ADVANCES IN INORGANIC CHEMISTRY, VOL. 31

POLYSULFIDE COMPLEXES OF METALS

A. MÜLLER and E. DIEMANN

Fakultät für Chemie der Universität, D-4800 Bielefeld,
Federal Republic of Germany

I. Introduction

Many complexes with stable homonuclear diatomic ligands like O_2 and N_2 are well known and have been extensively studied. Only in recent years has the chemistry of metal complexes containing one or more coordinated homonuclear *sulfur ligands*, S_n^{2-} (with $n = 2$ or $n > 2$), been developed systematically. Complexes with S_n^{2-} units can be obtained for many metals under a variety of conditions, and coordinated S_n^{2-} ligands exhibit an especially rich structural chemistry.

Sulfide minerals were formed mostly hydrothermally from postmagnetic fluids; it appears remarkable that the formation of many ore deposits cannot be conclusively explained because of the very low solubility of the corresponding sulfide. Though it was postulated earlier (*28, 29, 95*) that polysulfido complexes might have been responsible for "the transport of metals and sulfur together" (*80*), it was later proved that many discrete polysulfido complexes and clusters of metals exist in polysulfide solutions (see, e.g., *136, 138*).

The formation of soluble polysulfido clusters or complexes is also responsible for the fact that some classical analytical separation procedures based on polysulfide solutions (distinguishing between the classical thioanion-forming elements like As, Sb, Sn, and others like Cu) sometimes fail (*51*).

It is now evident that S_n^{2-} ions are fascinating and versatile (polydentate) ligands from the structural point of view, and that metal aggregates can be nicely "glued" by these ligands according to their high (and variable) number of coordination sites, which keeps the charge of the cluster low (*134*). In $[Cu_6(S_4)_3(S_5)]^{2-}$ only four ligands are capable of stabilizing a cluster with six metal atoms (*134*). It is remarkable that all possible S_n^{2-} ions ($n = 2$–9) occur in complexes, although S_9^{2-} has not been reported until now as an isolated ion.

It should also be noted that polysulfido complexes are not only interesting because of their structures and reactivity, but also because of their possible applications. They can, for example, be used to prepare sulfur rings of predetermined size and they are also suspected to play a role in catalysis (particularly in hydrodesulfurization).

II. Polysulfide Ions and Solutions

Free polysulfide ions consist of sulfur chains. The atoms of an S_3^{2-} chain are necessarily coplanar. Longer chains, however, exhibit different possibilities of isomerism. For example, by addition of one sulfur atom *d*- and *l*-S_4^{2-} can be obtained (Fig. 1). To describe the structures, in addition to bond lengths and interbond angles, the dihedral angle must be specified. For polysulfides, this angle is found to be between 60 and 110° in various examples. In order to illustrate the isomerism, the interbond and dihedral angles in Fig. 1 have been idealized to 90°.

The S_5^{2-} chain derives from the S_4^{2-} one by addition of one more sulfur atom, so that the dihedral angle of 90° is maintained. In doing so, we obtain structures c and d (Fig. 1), the cis and (*d* and *l*) trans forms of the S_5^{2-} chain. Similarly, by further addition of one sulfur atom, it can be shown that for an S_6^{2-} chain three (enantiomorphic) isomers will result (cis,cis; trans,trans; and cis,trans, each *d* and *l*, respectively). The *cis*-S_5^{2-} and *cis,cis*-S_6^{2-} ions may be regarded as parts of the S_8 ring

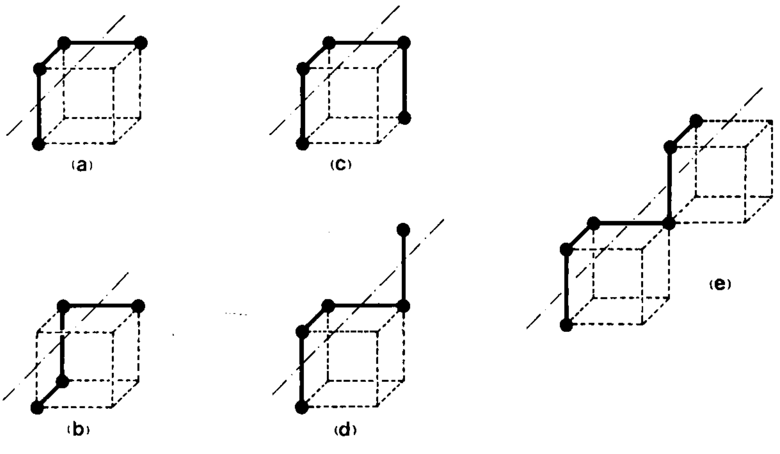


FIG. 1. Idealized stereochemistry (dihedral angle equal to 90°) for polysulfide ions (*191*). (a), (b), *d*- and *l*-S_4^{2-}; (c), (d), *cis*- and *trans*-S_5^{2-}; (e), *trans,trans*-S_6^{2-}

structure, while *trans*-S_5^{2-} and *trans,trans*-S_6^{2-} correspond to portions of an infinite helical chain (like that, e.g., in fibrous sulfur). All-trans conformations of the polysulfide chains have been found in, for example, Cs_2S_5 (*10*), Cs_2S_6 (*8*), and $(PPh_4)_2S_7$ (*70*); this is obviously the normal arrangement. However, the cis conformation has been detected in α-Na_2S_5 (*9*), the cis,trans conformation in $[(CH_3)_4N](NH_4)S_6$ (*112*), and the cis conformation for the five central sulfur atoms of S_7^{2-} in $(PPh_4)(NH_4)S_7 \cdot CH_3CN$ (*126*).

Solutions containing several S_n^{2-} species (but mainly S_4^{2-} and S_5^{2-}) are obtained upon digesting sulfur with aqueous sulfide. Solutions in methanol and ethanol may be prepared correspondingly. Salts of S_n^{2-} ($n = 2$–8) can be obtained not only from such solutions but also from liquid NH_3 and in dry reactions.

The average S—S bond length is shorter in S_n^{2-} ($n > 2$) than in S_2^{2-}, and the S—S terminal bond lengths decrease from S_3^{2-} (2.15 Å) to S_7^{2-} (1.992 Å) (*70*). These facts indicate that the negative charge (filling a π^*-antibonding molecular orbital) is delocalized over the whole chain, but the delocalization along the chain is less in higher polysulfides. This consideration is significant in comparing the S—S bond length of the free ions with those of the coordinated ones.

III. Survey of Compound Types

A. COMPLEXES WITH DIFFERENT TYPES OF COORDINATED S_2^{2-} LIGANDS

Complexes with S_2^{2-} ligands show a remarkable variety of structures, which result from the extension of the fundamental structural type Ia (side-on coordination) as well as IIa and IIb [cis and trans "end-on" (doubly) bridging coordination],[1] by using the remaining lone pairs of electrons (on sulfur) to coordinate additional metal atoms. Such coordination of additional metal atoms occurs for all three fundamental structural types (Ia, IIa, IIb). Representative examples (including structural type definitions) are summarized in Table I. End-on coordination of an S_2^{2-} ligand to a single metal atom to give a terminal MS_2 unit is unusual and has been claimed only for matrix-isolated MgS_2, ZnS_2, and CdS_2 (*94*).

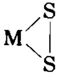
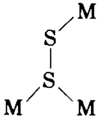
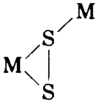
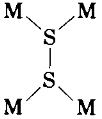
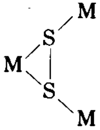
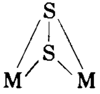
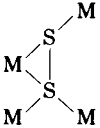
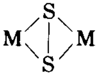
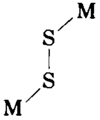
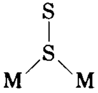
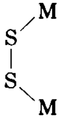
Another fundamental type of structural unit found in many cluster compounds is III, in which both sulfur atoms of the ligand are bonded to

---

[1] These types are also known for dioxygen complexes (*88, 186*).

TABLE I

TYPICAL GEOMETRIES OF S_2^{2-} COMPLEXES[a]

Structural type	Example	Structural type	Example
Ia 	$[Ir(dppe)_2(S_2)]^+$ **(1)**	IIc 	$Cp_4Co_4(S_2)_2S_2$
Ib 	$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$ **(4)**	IId 	$(SCo_3(CO)_7)_2(S_2)$ **(9)**
Ic 	$Mn_4(S_2)_2(CO)_{15}$ **(6)**	IIIa 	$[Mo_2(S_2)_6]^{2-}$ **(10)**
Id 	$Mn_4(S_2)_2(CO)_{15}$ **(6)**	IIIb 	$[(triphos)_2Ni_2(S_2)]^+$
IIa 	$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	IV 	$MeCp_2Cr_2(S_2)_2S$ **(12)**
IIb 	$[Mo_4(NO)_4(S_2)_6O]^{2-}$ **(8)**		

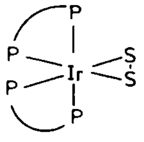
[a] For references see text and Table II.

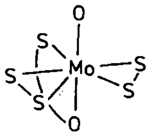
each of two metal atoms. The S—S bond is oriented approximately perpendicular to the metal–metal vector. A very remarkable, but uncommon, type of bridging ligand has been discovered in which two metal atoms are attached to the same sulfur atom of the ligand (structure type IV) (*16*).

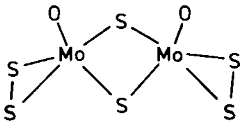
1. Type I Complexes

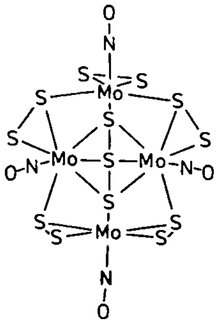
Complexes with type I structures are listed in Table II along with their S—S distances [*d*(S—S)] and S—S vibrational frequencies [ν(S—S)]. The most common mode of coordination is structure type Ia, in which the ligand occupies two coordination sites of the metal atom. One example of this type of binding is the complex $[\mathrm{Ir(dppe)_2(S_2)}]\mathrm{Cl}$ (**1**) (*7, 55*). The Ir atom is in a distorted octahedral environment, as would be expected for a six-coordinate metal with a d^6 electron configuration. Higher coordination numbers are found for complexes of the early transition elements. In $[\mathrm{MoO(S_2)_2(C_2O_3S)}]^{2-}$ (**2**) the Mo atom adopts pentagonal-bipyramidal coordination geometry with the S atoms of S_2^{2-} and of the thiooxalate ligand lying in the pentagonal plane (*100, 101*).

Several binuclear Mo(V) complexes contain type Ia ligands. The central $\{\mathrm{MoO(\eta^2\text{-}S)_2MoO}\}^{2+}$ structural unit in $\mathrm{(NMe_4)_2[Mo_2O_2S_2(S_2)_2]}$ (**3**) has the Mo=O groups in syn stereochemistry (*26, 161*). Related examples are $[\mathrm{Mo_2OS_7}]^{2-}$ (where one oxygen of **3** is substituted by sulfur) (*139*) and $[\mathrm{W_2S_{10}}]^{2-}$ (with one S_4^{2-} ligand at one tungsten atom) (*139*).


1


2


3


4

Ligands of structure type Ib also exist in the interesting compound $\mathrm{(NH_4)_4[Mo_4(NO)_4(S_2)_5S_3]\cdot 2H_2O}$ (**4**), which contains sulfur atoms in five different bonding situations (*118*). Four of the five S_2^{2-} ligands

