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SYNTHESES, STRUCTURES, AND REACTIONS OF BINARY AND TERTIARY THIOMOLYBDATE COMPLEXES CONTAINING THE (O)Mo(S_x) AND (S)Mo(S_x) FUNCTIONAL GROUPS ($x = 1, 2, 4$)

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I. Introduction

Molybdenum is one of the most abundant elements on the planet [found as molybdenite (MoS_2) and wulfenite ($PbMoO_4$)], and in the oceans molybdenum is the most abundant of the redox-active transition elements (*1*). As a result, in the course of evolution molybdenum has been widely adopted by bacteria, plants, and animals as a metal of choice for the development of active centers in redox-active enzymes.

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In biological systems Mo is present as the Fe/Mo cofactor of the nitrogenase enzymes (*2*) and of the multitude of oxidoreductases (*3*). In the latter the common molybdopterin cofactor (*4*), in addition to a dithiolene functionalized pyranopterin (*5*) ligand (Fig. 1), contains terminal oxo ligands and in the case of xanthine oxidase both oxo and thio ligands. Some aspects of molybdenum sulfur chemistry discussed in this work may be relevant to the biosynthesis of the molybdopterin cofactor and the function of xanthine oxidase (*6*).

The importance of molybdenum sulfur compounds in nonbiological catalysis is exemplified by the hydrodesulfurization (HDS) reaction. This reaction is carried out under H_2 at high temperatures and pressures and is used for the removal of sulfur (as H_2S) from organosulfur compounds present in crude petroleum (*7*). The catalyst consists of "sulfided" molybdates supported on γ-Al_2O_3 and usually contains Co^{II} or Ni^{II} as promoter ions. It has been suggested (*8*) that HDS catalysis occurs at the edges rather than on the basal planes of the γ-Al_2O_3-supported MoS_2 crystallites, and the promotion effects of Co^{II} or Ni^{II} may occur at the same sites. The Mo atoms found at the edges of the

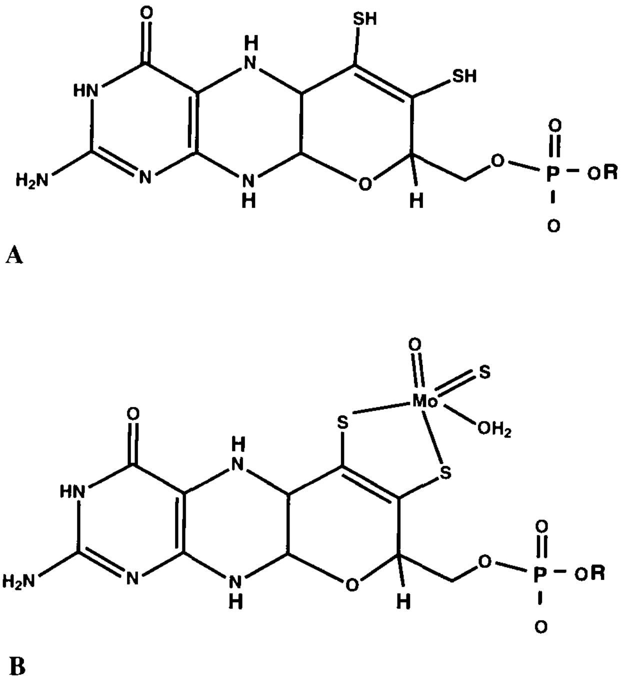


FIG. 1. (A) Molybdopyranopterin and (B) the molybdopyranopterin cofactor of the Mo oxidoreductases.

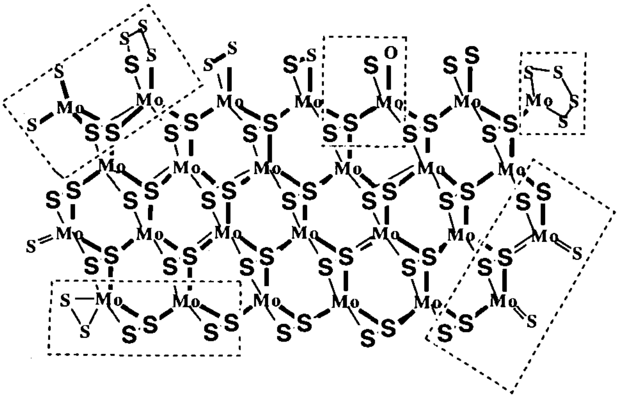


FIG. 2. Possible Mo/S and Mo/S/O groups at the edges of MoS_2. The outlined features have been observed in Mo/S and Mo/S/O complexes.

MoS_2 crystallites may be bound by any of several oxo, thio, or sulfido ligands (*8*) (Fig. 2) and these units may be directly or indirectly involved in the catalytic process.

A number of these "functional groups" (outlined in Fig. 2), often characterized by distinct reactivity properties, are known to exist in molybdothio anions that contain Mo in various formal oxidation states (Fig. 3). This review will concentrate on classes of Mo com-

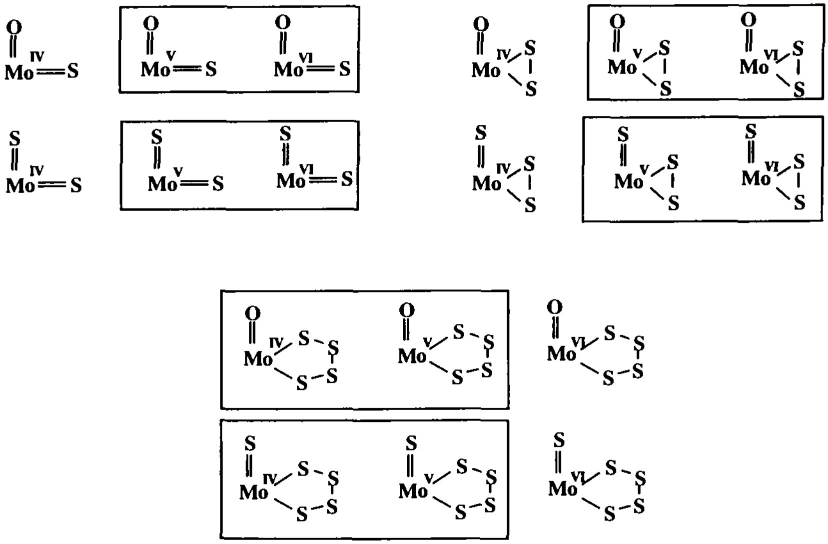


FIG. 3. Mo/S functional groups. The groups within boxes have been observed in crystallographically determined structures.

pounds that contain the chromophores shown in Fig. 3. These compounds possess as a common feature terminally bound S_x^{2-} ligands and include the tertiary $[MoS_xO_{4-x}]^{2-}$ anions, the binary $[(L)(Mo_2S_4)(L']^{2-}$ series, and the tertiary $[(L)(Mo_2O_2S_2)(L')]^{2-}$ and $[(L)(Mo_2OS_3)(L')]^{2-}$ series ($L, L' = S_x^{2-}$, $x = 1, 2, 4$). Throughout this article the Mo_2S_4, $Mo_2O_2S_2$, and Mo_2OS_3 designations represent the *syn*-$[(=S)_2Mo_2(\mu\text{-}S)_2]^{2+}$, *syn*-$[(=O)_2Mo_2(\mu\text{-}S)_2]^{2+}$, and *syn*-$[(=S)(=O)Mo_2(\mu\text{-}S)_2]^{2+}$ cores, respectively, unless otherwise indicated. Similarly the (S_2) and (S_4) ligands are $\eta^2\text{-}S_2^{2-}$ and $\eta^2\text{-}S_4^{2-}$ coordinated to the Mo atoms and the (=E) ligands ($E = S^{2-}$, O^{2-}) are terminally coordinated chalcogenide dianions.

Of direct relevance to this work are various other reviews that cover the chemistry of Mo/S complexes (*9*, *10*), the S_x^{2-} anions (*11*), the S_2^{2-} ligand (*12*), and the sulfur-bridged molybdenum and tungsten compounds (*13*).

II. Mo/S Chemistry

A. GENERAL CONSIDERATIONS

The chemistry of molybdenum ions with sulfur ligands is unique when compared to other transition metal ions. The diversity in structural and reactivity characteristics of Mo/S complexes derives mainly from a close matching of the S *3p* and Mo *4d* orbital energies (*14*), which provide low-energy superexchange pathways for intramolecular electron transfer processes (*15*). The latter allow for sulfur ligand transformations concomitant with Mo valence state interconversions that span oxidation states III, IV, V, and VI. An example of this diversity is available in the remarkable set of electron-redistribution isomers of the triad of $[(Cp)(Mo_2S_4)(Cp)]$ complexes (*16*) that have been reported as distinct $(Cp)_2Mo_2^{III}(\mu\text{-}S_2)_2$ (*17*), $(Cp)_2Mo_2^{IV}(\mu\text{-}S_2)(\mu\text{-}S)_2$ (*18*), and *anti*-$[(Cp)(Mo_2S_4)(Cp)]$ (*19*) units (Fig. 4). These isomers are thermally (*20*) or photochemically (*21*) interconvertible. A theoretical analysis of $[(Me\text{-}Cp\text{–}Mo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$ and its isomers explains how the central S_4 unit "traverses in many compounds a range in S–S bonding from ring to isolated S_2^{2-} bridges" (*22*).

At times, the ground states of electron-redistribution isomers of isoelectronic complexes are close enough in energy so that minor perturbations (crystal packing forces, solvent dielectrics, ion pairing) are sufficient to stabilize preferentially one isomer over another. A remarkable example of such an event is the existence, isolation, and structural characterization of the $[Mo_2^V(S_2)_6]^{2-}$ (*23*) and

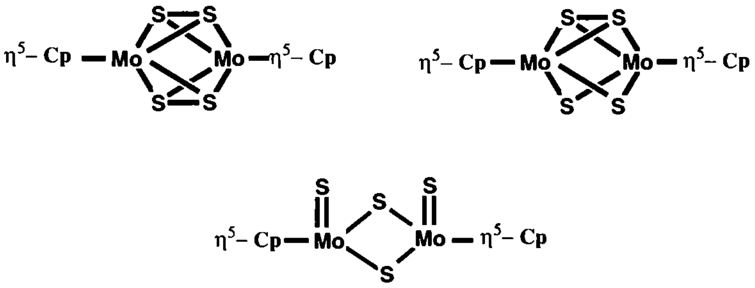


FIG. 4. Schematic representation of the three isomers of the $[(Cp)(Mo_2S_4)(Cp)]$ complexes.

$[(S_4)(Mo_2S_4(S_4)]^{2-}$ (*24*) anions (Fig. 5). The former, isolated from aqueous solution as an NH_4^+ salt, transforms to the latter on dissolution in dimethylformamide and addition of R_4N^+ cations (*25*).

Numerous examples of the redox interplay between molybdenum and sulfur have been reported (*26–28*). The synthesis of the $[S{=}Mo^{IV}(S_4)_2]^{2-}$ anion (*24a*, *29*) from the reaction of $[Mo^{VI}S_4]^{2-}$ with elemental sulfur or organic trisulfides paradoxically involves the reduction of the Mo^{VI} ion under oxidizing conditions. This reaction is rationalized in terms of the internal oxidation of S_2^{2-} ligands (*vide*

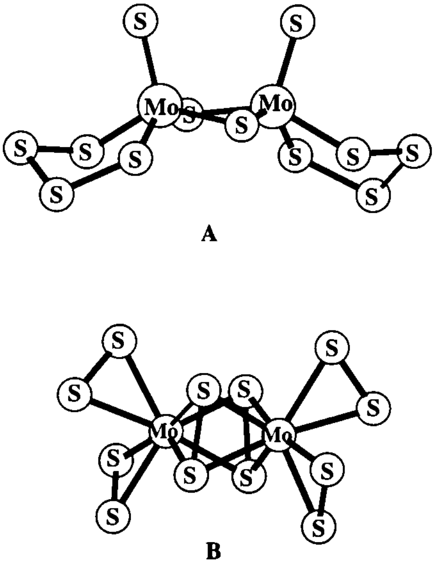


FIG. 5. Two $[Mo_2S_{12}]^{2-}$ isomers.

infra). The reactions of the VS_4^{3-} and MoS_4^{2-} anions with the oxidizing tetraalkylthiuram disulfides, or $(R_2Dtc)_2$, afford the $V_2^{IV}(\mu\text{-}S_2)_2(R_2Dtc)_4$ (*30–32*) and $Mo^{V}(S_2)(R_2Dtc)_3$ (*33*, *34*) dithiocarbamate complexes. Here also, the reduction of the metal is coupled to the oxidation of the S^{2-} ligands that form the S_2^{2-} disulfido groups. Other similar, internal redox, systems have been reported (*24c*, *35–36*). A kinetic study (*37*) of the reaction of MoS_4^{2-} with certain disulfides to form $[(S_2)(Mo_2S_4(S_2)]^{2-}$ has led to a mechanism based on the internal reduction of Mo^{VI} and a rate-determining step involving the formation of the $(L)_2Mo^{IV}(S_2)$ group from $(L)_2Mo^{VI}(S)_2$.

B. THE Mo=S BOND

The chemistry of the Mo=S bond is intimately associated with synthetic aspects or reactivity characteristics for the vast majority of the Mo–S complexes reviewed in this work. In six-coordinate $S{=}Mo(L)_5$ and five-coordinate $S{=}Mo(L)_4$ complexes, the involvement of the molybdenum (d_{xz} and d_{yz}) orbitals in π bonding with the sulfur *p* orbitals orthogonal to the Mo–S σ bond results in essentially a triple Mo–S bond (Fig. 6).

In the $(L)_5Mo{=}S$ complexes competition of π donor ligands (trans to the S atom in the Mo=S bond) for the same Mo *d* orbitals results in a weakening of the Mo=S bond. In the $(L)_4Mo{=}S$ square pyramidal complexes a similar energy level scheme (Fig. 7B) applies (*38*), although it is proposed that the energy of the σ^* orbital is lowered in the pyramidal complexes (*39*). The Mo–L triple bonds are predominant for the IV, V, and VI oxidation states or the d^2, d^1, and d^0 electronic configurations that do not involve population of the strongly antibonding π^* orbital. An examination of the energy level diagram (Fig. 6) shows the ready accessibility of the σ^* and π^* orbitals and justifies the contention (*40*) that the photochemistry of these compounds promises to be an exciting area.

