \rightarrow d(M)$LMCT (see text). [c] In CH_3CN. [d] Solid in reflectance. [e] In DMF.

(iii) Electronic absorption spectra

Table 9 lists the electronic absorption maxima and extinction coefficients for disulfur complexes. For bonding type Ia the π^* orbital of S_2^{2-} splits into a strongly interacting π_h^* orbital in the MS_2 plane and a weakly interacting π_v^* orbital perpendicular to the MS_2 plane. The longest wavelength band in the complexes $Cp_2Nb(S_2)X$ (X = Cl, Br, I), and $MoO(S_2)(dtc)_2$ occurs at ~20 kK and is assigned to a LMCT (ligand-to-metal charge transfer) of the type $\pi_v^*(S) \rightarrow d(M)$ [17]. This assignment is probably also correct for other complexes of structure type Ia which contain metal atoms in a high oxidation state, e.g. $[Mo_2O_2S_2(S_2)_2]^{2-}$.

The position of this first band is influenced by the oxidation state of the metal, by the metal–metal bonding and by the nature of the other ligands, which determine the energy of the LUMO and its metal character and thereby influence the optical electronegativity of the metal.

For disulfur complexes of structure type III the corresponding absorption band is expected to occur at higher energy because both π^* orbitals of the ligand interact strongly with the metals. Thus for $Nb_2(S_2)_2X_4$ (X = Cl, Br), $Mo_2(S_2)_2Cl_6$ and $Mo_3S(S_2)_3Cl_4$ the low-energy electronic absorption bands ≤ 20 kK are probably due to transitions within the metal–metal bond system. The same situation applies in $Fe_2(S_2)(CO)_6$, for which several MO calculations have been performed [137–139].

Especially interesting is the very intense band at 14.2 kK in $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]Cl_4$. A comparable band is not found in the related compounds with type IIa structures, $[(CN)_5Co(S_2)Co(CN)_5]^{6-}$ and aqueous $\{Cr(S_2)Cr\}^{4+}$. It has been proposed that the central unit in $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$ is best formulated as Ru^{II}–$(S_2)^-$–Ru^{III} [22,23]. Such a mixed valence complex could exhibit the intense band observed [140]. The isoelectronic mixed valence structure Fe^{II}–$(S_2)^-$–Fe^{III} has been proposed [24] for $Cp_2Fe_2(S_2)(SEt)_2$ (7) (structure type IIb) which exhibits an intense band at 11.9 kK [60].

F. DISCUSSION OF THE BONDING

One bonding framework for discussing the properties of metal complexes of diatomic molecules is to partition conceptually the complex into M^{m+} and Y_2^{n-}. The values for m and n are determined by comparing the physical properties of the complex [Y–Y distance, ν(Y–Y) (band position and intensity), electronic spectra, XP spectra, magnetic properties] with those of the isolated Y_2^{n-} species. This empirical basis for interpreting the physical data of dioxygen complexes has been discussed in detail elsewhere [16,17]. Here it is sufficient to note that complexes have been divided into super-

TABLE 10

Comparison of the distances and frequencies for X_2^{n-} (X=O, S; *n* =0–2)

Parameter	X_2 ($^3\Sigma_g^-$)	X_2^- ($^2\Pi_g$)	X_2^{2-} ($^1\Sigma_g^+$)
d(O–O)(pm)	121 [a]	133 [a]	149[a]
d(S–S)(pm)	189 [b]	200 [c]	213 [d]
ν(O–O)(cm^{-1})	1580 [a]	1097 [a]	802 [a]
ν(S–S)(cm^{-1})	725 [e]	589 [f]	446 [e]

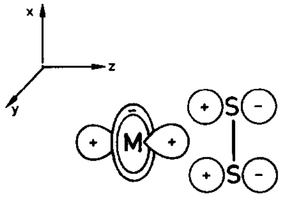
[a] Ref. 16. [b] Refs. 90 and 91. [c] Estimated value [122]. [d] Ref. 92. [e] Ref. 50. [f] Ref. 122.

oxide complexes (O_2^-) and peroxide (O_2^{2-}) complexes, primarily on the basis of O–O distance and ν(O–O) (Table 10). The superoxide ligand has $d_{O\text{-}O} \sim 130$ pm and $\nu(O–O) \sim 1125$ cm^{-1}; the peroxide ligand has $d_{O\text{-}O} \sim 145$ pm and $\nu(O–O) \sim 860$ cm^{-1} [16]. The electronic spectra of the complexes have also been used to classify dioxygen complexes [17,141].