TABLE II

REPRESENTATIVE EXAMPLES OF COMPLEXES WITH TYPES I–III S_2^{2-} LIGANDS

Formula	Type	d(S—S)[a] (Å)	ν(S—S)[a] (cm^{-1})	Color	Reference
$[Ir(dppe)_2(S_2)]^+$	Ia	2.07	528	Orange	*7, 55*
$[Rh(dmpe)_2(S_2)]^+$	Ia	—	525	Orange	*55*
$RhL1(S_2)Cl$[b]	Ia	—	546	Orange	*151, 152*
$Os(CO)_2(PPh_3)_2(S_2)$	Ia	—	—	Orange	*23, 47*
$[Rh(vdiars)_2(S_2)]^+$[c]	Ia	—	554	Red-brown	*89*
$[Rh(L2)_2(S_2)]^+$[d]	Ia	—	—	Brown	*46*
$[MoO(S_2)_2(mtox)]^{2-}$[e]	Ia	2.01	530	Dark red	*100, 101*
$MoO(S_2)(dtc)_2$[f]	Ia	2.02	558	Blue	*36, 37*
$Cp_2Mo(S_2)$	Ia	—	536	Red	*77*
$Cp_2Nb(S_2)Cl$	Ia	—	540	Red	*184*
$Cp_2Nb(S_2)Me$	Ia	2.01	540	Orange	*1, 102*
$[Mo_2O_2S_2(S_2)_2]^{2-}$	Ia	2.08	510	Red-orange	*26, 27, 161*
$[Mo_2S_4(S_2)(S_4)]^{2-}$	Ia	2.07	—	Red-violet	*25*
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	Ia	2.04	536	Red	*118*
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	Ib	2.05	550	Red	*118*
$Cp_2Fe_2(S_2)_2CO$	Ib	1.99	—	Green	*52*
$Mn_4(S_2)_2(CO)_{15}$	Ic	2.07	—	Red	*84, 85*
$Mn_4(S_2)_2(CO)_{15}$	Id	2.09	—	Red	*84, 85*
$[(CN)_5Co(S_2)Co(CN)_5]^{6-}$	IIa	—	490	Red-brown	*174*
$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	IIa	2.01	514	Green	*15, 44*
$Cp(CO)_2Mn(S_2)MnCp(CO)_2$	IIa	2.01	—	Dark green	*62*
$\{(Re_6S_8)S_{4/2}(S_2)_{2/2}{}^{4-}\}_n$	IIa	2.09	—	Dark red	*14, 22, 171*
$Cp_2Fe_2(S_2)(SEt)_2$	IIb	2.02	507	Dark green	*82, 83, 183*
$[Mo_4(NO)_4(S_2)_6O]^{2-}$	IIb	2.08	480	Violet	*115*
$Cp'_2Mo_2(S_2)_5$[g]	IIb[h]	2.04	—	Black	*158*
$Cp_4Co_4(S_2)_2S_2$	IIc	2.01	—	Black	*185*
$Cp_4Fe_4(S_2)_2S_2$	IIc	2.04	503	Black	*82, 187*
$(SCo_3(CO)_7)_2(S_2)$	IId	2.04	—	Black	*93, 180*
$\{CpMn(NO)(S_2)\}_n$	IId	—	491(?)	Red-brown	*154*
$[(Cp_4Fe_4(S_2)_2S_2)_2Ag]^+$	IId	2.05	478	Black	*82, 187*
$[Mo_2(S_2)_6]^{2-}$	IIIa	2.04	550	Green-black	*127, 128*
$\{Mo_2(S_2)_2Cl_4Cl_{4/2}\}_n$	IIIa	1.98	561	Dark brown	*92*
$Nb_2(S_2)_2Cl_4$	IIIa	2.03	588	Brown	*155, 170*
$[Mo_3S(S_2)_6]^{2-}$	IIIa	2.02	545	Red	*129, 140*
$Mo_3S(S_2)_3Cl_4$	IIIa	2.03	562	Red	*92*
$Fe_2(S_2)(CO)_6$	IIIa	2.01	555	Red	*63, 71, 190*
$Ta_2(S_2)_2(PS_4)_2$	IIIa	2.05	—	Grey	*49*
$Mo_2(n\text{-}BuCp)_2(S_2)Cl_4$	IIIa	2.02	—	Black	*17, 103*
$Mo_2(S_2)(S_2C_2Ph_2)_4$	IIIa	2.04	518	Green-black	*193*
$Nb_2S(S_2)Br_4(tht)_4$[i]	IIIa	2.01	—	Green	*41*
$[Mo_2(S_2)(SO_2)(CN)_8]^{4-}$	IIIa	2.00	520	Violet	*157*
$[(triphos)_2Ni_2(S_2)]^+$	IIIb	2.21	—	Brown	*99*

[a] Mean value.

[b] L1 = $PPh(CH_2CH_2CH_2PPh_2)_2$.

[c] vdiars = $Ph_2AsCHCHAsPh_2$.

[d] L2 = R_2PNHPR_2.

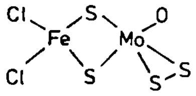
[e] mtox = O_2CCOS^{2-}.

[f] dtc = S_2CNPr_2.

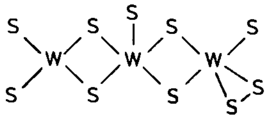
[g] Cp′ = Me_5Cp.

[h] Mo—S—S—Mo angle ≈ 59.7°.

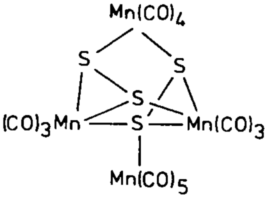
[i] tht = tetrahydrothiophene.



5a



5b



6

bridge pairs of Mo atoms unsymmetrically (structure type Ib). One S_2^{2-} ligand is "side-on" coordinated to a single Mo atom (structure type Ia).

It is also interesting to note that in $[Cl_2FeS_2MoO(S_2)]^{2-}$ (**5a**) (*141*) and $[S_2WS_2(WS)S_2(WS)(S_2)]^{2-}$ (**5b**) (*194*) (with type Ia ligands) the units $\{S_2MoO(S_2)\}^{2-}$ and $\{S_2WS(S_2)\}^{2-}$ may be regarded as perthio derivatives of the thiometalates $MoOS_3^{2-}$ and WS_4^{2-}, respectively.

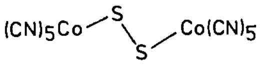
Structure types Ic and Id (Table I), in which the ligand is coordinated to three and four metal atoms, respectively, both occur in $Mn_4(S_2)_2(CO)_{15}$ (**6**) (*84, 85*).

2. *Complexes with Type II Structure*

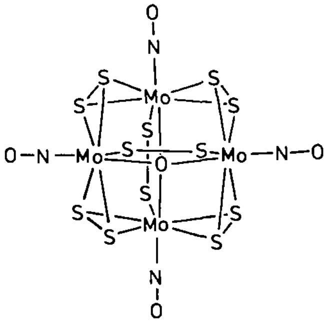
Complexes with type II structures are compiled in Table II along with their S—S distances and S—S vibrational frequencies. There are several examples of complexes of structure type IIa (planar trans end-on bridging coordination). Vibrational spectroscopy (*174*) indicates that this structure occurs in $[(CN)_5Co(S_2)Co(CN)_5]^{6-}$ (**7**). Trans arrangement of the metal atoms has been proved by X-ray structure determination for $[(NH_3)_5Ru(S_2)Ru(NH_3)_5]Cl_4 \cdot 2H_2O$ (*15, 44*).

Structure type IIb (cis end-on bridging coordination) is found in $Cp_2Fe_2(S_2)(SEt)_2$ (*83, 183*), where it is dictated by the two bridging SEt groups. The $Fe(S_2)Fe$ group is planar (as in type IIa structures). The same kind of coordination occurs in $[Mo_4(NO)_4(S_2)_6O]^{2-}$ (**8**) (*115*). This complex represents a tetragonal bisphenoid of Mo atoms with an interstitial oxygen atom. The two nonadjacent edges of the metal cage are bridged by type IIb S_2^{2-} ligands. The remaining four edges are bridged by ligands of structure type IIIa (*vide infra*).

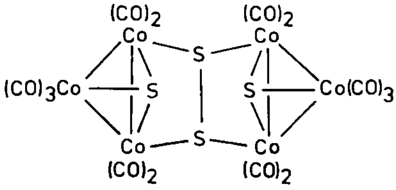
The complex $Cp_4Co_4(S_2)_2S_2$ has a cage structure with two S_2^{2-} ligands, each of which bridges three Co atoms (type IIc) (*185*). A few complexes have been structurally characterized in which an S_2^{2-} ligand bridges four metal atoms (structure type IId, Tables I and II). In the cluster compound $(SCo_3(CO)_7)_2(S_2)$ (**9**), the ligand is bound to one edge of each of two Co_3 triangles (*93, 180*). The resulting structure consists of two Co_3S_2 planes which have a common S_2^{2-} edge.



7



8

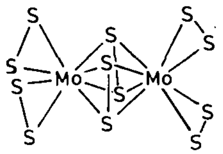


9

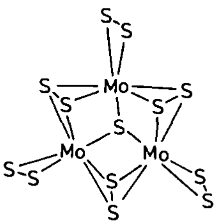
3. *Complexes with Type III Structures*

Type III complexes are included in Table II. The binuclear compound $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ (**10**) incorporates only $S_2{}^{2-}$ ligands (*127, 128*). Two of the $S_2{}^{2-}$ ligands bridge the two Mo atoms (type IIIa) and four of the $S_2{}^{2-}$ ligands are bonded to a single Mo atom (type Ia geometry). The coordination geometry about each Mo atom is distorted dodecahedral. An interesting feature of the type IIIa bridging $S_2{}^{2-}$ ligands is their asymmetric bonding to the Mo atoms. A second structural isomer of $[Mo_2S_{12}]^{2-}$, with two terminal and two bridging sulfides and one $S_4{}^{2-}$ ligand at each Mo atom, and the corresponding tungsten species $[W_2S_4(S_4)_2]^{2-}$ (**30b**), have also been reported (*40, 139*).

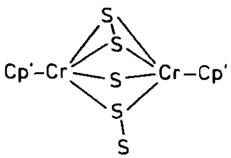
Another cluster anion with type IIIa ligands which contains only molybdenum and sulfur occurs in $(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O$ (**11**) (*111, 129*) ($n = 0$–2, with variable nonstoichiometric amounts of water, which are disordered in the crystal lattice) (*35*). This type of ligand has



10



11



12

also been found in a compound containing two isostructural anions in the crystal lattice, i.e., the mixed valence $[(\mathrm{Mo}^{\mathrm{III/IV}})_2(\mathrm{SO}_2)(\mathrm{S}_2)(\mathrm{CN})_8]^{5-}$ (paramagnetic) and $[\mathrm{Mo}_2{}^{\mathrm{IV}}(\mathrm{SO}_2)(\mathrm{S}_2)(\mathrm{CN})_8]^{4-}$ (diamagnetic) (*117*).

Structure type IIIb with an η^2-$\mathrm{S}_2{}^{2-}$ ligand that is coplanar with the two metal atoms has been detected in $[(\text{triphos})\mathrm{Ni}(\mu\text{-}\mathrm{S}_2)\text{-}\mathrm{Ni}(\text{triphos})]\mathrm{ClO}_4$[triphos = bis(2-diphenylphosphinoethyl)phenylphosphine] (*99*).

In $\mathrm{Cp'}_2\mathrm{Cr}_2\mathrm{S}(\mathrm{S}_2)_2$ (**12**) two Cr atoms are bridged by a type IIIa $\mathrm{S}_2{}^{2-}$ ligand, by a sulfido group, and by a type IV ligand (*16*). This compound is the first known example of the latter type. Both the type IIIa and type IV S—S bonds are surprisingly long (2.15 and 2.10 Å, respectively).

B. COMPLEXES WITH RING SYSTEMS GENERATED BY $\mathrm{S}_n{}^{2-}$ IONS ($n > 2$)

Different types of coordination of $\mathrm{S}_n{}^{2-}$ ligands are shown in Fig. 2.

1. *Mononuclear Complexes with* $\mathrm{M}(\mu_2\text{-S})_n$ *Ring Systems (Bidentate Ligands)*

Only a few compounds containing the $\mathrm{S}_3{}^{2-}$ ligand are known. The compound $(\mathrm{MeCp})_2\mathrm{Ti}(\mathrm{S}_3)$ (**13**) contains a nonplanar four-membered TiS_3 ring with a dihedral angle of 49° between TiS(1)S(2) and

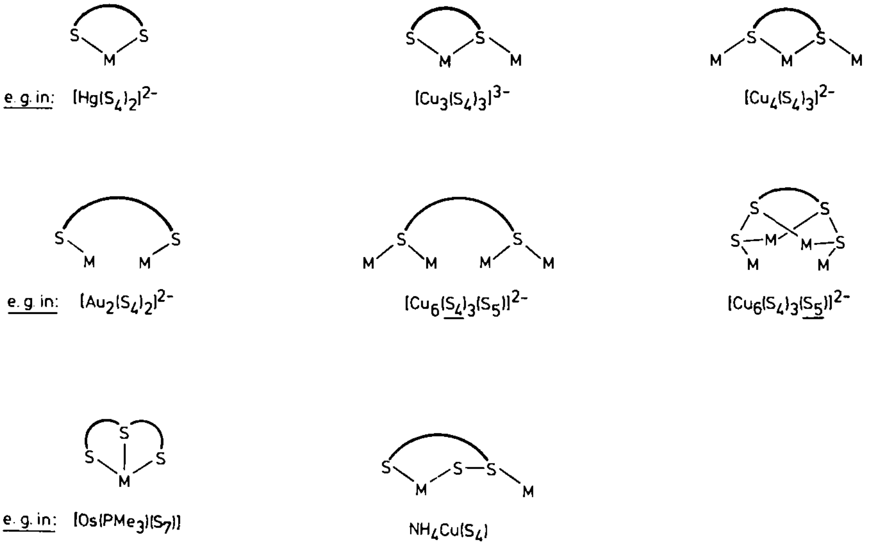
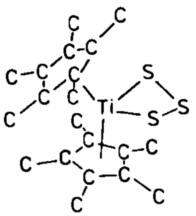


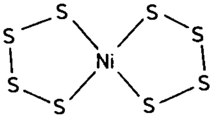
FIG. 2. Important structure types observed for $\mathrm{S}_n{}^{2-}$ complexes (mainly with $n = 4$).

S(1)S(2)S(3) (*2*). On the other hand quite a number of complexes with S_4^{2-} ligands have been prepared and structurally characterized. In compounds where the ion acts as a bidentate ligand, an "envelope" as well as a "half-chair" conformation is possible. In $Cp_2M(S_4)$ (M = Mo, W) (complexes with tetrahedral coordination of the metal ions) (*34, 73*) and in $[M(S_4)_2]^{2-}$ [M = Ni (**14**), Pd] the half-chair conformation is found (*123*) whereas several complexes with a square-pyramidal coordination of Mo and W show the envelope conformation (*25, 40, 139*). The S_4^{2-} ligand has also been found in $[Sn(S_4)_3]^{2-}$, $[Sn(S_4)_2(S_6)]^{2-}$ (*143*), and $[M(S_4)_2]^{2-}$ [M = Zn (*31*), Hg (**17b**) (*142*)].