The energy level schemes for the $E{=}Mo(L)_3$ (C_{3v}) and $E{=}Mo(L)_4$ (C_{4v}) complexes are shown in Fig 7. In C_{3v} geometry the $d_{x^2-y^2}$ orbital is less antibonding and the bond order of the terminal (axial) ligand is reduced from being a triple bond. The energies of the a_1, b_1, e, and b_2 orbitals in $[MoOCl_4]^-$ have been calculated as 4.63, 3.66, 2.80, and 0.87 eV, respectively; they are above the Cl *3p* in-plane (a_2 and b_2) orbitals at -1.45 eV and the Cl *3p* out-of-plane (b_1, e, and a_1) orbitals at -2.14, -2.43, and -2.91 eV, respectively (*41*). Certain reactions of the trigonal pyramidal $E{=}Mo(L)_3$ complexes lead to square pyramidal

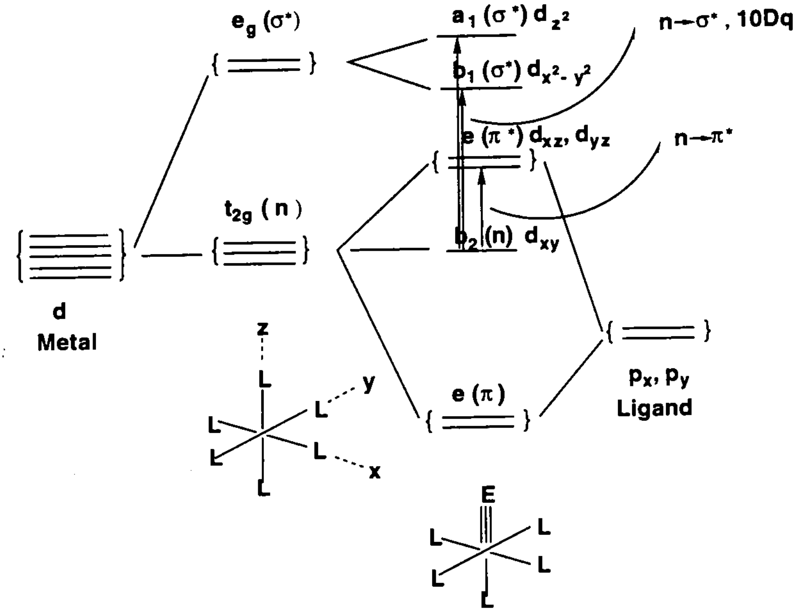


Fig. 6. Energy level schemes for the $Mo(L)_6$ and $E{=}Mo(L)_5$ complexes.

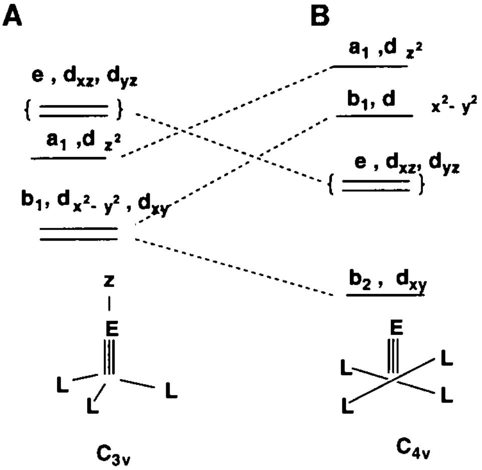


Fig. 7. Energy level schemes for the $E{=}Mo(L)_3$ and $E{=}Mo(L)_4$ complexes.

$E{=}Mo(L)_4$ complexes. The energetics of this transformation have profound effects on reactivity (see Section IV,B).

III. Binary Thiomolybdates and Tertiary Oxo/thiomolybdates

A. THE $(MoS_xO_{4-x})^{2-}$ ANIONS

The reactions of oxomolybdates $[(MoO_4)^{2-}$ or $(Mo_7O_{24})^{6-}]$ with H_2S or $(NH_4)_2S_x$ under basic conditions give thiomolybdate products that, depending on reaction times or conditions, contain $Mo{=}S$ and $Mo{=}O$ units in various combinations (*42*). The chemistry and spectroscopic properties of the tetrahedral $(MoS_nO_{4-n})^{2-}$ anions have been reviewed (*43–45*) and the structures of various thiomolybdates have been determined (*46*).

The kinetics of the interconversion of sulfido and $(MoO_nS_{4-n})^{2-}$ species in aqueous solution have been studied (*47*). The results indicate that crowding by the larger S^{2-} ligands at the reaction site makes associative substitution more difficult and results in slower rates as the S^{2-}/O^{2-} ratio increases.

Investigations of bonding in the $(MoO_nS_{4-n})^{2-}$ anions using ^{33}S and ^{17}O NMR spectroscopy have been reported (*48*, *49*). The monotonic deshielding observed in the ^{95}Mo NMR as oxygens are successively replaced by sulfur is explained by *ab initio* calculations (*49*) that show an increase in the electron density on the Mo atom as oxygen atoms are successively replaced by sulfur atoms. Theoretical studies of the bonding in the $(Mo_{4-n}S_n)^{2-}$ anions have been published (*50*). The solution chemistry of the $(MoS_4)^{2-}$ anion has been investigated (*51*) electrometrically and the formation of various thioanions, including $(Mo_2S_7)^{2-}$, was detected. A multitude of heterometallic complexes have been obtained whereby the thiomolybdate anions serve as ligands. The vast majority of these complexes are $(MoS_4)^{2-}$ derivatives. Various reviews have been published on these compounds (*23c*, *43*, *44*, *52*). The first reports of $\{M[MoS_4]_2\}^{2-}$ complexes (M = Ni, Fe, Co, Zn) and the use of the $(MoS_4)^{2-}$ anion as a ligand appeared in 1971 (*53*, *54*) and the structure of the $(Ph_4P)_2\{Ni[MoS_4]\}$ complex was subsequently determined (*55*) ($Mo{-}S_b = 2.23$ Å, $Mo{=}S = 2.15$ Å; $Ni{-}Mo = 2.80$ Å). The electrochemistry of the $\{M[MoS_4]_2\}^{2-}$ anions (M = Ni, Pd, Pt) shows (*56*) a $2e^-$ reversible reduction for the Ni complex and a $1e^-$ reduction for the Pt complex. The calculation of electronic structure for a wide range of $[M(MS_4)_2]^{2-}$ complexes (M = Mo, W) has been reported (*50b*).

In later years a great number of $(MoS_4)^{2-}$ complexes with iron were reported (Fig. 8). The syntheses of these compounds were inspired by the Fe/Mo/S center in nitrogenase. Among them are included complexes such as $[L_2FeS_2MS_2]^{2-}$ [L = PhS^- (*57a,b*), Cl^- (*58*), PhO^- (*59*), NO^+ (*60a*); L_2 = S_5^{2-} (*61*)], $[Cl_2FeS_2MS_2FeCl_2]^{2-}$ (*58a*), $[Fe(MoS_4)_2]^{3-}$ (*62*), $[(S_2)OMoS_2FeCl_2]^{2-}$ (*63*), and $[S_2MoS_2FeS_2Fe(S\text{-}p\text{-}C_6H_4Me)_2]^{3-}$ (*59, 64*). The synthesis and structural characterization of the $[(PhS)_2FeS_2MoO_2]^{2-}$ complex were reported more recently (*57c*). The spectroscopic and structural properties of these complexes have been reviewed (*52*). An electron paramagnetic resonance (EPR) study of the reactions of $(MoS_4)^{2-}$ with Roussin's salts $Fe_2(SR)_2(NO)_4$ and

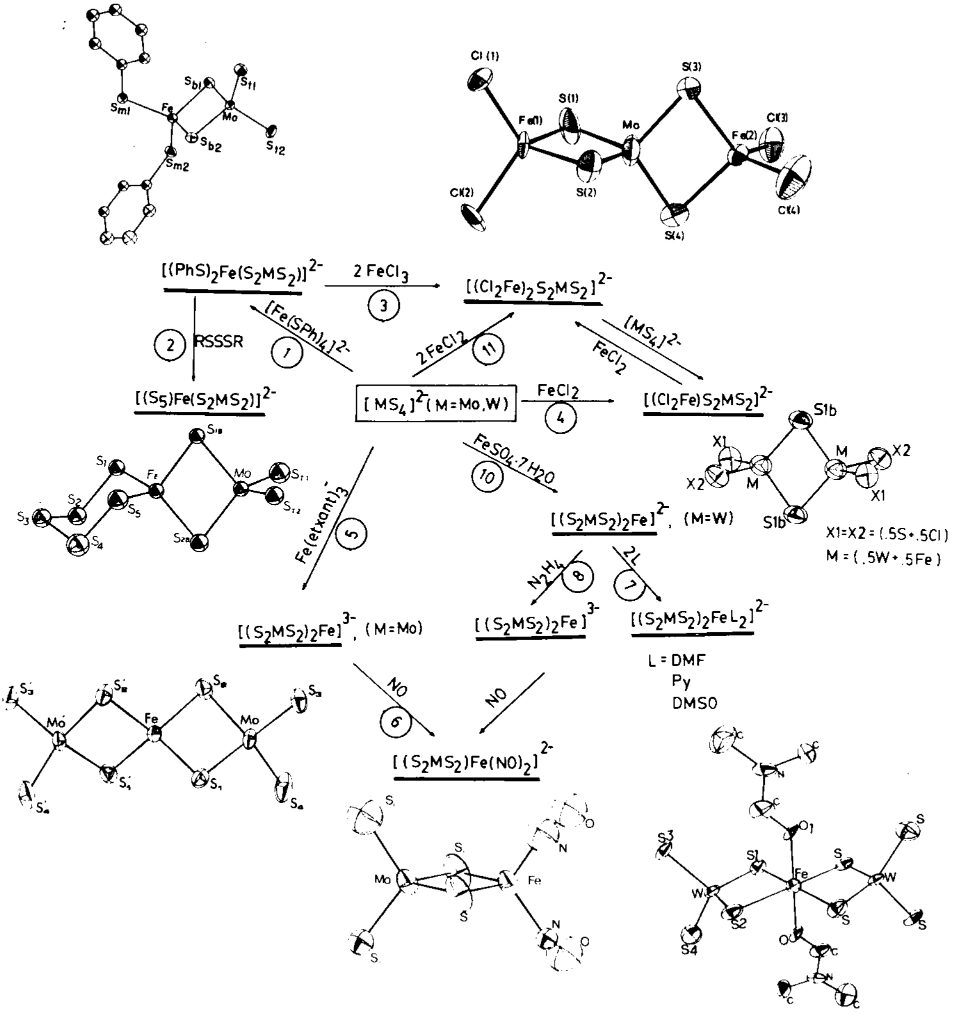


FIG. 8. The $[MoS_4]^{2-}$ anion as a ligand; Fe/MoS_4 complexes.

$[Fe_4S_3(NO)_7]^-$ has detected the formation of nitrosyl complexes such as $[Fe(NO)_2(S_2MoS_2)]^-$ and $[Fe(NO)(S_2MoS_2)_2]^{2-}$ (*60b*).

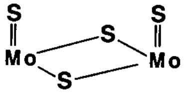
The use of the $(MoS_4)^{2-}$ anion as a ligand for $Mo(CO)_4$ led to the unusual $[(CO)_4MoS_2MoS_2]^{2-}$ and $\{[(CO)_4Mo]_2[MoS_4]\}^{2-}$ complexes (*65*) that contain two Mo atoms within the same molecule in two widely different oxidation states, 0 and VI. The trinuclear $W^{VI}(W^0)_2$ analog also has been obtained (*65b*).

The $[MoFe_3S_6(CO)_6]^{2-}$ complex (*66*) contains the $[(CO)_6Fe_2(\mu\text{-}S)_2]^{2-}$ "ligand" and could be described as a structural derivative of the $[Cl_2Fe(MoS_4)]^{2-}$ complex wherein the two Cl^- ligands have been replaced by the $[(CO)_6Fe_2(\mu\text{-}S)_2]^{2-}$ anion. The synthesis and structure of the $(MeCp)_2M(MoS_4)]$ complexes (M = Mo, W) have been reported (*67*). A variety of mixed-ligand heterometallic complexes with $(MoS_4)^{2-}$ as one of the coligands has been reported, including $(bipy)_2Mn(MoS_4)$, obtained (*68*) in a straightforward manner from MoS_4^{2-}, bipy, and Mn^{2+}; the Cu^I dimers (*69*) $LCu(MoS_4)CuL$ (L = 2,2-bipyridine, 1,10-phenanthroline); and polymeric $[(CuNCS)_4MS_4]^{2-}$ heterobimetallic clusters (*70*) of Cu^I with $(MoS_4)^{2-}$. A multitude of neutral $(MS_4)^{2-}/M'L$ complexes are known for M′ = a coinage metal, L = CN^-, Cl^-, or NCS^-. These complexes include $[WS_4(CuCN)_2]^{2-}$ (*71a,b*) and $[MoS_4(CuCl)_3]^{2-}$ and variants (*71c,f*). The reduction of Cu^{II} in aqueous solution by $(NH_4)_2MoS_4$ gives (*72a*) polymeric NH_4CuMoS_4. The linear trimetallic $(AuPEt_3)(S_2MoS_2)(AuPEt_3)$ complex contains a $\mu\text{-}(MoS_4)^{2-}$ ligand and has been structurally characterized (*72b*). The synthesis of the $[(PhS)_2Mo(O)(MoS_4)]^{2-}$ anion is accomplished (*73*) in DMF solution by substitution of two of the thiophenolate ligands in the $[(PhS)_4Mo(O)]^-$ complex (*74*) by the $(MoS_4)^{2-}$ chelating ligand. An infrared (IR)–Raman study of the Cu^I–MoS_4 complexes has been reported (*75*) and redox-based intercoversions (*76*) between $[(CuCN)(MoS_4)]^{2-}$ and $[(CuCN)_2(MoS_4)]^{2-}$ have been investigated.

Other trinuclear and tetranuclear univalent coinage metal derivatives of thiomolybdate and thiotungstate dianions include $[(O)MoS_3Cu_2(Py)_2(PPh_3)_2]$ (*77a*), $[(O)MoS_3Cu_3(NCS)_3]^{2-}$ (*77b,d*), $[(O)MoS_3Cu_3(\mu_3\text{-}Cl)_2(PPh_3)_3]$ (*77c*), and the "incomplete cubanes" $[(Edt)_2M_2S_4Cu(PPh_3)]^-$ (*77e*) (M = Mo, W). The silver analogues of the latter also have been reported (*77f*). The neutral cubane clusters $[(Edt)_2M_2S_4Cu_2(PPh_3)_2]$ (*77g*) are structural derivatives of the incomplete cubanes (see above) and contain an additional $[Cu(PPh_3)]^+$ unit (*77g*). The heterometallic $[MS_4(CuCl)_4)]^{2-}$ (M = Mo, W) complexes (*78*) contain a central $\mu_4\text{-}(MS_4)^{2-}$ bridge that symmetrically binds four CuCl units. These dianions oligomerize and form interionic Cu_2Cl_2 rhombic bridging units. The oligomerization process depends on the types of counterions that accompany the $[MS_4(CuCl)_4)]^{2-}$ anions.