For the known disulfur complexes, however, a similar empirical classification is not possible. The S–S distances are in the continuous range 198–215 pm, and do not strongly correlate with structure type [Section B(v)]. The ν(S–S) frequencies are in the continuous range 480–600 cm^{-1}. Moreover the ν(S–S) vibration is strongly coupled to the ν(M–S) vibrations so that the ν(S–S) frequencies are not a simple indicator of the formal charge on the S_2 ligand. However, comparison of the S–S distances and frequencies in Table 10 with those in Tables 2–4 indicates that an effective charge on the ligand in disulfur complexes between -1 and -2 seems reasonable. A similar conclusion can be drawn from the sulfur and metal binding energies of the ESCA spectra. All the physical data are consistent with a charge delocalisation from the polarizable (soft) S_2^{2-} ligand to the metal.

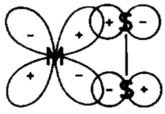
The Y_2^- ligand seems to be less important for disulfur complexes than for dioxygen complexes. Most disulfur complexes are diamagnetic, although a few show a weak paramagnetism. Consequently EPR spectroscopy cannot be used to probe the electron distribution in the HOMO in these complexes. The S_2^- classification has been advocated for the ligand in $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$ from analysis of the electronic spectra [22,23], and for $Cp_2Fe_2(S_2)(SR)_2$ [24,110] from similarities of the ligand geometry to the geometry of the O_2 ligand in superoxide complexes.

An alternative approach to describe the bonding in MY_2 complexes is to consider the triatomic MY_2 unit as a covalent inorganic functional group. Enemark and Feltham have shown [142] that the diverse properties of metal nitrosyl complexes can be conveniently interpreted by describing the complexes as derivatives of the $\{MNO\}^n$ group, where n is the total number of electrons in the d orbitals of the metal and the π^* orbitals of the nitrosyl ligand. This qualitative concept has been extended to other diatomic ligands [143]. Particularly germane to this review is the analysis of the bonding in η^2 (side-on) MO_2 complexes which show that the primary bonding interaction involves the metal d_{xz} orbital and the $\pi_z^*(\pi_h^*)$ orbital of the O_2 ligand (π-bonding) (**17**) and the d_{z^2} orbital and the $\pi_z(\pi_h)$ orbital (σ-bonding) (**16**)



σ-bonding ($\pi_z \rightarrow d_{z^2}$)

(16)



π-bonding ($\pi_z^* \rightarrow d_{xz}$)

(17)

according to the qualitative Dewar–Chatt–Duncanson bonding scheme [144–146] [the interaction of the $\pi_y(\pi_v)$ and the $\pi_y^*(\pi_v^*)$ orbitals are considered to be negligible]. The major contribution is the π-bonding as shown by more quantitative molecular orbital calculations of side-on MO_2 complexes [147].

For type Ia disulfur complexes the π-bonding should also be the major bonding interaction. For type III $\{M1–S_2–M2\}$ complexes this bonding interaction (**17**) would occur twice, once between π_z^* of S_2 and M1 and once between π_y^* of S_2 and M2. If M2 is a positively charged metal ion with few d electrons then there should be less electron density on the disulfur unit in a type III complex relative to a type Ia complex. Such depopulation of the π^* orbitals of the disulfur ligand is consistent with the greater susceptibility of type III complexes to nucleophilic attack and with the shorter S–S distances and higher ν(S–S) values for such complexes. These properties are consistent with the π-donor character of the disulfur ligand and the empirical assignment of the charge on the ligand as approximately −2.

The facile formation and cleavage of S–S bonds in chemical reactions suggests that the $\sigma^*(p)$ orbital of the S–S bond in disulfur complexes may also be relatively close in energy to the metal d and disulfur π^* orbitals. In fact, the σ^* orbital of the coordinated S_2 ligand is of the same symmetry as the major component of the bonding (**17**) between the metal and the S_2 ligand. Further interpretation of the properties of disulfur complexes must await more quantitative descriptions of the bonding.

G. CONCLUSION

The chemistry of disulfur complexes is still in its early stages. However, there is no other simple ligand that is as versatile in its coordination to metals. The range of structures and chemical reactions already known augur well for the future of this area of metal–sulfur chemistry.

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