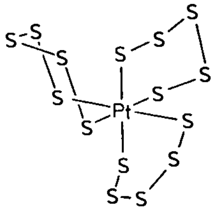
Quite a few complexes with the bidentate pentasulfido ligand are also known. The first reported was the homoleptic and optically active complex $[Pt(S_5)_3]^{2-}$ (**15**) (*53, 64, 65, 68, 69, 176*). Brick-red $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$ is formed from the reaction of $K_2[PtCl_6]$ with aqueous $(NH_4)_2S_n$ solution. Addition of concentrated HCl results in the separation of maroon $(NH_4)_2[PtS_{17}]\cdot 2H_2O$ (*54*). The $[Pt(S_5)_3]^{2-}$ ion crystallizes from the solution as a racemate, which can be resolved by forming diastereoisomers. Upon crystallization, $[PtS_{17}]^{2-}$ undergoes a second-order asymmetric transformation, so that the solid contains an excess of the (−) enantiomer (*54*).



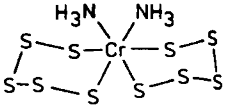
13



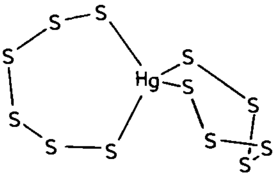
14



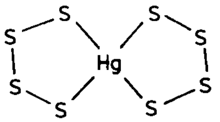
15



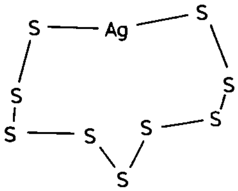
16



17a



17b



18

The compound $Cp_2Ti(S_5)$ (*76, 167*), which has been prepared by various different routes (*vide infra*), is probably the most thoroughly studied polysulfido compound. Some of the more important reactions of this complex will be discussed below. The corresponding compounds of zirconium, hafnium, and vanadium have been obtained by the reaction of Cp_2MCl_2 with $Li_2S_2/3S$ or $(NH_4)_2S_5$, respectively (*78, 97*). The spectroscopic properties of the black paramagnetic complex $Cp_2V(S_5)$ are particularly interesting and helpful for a general description of the electronic structure of Cp_2ML_2 compounds (*156*).

The MS_5 moiety has the chair conformation in all known mononuclear complexes. Examples are $[Cr(NH_3)_2(S_5)_2]^{2-}$ (**16**) (*143*) and $[(S_5)Mn(S_6)]^{2-}$ (*31*). It is worth noting that the "bite" of $S_5{}^{2-}$ varies strongly [a very large one is found in $[(S_5)Fe(MoS_4)]^{2-}$ (*30, 32*)].

Some mononuclear complexes containing bidentate $S_6{}^{2-}$ ligands can also be isolated. Examples include the homoleptic $[M(S_6)_2]^{2-}$ [M = Zn, Cd, Hg (**17a**)] (*144, 145*) and two containing the $S_9{}^{2-}$ ligand, namely $[AuS_9]^-$ (*91*) and $[AgS_9]^-$ (**18**) (*137, 143*), both with ring structure. The following homoleptic mononuclear complexes are known at present: $[M(S_4)]^{2-}$ [M = Zn (*31*), Ni (*123*), Pd (*123*), Hg (*142*)], $[Pt(S_5)_2]^{2-}$ (*168, 192*), $[M(S_5)_3]^{m-}$ [M = Pt, $m = 2$ (*53, 64, 65, 69*); M = Rh, $m = 3$ (*79*)], $[M(S_6)_2]^{2-}$ [M = Zn, Cd (*142*), Hg (*144*)], and $[M(S_9)]^-$ [M = Ag (*137, 143*), Au (*91*)].

Monocyclic MS_n units are known for $n = 3–7$ and 9. Among the mononuclear complexes there is also an example where a polysulfide acts as a tridentate ligand, namely the $S_7{}^{2-}$ ion in $(Me_3P)_3M(S_7)$ (M = Ru, Os). The OsS_7 bicycle shows a similar exo-endo conformation as the $S_8{}^{2+}$ ion in $S_8(AsF_6)_2$ (*58*).*

2. *Binuclear Complexes with* $M(\mu_2 - S)_nM$ *Units (Doubly Bridging Ligands)*

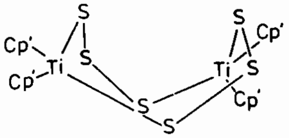
Only a few binuclear complexes are known in which $S_n{}^{2-}$ ($n = 3–8$) acts as a doubly bridging ligand. The structure of $(MeCp)_4Ti_2S_6$ (**19**) consists of an eight-membered ring containing alternating Ti atoms and S_3 fragments. In contrast to cyclo-S_8, the ring adopts a "cradle" conformation with the Ti atoms positioned at the sites adjacent to the apical S atoms. In the complex, the S—S—S angles are expanded relative to those known for other cyclic sulfur ring species (*6*).

The $\{S_5Mo_2(S')\}$ moiety in $[Mo_2(NO)_2(S_2)_3(S_5)(OH)]^{3-}$ (**20a**), however, has practically the same geometry as that of cyclooctasulfur [if one ring member is assumed to be at the center of the bridging $S_2{}^{2-}$ group ("S′")] (*114*). The highest known oxidation state (+5) of a metal atom in a polysulfido ($S_n{}^{2-}$, $n > 2$) was found in $[Nb_2(OMe)_2(S_2)_3(S_5)O]^{2-}$ (**20b**), in which the $\{Nb_2S'S_5\}$ fragment has the conformation of $S_8{}^{2+}$ (*143*). The compound Os_2-μ-(S_5)-μ-(S_3CNR_2)-$(S_2CNR_2)_3$ (**21**) contains the $S_5{}^{2-}$ ion as a "half-bridging" ligand (*90*).

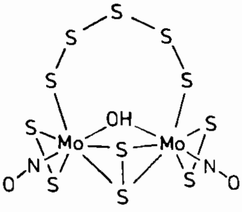
---

* Polynuclear species with monocyclic MS_4 entities such as $W_2S_{12}{}^{2-}$ (**30b**) are not discussed separately.

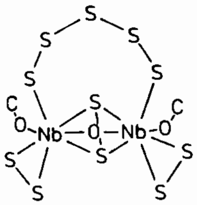
The six-membered OsS_5 ring has the chair conformation. A seven-membered 1,4-dirheniacycloheptasulfur ring has been found in $Cp_2Re_2(CO)_2(\mu\text{-}S_2)(\mu\text{-}S_3)$ (**22**) (*61*).



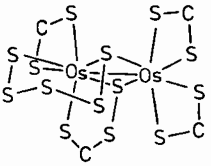
19



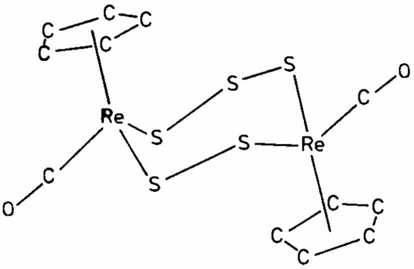
20a



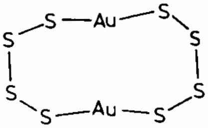
20b



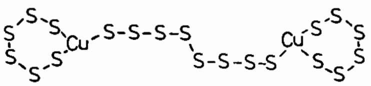
21



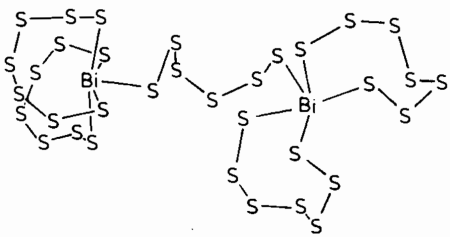
22



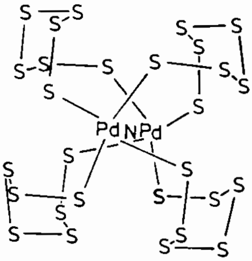
23



24



25a



25b

The remarkable 10-membered highly symmetrical $[Au_2S_8]^{2-}$ ring (**23**) consists of two Au atoms and two bridging $S_4{}^{2-}$ ligands and has approximately D_2 symmetry (*136*). The binuclear complexes

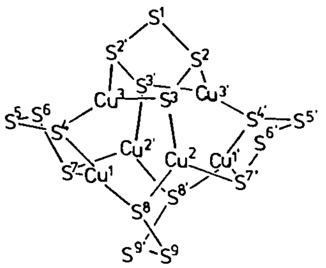
$[(S_6)M(S_8)M(S_6)]^{4-}$ (M = Cu (**24**), Ag) have two bidentate $S_6{}^{2-}$ ligands (forming rings) and the doubly bridging $S_8{}^{2-}$ ligand (*109, 133*). A novel bismuth polysulfido compound with the highest portion of sulfur known so far, $[Bi_2(S_6)(S_7)_4]^{4-}$ (**25a**), has also been prepared (*149*).

An interesting example of doubly bridging $S_7{}^{2-}$ ligands has been found in $[Pd_2(S_7)_4]^{2-}$ (**25b**) (*148*) (with a $NH_4{}^+$ ion captured in the center of the cage).

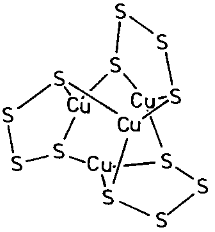
3. Polynuclear Complexes with Condensed Ring Systems (Polydentate Ligands)

One would expect (according to the high number of coordination sites) that "soft metal aggregates" could be "glued" by $S_n{}^{2-}$ ions.

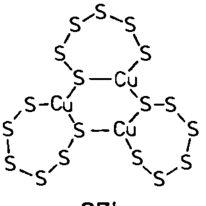
A remarkable species with very different types of coordination is the hexanuclear complex $[Cu_6S_{17}]^{2-}$ (**26**) containing 10 μ_3-sulfur atoms and an aggregate of six Cu(I) ions which can be approximately described as two Cu_4 tetrahedra sharing one edge (*134, 135*). Whereas only the two terminal sulfur atoms of the three $S_4{}^{2-}$ ligands in **26** are bonded to copper atoms, coordination of four sulfur atoms of the $S_5{}^{2-}$ ligand is found. Each of the two equivalent $S_4{}^{2-}$ ions acts as a bridging and chelating ligand for the two "Cu tetrahedra," with coordination to three different Cu atoms. The S4 and S7 atoms (correspondingly S4′ and S7′) are bonded not only to the same atom Cu1 (Cu1′), but also to Cu3 and Cu2′ (Cu3′ and Cu2), respectively. The other $S_4{}^{2-}$ (S8—S9—S9′—S8′) and the $S_5{}^{2-}$ ligands are responsible for the connection of the "tetrahedra." Both ligands show coordination to four different Cu atoms.



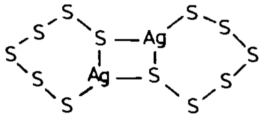
26



27a



27b



28

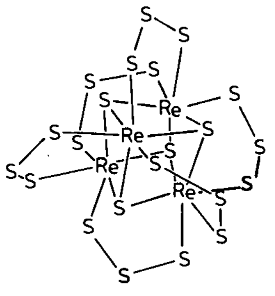
The tetranuclear clusters $[Cu_4(S_n)_3]^{2-}$ ($n = 4$ (**27a**), 5) [including $[Cu_4(S_5)_2(S_4)]^{2-}$ and $[Cu_4(S_5)(S_4)_2]^{2-}$] have six μ_3-S atoms from three S_n^{2-} ligands as bridges for the six edges of the metal tetrahedra. The trinuclear species $[Cu_3(S_6)_3]^{3-}$ (**27b**) and $[Cu_3(S_4)_3]^{3-}$ have three μ_3-S atoms forming the central Cu_3S_3 ring with the chair conformation (*109, 135, 136*).

The basic structure of the species $[Cu_4(S_n)_3]^{2-}$ can formally be obtained from $[Cu_3(S_n)_3]^{3-}$ (a novel polycyclic inorganic species with different puckered copper sulfur heterocycles, a central Cu_3S_3 ring with the chair conformation, and three outer CuS_6 or CuS_4 rings) by coordination of each of the three "end-on bonded sulfur atoms" of the three polysulfide ligands to an additional fourth Cu(I) (*135, 136*). The structure of $[Cu_6S_{17}]^{2-}$ can formally be derived by connecting two $Cu_3(\mu\text{-}S)_3$ rings by four polysulfido ligands.

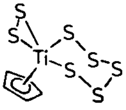
It turns out that the six-membered $Cu_3(\mu\text{-}S)_3$ rings are paradigmatic units. This type of ring system has been incorporated into current models of metallothioneins [low-molecular-weight proteins which are believed to play a key role in metal metabolism (cf. references in *136*)]. The structural chemistry of the Ag complexes seems to be different. Monocyclic $\{Ag(S_n)\}^-$ rings can be linked via bridging ligands as in $[(S_6)Ag(S_8)Ag(S_6)]^{4-}$ (*133*) or condensed as in $[Ag_2(S_6)_2]^{2-}$ (**28**) (*126*).