B. BINARY THIOMOLYBDATES

1. *The* $[S{=}Mo(S_4)_2]^{2-}$ *Anion and the* $[(S_x)(Mo_2S_4)(S_y)]^{2-}$ *Series*



The $[Mo_2S_4]^{2+}$ *unit*

Explorations of the chemistry of the binary molybdenum sulfides started with initial reports on the synthesis and structural characterization of the $[(S_2)_2Mo(\mu\text{-}S_2)]_2^{2-}$ (*23*) (Fig. 5B) and the $[Mo_3S_{13}]^{2-}$ (Fig. 9) thioanions by Muller and co-workers (*23d–j*). Soon thereafter, the discovery and detailed characterization of new thiomolybdates such as $[S{=}Mo(S_4)_2]^{2-}$ (*24a*), $[(S_2)(Mo_2S_4)(S_2)]^{2-}$ (*35*, *79*), $[(S_4)(Mo_2S_4)(S_2)]^{2-}$ (*24*), and $[S{=}Mo(MoS_4)_2]^{2-}$ (*80*) revealed the remarkable complexity of the Mo/S system.

The reaction of $(Et_4N)_2(MoS_4)$ (*46*) with either elemental sulfur or organic trisulfides in CH_3CN solution affords (*24*) highly crystalline $[Et_4N]_2[S{=}Mo(S_4)_2]$. The $[S{=}Mo(S_4)_2]^{2-}$ anion also can be made from $(NH_4)_2S_3$ and $(NH_4)_2MoS_4$ in aqueous solution and crystallizes as an Et_4N^+ salt on addition of Et_4NCl. The formation of this interesting Mo^{IV} complex (Fig. 10) under oxidizing conditions has been discussed in terms of internal electron transfer (see Section II,A).

Crystalline $[Et_4N]_2[O{=}Mo(S_4)_2]$ is obtained by hydrolysis of $[Et_4N]_2$ $[S{=}Mo(S_4)_2]$ in hot "wet" DMF. Attempts to exchange the Et_4N^+ cations in $[Et_4N]_2[S{=}Mo(S_4)_2]$ with Ph_4P^+ resulted in the isolation of Ph_4P^+ salts of the $[(S_4)(Mo_2S_4)(S_4)]^{2-}$ (Fig. 5A) and $[(S_2)(Mo_2S_4)(S_4)]^{2-}$ anions (*24*). The same anions also are isolated following addition of

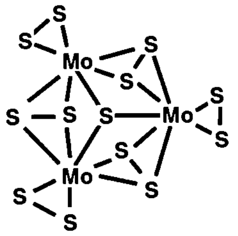


FIG. 9. Schematic representation of the $[Mo_3S_{13}]^{2-}$ anion.

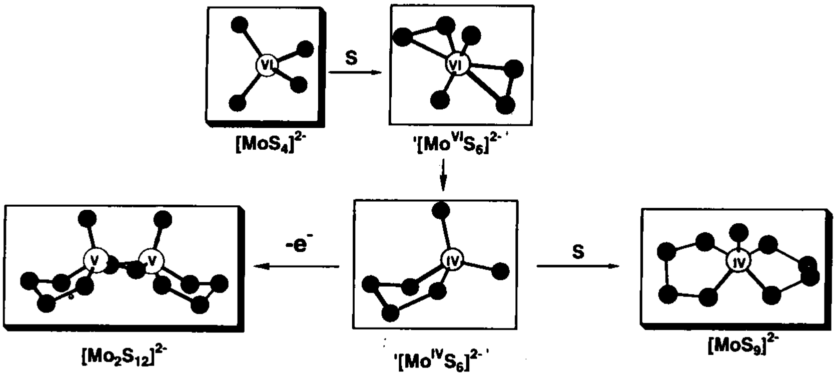


FIG. 10. Proposed pathway in the synthesis of the $[S{=}Mo(S_4)_2]^{2-}$ anion. (In this and in all subsequent figures the structures within solid-line frames have been plotted from crystallographically determined coordinates.)

Ph_4PCl to CH_3CN solutions of $(NH_4)_2[Mo_2(S_2)_6]$ (Fig. 5B). The $[(S_2)(Mo_2S_4)(S_2)]^{2-}$ anion was obtained by oxidation of $(NH_4)_2MoS_4$ with diphenyl disulfide or diselenide in DMF solution and was isolated as a $(Ph_4P)^+$ salt in 80% yield (*35*). These early observations in Mo/S chemistry revealed the rich chemistry of the system and led to proposals of complex equilibria between various thioanions.

Among the thioanions that were proposed to coexist in equilibria or to be possible intermediates in the formation of the $[S{=}Mo(S_4)_2]^{2-}$, $[(S_4)Mo(Mo_2S_4)Mo(S_2)]^{2-}$ (*24a,b*), and $[S{=}Mo(MoS_4)_2]^{2-}$ (*80*) complexes are the $[Mo_2S_7]^{2-}$ (*24a,b, 79*) and $[(S)(Mo_2S_4)(S_4)]^{2-}$ (*24a, 79*) anions. The former has been reported (*51*) to form in aqueous $(MoS_4)^{2-}$ solutions at pH ~5, and to exist as a ligand in the [Fe (Salen)]$_2$(Mo_2S_7) complex (*81*), but had not been isolated in the solid state, whereas the latter, a possible precursor to $(Mo_2S_7)^{2-}$, was until then an unknown derivative of the $(Mo{=}S)^{2+}$ (*24a*) unit.

Subsequent studies of the reactivity of the known thiomolybdates (and particularly the $[(S_4)(Mo_2S_4)S_2)]^{2-}$ complex) with Ph_3P have resulted (*82, 83*) in the systematic synthesis of the $[(S_x)(Mo_2S_4)(S_y)]^{2-}$ anions (Fig. 11; Table I).

A mixture of $[(S_4)(Mo_2S_4)(S_2)]^{2-}$ and $[(S_4)(Mo_2S_4)(S_4)]^{2-}$ (Fig. 11, structures 4A and 6A) and also $[(S_2)(Mo_2S_4)(S_2)]^{2-}$ (Fig. 11, structure 2B) is obtained by oxidation of the $[S{=}Mo(S_4)_2]^{2-}$ anion with diphenyl disulfide (*35, 83*). The possibility of internal electron transfer processes, mediated by the S_x^{2-} ligands, often presents the choice of more

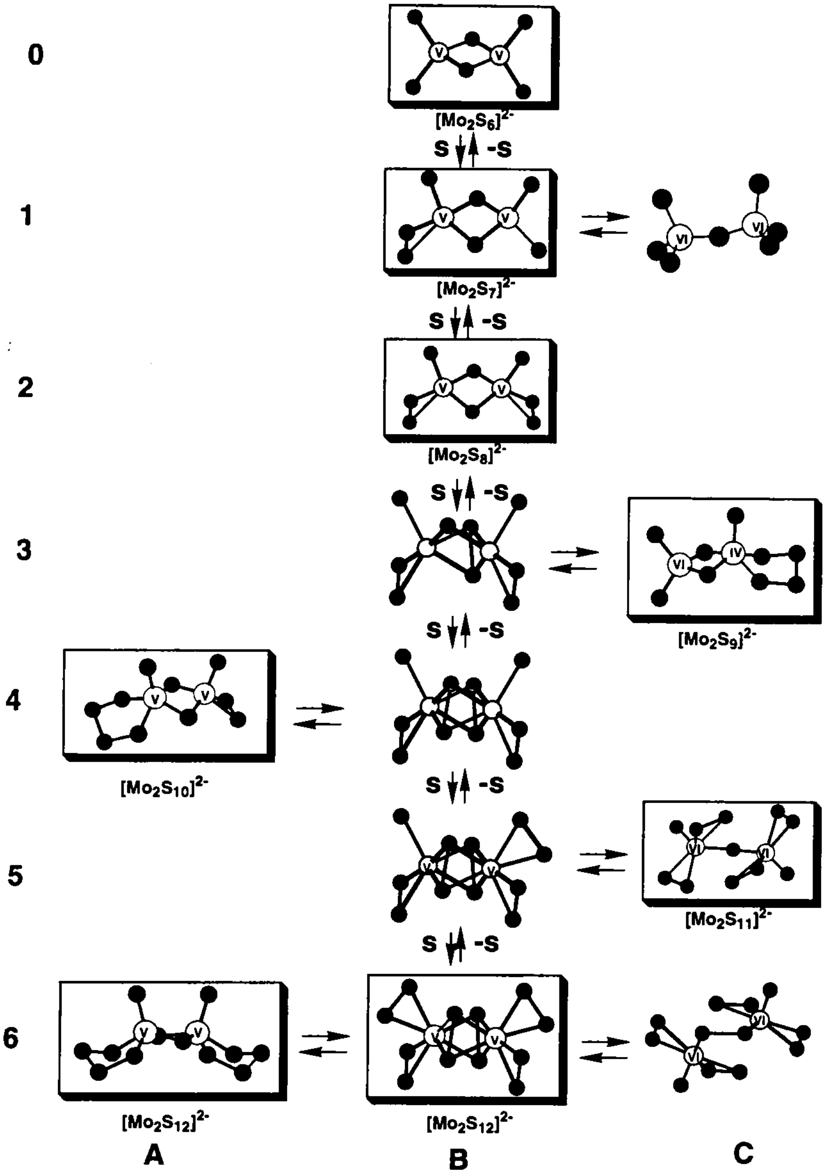
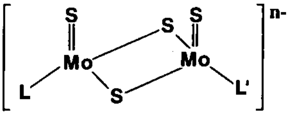


FIG. 11. The $[(S_x)(Mo_2S_4)(S_y)]^{2-}$ anions.

TABLE I

DISTANCES AND ANGLES IN BINARY Mo/S COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[Mo_2S_4]^{2+}$ CORE[a]



L	L'	n	Mo—Mo (Å)	Mo—S_b (Å)	Mo=S_t (Å)	Mo—L (Å)	Mo—L' (Å)	Mo—S—Mo (°)	S—Mo—S (°)	Reference
S^2	S^2	2	2.856(1)	2.301(1)	2.157	2.145	2.145	76.8(1)	103.2(1)	*82a,b*
S^2	S_2^2	2	2.848(2)	2.323 2.283^b	2.103	2.174(3)	2.405	76.3(1)	101.3(1) $103.7(1)^a$	*82a,b*
S^{2-}	S_4^2	2	2.859(1)	$2.271(3)^c$ $2.237(5)^c$ $2.342(4)^d$ $2.368(4)^d$	$2.142(4)^c$ $2.105(3)^d$	2.157(3)	2.387	76.6	$105.2(1)^b$ $99.0(1)^c$	*82a,b*
S_2^2	S_2^{2-}	2	2.821(1)	2.310(4,2)	2.118	2.393(4,8)	2.393(4,8)	75.3	101.2	*35*
S_2^{2-}	S_4^{2-}	2	2.846(1)	2.342^e 2.295^f	2.118	2.432	2.412	75.70	102.0	*24a*
S_2^2	S_4^{2-}	2	2.837(1)	2.341^e 2.296^f	2.110	2.395	2.406	75.5	102.0	*24b*
$(CS_3)^{2-}$	$(CS_3)^2$	2	2.823(1)	2.300(7)	2.100(2)	2.433(8)	2.433(8)	75.6(1)	100.8(1)	*161a*
$(CS_4)^2$	$(CS_4)^2$	2	2.840(3)	2.316(5)	2.108(5)	$2.412(5)^g$ $2.391(4)^h$	$2.413(5)^g$ $2.391(4)^h$	75.6(1)	101.4(3)	*160, 161a*
$(Edt)^{2-}$	$(Edt)^{2-}$	2^i	2.863(2)	2.319(4)	2.089(4) 2.112(3)	2.405(3)		76.22	99.84	*89b*
			2.855(1)	2.315(2)	2.103(2)	2.394(2)		76.2(1)	100.6(1)	*89c*
$(Edt)^2$	$(Edt)^2$	2^j	2.878(2)	2.298(2) 2.344(2)	2.129(2)	2.400		76.62(7)	103.38(7)	*89b*
$[S{=}Mo(S_4)_2]^{2-}$		—	—	—	2.128(1)	2.331(1) 2.387(1)		—	—	*24a*

[a] In this and the rest of the tables that report crystallographic data the average values of chemically equivalent distances or angles are given. The number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\Sigma_{i=1}^{N}(x_i - x)^2/N(N - 1)]^{1/2}$. If only two values are available for a given distance or angle, the average value is reported without a standard deviation in parentheses.

[b] Involves the Mo bound to L = S.

[c] Bound to the Mo^{IV} ion.

[d] Bound to the Mo^{VI} ion.

[e] Bound to the $Mo(S_4)$ unit.

[f] Bound to the $Mo(S_2)$ unit.

[g] Bond with the C–S group of the ligand.

[h] Bond with the C–S–S group of the ligand.

[i] Syn isomer.

[j] Anti isomer.

than one structure for a given complex, and the structures formally described in Fig. 11 as 4B and 5B have been obtained in different isomeric forms (Fig. 11, structures 4A and 5C).

The $[(S_4)(Mo_2S_4)(S)]^{2-}$ anion (Fig. 11, structure 3C) can only be obtained by the BH_4^- reduction of the $[(S_4)(Mo_2S_4)(S_2)]^{2-}$ complex in DMF solution. A possible pathway for this reaction has been sug-

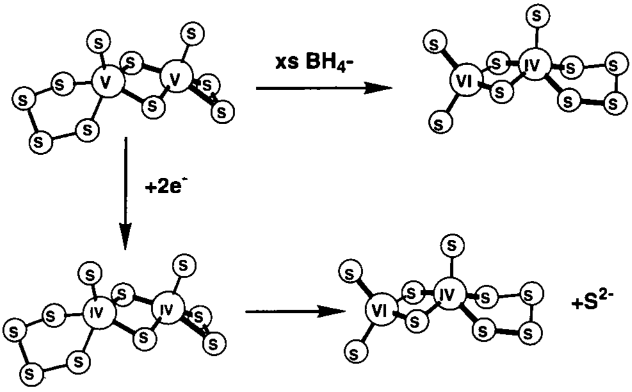


FIG. 12. The synthesis of the $[(S_4)(Mo_2S_4)(S)]^{2-}$ anion.

gested (*83*) (Fig. 12). The description of this complex as the valence-localized $[(S{=}Mo^{IV}(S_4)(Mo^{VI}S_4)]^{2-}$ ion is prompted by the asymmetric $[Mo_2S_4]^{2+}$ core (Table I) that shows two sets of Mo–μ-S bonds at 2.355 and 2.254 Å, respectively. Abstraction of two sulfur atoms from the S_4^{2-} ligand in this complex leads to the $[(S{=}Mo^{IV}(S_2)(Mo^{VI}S_4)]^{2-}$ ion (Fig. 11, structure 1B). A detectable structural asymmetry in this ion (Table I) suggests that a valence-localized form contributes somewhat to the description of its structure. The $[Mo^{VI}S_3)_2S]^{2-}$ form of this ion (Fig. 11, structure 1C) would be isostructural to that of the known $[Mo_2O_7]^{2-}$ anion (*84*). Attempts to obtain $[(Mo^{VI}S_3)_2S]^{2-}$ by the reaction of $[(Mo^{VI}O_3)_2O]^{2-}$ with $(Me_3Si)_2S$ have led to the monomeric $[(Mo^{VI}O_3OSiMe_3]^-$ complex (*85*).

The $\{[(S_2)_2Mo(\mu\text{-}S_2)]_2\}^{2-}$ anion [Fig. 5B; Mo–Mo, 2.826(2), 2.828(2) Å; S–S, 2.038(5)–2.056(5) Å] (*23*) is unique among the binuclear binary Mo/S complexes in that it contains the $Mo_2(\mu\text{-}S_2)_2$ rather than the $Mo_2(\mu\text{-}S)_2$ bridging unit. The complex is obtained as a black crystalline dihydrate by the reaction of $(NH_4)_2MoS_2O_2$ with $(NH_4)_2S_x$ (*23f*). The lability of this complex, which in the solid state exists as an NH_4^+ salt, already has been noted in its remarkable, cation-induced, transformation to the isomeric $[(S_4)(Mo_2S_4)(S_4)]^{2-}$ anion. The latter can be obtained from DMF solutions of $(NH_4)_2\{[(S_2)_2Mo(\mu\text{-}S_2)]_2\}$ on addition of Et_4NCl.

The $[Mo(\mu\text{-}S_2)_2Mo]^{6+}$ core in the $[X_4Mo(\mu\text{-}S_2)_2MoX_4]^{2-}$ anions (*86*) shows slightly longer Mo–Mo bonds and shorter S–S bonds [Mo–Mo, 2.857(1)–2.852(4) Å; S–S, 1.998(9)–1.969(9) Å] by comparison to $\{[(S_2)_2Mo(\mu\text{-}S_2)]_2\}^{2-}$. The former is obtained in very good yield from

$Mo(S_2)X_3$ ($X = Cl^-$, Br^-). The expected lability of the X^- ligands in this molecule should make it a good reagent for the synthesis of other complexes with the $Mo(\mu\text{-}S_2)_2Mo$ unit. The $[Mo(\mu\text{-}S_2)_2Mo]^{6+}$ core also is found in the solid-state structure of $[Cl_{4/2}Mo(\mu\text{-}S_2)_2MoCl_{4/2}]$ (*87*) and in the structure of the $\{(Et_2Dtc)_2[Mo(\mu\text{-}S_2)_2Mo](Et_2Dtc)_2\}^{2+}$ complex (*88*). The extraordinary H_2 activation chemistry associated with certain isomeric forms of the $[(Cp)(Mo_2S_4)(Cp)]$ complex has been studied in detail mainly by M. Rakowski-DuBois and co-workers (*19a*). This work poses the question whether other complexes that contain the $[Mo_2S_4]^{2+}$ core might not display similar reactivity.

Reduction of the S_2^{2-} ligands in $\{[(S_2)_2Mo(\mu\text{-}S_2)]_2\}^{2-}$ by an excess of other oxidizable sulfur ligands L ($L = Et_2Dtc^-$, PhS^-, Edt^{2-}) leads to generation of the $[Mo_2S_4]^{2+}$ core and concomitantly to $[(L)_n(Mo_2S_4)(L)_n]$ complexes (*89a*). Both the syn (*89b,c*) and *anti* (*89b*) isomers of the $[(Edt)(Mo_2S_4)(Edt)]^{2-}$ complex have been synthesized and structurally characterized. The bonding in these molecules has been examined through extended Hückel and Fenske–Hall calculations that show a greater Mo–Mo *4d* overlap for the syn isomer relative to the anti isomer and a greater relative stability of the syn isomer (*89d*). A compilation of characteristic infrared data and of electronic spectra for mainly binary sulfide complexes that contain the $[Mo_2S_4]^{2+}$ core can be found in Table II.

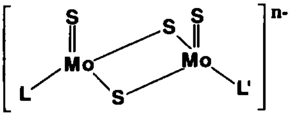
2. *Other Binary and Tertiary Group VI Chalcogenides M/E (M = W; E = S, Se, Te)*

A number of W/S complexes analogous and often isostructural to corresponding Mo/S complexes have been reported, including $(W_2S_{11})^{2-}$ (*90c*), $(W_2S_{12})^{2-}$ (*24c*), $[S{=}W(WS_4)_2]^{2-}$ (*90d*), $[(WS_4)(S)W(\mu\text{-}S)_2W(S)(S_2)]^{2-}$ (*90e*), and $[(WS_4)(S)W(\mu\text{-}S)_2W(S)(WS_4)]^{2-}$ (*90f*). The very interesting $[W(WS_4)_2]^{2-}$ anion contains a four-coordinate square, formally W^{II}, central ion bound by two tetrathiotungstate dianions (*90a,b*). A doubt has been raised concerning the identity of this unusual molecule (*90c*).

From the synthetic and crystallographic studies of W/Se chemistry (*91*) it has been revealed that certain aspects of this chemistry do not parallel those of W/S chemistry. This is particularly true for the degree of catenation found with the E_x^{2-} chalcogenide ligands. Thus the Se_3^{2-} ligand found in the $[(Se_3)(Se)W(\mu\text{-}Se)]_2^{2-}$ and $[(Se_3)(Se)W(\mu\text{-}Se)_2W(Se)(Se_2)]^{2-}$ complexes (*91*) has no counterpart in Mo/S or W/S chemistry. As a general rule, selenide chemistry appears more complex and the compounds are less stable.

TABLE II

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF BINARY Mo/S COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[Mo_2S_4]^{2+}$ CORE



L	L′	Infrared absorption $(cm^{-1})^a$	λ_{max} (nm: $\varepsilon \times 10^{-3})^b$	Reference
S^{2-}	S^{2-}	503(m); 475(m); 452(w)	290(26.0); 310(19.3); 362(sh); 454(9.9); 482(sh)	*82b*
S^{2-}	S_2^{2-}	504(m); 480(m); 454(w)	295(sh); 362(sh); 422(sh); 452(5.2); 560(2.4)	*82b*
S^{2-}	S_4^{2-}	506(m); 487(m); 456(w)	298(23.8); 350(sh); 422(7.0)	*82b*
S_2^{2-}	S_2^{2-}	512(sh); 453(w)	290(sh); 464(2.7); 574(3.3)	*82b*
S_4^{2-}	S_4^{2-}	523(s); 496(w); 439(m); 416(w); 348(w); 325(w); 315(w); 298(m)	—	*24c*
$(CS_3)^{2-}$	$(CS_3)^{2-}$	C=S, 982(s); Mo–S_b, 464(w)	344; 444(sh)	*161*
$(CS_4)^{2-}$	$(CS_4)^{2-}$	C=S, 1052(s); Mo–S_b, 460(w)	314(sh); 365(sh); 470(sh); 610(sh)	*161*
$[(S{=}Mo(S_4)_2]^2$		S=Mo, 525(s)	316(15.7); 340(sh); 405(sh); 470(sh)	*24a*

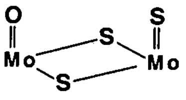
[a] In KBr disk.
[b] In DMF.

The $[(E)M_2E_4(E)]^{2-}$ series (Fig. 11, structure 0B), structurally described in terms of two edge-sharing ME_4 tetrahedra, are represented only by the $[Mo_2S_6]^{2-}$ (*82*) and $[W_2Se_6]^{2-}$ (*92*) ions. In the series $[E{=}M(Se_4)_2]^{2-}$ (M = Mo, W; E = S, Se, O), the anions $[Se{=}W(Se_4)_2]^{2-}$, $[Se{=}Mo(Se_4)_2]^{2-}$, $[S{=}W(Se_4)_2]^{2-}$, $[S{=}Mo(Se_4)_2]^{2-}$, $[O{=}W(Se_4)_2]^{2-}$, and $[O{=}Mo(Se_4)_2]^{2-}$ have been reported (*93*).

The Mo and W oxytellurides, $[O{=}Mo(Te_4)_2]^{2-}$ and $[O{=}W(Te_4)_2]^{2-}$, obtained from soluble polytellurides and high-valent metal chlorides, are known and their structures have been determined (*94*). These complexes have structures that are similar to those of the previously reported (*93*) sulfides (*24*) and selenides (*93*). Their ^{125}Te NMR spectra are consistent with their structures.

C. TERTIARY OXO/THIOMOLYBDATES

1. *The $[(S_x)(Mo_2OS_3)(S_y)]^{2-}$ Series*



The $[Mo_2OS_3]^{2+}$ unit

Molybdothio anion dimers that contain both Mo=S and Mo=O units are rare and the small number of such complexes that have been reported, such as $[(\eta^2\text{-}S_2)Mo(=O)(\mu\text{-}S)_2Mo(=O)(\mu\text{-}S)_2Mo(=O)(=S)]^{2-}$ (*95*) and $[(S_2)Mo_2OS_3)(S_2)]^{2-}$ (*97*), have been obtained by serendipitous means.

Oxidation of the RS^- ligands in thiolate complexes by S_x^0 fragments [present in solutions of either dibenzyl trisulfide (*73d*) or elemental sulfur] generates S_x^{2-} anions that replace the thiolate complexes. This reaction has been used effectively (*98*) in the synthesis of $[M(S_x)_2]^{2-}$ complexes from $[M(SPh)_4]^{2-}$ thiolates (*99*) (M = Mn, Ni, Zn; $x = 4$, 5, or 6). A similar reaction has been employed for the synthesis of complexes that contain both Mo=S and Mo=O units within a central $[Mo_2OS_3]^{2+}$ core. These compounds were obtained by the oxidative removal of the coordinated PhS^- ligands from the $[(O{=}Mo(PhS)_2(MoS_4)]^{2-}$ anion (*73a,b,c*) (Fig. 13, structure 1A; Table III). The latter was made in DMF solution via the substitution of two of the thiophenolate ligands in the $[O{=}Mo(PhS)_4]^-$ complex (*74*) by the MoS_4^{2-} chelating liquid (Fig. 13).

The various $[(S_x)(Mo_2OS_3)(S_y)]^{2-}$ derivatives (Fig. 13) can be obtained in a rational manner by S addition reactions (*73a,b*) using elemental sulfur or sulfur abstraction reactions using Ph_3P. The $[(S_4)(Mo_2OS_3)(S_2)]^{2-}$ complex (Fig. 13, structure 1C) exists in two isomers with the S_2^{2-} ligand adjacent to either the Mo=S or the Mo=O groups. The reaction of a 50:50 mixture of these isomers with one-half equivalent of Ph_3P results in sulfur abstraction from the S_2 ligand adjacent to the Mo=S chromophore and gives exclusively one product (Fig. 13, structure 2C). A similar reaction of $[(S_2)(Mo_2OS_3)(S_2)]^{2-}$ (Fig. 13, structure 2A) with one equivalent of Ph_3P also results in sulfur abstraction from the S_2^{2-} ligand adjacent to the Mo=S unit (Fig. 13, structure 2B). This preference for sulfur abstraction has been attributed to a release of steric crowding, which is more pronounced around the $(\mu\text{-}S)_2(S)Mo(S_2)$ unit than the $(\mu\text{-}S)_2(O)Mo(S_2)$ unit (*73*). An alternate explanation is based on the

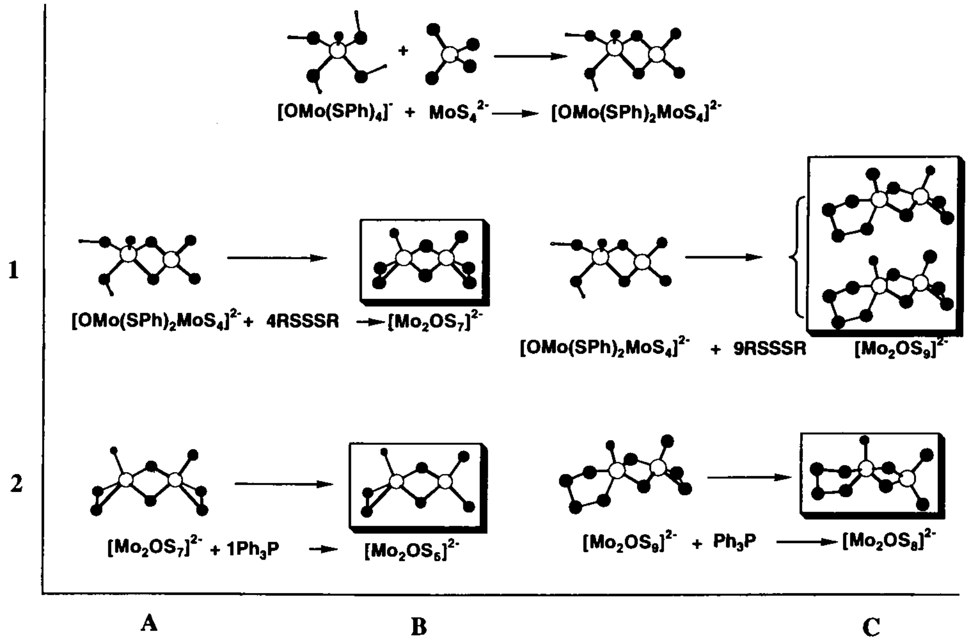
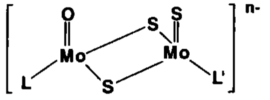


FIG. 13. The $[(S_x)(Mo_2OS_3)(S_y)]^{2-}$ complexes.