4. *Ring Systems with Strong Metal–Metal Bonds*

The cubane cluster $[Re_4S_4(S_3)_6]^{4-}$ (**29a**) with six bridging S_3^{2-} ligands has been reported recently (*124*). This is the only known species where metal–sulfur rings with strong metal-to-metal bonds occur. The six Re_2S_3 rings have planar Re_2S_2 moieties and, therefore, an envelope conformation. Complexes of the type $[Re_4S_4(S_3)_n(S_4)_{6-n}]^{4-}$ can also be obtained (*107*).



29a



29b

5. *Mixed (Polysulfido) Ligand Complexes*

Several complexes, particularly the labile ones discussed above, contain two different S_n^{2-} ligands (e.g., **27a**). Another nice example is $CpTi(S_2)(S_5)$ (**29b**) (*107*) with a pseudo-sandwich structure.

C. SOLID-STATE STRUCTURES

Many solid-state structures with S_n^{2-} groups are known (e.g., $Na_2Re_3S_6$, NbS_2Cl_2, MoS_2Cl_3, or $Mo_3S_7Cl_4$; all having S_2^{2-} ligands). The reviews of Rabenau and co-workers (*48*) and of Bronger (*13*) cover the most important literature in this field. Regarding the ability of S_n^{2-} species to glue metal aggregates together we restrict ourselves here to two characteristic examples. The complex $(NH_4)_2PdS_{11}\cdot 2H_2O$ (*60*) contains Pd atoms linked via S_6^{2-} chains in a three-dimensional array. The crystal structure is a composite of different possible linkages, whereby sulfur absences account for the PdS_{11} composition. In $(NH_4)Cu(S_4)$, well known from laboratory courses, CuS_4 chelate rings are linked via "additional" Cu—S bonds to form one-dimensional polymeric anions (*18*).

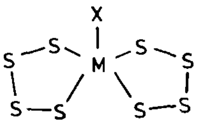
IV. Syntheses

There are several routes for the synthesis of polysulfido complexes. Oxidative addition of elemental sulfur to a coordinatively unsaturated electron-rich metal is a convenient method for preparing S_n^{2-} complexes. Examples are the reactions of $CpRh(PPh_3)_2$ to yield $CpRh(PPh_3)(S_5)$ (*189*) or of ML_4 ($M = Pd, Pt$; $L = PPh_3$) to yield $L_2M(S_4)$ (*21*). Examples of the preparation of complexes by using sulfur as reagent are the preparation of $Cp_2Ti(S_5)$ from $Cp_2Ti(CH_3)_2$ or $Cp_2Ti(SH)_2$ (*76, 163*) and the following reactions (*77*), which proceed without a change in the oxidation state of Mo (see also section V).

$$Cp_2Mo(S_2) + \tfrac{1}{4}S_8 \longrightarrow Cp_2Mo(S_4)$$

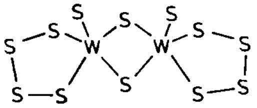
$$Cp_2Mo(SH)_2 + \tfrac{3}{8}S_8 \longrightarrow Cp_2Mo(S_4) + H_2S$$

By reacting thioanions of molybdenum, tungsten, or rhenium (e.g., MoS_4^{2-}, $MoOS_3^{2-}$, WS_4^{2-}, and ReS_4^{-}) with sulfur, complexes containing MS_4 ring systems like $[SM(S_4)_2]^{n-}$ (**30a**), $[OMo(S_4)_2]^{2-}$ (**30a**) ($M =$ Mo, Re), $[Mo_2O_2S_2(S_4)_2]^{2-}$, and $[W_2S_4(S_4)_2]^{2-}$ (**30b**) have been obtained (*25, 40, 107, 139*).



M = Mo, Re
X = O, S

30a



30b

Several compounds with network structures have been prepared, by high-temperature reaction of metals or metal halides with S_8 and/or S_2Cl_2, as for example in the reaction of a metal halide with sulfur and S_2Cl_2 (*92*) (see also Section V).

$$MoCl_3 + S_8/S_2Cl_2 \longrightarrow Mo_3S(S_2)_3Cl_4 + Mo_2(S_2)_2Cl_6$$

Reaction of metal complexes with S_n^{2-} is a convenient method for directly introducing the ligand by substitution of other ligands. For example, Na_2S_2 or polysulfide solutions can be used for this purpose (*77, 107, 108, 120, 146*).

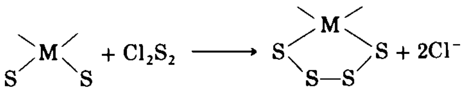
$$\begin{aligned}
Cp_2MoCl_2 + Na_2S_2 &\longrightarrow Cp_2Mo(S_2) + 2NaCl \\
[Mo_3S_4(CN)_9]^{5-} + S_n^{2-} &\longrightarrow [Mo_3S(S_2)_6]^{2-} \\
Mo_3S(S_2)_3Cl_4 + S_n^{2-} &\longrightarrow [Mo_3S(S_2)_6]^{2-} \\
FeCl_3 + S_n^{2-} &\longrightarrow [Fe_2S_2(S_5)_2]^{2-} \\
MoO_4^{2-} + S_n^{2-} &\longrightarrow [Mo_3S(S_2)_6]^{2-} + [Mo_2(S_2)_6]^{2-}
\end{aligned}$$

In the latter reaction, S_n^{2-} acts as a reducing agent.

Nearly all homoleptic complexes have been prepared from reactions with polysulfide solutions. Solvents used in most cases were H_2O, CH_3OH, C_2H_5OH, CH_3CN, or dimethylformamide (DMF). It seems that the type of S_n^{2-} ligand occurring in the complex need not necessarily have a high abundance in the polysulfide reaction solution: Cp_2TiCl_2 reacts with Na_2S_n ($n = 2$–7) to yield $Cp_2Ti(S_5)$ in all cases (*75*), i.e., the most stable M_yS_n system is formed. This consideration applies also to the very simple reaction of metal ions with H_2S in the presence of oxygen, where the formation of only small amounts of a "matching" ligand suffices for the preparation of a particular complex, like $[Fe_2S_2(S_5)_2]^{2-}$ (*107*).

On the other hand, the compounds in the system $Cu(I)/S_n^{2-}$ are obviously kinetically labile. Here, n can be influenced simply by passing H_2S through the S_8-containing reaction mixture (keeping all other conditions constant). Chains with high n are formed when the portion of S^{2-} (from H_2S) is low. With decreasing S_8/S^{2-} ratio, the chain size decreases. By controlling this ratio a series of different copper clusters has been obtained (see Section III,B,3) (*107*).

The formation of polysulfido complexes with other reagents containing S_n bonds, such as Cl_2S_n and R_2S_n, is also possible (*43, 74*). The former offers a particularly interesting reaction (*43*).



It has been pointed out (*33*) that synthesis of $[Fe_2S_2(S_5)_2]^{2-}$ from $[Fe(SPh)_4]^{2-}$ and dibenzyl trisulfide would have implications regarding the enzymatic biosynthesis of the metal clusters in Fe_2 ferredoxins, since trisulfides seem to be present in biological systems.

The complexes $\{CpFe(CO)_2\}_2S_n$ have been prepared by several routes (*45*) (at low temperatures to avoid redox reactions):

$$\left.\begin{array}{rcl} {[}CpFe(CO)_2]^- + SCl_2 & \longrightarrow & (n = 3) \\ {[}CpFe(CO)_2]^- + S_2Cl_2 & \longrightarrow & (n = 3, 4) \\ {[}CpFe(CO)_2]^- + SOCl_2 & \longrightarrow & (n = 3) \\ \{CpFe(CO)_2\}_2 + S_8 & \longrightarrow & (n = 3) \\ {[}CpFe(CO)_2Br] + Li_2S_2 & \longrightarrow & (n = 2, 3) \\ {[}CpFe(CO)_2Br] + Li_2S_4 & \longrightarrow & (n = 3, 4) \end{array}\right\} Cp(CO)_2FeS_nFe(CO)_2Cp$$

Although there is a systematic variation of reactants the trisulfido complex is formed in all the reactions.

Some preparations of polysulfido complexes with sulfur-abstracting reagents have been reported. For example, $[Pt(S_5)_3]^{2-}$ (**15**), reacts with CN^- to yield $[Pt(S_5)_2]^{2-}$ (*168, 192*). During the course of this reaction, an interesting two-electron transfer occurs, reducing Pt(IV) to Pt(II). The same substrate reacts with Ph_3P in the following way (*42, 81*):

$$[Pt(S_5)_3]^{2-} + 12Ph_3P \longrightarrow S^{2-} + (Ph_3P)_2Pt(S_4) + 10Ph_3PS$$

Intramolecular redox reactions within metal–sulfido moieties provide an interesting route to $S_2{}^{2-}$ complexes. An example is the formation of $[Mo_2O_2S_2(S_2)_2]^{2-}$ from $MoO_2S_2{}^{2-}$ (*161*). The following redox processes could be involved (see note added in proof).

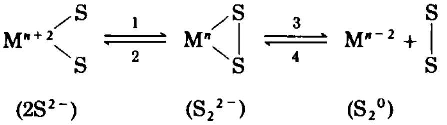
$$\mathrm{Mo^{VI}} \xrightarrow{\text{red}} \mathrm{Mo^{IV}}$$

$$(\mathrm{Mo^{IV}} + \mathrm{Mo^{VI}} \longrightarrow 2\mathrm{Mo^{V}})$$

$$2S^{2-} \xrightarrow{\text{ox}} S_2{}^{2-}$$

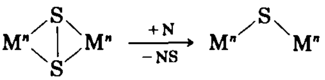
V. Reactions of Coordinated Ligands

Electron-transfer and intramolecular redox reactions (related to S_2^{2-} *complexes).* The redox behavior of S_2^{2-} complexes is of particular interest because it can probably provide a foundation for understanding the course of reactions involved in relevant enzymes and catalysts (especially hydrodesulfurization catalysts). Intramolecular redox reactions related to type Ia S_2^{2-} ligands can be summarized as follows:



Examples of step 1 are provided by oxidation of =S and —SR groups (*85, 132, 159, 161*). Step 2 involves reduction of the S—S bond to form two sulfido groups (*172, 173*). An example of step 3 is thermal decomposition of $Cs_2[Mo_2(S_2)_6]\cdot nH_2O$ to give S_2 as the main gaseous product (*67*) (*vide infra*), and examples of step 4 include synthesis of S_2^{2-} complexes from reactions employing elemental sulfur (*vide supra* and note added in proof).

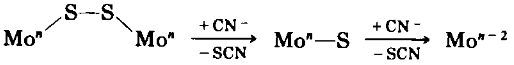
Reactions with nucleophiles (with abstraction of neutral sulfur). A characteristic reaction of S_n^{2-} ligands is abstraction of a sulfur atom by nucleophiles (N) such as PR_3, SO_3^{2-}, SR^-, CN^-, and OH^-, e.g., the reaction (*87, 105, 110, 116, 125, 130*)



The reaction involves transfer of a neutral sulfur atom from the complex (no change in the oxidation state of the metal atoms occurs). The reaction of $[Mo_3S(S_2)_6]^{2-}$ with CN^- [giving $[Mo_3S_4(CN)_9]^{5-}$] is particularly interesting. The bridging S_2^{2-} ligands are converted into bridging sulfido ligands and the terminal S_2^{2-} ligands are replaced by CN^- groups (*130*).

In $[Mo_4(NO)_4(S_2)_4(S_2)_2O]^{2-}$ (8) both end-on bridging S_2^{2-} ligands of type IIb and the type III bridging S_2^{2-} ligands react with CN^- to yield mainly $[Mo_2S_2(NO)_2(CN)_6]^{6-}$ and (some) $[Mo_4S_4(NO)_4(CN)_8]^{8-}$ (*116, 121*).

The strongly distorted $\{Mo_4S_4\}$ cube of the latter species is produced by abstraction of a sulfur atom from each of the four type III ligands. A reasonable mechanism for the reaction of the two type IIb ligands would be the stepwise sequence



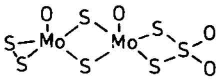
$$\mathrm{Mo}^{n}\overset{\mathrm{S{-}S}}{\diagup\quad\diagdown}\mathrm{Mo}^{n} \xrightarrow[-\mathrm{SCN}]{+\mathrm{CN}^{-}} \mathrm{Mo}^{n}\text{—}\mathrm{S} \xrightarrow[-\mathrm{SCN}]{+\mathrm{CN}^{-}} \mathrm{Mo}^{n-2}$$

in which a two-electron reduction occurs parallel to the formation of two metal-to-metal bonds within the $\{Mo_4S_4\}$ cube (or one in $\{Mo_2S_2\}$, respectively.) (*116*).

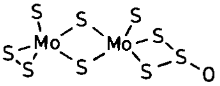
Type III bridging S_2^{2-} ligands are more susceptible to nucleophilic attack with extrusion of a neutral sulfur atom than are type Ia ligands. This is consistent with a generally lower electron density on the S atoms of type III ligands (bonded to two metal atoms) than of type Ia ligands (bonded to one metal atom).

The compound $Cp_2Ti(S_5)$ (**33**) reacts with PPh_3 to yield the binuclear complex $[Cp_2Ti(S_3)]_2$ (with two S_3^{2-} ligands) (*6*) and with PBu_3 to yield the related $[Cp_2Ti(S_2)]_2$ (with two type IIb S_2^{2-} ligands) (*4*) (for further corresponding reactions of S_n^{2-} ligands with $n > 2$, see below).

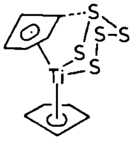
Oxidation of the ligand by external agents. In $Ir(dppe)_2(S_2)Cl$, for instance, the S_2^{2-} ligand can be oxidized stepwise (on the metal) to form "S_2O" and "S_2O_2" (*165, 166*). Complexes with bridging "S_2O" ligands are also known (*37*) (a more reasonable classification is as $S_xO_y^{2-}$ ligands).



31



32



33

Particularly interesting is the oxidation of S_n^{2-} ligands ($n > 2$). The compound $[(S_2)Mo(S)(S)_2Mo(S)(S_4)]^{2-}$ can be oxidized to yield $[(S_2)Mo(O)(S)_2Mo(O)(S_3O_2)]^{2-}$ (**31**) (*131*) and $[(S_2)Mo(S)(S)_2$-$Mo(S)(S_3O)]^{2-}$ (**32**) (*160*). The former species is obtained in pure form from a solution containing MoS_4^{2-} simply upon exposure to air (*131*).

Thermal decomposition (with generation of neutral sulfur species, e.g., 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 by reductive elimination. This has been proved by mass spectroscopy and matrix isolation Raman, UV/VIS, and IR spectroscopy (*67, 107*).

Of general interest also is the thermal decomposition of $(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O$ with MoS_2 as the final product (*35, 113*). This implies a reaction without a change of the oxidation state of the metal atoms, according to the equation:

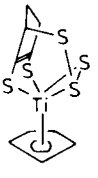
$$(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O \longrightarrow 2NH_3 + H_2S + 3MoS_2 + 6S^0 + nH_2O$$

Some additional special reactions of general significance should be mentioned here: $Cp_2Ti(S_5)$ (**33**) has been used as a standard reagent (*167*) for the preparation of new cyclo-S_n species by ligand-transfer reactions [$n = 5 + m$ with S_mCl_2 (*164, 169, 177*); $n = 10$, 15, 20 with SO_2Cl_2 (*179*); with Se_2Cl_2 the cyclo-1,2,3-Se_3S_5 is obtained as final product (*86, 178*)]. Intermediates resulting from the cleavage of the $\{TiS_5\}$ ring with S^{2-} can be trapped with aliphatic ketones or halides. For example, the isomers $Cp_2Ti(S_2)_2CH_2$ and $Cp_2TiS(S_3)CH_2$ have been obtained from the reaction of **33** with dibromomethane and ammonium sulfide (*56*).

The reactions of polysulfido complexes with activated acetylenes have been studied in some detail (*4, 5*). 1,4- $(MeCp_2Ti)_2(S_2)_2$ reacts with dimethylacetylene dicarboxylate (DMAD) to yield $MeCp_2TiS_2C_2R_2$ with a five membered $\overline{\mathrm{Ti{-}S{-}C{=}C{-}S}}$ ring as the final product (*4*). Similarly, insertions have also been observed during the reaction of $[Mo_2O_2(S)_2(S_2)_2]^{2-}$ (**3**) with DMAD (*59*). $[MoS(S_4)_2]^{2-}$ (**30a**) reacts with DMAD to yield $[Mo(S_2C_2(COOMe)_2)_3]^{2-}$ (*39*).

Reactions have been observed in which S^{2-}, $S_2{}^{2-}$, and $S_4{}^{2-}$ are formed from each other (particularly in Mo chemistry; cf. ref. (*108*). The formal oxidation state of the metal may also change. With sulfur, $MoS_4{}^{2-}$ yields $[MoS(S_4)_2]^{2-}$ (**30a**) (*40, 175*), which reacts again with thiolates to form $MoS_4{}^{2-}$ (*181*). With Ph_2S_2, $MoS_4{}^{2-}$ forms $[(S_2)MoS(\mu\text{-}S)_2MoS(S_2)]^{2-}$ (*153*) [which inserts (reversibly) CS_2 into the $S_2{}^{2-}$ groups (*38*) to form a five-membered Mo—S—(C=S)S—S ring]. Upon heating, $MeCp_2V(S_5)$ forms the dinuclear species $MeCpV(\mu\text{-}S)(\mu\text{-}S_2)_2VCpMe$ (*3*).

A transformation reaction occurs when $Cp_2Ti(S_5)$ (**33**) is refluxed for one day. The formation of a second structural isomer (**34**) provides an interesting example for the migration of a π-complexed organic unit to an inorganic sulfur ligand (*57*).



34

VI. Spectroscopic Properties

A. Disulfido Complexes

The ν(S–S) vibrational frequencies range from ~480 to 600 $\mathrm{cm^{-1}}$. Comparison of the ν(S–S) values for the discrete diatomic sulfur species S_2 ($^3\Sigma_g^-$: 725 $\mathrm{cm^{-1}}$) (*182*), S_2^- ($^2\Pi_g$: 589 $\mathrm{cm^{-1}}$) (*24, 66*), and S_2^{2-} ($^1\Sigma_g^+$: 446 $\mathrm{cm^{-1}}$) (*67*) leads to the conclusion that the approximate charge distribution is somewhere between that for S_2^- and that for S_2^{2-}. However, here 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 proved by the shift of 1–2 $\mathrm{cm^{-1}}$ observed in some ν(S–S) stretching vibrations upon substitution of ^{92}Mo by ^{100}Mo in $[Mo_2(S_2)_6]^{2-}$ and $[Mo_3S(S_2)_6]^{2-}$ (*67*).

Frequencies of type IIIa bridging disulfido ligands are generally higher than those for species with type I structures. In the case of $[Mo_3S(S_2)_6]^{2-}$ with both types of S_2^{2-} ligands the vibrational band at 545 $\mathrm{cm^{-1}}$ can be assigned to type IIIa ligands. The higher frequencies found for type IIIa ligands are consistent with the slightly shorter S—S distances for this structural type (see Table II). The intensities of the ν(S–S) bands of type IIIa ligands are normally high in the IR as well as in the Raman spectra. The type Ia ligands show intensive ν(S–S) bands in the IR, but in the Raman spectrum these bands are usually weak (*67*).

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

X-Ray photoelectron spectra (XPS) have been measured in order to obtain additional information about the effective charge on the sulfur atoms in these ligands. The sulfur 2*p* binding energies lie between ~162.9 and 164.4 eV, indicating that the sulfur atoms here are generally more negatively charged than in neutral sulfur [E_B (2*p*) for S_8 is 164.2 eV] (*19*). The corresponding binding energy for sulfur in complexes with reduced sulfur-containing ligands such as S^{2-}, —C—S^-, —C—S—C—, or =C=S are in the range 161.5–163.5 eV; in Na_2S it has a binding energy of 162.0 eV (*19*), and thiometallates show binding energies of 162.2–163.4 eV (*119*). Thus, the S 2*p* binding energies for disulfido complexes are consistent with the conclusion drawn from S—S distances and from vibrational spectroscopy, i.e., the effective charge on the sulfur atoms in the disulfido ligand in metal complexes is between 0 and −2.

Additional evidence about the oxidation state of the sulfur can be obtained by comparing the metal-binding energies in S_2^{2-} complexes with the electron-binding energies of the metal atom in complexes with known oxidation states. In particular it has become 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 ligands are formulated as S_2^{2-} units rather than neutral S_2 fragments (*122*).[2] Similar results apply for the metal-binding energies of iridium and osmium complexes (*47, 72*). However, neither the sulfur nor the metal XPS data are sufficiently sensitive to distinguish between the various modes of coordination of the S_2^{2-} ligands.

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 less-interacting π^*_v orbital perpendicular to the MS_2 plane (cf. Section VII). The longest wavelength band in the electronic spectra of the complexes $Cp_2Nb(S_2)X$ (X = Cl, Br, I) (*184*) and $MoO(S_2)(dtc)_2$ (*98*) occurs at ~20 kK and is assigned to ligand to metal charge transfer (LMCT) of the type $\pi^*_v(S) \rightarrow d(M)$. This assignment probably also applies to the corresponding bands of the other complexes of type Ia which contain metal atoms in a high oxidation state. The position of this first band is influenced by the oxidation state of the metal, by the kind of metal–metal bonding, and by the nature of the other ligands, which determine the energy of the LUMO and its metal character.

For S_2^{2-} complexes of type III, the corresponding absorption band is expected to occur at higher energy because both π^* orbitals of the ligand interact strongly with the metal atoms. Particularly 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 of type IIa structure [e.g., $[(CN)_5Co(S_2)Co(CN)_5]^{6-}$ 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 $Ru^{II}—(S_2)^-—Ru^{III}$ (*15, 44*). Such a mixed-valence complex could exhibit the intense band observed (*106*).

B. S_n^{2-} ($n > 2$) COMPLEXES

The interpretation of vibrational and electronic spectra of these complexes is much more complicated. Whereas IR spectra generally show only bands of low intensity, the Raman spectra often display intense and characteristic lines. Rigorous assignments have not been published so far, but the most simple $M(\mu_2\text{-}S)_n$ ring systems can easily be

---

[2] In the older literature, *disulfur* ligands were often regarded as being neutral (see, e.g., *55, 184*).

recognized from the Raman data (the highest wavenumber line is shifted to higher energies with increasing n).

The color and the corresponding electronic spectra are often dominated by ligand internal electronic transitions, the energies of which show a red shift with increasing n. The average negative charge on the sulfur atoms of the S_n^{2-} ligands, of course, decreases with increasing n, as can be seen from XPS data (*107*).

NMR spectroscopy on polysulfido complexes has mainly been used for conformational studies. It has been found that in solution the chair conformation of the TiS_5 cycle in $Cp_2Ti(S_5)$ (**33**) is retained. The ring inversion barrier has been determined for the three $Cp_2M(S_5)$ species with M = Ti, Zr, and Hf (76.3, 48.6, and 58.0 kJ/mol, respectively) (*97*).

VII. Some Structural Features and Chemical Bonding

A. S_2^{2-} COMPLEXES

Structural diversity is achieved through the use of nonbonded pairs of electrons on the S_2^{2-} ligand of both type II complexes to coordinate additional metal atoms. The S—S distances of known complexes range from ~1.98 to 2.15 Å. Most S—S distances are intermediate between the distance of 1.89 Å for S_2 ($^3\Sigma_g^-$) (*104*) and 2.13 Å for S_2^{2-} ($^1\Sigma_g^+$) in Na_2S_2 (*50*). The main S—S distances show no clear systematic trend with structural type (cf. Table II).

The average type Ia S—S distances in $[Mo_2(S_2)_6]^{2-}$ (*128*) and $[Mo_3S(S_2)_6]^{2-}$ (*129*) are slightly longer than the average type IIIa S—S distances. The data for $[Mo_4(NO)_4(S_2)_6O]^{2-}$ (*115*) indicate that type IIb S—S distances may be slightly longer than type IIIa distances. However, caution must be exercised in interpreting these trends because of the known tendency for type IIIa ligands to be slightly asymmetrically bound to the metal atoms.

High coordination numbers of the metal atom are favored for type I and type IIIa structures by the small coordination angles of the bidentate S_2^{2-} ligand. High coordination numbers also protect the metal center from nucleophilic attack, an important factor for the stabilization of metal–metal bonds.

The physical data for dioxygen complexes have been discussed in detail elsewhere (*88, 186*). We note here only that the complexes have been divided into superoxide (O_2^-) and peroxide (O_2^{2-}) ones, primarily on the basis of the O—O distance and ν(O–O) frequencies: The coordinated superoxide ligand has $d(O–O) \approx 1.30$ Å and

TABLE III

BOND DISTANCES AND VIBRATIONAL FREQUENCIES FOR X_2^{n-}

	X_2 ($^3\Sigma_g^-$)	X_2^- ($^2\Pi_g$)	X_2^{2-} ($^1\Sigma_g^+$)
d(O—O) (Å)	1.21[a]	1.33[a]	1.49[a]
d(S—S) (Å)	1.89[b]	2.00[c]	2.13[d]
ν(O—O) (cm^{-1})	1580[a]	1097[a]	802[a]
ν(S—S) (cm^{-1})	725[c]	589[e]	446[f]

[a] Ref. *186*.
[b] Ref. *96, 104*.
[c] Estimated, see ref. *24*.
[d] Ref. *50*.
[e] Ref. *24*.
[f] Ref. *67*.

$\nu(O-O) \approx 1125$ cm^{-1}; the coordinated peroxide ligand has $d(O-O) \approx 1.45$ Å and $\nu(O-O) \approx 860$ cm^{-1} (*186*).