TABLE III

DISTANCES IN TERTIARY Mo/S/O COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[Mo_2S_3O]^{2+}$ CORE[a]



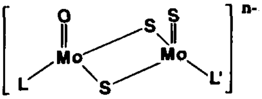
L′	L	n	Mo−Mo (Å)	Mo=S (Å)	Mo=O (Å)	O=Mo−S$_b$ (Å)	S=Mo−S$_b$ (Å)	O=Mo−L (Å)	S=Mo−L′ (Å)	Reference
S^{2}	S_2^{2}	2	2.864(1)	2.132(3)	1.680(7)	2.370(3)	2.285(3)	2.406	2.175(3)	*73a,b*
						2.331(3)	2.320(3)			
S^{2}	S_4^{2}	2	2.888(3)	2.135(7)	1.67(1)	2.382(8)	2.262(7)	2.388	2.182(7)	*73a,b*
						2.365(6)	2.275(7)			
S_2^{2}	S_2^{2}	2	2.820(1)	2.055(2)	1.677(4)	2.326	2.319	2.399	2.387	*73a,b*
		2	2.832(1)	2.111(3)	1.759(9)	2.326	2.308	2.392	2.396	*23c*
S_2^{2}	S_4^{2}	2	2.850(1)	1.862(7)[b]	2.014(5)[b]	2.302[b]	2.350[b]	2.400[b]	2.412[b]	*73a,b*

[a] See footnote *a*, Table I.

[b] Subject to site occupation disorder.

TABLE IV

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF TERTIARY Mo/S/O COMPLEXES THAT CONTAIN THE $[Mo_2S_3O]^{2+}$ CORE[a]

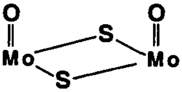


L′	L	*n*	Infrared absorption $(cm^{-1})^b$	λ_{max} (nm; $\varepsilon \times 10^{-3})^c$
S^{2-}	S_2^{2-}	2	945(m); 503(m); 483(w); 461(w)	412; 476(sh)
S^{2-}	S_4^{2-}	2	944(m); 506(m); 489(m); 482(w)	408
S_2^{2-}	S_2^{2-}	2	938(m); 546(w); 354(w)	390; 470; 550(sh)
S_2^{2-}	S_4^{2-}	2	949(m); 932(m); 458(w); 354(w)	370; 430

[a] Data from Refs. *73a,b*.
[b] In CsI disk.
[c] In DMF.

argument that the $S_2 \rightarrow Mo$ charge transfer depletes more electron density from the antibonding π^* orbital of the S_2^{2-} ligand in the $O{=}Mo{-}S_2$ than in the $S{=}Mo{-}S_2$ unit and results in a stronger S–S bond in the former (*28a*). This latter argument is not supported by crystallographic data (Table II) that show a wide range in S–S distances instead of consistently longer S–S bonds in the $(S_2)Mo(S)$ units. The electronic and infrared spectral data (Table IV) also are mainly inconclusive in this respect.

2. *The $[O{=}Mo(S_4)]^{2-}$ Anion and the $[(S_x)(Mo_2O_2S_2)(S_y)]^{2-}$ Series*



The $[Mo_2O_2S_2]^{2+}$ unit

Tertiary oxo/thiomolybdates that contain the $[Mo^V{}_2O_2S_2]^{2+}$ cores are very common and have been reported with a wide variety of terminal ligands. The binary complexes within the $[(S_x)(Mo_2O_2S_2)(S_y)]^{2-}$ series include $[(S_2)(Mo_2O_2S_2)(S_2)]^{2-}$ (*100*), $[(S_2)(Mo_2O_2S_2)(S_3O_2)]^{2-}$ (*101*), the $[(S_2)(Mo_2O_2S_2)(MoS_4)]^{2-}$ and $[(S_2)(Mo_2O_2S_2)(MoOS_3)]^{2-}$ anions (*102*) (which were isolated in a crystalline solid that contained virtually equimolar amounts of both of these trimetallic complexes), the monomeric $[(S)(Mo_2O_2S_2)(S_4)]^{2-}$ and its dimeric form

$\{[(S)(Mo_2O_2S_2)(S_4)]_2\}^{4-}$ (*103*), the $[(S_4)(Mo_2O_2S_2)(S_2)]^{2-}$ anion (*104*), and $[(S_4)(Mo_2O_2S_2)(S_4)]^{2-}$ (*97*).

A general approach that has been found effective in the systematic synthesis of most of the $[(S_x)(Mo_2O_2S_2)(S_y)]^{2-}$ complexes (Fig. 14; Tables V and VI) is based on the $[(S_2)(Mo_2O_2S_2)S_4)]^{2-}$ complex (Fig. 14, structure 3A). Sequential, stoichiometric S addition or S abstraction reactions to or from Fig. 14 (structure 3A) afford various derivatives with the $(Mo_2O_2S_2)^{2+}$ core intact (*105*). The synthesis of structure 3A is carried out by the reaction of $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ with sulfur-enriched $(NH_4)_2S$ in water. The complex forms under aerobic conditions and is isolated as a Et_4N^+ salt after standing for 24 hr (*104*). In short reaction times but otherwise similar conditions this reaction affords in good yield the $[O{=}Mo(S_4)_2]^{2-}$ complex (*106*). The latter was obtained previously in low yield by the hydrolysis of the $[S{=}Mo(S_4)_2]^{2-}$ anion (*24a*). A probable pathway that leads to the $[O{=}Mo(S_4)_2]^{2-}$ and $[(S_2)(Mo_2O_2S_2)(S_4)]^{2-}$ complexes (Fig. 15) is based on an intramolecular redox process not unlike the one outlined for the synthesis of $[S{=}Mo(S_4)_2]^{2-}$ from $(MoS_4)^{2-}$ (Fig. 10).

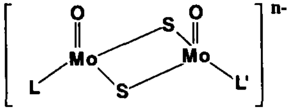
3. *The Solvated $[Mo_2O_2S_2]^{2+}$ Core and Derivatives*

Stoichiometric reactions of the $[(S_4)(Mo_2O_2S_2)(S_2)]^{2-}$ complex with I_2 in DMF solution result in the sequential oxidation of the S_4^{2-} and S_2^{2-} ligands and formation of the neutral $[(DMF)_3(Mo_2O_2S_2)(S_2)]$ and the cationic $[(DMF)_3(Mo_2O_2S_2)(DMF)_3]^{2+}$ complexes (*104*) (Fig. 16, structures 2B and 1B; Table V). The latter, isolated as an I^- salt, is a 2:1 electrolyte soluble in both water and nonaqueous solvents. The structure of $[(DMF)_3(Mo_2O_2S_2)(S_2)]$ has been determined (*103*). The lability of the DMF ligands in both structures 2B and 1B (Fig. 16) makes these compounds excellent reagents for the synthesis of a great number of complexes that contain the $[Mo_2O_2S_2]^{2+}$ core. Representative derivatives of structure 2B (Fig. 16) are the $[(L)(Mo_2O_2S_2)(L')]^n$ complexes (*104*) with $L = S_2^{2-}$, $L' = [S_2C_2O_2]^{2-}$, CS_3^{2-}, $2Cl^-$ ($n = -2$); $L = S_2^{2-}$, L' = trithiacyclononane (TTN) ($n = 0$); or $L = S_2^{2-}$, $L' = Cp$ ($n = -1$). All of these complexes (*105*) are expected to be well suited for the synthesis of "mixed-ligand" derivatives with ligands L other than S_2^{2-} using their $[(Cl)_2(Mo_2O_2S_2(L')]^n$ derivatives. The latter are obtained by the reaction of benzoyl chloride with the Mo-coordinated S_2^{2-} ligands. In these reactions the S_2^{2-} ligands are converted to the $(PhCOS)_2$ disulfide and are replaced by two Cl^- ions (*73b*, *113*). This reaction is clean and could also be useful in the synthesis of monothio aryl carboxylic acid derivatives.

The $[(S_2)(Mo_2O_2S_2)(Cp)]^-$ monoanion (Fig. 16, structure 2C, which

TABLE V

Distances and Angles in Tertiary Mo/S/O Complexes and Select Derivatives That Contain the $[Mo_2O_2S_2]^{2+}$ Core[a]



L	L'	n	Mo–Mo (Å)	M=O (Å)	(L)Mo–S$_b$ (Å)	(L')–S$_b$ (Å)	Mo–L (Å)	Mo–L' (Å)	M–S–M (°)	S–Mo–S (°)	Reference
$(DMF)_3$	S_2^{2-}	0	2.813(1)	1.686	2.317(3)		2.186(6) 2.212(6) 2.224(6)[b]	2.38	74.8	102.5	*103a*
S^{2-}	S_4^{2-}	2[c]	2.896(1)	1.692	2.277	2.372	2.167(3)	2.412	77.0	101.5	*103a*
S^{2-}	S_4^{2-}	4[d]	2.852(2) 3.554(2)[e]	1.664	2.324	2.350 2.420[f]	—	2.435	75.2	98.4 75.8[f]	*103a*
S_2^{2-}	S_2^{2-}	2	2.828(1)	1.683	2.322		2.394		75.0	102.1	*100c*
			2.825(2)	1.675	2.324		2.41(2)		74.9	101.8(2)	*100d*
S_2^{2-}	S_4^{2-}	2	2.829(1)	1.676	2.297(3) 2.316(3)	2.365(2) 2.353(3)	2.394	2.420	74.6	101.6(1) 98.5(1)	*83, 104*
S_2^{2-}	Cp^-	1	2.855(1)	1.673	2.310(4)		2.396	2.380(9)[g]	77.0	101.5	*103a*
S_4^{2-}	S_2^{2-}	2	2.853(3)	1.691	2.330		2.43(1)		75.5	101.5	*97a*
$(CS_3)^{2-}$	$(CS_4)^{2-}$	2	2.835(2)	1.678(9)	2.305(5)		2.433(6)	2.401(5)	75.4(2)	100.5(2)	*161*
Cp^-	$(SO_3)^{2-}$	1	2.838(2)	1.681(6)	2.308(3)		2.063(7)	2.38(2)	75.9(1)	101.9(1)	*113, 175*
Cp^-	$(S_2O_3)^{2-}$	1	2.850(2)	1.69(1)	2.296(3)		2.08(1)	2.40(4)	76.8(2)	101.2(2)	*113, 175*
Cp^-	$(SO_4)^{2-}$	1	2.831(1)	1.685(3)	2.303(2)		2.087(4)	2.374(7)	75.9(1)	101.8(1)	*113, 175*
$(S_2O_2)^{2-}$	$(S_2O_3)^{2-}$	2[h]	2.810(3)	1.65(2)	2.315(5)		—[h]	—[h]	74.7(2)	101.3(1)	*113*
S_2^{2-}	$(S_2O_3)^{2-}$	2	2.794(1)	1.678(9)	2.316(4)[i] 2.269(4)[j]		2.44	2.395(5)[k] 2.26(1)[l]	74.6(1)	103.5(2) —[m]	*113*
$(SO_4)^{2-}$	$(SO_4)^{2-}$	2	2.818(1)	1.675(5)	2.304(2)		2.08(1)	2.08(1)	75.5(1)	101.7(1)	*113*
$(DMF)_3$	$(SO_4)^{2-}$	0	2.823(1)	1.655(5)	2.300(2)		2.146(6) 2.189(6) 2.245(6)[n]	2.081)6)	75.6(1)	102.6(1)	*113*
$(SO_4)^{2-}$	$(SO_4)^{2-}$ [o]	2	2.775(2)	1.638(7)	2.316(4) 2.278(7)		2.104(6)	2.09(2)	75.1(1)	101.9(1)	*174*

$(S_2O_3)^{2-}$	$(S_2O_3)^{2-}$	2[p]	2.686(1)	1.662	2.312 1.916	2.408(2)[q] 2.099(5)[r]	2.397(2)[q] 2.074(5)[r]	89.0(2)[s] 71.0(1)[t]	96.7(2)[u]	*113*
$(VDS)^{2-}$	$(VDS)^{2-}$	2	2.882(1)	1.676(6)	2.328	2.215(8)[v] 2.382(3)[w]		—	—	*169*
DMAD, DMAD		2								
—[x]			2.853(1)	1.675	2.331(3)	2.425(8)		75.5	100.9	*25*
—[y]			2.904(1)	1.684(2)	2.328	2.419		77.1(1)	100.9(1)	*25*
$[O{=}Mo(S_4)_2]^{2-}$		2	—	1685(7)	—	2.363(2) 2.395(2)		—	—	—
$(Edt)^{2-}$, $(Edt)^{2-}$		2	2.866(3)	1.659(3)	2.341(9)	2.412(9)		75.5(4)	100.5(4)	*89c*

[a] See footnote *a*, Table I.

[b] Trans to the Mo=O group.

[c] Dimeric Ph_4P^+ salt.

[d] Tetrameric $\{S_4(Mo_2S_2S_2)S]_2^{4-}$ Et_4N^+ salt.

[e] Interdimer Mo–Mo distance.

[f] Associated with the central Mo_2S_2 unit.

[g] Mo–C distances to the η^5-Cp carbon atoms.

[h] Positionally disordered L and L′.

[i] Trans to the $(S_2O_3)^{2-}$ S donor.

[j] Trans to the $(S_2O_3)^{2-}$ O donor.

[k] The $(S_2O_3)^{2-}$ S donor.

[l] The $(S_2O_3)^{2-}$ O donor.

[m] Intrabridge angle.

[n] Trans to the Mo=O group.

[o] From the $\{[(SO_4)(Mo_2O_2S_2)(SO_4)]_2^{2-}(\eta^4-SO_4)\}^{6-}$ tetramer.

[p] The central core in this complex is the mixed-ligand bridged $[Mo_2(O)_2(\mu-S)(\mu-O)]^{2+}$ unit.

[q] Mo–S.

[r] Mo–O.

[s] Mo–O–Mo.

[t] Mo–S–Mo.

[u] S–Mo–O angle.

[v] Mo–C bond.

[w] Mo–S bond.

[x] Syn isomer.

[y] Anti isomer.

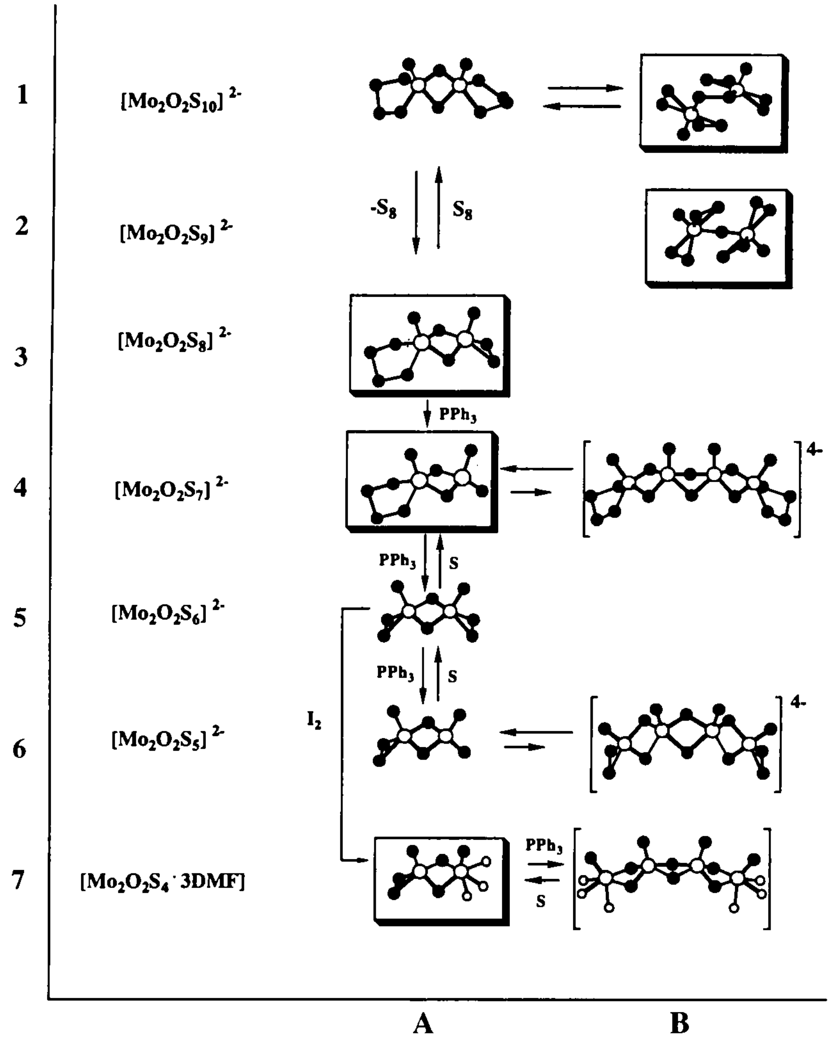


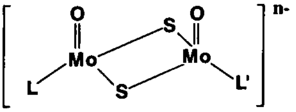
FIG. 14. The $[(S_x)(Mo_2O_2S_2)(S_y)]^{2-}$ complexes.

is readily available from structure 2B) and its derivatives have been used extensively in ^1H NMR studies of reactions of the $(S_x)Mo{=}O$ chromophore. The Cp^- ligand is a convenient spectroscopic "handle" and has been used as a "reporter" of the changes that accompany reactions of the $[(S_x)(Mo_2O_2S_2)(Cp)]^-$ complexes (*28b*) (*vide infra*).

The $[(DMF)_3(Mo_2O_2S_2)(DMF)_3]^{2+}$ complex (Fig. 16, structure 1B) also has been used effectively in the synthesis of a plethora of

TABLE VI

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF TERTIARY Mo/S/O COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[Mo_2O_2S_2]^{2+}$ CORE



L'	n	Infrared absorption (cm^{-1})	κ_{max} (nm)	Reference
$(DMF)_3$, $(DMF)_3$	2+	Mo=O, 928(m), 947(s); Mo–S_b, 469(m)[a]	276; 286(br, sh); 358(sh)[b]	*104, 105*
$(DMF)_3$, S_2^{2-}	0	Mo=O, 948(s), 954(s), Mo–S_b, 469(m); Mo–S_n, 527(m)[a]	269(br, sh)[b]	*104, 105*
S^{2-}, S_4^{2-}[c]	2	Mo=O, 890(m), 943(m); Mo–S_b, 465(m); Mo–S_n, 494(m), 420(w)[a]	270; 365[b]	*104, 105*
S^{2-}, S_4^{2-}[f]	4	Mo=O, 933(s); Mo–S_b, 462(m); Mo–S_n, 410(w)	365; 270[b]	*103*
S_2^{2-}, Cp^-	1	Mo=O, 909(m), 948(s); Mo–S_b, 462(m); Mo–S_n, 527(m)[d]	270; 311[b]	*103*
S^{2-}, Cp^-	1	Mo=O, 903(s), 914(m), 930(s); Mo–S_b, 464(m)[a]	270; 320[b]	*103*
$(CS_3)^{2-}$, Cp^-	1	Mo=O, 911(m), 951(s); Mo–S_b, 466(m)[a]	270(sh); 298(sh); 313(sh)[b]	*103*
$(VDS)^{2-}$, Cp^-	1	Mo=O, 932(s), 950(m); Mo–S_b, 460(w); Mo–S_n, 526(s), 420(w)[a]	274(br); 296(sh); 360(sh); 467(sh)[b]	*103*
$(CS_3)^{2-}$, $(CS_4)^{2-}$	2	Mo=O, 953(s); Mo–S_b, 466(w)[a]	—	*103*
$(CS_3)^{2}$, S_4^{2-}	2	Mo=O, 949(s); Mo–S_b, 468(w); Mo–S_n, 422(s)[d]	258; 310[b]	*103*
$(VDS)^{2-}$, $(VDS)^{2-}$	2[g]	Mo=O, 947; Mo–S_b, 473; S–S, 520[a]	—	*169*
$(VDS)^{2-}$, $(VDS)^{2-}$	2[g]	Mo=O, 940(s); Mo–S, 469(w), 420(VW), 382(w), 358(w), 331(w)[a]	—	*25*
$(DMDA)^{2-}$, $(DMDA)^{2-}$	2[h]	Mo=O, 942(m); Mo–S_b, 463(w)[a]	—	*25*
$(DMDA)^{2-}$, $(DMDA)^{2-}$	2[i]	Mo=O, 923(s); 911(w); Mo–S_b, 462(w)[a]	318; 380(sh)[e]	*25*
$(SO_3)^{2-}$, Cp	1	Mo=O, 962(s), 903(m); $\nu-SO_3^{2-}$, 1166, 646, 571, 502[d]	—	*175*
$(S_2O_3)^{2}$, Cp^-	1	Mo=O, 955(s), 915(m); $\nu-S_2O_3^{2-}$, 1277, 1172, 1150, 662, 542; Mo–S_b, 483, 470[d]	—	*175*
$(SO_4)^{2-}$, $(SO_4)^{2-}$[j]	2	Mo=O, 960(s), 903(m); $\nu-SO_4^{2-}$, 1280, 1157, 1114, 660, 618, 582[d]	—	*174*

[a] In KBr disk.

[b] In DMF.

[c] Ph_4P^+ salt dimer.

[d] In CsI disk.

[e] In CH_3CN solution.

[f] Et_4N^+ salt tetramer.

[g] The cis, syn isomer.

[h] Syn isomer.

[i] Anti isomer.

[j] From the $\{[(SO_4)(Mo_2O_2S_2)(SO_4)]_2^{2-}(\eta^4-SO_4)\}^{6-}$ tetramer.

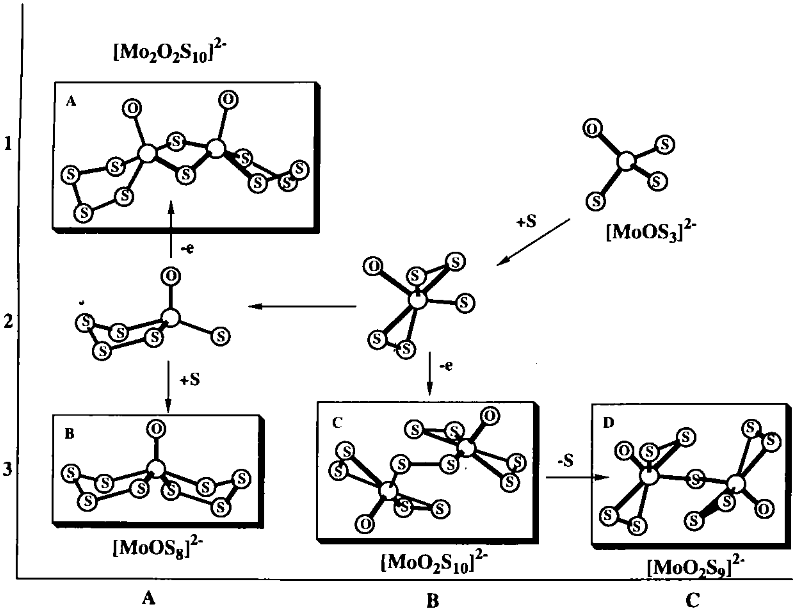


FIG. 15. Proposed pathways in the synthesis of the $[O{=}Mo(S_4)_2]^{2-}$ anion.

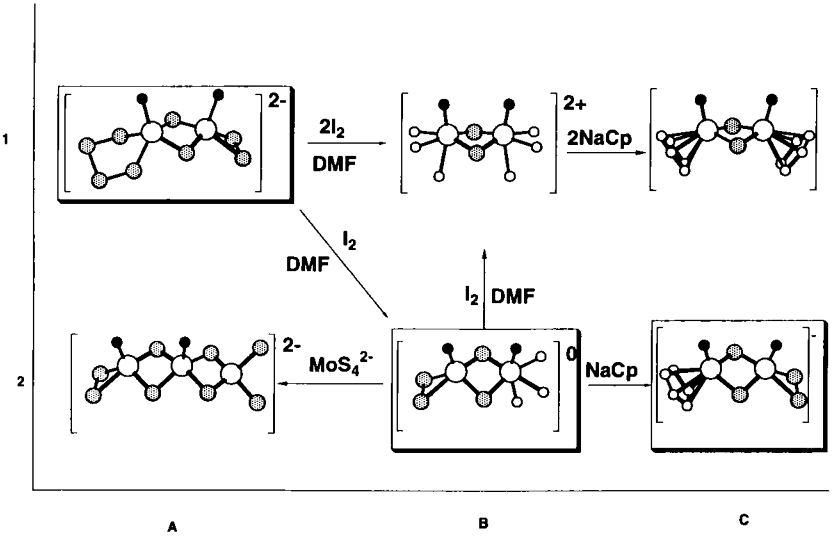
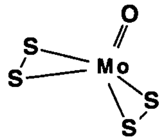


FIG. 16. The synthesis of the solvated $[Mo_2O_2S_2]^{2+}$ core and derivatives.

$[(L)(Mo_2O_2S_2)(L)]^n$ molecules (*105*) (Fig. 17). Of these, some have been reported previously, including L = $(NCS)_3$, n = −4 (*107*); L = EDTA, $n = -2$ (*108*); L = $S_2P(i\text{-}Pr)_2$, $n = 0$ (*109*); L = n-Bu_2Dtc, $n = 0$ (*110*); and L = Cp^-, $n = 0$ (*111*). The synthetic utility of structure 1B (Fig. 16) parallels that of the similarly water soluble $[(H_2O)_3(Mo_2O_2S_2)(H_2O)_3]^{2+}$ complex (*112*). The syntheses of the $[(H_2O)_3(Mo_2O_2S_2)(H_2O)_3]^{2+}$ complex by acidification of $Na_2[(Cys)(Mo_2O_2S_2)(Cys)]$ and various other $[(L)(Mo_2O_2S_2)(L)]^n$ complexes have been reported in detail (*112b*). The same synthetic procedure has been found successful for the synthesis of various $[(L)(Mo_2O_3S)(L)]^{2-}$ complexes from $Na_2[(Cys)(Mo_2O_3S)(Cys)]$ (*112b*). These complexes contain both μ-S^{2-} and μ-O^{2-} bridges (*112c–f*). A convenient, high-yield synthesis of the "mixed-bridge" $[Mo_2O_3S]^{2+}$ core has been reported by the reaction of $(Et_4N)_2[MoS_2O_2]$ with SO_2 in CH_3CN. This reaction affords the crystalline $(Et_4N)_2[(S_2O_3)(Mo_2O_3S)(S_2O_3)]$ complex. The lability of the $(S_2O_3)^{2-}$ ligands in this structurally characterized (*113*) molecule makes it an excellent reagent for the synthesis of other complexes with the $[Mo_2O_3S]^{2+}$ core. Selected features in the structures of the $[(L)(Mo_2O_2S_2)(L)]^n$ complexes are given in Table V and characteristic features of the electronic and infrared spectra of these complexes are included in Table VI.

4. *The $[(S_2)_2Mo(O)]$ Structural Unit and Derivatives*



The $[O{=}Mo^{VI}(S_2)_2]$ unit

Oxidation of $[O{=}Mo^{IV}(S_4)_2]^{2-}$ with $[(Cp)_2Fe]^+$ affords the $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$ and $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}^{2-}$ complexes (*106*) (Fig. 18, structures 2A and 3B; Table VII). In the structures of these complexes (Table VII), the η^2-S_2 ligands and the μ-S ligands occupy the equatorial positions of the pentagonal pyramidal structure of the Mo^{VI} ion. The oxo ligand is located at the apical position and trans to a weakly interacting S_2 ligand from the second $[O{=}Mo^{VI}(S_2)_2]$ subunit.

The $[O{=}Mo^{VI}(S_2)_2]$ chromophore in these complexes is derived by internal electron transfer within the $[O{=}Mo^{IV}(S_4)]$ unit. As indicated previously, this process in reverse accounts for the synthesis of $[O{=}Mo^{IV}(S_4)]$ and the $[O{=}Mo^{IV}(S_4)_2]^{2-}$ anion from $(MoOS_3)^{2-}$ (Fig. 15). Indeed, it appears likely that, under certain circumstances, the $[O{=}Mo^{VI}(S_2)_2]$ and $[O{=}Mo^{IV}(S_4)]$ units may exist in equilibrium. This

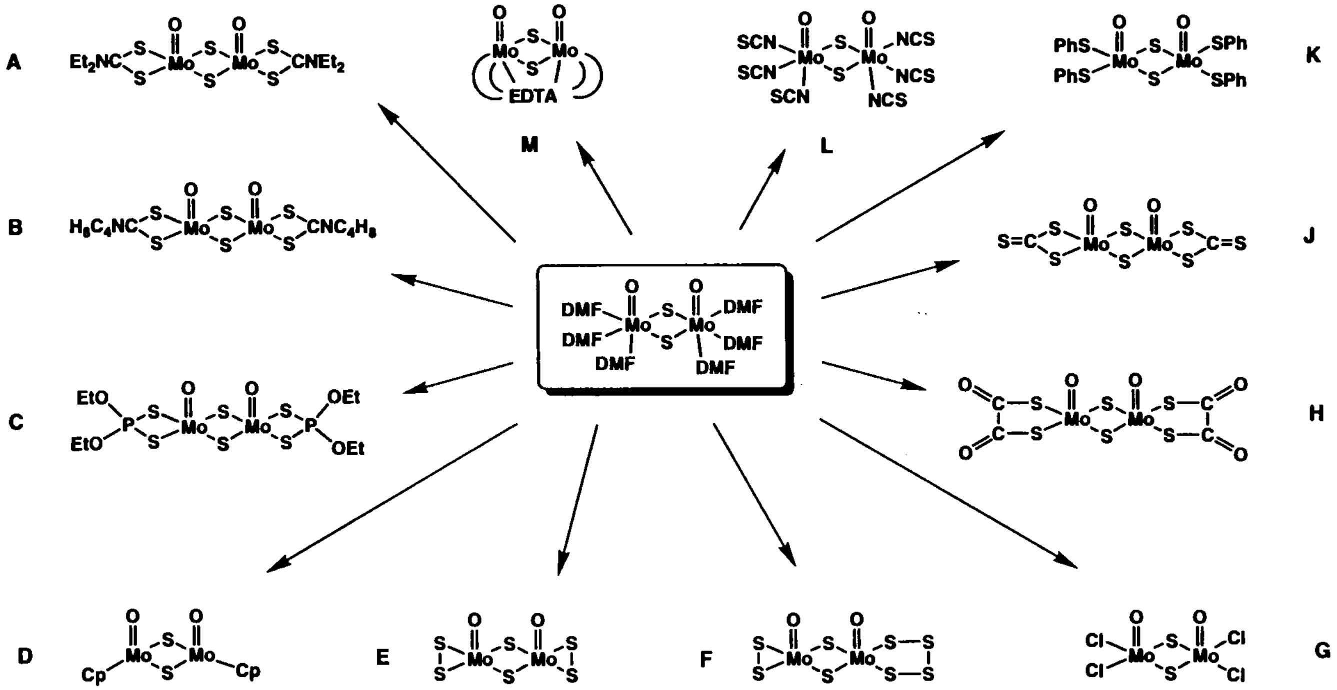


FIG. 17. The synthetic utility of the $[(DMF)_3(Mo_2O_2S_2)(DMF)_3]^{2+}$ complex.