Comparison of the S—S distances and frequencies in Table III indicates that the effective charge on the ligand in the complexes quoted in Table II is between −1 and −2. The S_2^- ligand seems to be much less abundant compared to the corresponding situation with dioxygen 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 (*15, 44*) and for $Cp_2Fe_2(S_2)(SR)_2$ (*83, 188*) from similarities of the ligand geometry to the geometry of the O_2 ligand in superoxide complexes.

Relevant to our case is the analysis of the bonding in η^2 side-on S_2^{2-} complexes. Figure 3 shows that the principal bonding interaction is produced by the metal d_{xz} orbital and the π^*_z (π^*_h) orbital of the S_2^{2-} ligand (π-bonding) and also by the d_{z^2} of the metal and the π_z (π_h) (σ-bonding) orbitals. [According to the qualitative Dewar–Chatt–Duncanson bonding scheme (*20*) the interaction of the π_y (π_v) and the π^*_y (π^*_v) orbitals is considered to be negligible]. The major contribution is expected to be the π-bonding as implied by more quantitative molecular orbital calculation of MO_2 complexes with side-on bonded ligands (*162*).

For type Ia S_2^{2-} complexes, π-bonding should also be the major bonding interaction. For type IIIa M1—(S_2)—M2 complexes this bonding interaction would occur twice, once between π^*_z of S_2^{2-} and M1 and once between π^*_y of S_2^{2-} and M2. If M2 is a positively charged

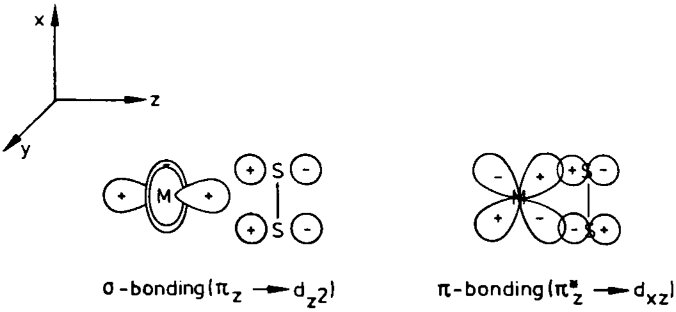


FIG. 3. Schematic bonding interactions between the metal d_{xz} orbital and the π^*_z orbital of the S_2^{2-} ligand (π-bonding) (right) and the d_{z^2} orbital of the metal with the π_z orbital of S_2^{2-} (σ-bonding) (left).

metal ion with few *d*-electrons, then there should be less electron density on the disulfur unit in a type IIIa complex relative to a type Ia complex. Such a depopulation of the π^* orbitals of the S_2^{2-} ligand is consistent with the greater susceptibility of type IIIa complexes to nucleophilic attack and with the shorter S—S distances and higher ν(S–S) vibrational frequencies for such complexes. These properties are consistent with the π-donor character of the S_2^{2-} ligand.

B. S_n^{2-} ($n > 2$) COMPLEXES

Whereas the coordination of S_2^{2-} ligands to metal atoms always results in a significant shortening of the S—S bond length, the corresponding situation is much more complicated in the case of the S_n^{2-} ($n > 2$) complexes. In general, the shortening of the S—S bond is less pronounced in this type of complex. A semiempirical MO calculation on $[Pt(S_4)(PH_3)_2]$ indicates a substantial donation of electron density from the S_4 ligand to the $\{Pt(PH_3)_2\}$ fragment, leading to a charge distribution for the coordinated ligand intermediate between those for S_4 and S_4^{2-} (*12*).

Table IV compares bond lengths for S—S bonds in compounds with S_4 structural units (uncoordinated and coordinated). In several S_4^{2-} complexes (in addition to a shortening of the S—S bonds compared to the length in S_4^{2-} units in $BaS_4 \cdot H_2O$), variations of the S—S bond length in the S_4^{2-} chelate are observed. It has been postulated that the high oxidation state of Mo and W in the corresponding complexes contributes to ligand-to-metal π-backbonding and to a shortening of the central S(2)—S(3) bond of the $[\text{—S(1)—S(2)—S(3)—S(4)—}]^{2-}$ ligand.

The different conformations occurring in MS_4 ring systems have been explained by the varying degree of interligand interactions. In the

TABLE IV

BOND LENGTHS FOR S—S BONDS IN COMPLEXES WITH BIDENTATE S_4^{2-} LIGANDS[a,b,c]

	d[S(1)—S(2)] (Å)	d[S(2)—S(3)] (Å)	d[S(3)—S(4)] (Å)
	S_4 Ligand in Complex		
$(Ph_3P)_2Pt(S_4)$	2.024(8)	2.022(10)	2.081(10)
$[PPh_4]_2[Hg(S_4)_2]$	2.050	2.043	2.048
$[Et_4N]_2[Ni(S_4)_2]$	2.073(2)	2.037(4)	2.073(2)
$[Et_4N]_2[Pd(S_4)_2]$	2.062(8)	2.054(6)	2.065(8)
$[AsPh_4]_2[Mo_2S_2(S_4)_2]$[d]	2.019(5)	1.970(6)	2.115(5)
$[AsPh_4]_2[Mo_2S_2(S_4)_2]$[d]	2.096(16)	1.936(19)	2.169(14)
$[PPh_4]_2[Mo_2O_2S_2(S_4)_2]$	2.066	2.024	2.084
$[PPh_4]_2[W_2S_4(S_4)_2]\cdot 0.5DMF$	2.044(11)	2.013(14)	2.112(12)
$[PPh_4]_2[W_2O_2S_2(S_4)_2]\cdot 0.5DMF$	2.062	2.011	2.100
$[PPh_4]_2[W_2S_4(S_2)(S_4)]\cdot 0.5DMF$	2.039	2.016	2.067
$[Et_4N]_2[MoS(S_4)_2]$	2.107(1)	2.012(1)	2.166(1)
$(\eta^5\text{-}C_5H_5)_2Mo(S_4)$	2.081(8)	2.018(9)	2.085(7)
$(\eta^5\text{-}C_5H_5)_2W(S_4)$	2.105(7)	2.016(8)	2.116(9)
	Free S_4 Ligand in Salt		
$BaS_4\cdot H_2O$	2.079(3)	2.062(4)	2.079(3)
$C_6H_2(OEt)_2(S_4)_2$[d]	2.028(5)	2.068(5)	2.027(5)
$C_6H_2(OEt)_2(S_4)_2$[d]	2.034(5)	2.067(5)	2.024(5)

[a] Ligand notation is S1—S2—S3—S4—M.

[b] Compared to the corresponding values of the free ligand in different salts.

[c] Data from refs. *42, 139, 142.*

[d] District S_4 chains are involved..

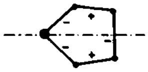
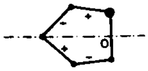
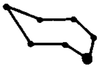
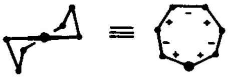
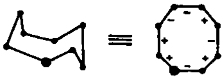
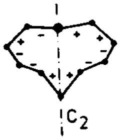
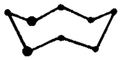
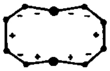
$Cp_2M(S_4)$ complexes with a tetrahedral coordination of the metal atoms and half-chair conformation of the MS_4 rings these interactions are insignificant (*25, 40*).

In molybdenum and tungsten complexes of the type $[M_2S_2X_2(S_4)(S_n)]^{2-}$ and $[XMo(S_4)_2]^{2-}$ ($X = O$, S; $n = 2$, 4) the envelope conformation for the five-membered rings and the obligatory orientation of the lone pairs on the molybdenum-bound sulfur atoms result in a structure with S—S interligand interactions within the XMS_4 pyramidal units being minimized. In these units the half-chair conformation would bring the lone pairs of the sulfur atoms bound to Mo in a position with closer interligand lone-pair contacts (*25, 40*).

For the six-membered MS_5 ring system the preferred conformation is that of a half-chair. The comparison of the molecular parameters of hetero atomic ring systems with those of S_6 in rhombohedral cyclohexasulfur is particularly interesting. The S_6 molecule also has a chairlike structure with an S—S bond length of 2.057(18) Å, an S—S—S bond

TABLE V

CONFORMATIONS OF MOST COMMON METAL–SULFUR RINGS

Type	Conformation	Structure	Example formula
MS_4	Half chair (C_2)		$[Ni(S_4)_2]^{2-}$ **(14)**
	Envelope (C_S)		$[Cu_4(S_4)_3]^{2-}$ **(27a)**
MS_5	Chair		$[Cp_2Ti(S_5)]$ **(33)**
MS_6	Chair		$[Ag_2(S_6)_2]^{2-}$ **(28)**
	Twist chair		$[Hg(S_6)_2]^{2-}$ **(17a)**
MS_7	Boat chair		$[Bi_2(S_6)(S_7)_4]^{4-}$ **(25a)**
MS_9			$[Ag(S_9)]^-$ **(18)**
M_2S_3	Envelope		$[Re_4S_{22}]^{4-}$ **(29a)**
$M_2S'S_5$	Crown		$[Mo_2(S_5)(S_2)_3(OH)(NO)_2]^{3-}$ **(20a)**
	Boat chair		$[Nb_2(S_5)(S_2)_3O(OCH_3)_2]^{2-}$ **(20b)**
M_2S_8			$[Au_2S_8]^{2-}$ **(23)**

angle of 102.2(1.6)°, and a torsional angle of ±74.5(2.5)°. Formal replacement of a sulfur atom by $\{TiCp_2\}$ or $\{VCp_2\}$ fragments, for instance, leads to longer M—S distances (2.40–2.46 Å) (compared to the S—S bond length). These are compensated by smaller S—M—S bond angles (89–95°). Therefore, the geometry of the resulting S_5 ligand is similar to that of the S_6 molecule (*150*).

Conformations of some simple ring systems are summarized in Table V. In some cases different ring systems are observed for the same metal in the same oxidation state [e.g., in $[Hg(S_n)_2]^{2-}$ ($n = 4, 6$) (**17a,b**)].

The metal–ligand interaction in S_n^{2-} complexes should be comparable to that in other complexes with sulfur-containing ligands, at least for higher values of n. Additionally, the observation that polysulfides with even n prefer coordination to closed-shell metal ions and those with odd n to open-shell ones indicates that the kind of metal-to-ligand interaction is obviously not restricted to the sulfur atoms attached directly to the metal.

It is interesting to note that $(NEt_4)_2[Ni(S_4)_2]$ exists in two polymorphic forms, which differ significantly in their Ni—S distances [d^4(NiS) = 2.185 Å (site symmetry D_2) and d^2(NiS) = 2.143 Å and trans to these bonds 2.270 Å (site symmetry of Ni is C_2), respectively). Both forms have also been identified and characterized by spectroscopy (*147*).

NOTE ADDED IN PROOF. According to new studies we have to distinguish between *balanced* intramolecular redox processes (*194*) and *unbalanced* ones induced by external reductants or oxidants (*108, 195*).

ACKNOWLEDGMENTS

Our own work reported in this article has been supported by grants from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung, North Rhine-Westphalia. We gratefully acknowledge the contributions of several colleagues and co-workers to these results. We particularly thank Dr. H. Bögge and Dr. K. Schmitz for helpful discussions and for reviewing the manuscript.

REFERENCES

1. Amaudrut, J., Guerchais, J. E., and Sala-Pala, J., *J. Organomet. Chem.* **157,** C 10 (1978).
2. Bird, P. H., McCall, J. M., Shaver, A., and Sirwardane, U., *Angew. Chem.* **94,** 375 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 384 (1982).
3. Bolinger, C. M., Rauchfuss, T. B., and Rheingold, A. L., *Organometallics* **1,** 1551 (1982).

4. Bolinger, C. M., Hoots, J. E., and Rauchfuss, T. B., *Organometallics* **1,** 223 (1982).

5. Bolinger, C. M., and Rauchfuss, T. B., *Inorg. Chem.* **21,** 3947 (1982).

6. Bolinger, C. M., Rauchfuss, T. B., and Wilson, S. R., *J. Am. Chem. Soc.* **103,** 5620 (1981).

7. Bonds, W. D., Jr., and Ibers, J. A., *J. Am. Chem. Soc.* **94,** 3413 (1972).

8. Böttcher, P., Buchkremer-Hermanns, H., and Baron, J., *Z. Naturforsch. B Anorg. Chem. Org. Chem.* **39b,** 416 (1984).

9. Böttcher, P., and Keller, R., *Z. Naturforsch. B Anorg. Chem. Org. Chem.* **39b,** 577 (1984).

10. Böttcher, P., and Kruse, K., *J. Less-Common Met.* **83,** 115 (1982).

11. Bravard, D. C., Newton, W. E., Huneke, J. T., Yamanouchi, K., and Enemark, J. H., *Inorg. Chem.* **21,** 3795 (1982).

12. Briant, C. E., Calhorda, M. J., Hor, T. S. A., Howells, N. D., and Mingos, D. M. P., *J. Chem. Soc., Dalton Trans.* p. 1325 (1983).