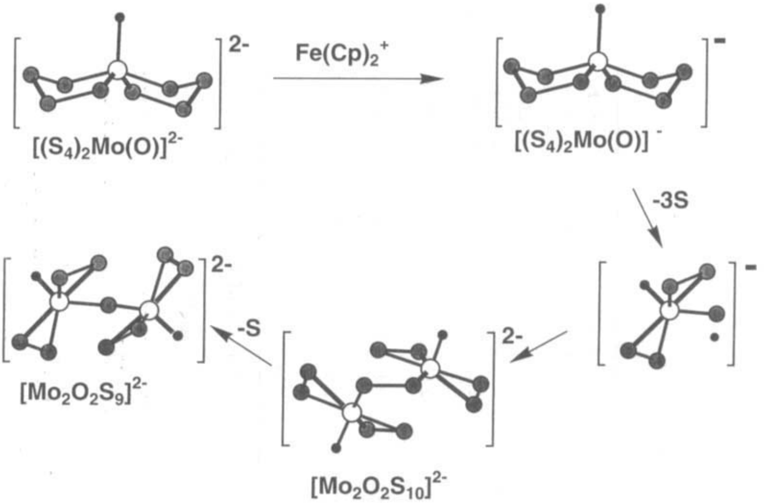


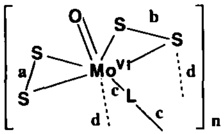
FIG. 18. A proposed pathway toward the synthesis of $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$.

type of equilibrium would be consequence of the close energy matching between the Mo *4d* orbitals and the sulfur *3p* orbitals and would account for the apparent similar energies between the pentagonal bipyramidal $[E{=}Mo^{VI}(S_2)_2L)]^n$ complexes and the square pyramidal $[E{=}Mo^{IV}(S_4)(L)]^n$ complexes (L = a bidentate chelating ligand). The pentagonal bipyramidal complexes with the $O{=}Mo^{VI}(S_2)_2$ structural unit are quite common. This is not the case for the square pyramidal complexes with the $O{=}Mo^{IV}(S_4)$ unit. With the exception of the $[E{=}Mo(S_4)_2]^{2-}$ and the $[(Cp)Mo(S_4)_2]^-$ (*116*) complexes, the only other square pyramidal complex of this structural type is the structurally characterized $[O{=}Mo^{IV}(S_4)(MNT)]^{2-}$ obtained by a substitution reaction between the $\{[O{=}Mo^{VI}(S_2)_2]_2Cl\}^-$ complex and Na_2MNT (*106b*). An interesting question can be raised whether, in solution, the $[O{=}Mo^{IV}(S_4)(Mo^{VI}S_4)]^{2-}$ and $[O{=}Mo^{IV}(S_4)(Mo^{VI}OS_3)]^{2-}$ complexes (Figs. 13 and 14, structures 2C and 4A, respectively) exist in equilibrium with their pentagonal bipyramidal, internal redox isomers, $[O{=}Mo^{VI}(S_2)_2(Mo^{VI}S_4)]^{2-}$ and $[O{=}Mo^{VI}(S_2)_2(Mo^{VI}OS_3)]^{2-}$, respectively. A spectroscopic handle that can differentiate between the two different isomers is not available in the rather uninformative infrared or electronic spectra (Table VIII).

A proposed pathway (*83*, *106*) for the oxidative coupling and formation of $\{[O{=}Mo^{VI}(S_2)_2]_2S\}^{2-}$ and $\{[O{=}Mo^{VI}(S_2)_2]_2S_2\}^{2-}$ has been suggested (Fig. 18). The removal of S^{2-} (as NiS) by the reaction of structure 2A (Fig. 19) with $NiCl_2$ affords the $\{[O{=}Mo^{VI}(S_2)_2]_2Cl\}^-$ complex

TABLE VII

DISTANCES IN TERTIARY Mo/S/O COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[O{=}Mo(S_2)_2]$ UNIT[a]



L	n	Mo–Mo (Å)	Mo=O (Å)	Mo–S (**a**) (Å)	Mo–S (**b**) (Å)	Mo–S(L′) (**d**) (Å)	Mo–L (**c**) (Å)	S–S (**a**) (Å)	S–S (**b**) (Å)	Reference
½S	2	3.606(1)	1.676(6)	2.37(2)	2.409(6)	2.856(3)	2.50(2)	2.028(8)	2.042(4)	*105*
½SMe	2	3.570(1)	1.672(6)	2.380(3)	2.420(5)	2.84(2)	2.526(3)	2.037(4)	2.046(4)	*105*
½S	4	3.606(1) 3.561(1)	1.676(8)	2.386(4)	2.380(4) 2.387(7)	2.919(9)	2.538(8)[b]	2.043(5)	2.051(5)	*105*
½Cl	2[c]	3.550(1)	1.654(10)	2.377(4)	2.379(3) 2.392(4)	2.88(3)[d]	2.535(3)[b]	2.055(6)	2.038(5)	*105*
½S_7^{2-}	2[e]	—	1.670(6)	2.390(8)	2.390(8)	2.490(8)[f]	2.472(4)[g]	2.038(5)	2.038(5)	*117a*
η^2-Monothiooxalate	1	—	1.70(4)	2.38(2)	2.38(2)	2.31(4)[h]	2.53(2)[i]	2.03(2)	2.03(2)	*119*
η^2-Bipy	1	—	1.690(10)	2.371(7)[j] 2.431(7)[k]	—	2.207(12)[l]	2.351(2)[m]	2.055(6) 2.038(6)	—	*118a*
½S_2	2[n]	4.108(1)	2.420(11)[o]	2.430(3)	2.420(3)	2.648(2)	2.523(3)	2.037(5)	2.026(4)	*115*

[a] See footnote *a*, Table I. Bold letters in parentheses correspond to letters in the structure at the top of this table, identifying the different types of S_2^{2-} bonding.

[b] Equatorially bound μ-η^2, η^1-disulfido ligand.

[c] This complex contains an η^1-Cl^- ligand bound to one of the Mo atoms and a μ-η^2, η^1-disulfido bridging ligand (see Fig. 19, structure 2C).

[d] Axially bound μ-η^2, η^1-disulfido ligand.

[e] $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}^{2-}$ anion.

[f] $Mo{-}\mu\text{-}H_2N{-}NH_2$ bond.

[g] Bonds to the μ-S_7^{2-} ligand.

[h] Axially bound oxygen atom of the monothiooxalate ligand.

[i] Equatorially bound S atom of the monothiooxalate ligand.

[j] η^2-S_2 sulfur atoms neighboring the equatorial N atom and nearly trans to each other.

[k] η^2-S_2 sulfur atoms distant from the equatorial N atom.

[l] Axial Mo–N bond.

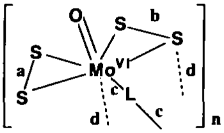
[m] Equatorial Mo–N bond.

[n] Instead of terminal O or S groups the complex contains Me_5-Cp ligands bound to the Mo atoms.

[o] Mo–C distances to the Me_5-Cp ligand.

TABLE VIII

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF TERTIARY Mo/S/O COMPLEXES AND SELECT DERIVATIVES THAT CONTAIN THE $[O{=}Mo(S_2)_2]$ CORE



L	n	Infrared absorption (cm $^{-1}$)	λ_{max} (nm; $\varepsilon \times 10^{-3}$)	Reference
$\frac{1}{2}$S	2	Mo=O, 926(s), 528(m), 358(m), 352(m), 341(m)[a]	392(3.8); 432(4.0); 522(1.9)[b]	*105*
$\frac{1}{2}$SMe	2	Mo=O, 957(w), 939(vs), 927(vs); 545(m), 535(m), 358(m), 347(m)[a]	354(sh); 382(2.9); 436(3.0); 530(2.5)[b]	*105*
$\frac{1}{2}$S	4	Mo=O, 940(vs), 930(vs), 912(w), 534(m)[a]	338(10.4); 414(8.1); 510(7.9)[b]	*105*
$\frac{1}{2}$Cl	2	Mo=O, 949(s), 936(vs), 539(m), 378(m), 366(m), 297(m)[a]	350(3.0); 390(sh); 474(2.7); 530(sh)[b]	*105*
$\frac{1}{2}$S	2	Mo=S, 520(s), 530(s)[a]	360; 400; 485; 590[d]	*121*[c]
$\frac{1}{2}S_7^{2-}$	2	Mo=O, 925(vs), 532(s), 485(w, sh); 470(w), 344(s)[e]	248(25); 317(14.9); 452(4.0); 530(2.43)[d]	*117*[f]
Bipy	1	Mo=O, 930(s); S–S, 540(s), 370(m), 340(m)[e]	305(9.5); 330(3.9); 418(.25); 483(1.0); 565(1.0)[b]	*118a*
η^2-Monothiooxalate	1	Mo=O, 930(s); S–S, 530	—	*119*

[a] In CsI disk.
[b] In DMF.
[c] Data for the $\{[S{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}^{2-}$ anion.
[d] In CH_3CN.
[e] In KBr disk.
[f] Data for the $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu_2\text{-}S_7)(\mu_2\text{-}H_2NNH_2)\}^{2-}$ anion.

(Fig. 19, structure 2C). The μ-S ligand in structure 1A (Fig. 19) is unusually labile and is replaced by an η^2-S_2 ligand in a transformation that converts the $\{[(\eta^2\text{-}S_2)_2Mo(O)]_2(\mu\text{-}S)\}^{2-}$ complex, structure 1A, into $[O{=}Mo(\mu\text{-}\eta^2,\eta^1\text{-}S_2)(\eta^2\text{-}S_2)][O{=}Mo(\eta^2\text{-}S_2)_2({=}S)]^{2-}$, structure 1C (Fig. 19). In this form the complex is probably oxidized to the structurally characterized $\{[O{=}Mo(\mu\text{-}\eta^2,\eta^1\text{-}S_2)(\eta^2\text{-}S_2)]O{=}Mo(\eta^2\text{-}S_2)_2(S)]\}_2^{2-}$ tetramer (Fig. 19, structure 3B). The ready dissociation of structure 2C to the $[O{=}Mo^{VI}(S_2)_2]$ and $[O{=}Mo^{VI}(S_2)_2(Cl)]^-$ fragments makes this complex ideally suited as a reagent for the synthesis of $(\eta^2$-$[O{=}Mo^{VI}(S_2)_2(L)]$ complexes in reactions with bidentate chelating ligands (L). These complexes usually have a seven-coordinate pentagonal bipyramidal structure. At times, certain ligands (such as MNT) promote internal redox, and the square pyramidal complexes, $[O{=}Mo^{IV}(S_4)(L)]$, are isolated (*106b*) rather than their pentagonal bipyramidal internal redox isomers.

The $(\eta^2\text{-}S_2)_2Mo(O)$ unit structurally resembles the oxo/peroxomolybdate units studied extensively by Stomberg and co-workers in

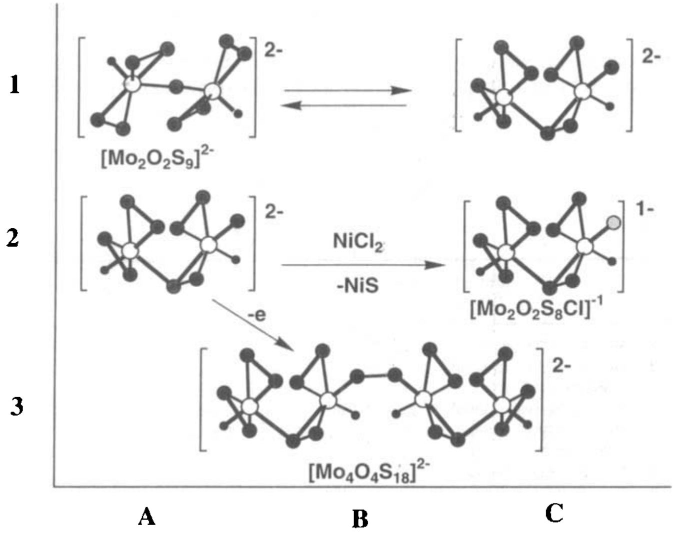


FIG. 19. Reactions of the $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$ complex.

complexes such as $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ (*114a*), $[Mo_3O_7(O_2)_4]^{4-} \cdot 2H_2O$ (*114b*), $[Mo_4O_{12}(O_2)_2]^{4-}$ (*114c*), $[Mo_5O_{10}(O_{28})^{6-} \cdot 5H_2O$ (*114d*), $[Mo_7O_{22}(O_2)_2]^{6-} \cdot 8H_2O$ (*114e*), and $[Mo_{10}O_{22}(O_2)_{12}]^{8-} \cdot 16H_2O$ (*114f*). Thus far the diversity in nuclearity apparent in the oxo/peroxomolybdate series has not been found with the oxo/disulfido complexes.