13. Bronger, W., *Angew. Chem.* **93,** 12 (1981); *Angew. Chem. Int. Ed. Engl.* **20,** 52 (1981).

14. Bronger, W., and Spangenberg, M., *J. Less-Common Met.* **76,** 73 (1980).

15. Brulet, C. R., Isied, S. S., and Taube, H., *J. Am. Chem. Soc.* **95,** 4758 (1973).

16. Brunner, H., Wachter, J., Guggolz, E., and Ziegler, M. L., *J. Am. Chem. Soc.* **104,** 1765 (1982).

17. Bunker, M. J., and Green, M. L. H., *J. Chem. Soc., Dalton Trans.*, p. 847 (1981).

18. Burschka, C., *Z. Naturforsch. B Anorg. Chem. Org. Chem.* **35b,** 1511 (1980).

19. Carlson, T. A., "Photoelectron and Auger Spectroscopy." Plenum, New York, 1975.

20. Chatt, J., and Duncanson, L. A., *J. Chem. Soc.*, p. 2939 (1953).

21. Chatt, J., and Mingos, D. M. P., *J. Chem. Soc., A*, p. 1243 (1970).

22. Chen, S., and Robinson, W. R., *J. Chem. Soc., Chem. Commun.*, p. 879 (1978).

23. Clark, G. R., Russell, D. R., Roper, W. R., and Walker, A., *J. Organomet. Chem.* **136,** C 1 (1977).

24. Clark, R. J. H., and Cobbold, D. G., *Inorg. Chem.* **17,** 3169 (1978).

25. Clegg, W., Christou, G., Garner, C. D., and Sheldrick, G. M., *Inorg. Chem.* **20,** 1562 (1981).

26. Clegg, W., Mohan, N., Müller, A., Neumann, A., Rittner, W., and Sheldrick, G. M., *Inorg. Chem.* **19,** 2066 (1980).

27. Clegg, W., Sheldrick, G. M., Garner, C. D., and Christou, G., *Acta Crystallogr. Sect. B* **36,** 2784 (1980).

28. Cloke, P. L., *Geochim. Cosmochim. Acta* **27,** 1265 (1963).

29. Cloke, P. L., *Geochim. Cosmochim. Acta* **27,** 1299 (1963).

30. Coucouvanis, D., Baenziger, N. C., Simhon, E. D., Stremple, P., Swenson, D., Kostikas, A., Simopoulos, A., Petrouleas, V., and Papaefthymiou, V., *J. Am. Chem. Soc.* **102,** 1730 (1980).

31. Coucouvanis, D., Patil, P. R., Kanatzidis, M. G., Detering, B., and Baenziger, N. C., *Inorg. Chem.* **24,** 24 (1985).

32. Coucouvanis, D., Stremple, P., Simhon, E. D., Swenson, D., Baenziger, N. C., Draganjac, M., Chan, L. T., Simopoulos, A., Papaefthymiou, V., Kostikas, A., and Petrouleas, V., *Inorg. Chem.* **22,** 293 (1983).

33. Coucouvanis, D., Swenson, D., Stremple, P., and Baenziger, N. C., *J. Am. Chem. Soc.* **101,** 3392 (1979).

34. Davis, B. R., Bernal, I., and Köpf, H., *Angew. Chem.* **83,** 1018 (1971); *Angew. Chem. Int. Ed. Engl.* **10,** 921 (1971).

35. Diemann, E., Müller, A., and Aymonino, P. J., *Z. Anorg. Allg. Chem.* **479,** 191 (1981).

36. Dirand, J., Ricard, L., and Weiss, R., *Inorg. Nucl. Chem. Lett.* **11,** 661 (1975).
37. Dirand-Colin, J., Schappacher, M., Ricard, L., and Weiss, R., *J. Less-Common Met.* **54,** 91 (1977).
38. Draganjac, M., Ph.D. Thesis, University of Iowa, Ames, 1983.
39. Draganjac, M., and Coucouvanis, D., *J. Am. Chem. Soc.* **105,** 139 (1983).
40. Draganjac, M., Simhon, E. D., Chan, L. T., Kanatzidis, M., Baenziger, N. C., and Coucouvanis, D., *Inorg. Chem.* **21,** 3321 (1982).
41. Drew, M. G. B., Baba, I. B., Rice, D. A., and Williams, D. M., *Inorg. Chim. Acta* **44,** L217 (1980).
42. Dudis, D., and Fackler, J. P., Jr., *Inorg. Chem.* **21,** 3577 (1982).
43. Egen, N. B., and Krause, R. A., *J. Inorg. Nucl. Chem.* **31,** 127 (1969).
44. Elder, R. C., and Trkula, M., *Inorg. Chem.* **16,** 1048 (1977).
45. El-Hinnawi, M. A., Aruffo, A. A., Santarsiero, B. D., McAlister, R., McAlister, D. Q., and Schomaker, V., *Inorg. Chem.* **22,** 1585 (1983).
46. Ellermann, J., Hohenberger, E. F., Kehr, W., Pürzer, A., and Thiele, G., *Z. Anorg. Allg. Chem.* **464,** 45 (1980).
47. Farrar, D. H., Grundy, K. R., Payne, N. C., Roper, W. R., and Walker, A., *J. Am. Chem. Soc.* **101,** 6577 (1979).
48. Fenner, J., Rabenau, A., and Trageser, G., *Adv. Inorg. Chem. Radiochem.* **23,** 329 (1980).
49. Fiechter, S., Kuhs, W. F., and Nitsche, R., *Acta Crystallogr. Sect. B* **36,** 2217 (1980).
50. Föppl, H., Busmann, E., and Frorath, F.-K., *Z. Anorg. Allg. Chem.* **314,** 12 (1962).
51. Furman, N. H., (Ed.), "Standard Methods of Chemical Analysis," 6th Ed., Vol. I, p. 398. Krieger, Huntington, NY, 1975.
52. Giannotti, C., Ducourant, A. M., Chanaud, H., Chiaroni, A., and Riche, C., *J. Organomet. Chem.* **140,** 289 (1977).
53. Gillard, R. D., and Wimmer, F. L., *J. Chem. Soc., Chem. Commun.* p. 936 (1978).
54. Gillard, R. D., Wimmer, F. L., and Richards, J. P. G., *J. Chem. Soc., Dalton Trans.,* p. 253 (1985).
55. Ginsberg, A. P., and Lindsell, W. E., *J. Chem. Soc., Chem. Commun.,* p. 232 (1971).
56. Giolando, D. M., and Rauchfuss, T. B., *Organometallics* **3,** 487 (1984).
57. Giolando, D. M., and Rauchfuss, T. B., *J. Am. Chem. Soc.* **106,** 6455 (1984).
58. Gotzig, J., Rheingold, A. L., and Werner, H., *Angew. Chem.* **96,** 813 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 814 (1984).
59. Halbert, T. R., Pan, W.-H., and Stiefel, E. I., *J. Am. Chem. Soc.* **105,** 5476 (1983).
60. Haradem, P. S., Cronin, J. L., Krause, R. A., and Katz, L., *Inorg. Chim. Acta* **25,** 173 (1977).
61. Herberhold, M., Reiner, D., Ackermann, K., Thewalt, U., and Debaerdemaeker, T., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **39b,** 1199 (1984).
62. Herberhold, M., Reiner, D., Zimmer-Gasser, B., and Schubert, U., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **35b,** 1281 (1980).
63. Hieber, W., and Gruber, J., *Z. Anorg. Allg. Chem.* **296,** 91 (1958).
64. Hofmann, K. A., and Höchtlen, F., *Ber. Dtsch. Chem. Ges.* **36,** 3090 (1903).
65. Hofmann, K. A., and Höchtlen, F., *Ber. Dtsch. Chem. Ges.* **37,** 245 (1904).
66. Holzer, W., Murphy, W. F., and Bernstein, H. J., *J. Mol. Spectrosc.* **32,** 13 (1969).
67. Jaegermann, W., Ph.D. Thesis, University of Bielefeld, Federal Republic of Germany, 1981.
68. Jones, P. E., and Katz, L., *J. Chem. Soc., Chem. Commun.,* p. 842 (1967).
69. Jones, P. E., and Katz, L., *Acta Crystallogr. Sect. B* **25,** 745 (1969).
70. Kanatzidis, M. G., Baenziger, N. C., and Coucouvanis, D., *Inorg. Chem.* **22,** 290 (1983).
71. Kettle, S. F. A., and Stanghellini, P. L., *Inorg. Chem.* **16,** 753 (1977).

72. Knecht, J., and Schmid, G., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **32b,** 653 (1977).
73. Köpf, H., *Angew. Chem.* **81,** 332 (1969); *Angew. Chem. Int. Ed. Engl.* **8,** 375 (1969).
74. Köpf, H., *Chem. Ber.* **102,** 1509 (1969).
75. Köpf, H., and Block, B., *Chem. Ber.* **102,** 1504 (1969).
76. Köpf, H., Block, B., and Schmidt, M., *Chem. Ber.* **101,** 272 (1968).
77. Köpf, H., Hazari, S. K. S., and Leitner, M., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **33b,** 1398 (1978).
78. Köpf, H., Wirl, A., and Kahl, W., *Angew. Chem.* **83,** 146 (1971); *Angew. Chem. Int. Ed. Engl.* **10,** 137 (1971).
79. Krause, R. A., *Inorg. Nucl. Chem. Lett.* 7, 973 (1971).
80. Krauskopf, K. B., "Introduction to Geochemistry," p. 393. McGraw-Hill, New York, 1979.
81. Kreutzer, B., Kreutzer, P., and Beck, W., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **27b,** 461 (1972).
82. Kubas, G. J., and Vergamini, P. J., *Inorg. Chem.* **20,** 2667 (1981).
83. Kubas, G. T., Spiro, T. G., and Terzis, A., *J. Am. Chem. Soc.* **95,** 273 (1973).
84. Küllmer, V., Röttinger, E., and Vahrenkamp, H., *J. Chem. Soc., Chem. Commun.*, p. 782 (1977).
85. Küllmer, V., Röttinger, E., and Vahrenkamp, H., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **34b,** 224 (1979).
86. Laitinen, R., Rautenberg, N., Steidel, J., and Steudel, R., *Z. Anorg. Allg. Chem.* **486,** 116 (1982).
87. Leonard, K., Plute, K., Haltiwanger, R. C., and Rakowski DuBois, M., *Inorg. Chem.* **18,** 3246 (1979).
88. Lever, A. B. P., and Gray, H. B., *Acc. Chem. Res.* **11,** 348 (1978).
89. Mague, J. T., and Davis, E. J., *Inorg. Chem.* **16,** 131 (1977).
90. Maheu, L. J., and Pignolet, L. H., *J. Am. Chem. Soc.* **102,** 6346 (1980).
91. Marbach, G., and Strähle, J., *Angew. Chem.* **96,** 229 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 246 (1984).
92. Marcoll, J., Rabenau, A., Mootz, D., and Wunderlich, H., *Rev. Chim. Miner.* **11,** 607 (1974).
93. Markó, L., Bor, G., Klumpp, E., Markó, B., and Almásy, G., *Chem. Ber.* **96,** 955 (1963).
94. Martin, T. P., and Schaber, H., *Spectrochim. Acta Part A* **38A,** 655 (1982).
95. Matthes, S., "Mineralogie, Eine Einführung in die spezielle Mineralogie, Petrologie und Lagerstättenkunde," p. 237. Springer-Verlag, Berlin and New York, 1983.
96. Maxwell, L. R., Mosley, V. M., and Hendricks, S. B., *Phys. Rev.* **50,** 41 (1936).
97. McCall, J. M., and Shaver, A., *J. Organomet. Chem.* **193,** C37 (1980).
98. McDonald, J. W., and Newton, W. E., *Inorg. Chim. Acta* **44,** L81 (1980).
99. Mealli, C., and Midollini, S., *Inorg. Chem.* **22,** 2785 (1983).
100. Mennemann, K., and Mattes, R., *Angew. Chem.* **89,** 269 (1977); *Angew. Chem. Int. Ed. Engl.* **16,** 260 (1977).
101. Mennemann, K., and Mattes, R., *J. Chem. Res. (M)*, p. 1372 (1979).
102. Mercier, R., Douglade, J., Amaudrut, J., Sala-Pala, J., and Guerchais, J., *Acta Crystallogr. Sect. B* **36,** 2986 (1980).
103. Meunier, B., and Prout, K., *Acta Crystallogr. Sect. B* **35,** 172 (1979).
104. Meyer, B., *Chem. Rev.* **76,** 367 (1976).
105. Miller, K. F., Bruce, A. E., Corbin, J. L., Wherland, S., and Stiefel, E. I., *J. Am. Chem. Soc.* **102,** 5102 (1980).
106. Miskowski, V. M., Robbinds, J. L., Treitel, I. M., and Gray, H. B., *Inorg. Chem.* **14,** 2318 (1975).

107. Müller, A., *et al.*, unpublished results.

108. Müller, A., *Polyhedron* **5,** 323 (1986): *Proc. 5th Int. Conf. Molybdenum, Newcastle,* 1985.

109. Müller, A., Baumann, F.-W., Bögge, H., Römer, M., Krickemeyer, E., and Schmitz, K., *Angew. Chem.* **96,** 607 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 632 (1984).

110. Müller, A., Bhattacharyya, R. G., Mohan, N., and Pfefferkorn, B., *Z. Anorg. Allg. Chem.* **454,** 118 (1979).

111. Müller, A., Bhattacharyya, R. G., and Pfefferkorn, B., *Chem. Ber.* **112,** 778 (1979).

112. Müller, A., Cyrankiewicz, R., and Bögge, H., unpublished results; Cyrankiewicz, R., Diploma thesis, University of Bielefeld, Federal Republic of Germany, 1985.

113. Müller, A., and Diemann, E., *Chimia* **39,** 312 (1985).

114. Müller, A., Eltzner, W., Bögge, H., and Krickemeyer, E., *Angew. Chem.* **95,** 905 (1983); *Angew. Chem. Int. Ed. Engl.* **22,** 884 (1983).

115. Müller, A., Eltzner, W., Bögge, H., and Sarkar, S., *Angew. Chem.* **94,** 555 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 535 (1982); *Angew. Chem. Suppl.*, p. 1167 (1982).

116. Müller, A., Eltzner, W., Clegg, W., and Sheldrick, G. M., *Angew. Chem.* **94,** 555 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 536 (1982).

117. Müller, A., Eltzner, W., Jostes, R., Bögge, H., Diemann, E., Schimanski, J., and Lueken, H., *Angew. Chem.* **96,** 355 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 389 (1984).

118. Müller, A., Eltzner, W., and Mohan, N., *Angew. Chem.* **91,** 158 (1979); *Angew. Chem. Int. Ed. Engl.* **18,** 168 (1979).

119. Müller, A., Jørgensen, C. K., and Diemann, E., *Z. Anorg. Allg. Chem.* **391,** 38 (1972).

120. Müller, A., Jostes, R., and Cotton, F. A., *Angew. Chem.* **92,** 921 (1980); *Angew. Chem. Int. Ed. Engl.* **19,** 875 (1980).

121. Müller, A., Jostes, R., Eltzner, W., Nie, C.-S., Diemann, E., Bögge, H., Zimmermann, M., Dartmann, M., Reinsch-Vogell, U., Che, S., Cyvin, S. J., and Cyvin, B. N., *Inorg. Chem.* **24,** 2872 (1985).

122. Müller, A., Jostes, R., Jaegermann, W., and Bhattacharyya, R. G., *Inorg. Chim. Acta* **41,** 259 (1980).

123. Müller, A., Krickemeyer, E., Bögge, H., Clegg, W., and Sheldrick, G. M., *Angew. Chem.* **95,** 1030 (1983); *Angew. Chem. Int. Ed. Engl.* **22,** 1006 (1983).

124. Müller, A., Krickemeyer, E., and Bögge, H., *Angew. Chem.* **98,** 258 (1986); *Angew. Chem. Int. Ed. Engl.* **25,** 272 (1986).

125. Müller, A., Krickemeyer, E., and Reinsch, U., *Z. Anorg. Allg. Chem.* **470,** 35 (1980).

126. Müller, A., Krickemeyer, E., Zimmermann, M., Römer, M., Bögge, H., Penk, M., and Schmitz, K., *Inorg. Chim. Acta* **90,** L69 (1984).

127. Müller, A., Nolte, W.-O., and Krebs, B., *Angew. Chem.* **90,** 286 (1978); *Angew. Chem. Int. Ed. Engl.* **17,** 279 (1978).

128. Müller, A., Nolte, W.-O., and Krebs, B., *Inorg. Chem.* **19,** 2835 (1980).

129. Müller, A., Pohl, S., Dartmann, M., Cohen, J. P., Bennett, J. M., and Kirchner, R. M., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **34b,** 434 (1979).

130. Müller, A., and Reinsch, U., *Angew. Chem.* **92,** 69 (1980); *Angew. Chem. Int. Ed. Engl.* **19,** 72 (1980).

131. Müller, A., Reinsch-Vogell, U., Krickemeyer, E., and Bögge, H., *Angew. Chem.* **94,** 784 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 796 (1982).

132. Müller, A., Rittner, W., Neumann, A., and Sharma, R. C., *Z. Anorg. Allg. Chem.* **472,** 69 (1981).

133. Müller, A., Römer, M., Bögge, H., Krickemeyer, E., Baumann, F.-W., and Schmitz, K., *Inorg. Chim. Acta* **89,** L7 (1984).

134. Müller, A., Römer, M., Bögge, H., Krickemeyer, E., and Bergmann, D., *J. Chem. Soc., Chem. Commun.*, p. 348 (1984).

135. Müller, A., Römer, M., Bögge, H., Krickemeyer, E., and Bergmann, D., *Z. Anorg. Allg. Chem.* **511,** 84 (1984).

136. Müller, A., Römer, M., Bögge, H., Krickemeyer, E., and Schmitz, K., *Inorg. Chim. Acta* **85,** L39 (1984).

137. Müller, A., Römer, M., Bögge, H., Krickemeyer, E., and Zimmermann, M., *Z. Anorg. Allg. Chem.* **534,** 69 (1986).

138. Müller, A., Römer, M., Krickemeyer, E., and Bögge, H., *Naturwissenschaften* **71,** 43 (1984).

139. Müller, A., Römer, M., Römer, C., Reinsch-Vogell, U., Bögge, H., and Schimanski, U., *Monatsh. Chem.* **116,** 711 (1985).

140. Müller, A., Sarkar, S., Bhattacharyya, R. G., Pohl, S., and Dartmann, M., *Angew. Chem.* **90,** 564 (1978); *Angew. Chem. Int. Ed. Engl.* **17,** 535 (1978).

141. Müller, A., Sarkar, S., Bögge, H., Jostes, R., Trautwein, A., and Lauer, U., *Angew. Chem.* **95,** 574 (1983); *Angew. Chem. Int. Ed. Engl.* **22,** 561 (1983); *Angew. Chem. Suppl.*, p. 747 (1983).

142. Müller, A., Schimanski, J., Schimanski, U., and Bögge, H., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **40b,** 1277 (1985).

143. Müller, A., Schimanski, J., Römer, M., Bögge, H., Baumann, F.-W., Eltzner, W., Krickemeyer, E., and Billerbeck, U., *Chimia* **39,** 25 (1985).

144. Müller, A., Schimanski, J., and Schimanski, U., *Angew. Chem.* **96,** 158 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 159 (1984).

145. Müller, A., Schimanski, J., Schimanski, U., and Bögge, H., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **40b,** 1277 (1985).

146. Müller, A., and Schladerbeck, N., *Chimia* **39,** 23 (1985).

147. Müller, A., Schmitz, K., Krickemeyer, E., Römer, M., Bögge, H., and Baumann, F.-W., *J. Mol. Struct.*, in press.

148. Müller, A., Schmitz, K., Krickemeyer, E., Penk, M., and Bögge, H., *Angew. Chem.* **98,** 470 (1986); *Angew. Chem. Int. Ed. Engl.* **25,** 453 (1986).

149. Müller, A., Zimmermann, M., and Bögge, H., *Angew. Chem.* **98,** 259 (1986); *Angew. Chem. Int. Ed. Engl.* **25,** 273 (1986).

150. Muller, E. G., Petersen, J. L., and Dahl, L. F., *J. Organomet. Chem.* **111,** 91 (1976).

151. Nappier, T. E., Jr., and Meek, D. W., *J. Am. Chem. Soc.* **94,** 306 (1972).

152. Nappier, T. E., Jr., Meek, D. W., Kirchner, R. M., and Ibers, J. A., *J. Am. Chem. Soc.* **95,** 4194 (1973).

153. Pan, W.-H., Harmer, M. A., Halbert, T. R., and Stiefel, E. I., *J. Am. Chem. Soc.* **106,** 459 (1984).

154. Piper, T. S., and Wilkinson, G., *J. Am. Chem. Soc.* **78,** 900 (1956).

155. Perrin-Billot, C., Perrin, A., and Prigent, J., *J. Chem. Soc., Chem. Commun.*, p. 676 (1970).

156. Petersen, J. L., and Dahl, L. F., *J. Am. Chem. Soc.* **97,** 6416 (1975).

157. Potvin, C., Brégeault, J.-M., and Manoli, J.-M., *J. Chem. Soc., Chem. Commun.*, p. 664 (1980).

158. Rakowski DuBois, M., DuBois, D. L., VanDerveer, M. C., and Haltiwanger, R. C., *Inorg. Chem.* **20,** 3064 (1981).

159. Ramasami, T., Taylor, R. S., and Sykes, A. G., *J. Chem. Soc., Chem. Commun.*, p. 383 (1976).

160. Reinsch-Vogell, U., Ph.D. Thesis, University of Bielefeld, Federal Republic of Germany, 1984.

161. Rittner, W., Müller, A., Neumann, A., Bäther, W., and Sharma, R. C., *Angew. Chem.* **91,** 565 (1979); *Angew. Chem. Int. Ed. Engl.* **18,** 530 (1979).

162. Sakaki, S., Hori, K., and Ohyoshi, A., *Inorg. Chem.* **17,** 3183 (1978).

163. Samuel, E., and Gianotti, G., *J. Organomet. Chem.* **113,** C17 (1976).

164. Sandow, T., Steidel, J., and Steudel, R., *Angew. Chem.* **94,** 782 (1982); *Angew. Chem. Int. Ed. Engl.* **21,** 788 (1982).

165. Schmid, G., and Ritter, G., *Angew. Chem.* **87,** 673 (1975); *Angew. Chem. Int. Ed. Engl.* **14,** 645 (1975).

166. Schmid, G., Ritter, G., and Debaerdemaeker, T., *Chem. Ber.* **108,** 3008 (1975).

167. Schmidt, M., Block, B., Block, H. D., Köpf, H., and Wilhelm, E., *Angew. Chem.* **80,** 660 (1968); *Angew. Chem. Int. Ed. Engl.* **7,** 632 (1968).

168. Schmidt, M., and Hoffmann, G. G., *Z. Anorg. Allg. Chem.* **452,** 112 (1979).

169. Schmidt, M., and Wilhelm, E., *J. Chem. Soc., Chem. Commun.*, p. 1111 (1970).

170. v. Schnering, H. G., and Beckmann, W., *Z. Anorg. Allg. Chem.* **347,** 231 (1966).

171. Schunn, R. A., Fritchie, C. J., Jr., and Prewitt, C. T., *Inorg. Chem.* **5,** 892 (1966).

172. Seyferth, D., and Henderson, R. S., *J. Am. Chem. Soc.* **101,** 508 (1979).

173. Seyferth, D., Henderson, R. S., and Gallagher, M. K., *J. Organomet. Chem.* **193,** C75 (1980).

174. Siebert, H., and Thym, S., *Z. Anorg. Allg. Chem.* **399,** 107 (1973).

175. Simhon, E. D., Baenziger, N. C., Kanatzidis, M., Draganjac, M., and Coucouvanis, D., *J. Am. Chem. Soc.* **103,** 1218 (1981).

176. Spangenberg, M., and Bronger, W., *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **33b,** 482 (1978).

177. Steidel, J., and Steudel, R., *J. Chem. Soc., Chem. Commun.*, p. 1312 (1982).

178. Steudel, R., and Strauss, E.-M., *Angew. Chem.* **96,** 356 (1984); *Angew. Chem. Int. Ed. Engl.* **23,** 362 (1984).

179. Steudel, R., and Strauss, R., *J. Chem. Soc., Dalton Trans.*, p. 1775 (1984).

180. Stevenson, D. L., Magnuson, V. R., and Dahl, L. F., *J. Am. Chem. Soc.* **89,** 3727 (1967).

181. Stiefel, E. I., *Proc. Int. Conf. Chem. Uses Molybdenum 4th* (1982).

182. Suchard, S. N., and Melzer, J. E., *in* "Spectroscopic Constants for Selected Homonuclear Diatomic Molecules," Vol. II. Report SAMSO-TR-76-31, 1976.

183. Terzis, A., and Rivest, R., *Inorg. Chem.* **12,** 2132 (1973).

184. Treichel, P. M., and Werber, G. P., *J. Am. Chem. Soc.* **90,** 1753 (1968).

185. Uchtman, V. A., and Dahl, L. F., *J. Am. Chem. Soc.* **91,** 3756 (1969).

186. Vaska, L., *Acc. Chem. Res.* **9,** 175 (1976).

187. Vergamini, P. J., and Kubas, G. J., *Prog. Inorg. Chem.* **21,** 261 (1976).

188. Vergamini, P. J., Ryan, R. R., and Kubas, G. J., *J. Am. Chem. Soc.* **98,** 1980 (1976).

189. Wakatsuki, Y., and Yamazaki, H., *J. Organomet. Chem.* **64,** 393 (1974).

190. Wei, C. H., and Dahl, L. F., *Inorg. Chem.* **4,** 1 (1965).

191. Wells, A. F., "Structural Inorganic Chemistry," 5th ed., p. 727. Oxford Univ. Press (Clarendon), London, 1984.

192. Wickenden, A. E., and Krause, R. A., *Inorg. Chem.* **8,** 779 (1969).

193. Yamanouchi, K., Huneke, J. T., and Enemark, J. H., *in* "Molybdenum Chemistry of Biological Significance" (W. E. Newton, and S. Otsuka, Eds.), p. 309. Plenum, New York, 1980.

194. Müller, A., Diemann, E., Wienböker, U., and Bögge, H., *Inorg. Chem.*, in press.

195. Stiefel, E. I., *Polyhedron* **5,** 341 (1986).