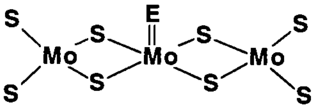
In the structure of $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$ a small amount of $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}^{2-}$ was found as a minor component at the same anion site. At a later date the $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$ was obtained apparently free of the disulfido minor component (*114g*). The $\{[(Cp^*)Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}$ complex (*115*) is very nearly isostructural to $\{[O{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}^{2-}$, with the oxo ligands in the latter replaced by the Cp* groups in the former. A similar situation prevails with the $[(Cp)Mo(S_4)_2]^-$ and $[(Cp)Mo(Se_4)_2]^-$ complexes (*116*) that are isostructural and formally isoelectronic to $[S{=}Mo(S_4)_2]^{2-}$. In $[(Cp)Mo(S_4)_2]^-$ the Mo coordinated S_4^{2-} anion shows the unusual alternation in the S–S distances similar to the one previously found in the $[S{=}Mo(S_4)_2]^{2-}$ anion. It would be of interest to investigate the extent to which the Mo=S and Cp–Mo groups are interchangeable in thiomolybdate complexes and how their chemistry may show comparative reactivity.

In the $[O{=}Mo(S_2)_2](\mu\text{-}S_7)(\mu\text{-}NH_2NH_2)[O{=}Mo(S_2)_2]$ complex (*117*) the $O{=}Mo(S_2)_2$ units are bridged by a S_7^{2-} ligand and by a hydrazine molecule. The $\mu_2\text{-}S_7^{2-}$ ligand coordinates in the equatorial planes of the pentagonal bipyramidal Mo^{VI} centers, satisfies the coordination requirements of the Mo^{VI} ions, and as a result the S_2^{2-} ligands are not used in the bridging mode. The bridging hydrazine N donor atoms are bound trans to the O=Mo groups at the rather long distances of 2.487(8) and 2.492(8) Å and occupy the positions occupied by the μ-η^2,η^1-S_2 ligands in structure 1A (Fig. 19).

A number of monomeric, pentagonal bipyramidal complexes of the type $[O{=}Mo(S_2)_2(L)$ have been reported. The complex with L = 2,2-bipyridyl (*118a*) is obtained from MoO_4^{2-} and aqueous S_x^{2-} in the presence of 2,2-bipyridyl. The corresponding W complex also is known and has been structurally characterized (*118b*). A similar complex with L = monothiooxalate $(C_2O_3S)^{2-}$ has been isolated (*119*) serendipitously by the reaction of $Cs_2[Mo_2O_4(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ with $Cs_2(S_2C_2O_2)$.

The tetrameric $(Nb_4Se_{22})^{6-}$ complex (*120*) is isostructural to the $\{[(O)Mo(\mu\text{-}\eta^2,\eta^1\text{-}S_2)(\eta^2\text{-}S_2)][(O)Mo(\eta^2\text{-}S_2)_2(S)]\}2^{2-}$, or $(Mo_4O_4S_{18})^{2-}$, tetramer (*105*) (Fig. 19, structure 3B). The $\{[(S_2)_2W(S)]_2(\mu\text{-}S)\}^{2-}$ and $[(S)W(\mu\text{-}\eta^2,\eta^1\text{-}S_2)(\eta^2\text{-}S_2)][(S)W(\eta^2\text{-}S_2)_2(SH)]^{2-}$ complexes, with structures similar to those shown in Fig. 19, have been synthesized and structurally characterized (*121a*). The $\{[O{=}W^{VI}(S_2)_2]_2(\mu\text{-}S)\}^{2-}$ complex is isostructural to the Mo analog (*121b*) and the $\{[S{=}Mo^{VI}(S_2)_2]_2(\mu\text{-}S_2)\}^{2-}$ complex has been synthesized and spectroscopically characterized (*121c*).

D. THE $[E{=}Mo(MoS_4)_2]^{2-}$ COMPLEXES (E = S, O) AND DERIVATIVES

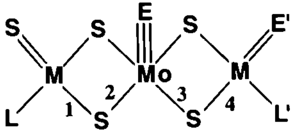


The $[E{=}Mo(MoS_4)_2]^{2-}$ Structural Unit

The pyramidal $[E{=}Mo(MoS_4)_2]^{2-}$ complexes (Tables IX and X) contain as a common structural feature the $(Mo^{IV}{=}S)^{2+}$ unit and are analogous to the $[E{=}Mo(S_4)_2]^{2-}$ complexes with $(MoS_4)^{2-}$ ligands replacing S_4^{2-} ligands. The $[S{=}Mo(MoS_4)_2]^{2-}$ complex and its structure were first reported in 1983 (*80c*). The anion was obtained by heating $(NH_4)_2MoS_4$ in DMF solution. The presence of moisture leads to hydrolysis and formation of the $[O{=}Mo(MoS_4)_2]^{2-}$ complex (*80c*). The synthesis and structure of the S=W analogue of the same compound had been reported earlier (*44*). The syntheses of $\{[(O{=}Mo(MoS_4)(Mo(O)(S)_2(S_2)\}^{2-}$ (*95a,b*) and $\{[(O{=}Mo(MoOS_3)(Mo(O)(S)_2(S_2)\}^{2-}$ (*95a*) have been reported. The former was obtained by stirring

TABLE IX

DISTANCES IN BINARY AND TERTIARY $[E{=}Mo(MS_4)_2]^{2-}$ COMPLEXES AND SELECT DERIVATIVES[a]



M	E	E′	L	L′	M—Mo (Å)	Mo=E (Å)	M=E′ (Å)	M=S (Å)	Mo—S_b (**1**) (Å)	Mo—S_b (**2**) (Å)	Mo—S_b (**3**) (Å)	Mo—S_b (**4**) (Å)	Mo—L′ (Å)	Reference
Mo	O	O	S	S_2^{2-}	3.030(1) 2.884(1)[b]	1.668(4)	1.691(4)	2.082(2)	2.231(2)	2.442(2)	2.363(2)	2.276(2)	2.391	*95b*
					3.047(1) 2.896(1)	1.654(5)	1.65(1)	2.144(3)	2.238(3)	2.458(2)	2.374(2)	2.287(3)	2.395	*95a*
Mo	S	S	S	S	2.953	2.086(4)	2.148(3)	2.145(4)	2.239	2.408	2.380	2.240	2.136(3)	*80a*
Mo	O	S	S	S	2.983	1.743(9)	2.132(5)	2.143(4)	—	2.411(5)		—	2.136	*80c*
W	O	S	S	S_2^{2-}	3.055(2)	1.64(1)	1.89(1)[c]	2.131	2.215(5)	2.435	2.335	2.275	2.374[d]	*96*
W[e]	O	O	S	S_2^{2-}	3.100(1) 2.899(1)[f]	1.671(8)	1.720(9)	2.139(3)	2.237	2.467	2.365	2.295	2.375	*96*

[a] See footnote *a*, Table I. Bold numbers in parentheses refer to numbers in the structure at the top of the table.

[b] Bound to the Mo coordinated by the S_2^{2-} ligand.

[c] The rather short distance and the high temperature factor of the E′ atom suggest that the site is partially occupied by oxygen and sulfur atoms.

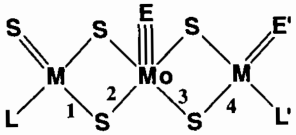
[d] The M=L bond length is 2.140(5) Å.

[e] In this complex the metal bound to E′ is Mo.

[f] Mo–Mo distance.

TABLE X

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF BINARY AND TERTIARY $[E{=}Mo(MS_4)_2]^{2-}$ COMPLEXES AND SELECT DERIVATIVES



M	E	E′	L	L′	Infrared absorption (cm^{-1})	λ_{max} (nm; $\varepsilon \times 10^{-3}$)	Reference
Mo	O	O	S	S_2^{2-}	Mo=O, 962, 943, 910(sh), 905; Mo=S, 527(m), 508(s); Mo–S, 480(m)[a]	272(19.6); 320(sh, 11.6); 376(10.2); 442(8.8); 480(sh, 5.64)[b]	*95a*
					Mo=O, 963, 943; Mo=S, 516(m), 501(s), 425[a]	230(41.0); 270(18.3); 287(17.1); 315(15.4); 378(8.2); 442(12.8)[b]	*95b*
					Mo=O, 958, 943; Mo=S, 520(m), 500(s); Mo–S, 478(m)[a]	268; 282(sh); 312; 436; 480(sh)[b]	*105a*
Mo	S	S	S	S	Mo=S, 509(m), 489(m), 471(w), 453(sh, vw)[a]	311(26.4); 340(sh); 373(sh); 465(18.0)[b]	*80c*
					W=S,[c] 517(m), 500(s), 492(s), 479(s), 465(m), 434(w)[a]	241(37.7); 271(28.6); 285(sh); 325(sh); 392(21.7)[b,c]	
W[e]	O	O	S	S_2^{2-}	Mo=S, 509(m), 489(m), 471(w), 453(sh, vw)[a]	272(19.6); 320(sh, 11.6); 376(10.2); 442(8.8); 480(sh, 5.64)[b]	*96*

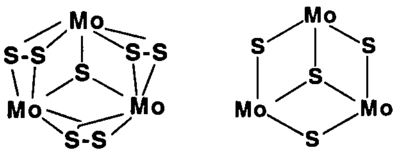
[a] In KBr disk.

[b] In CH_3CN solution.

[c] Data for the W derivative $W_3S_9^{2-}$.

$[Mo(O)_2(S)_2)]^{2-}$ in methanol at low temperatures (*95b*), acidifying solutions of $[Mo(O)(S)_3)]^{2-}$ (*95b*), or by the reaction of polyoxymolybdates with hexamethyldisilylthiane (*95a*). These two anions share the same lattice and in the crystal structure (*95a*) both molecules occupy the same site with approximately equal weight. The stepwise syntheses of linear trimetallic complexes of the type $[(S_2)(Mo_2O_2S_2)(MS_4)]^{2-}$ or $[(DMF)_3(Mo_2O_2S_2)(MS_4)]^{2-}$ are possible by reactions of the $[(DMF)_3(Mo_2O_2S_2)(DMF)_3]^{2+}$ cation or $[(S_2)(Mo_2O_2S_2)(DMF)_3]^{2+}$ with $(MS_4)^{2-}$ tetrathiometallate ligands (*96*, *105*). Further reaction of the $[(DMF)_3(Mo_2O_2S_2)(MS_4)]^{2-}$ complexes with the $(MS_4)^{2-}$ ligands affords the $\{[(O{=}Mo(MS_4)(Mo(S)_3(S_2)\}^{2-}$ complexes (*96*) rather than resulting in the anticipated $[(MS_4)(Mo_2O_2S_2)(MS_4)]^{2-}$ tetranuclear species, analogous to the known $[(WS_4)(W_2S_4)(WS_4)]^{2-}$ complex (*80a,b*). Apparently, the first step in these reactions is the formation of the linear tetranuclear complexes that dissociate to reactive dimeric $[(MS_4)(MoO)(S)]^{-}$ species. The structural data (Table IX) for this class of complexes consistently show long inner Mo–μ-S bonds by comparison to the shorter, outer, Mo–μ-S bonds. The data are suggestive of a central $E{=}Mo^{IV}$ unit bound by two Mo^{VI} thiomolybdate chelates to give a molecule with localized electronic structure and a Mo valence sequence of VI–IV–VI. There appears to be a tendency for delocalization to a VI–V–V system in situations wherein sulfur has been added to the terminal Mo^{VI} thioanions, as in the $\{[(O{=}Mo(MoS_4)(Mo(O)(S)_2(S_2)\}^{2-}$ and $\{[(O{=}Mo(MoOS_3)(Mo(O)(S)_2(S_2)\}^{2-}$ complexes (*95*, *96*).

E. The $[Mo_3S(S_2)_3]^{4+}$ Core and Derivatives



The $[Mo_3S(S_2)_3]^{4+}$ *and* $[Mo_3S(S)_3]^{4+}$ *units*

This class of clusters has been reviewed extensively by Shibahara (*13*) and consequently only a brief overview, designed to underscore the diversity in structure and reactivity, will be presented herein. The trinuclear $[(S_2)_3Mo_3S(S_2)_3]^{2-}$ complex anion (Fig. 9) contains three terminal S_2^{2-} ligands attached symmetrically to three Mo^{IV} ions triply bridged by a central μ_3-S^{2-} central ligand. This very interesting molecule, which has been proposed (*23k*) as a model for crystalline MoS_2, is synthesized as an NH_4^+ salt hydrate in 26% yield by the reaction of $(NH_4)_6Mo_7O_{24}$ with $(NH_4)_2S_x$ (*23f*). The same reaction also produces $(NH_4)_2[(S_2)_2Mo(\mu\text{-}S_2)]_2$ in 40% yield.

The S_2^{2-} ligands in $[Mo_3S_{13}]^{2-}$ undergo sulfur abstraction by CN^- to give the $[Mo_3S_4]^{4+}$ core that can be isolated as the $[Mo_3S_4(CN)_9]^{5-}$ complex (*23h*, *122*, *123*) [Eq. (1)].

$$[Mo_3S_{13}]^{2-} + 12CN^- \rightarrow [Mo_3S_4(CN)_9]^{5-} + 3SCN^- + 3S_2^{2-} \qquad (1)$$

A similar sulfur abstraction reaction from the core of $[Mo_3S_{13}]^{2-}$ has been reported [Eq. (2)].

$$[Mo_3S_{13}]^{2-} + 3edt^{2-} \rightarrow [Mo_3S_4(Edt)_3]^{2-} + S_x^{2-} \qquad (2)$$

It is suggested (*124*) that in this reaction the RS^- ligand abstracts a sulfur atom from the coordinated S_2^{2-} ligand [Eq. (3)].

$$RS^- + S_2^{2-} \rightarrow RSS^- + S^{2-} \qquad (3)$$

Electrochemical reduction of complexes that contain the $[Mo_3S(S_2)_3]^{4+}$ core in aqueous media have been reported and show that the reduction is not involving the Mo^{IV} ions. In the same study the synthesis of $[(L)_3Mo_3S(S)_3)^n$ complexes is reported (*125*). One of these complexes has been characterized structurally (L = 2-mercaptobenzoate dianion, $n = -2$). On reaction with excess HNTA the $[Mo_3S_{13}]^{2-}$ anion affords the $[Mo_3S_4(HNTA)_2(NTA)]^{3-}$ complex (*126a*). The structure of this complex has been determined. The Mo_3S_4 core also has been obtained by degradation of the $[Mo_4S_4]^{6+}$ core in $[Mo_4S_4(NCS)_{12}]^{6-}$ by a reaction with triazacyclononane, or [9]aneN_3, that gives (*126b*) $[Mo_3S_4([9]aneN_3)_3]^{4+}$. Another synthesis of a cluster that contains the Mo_3S_4 core involves coupling of $[(Cys)(Mo_2O_2S_2)(Cys)]^{2-}$ dimers that, through a Mo_4S_4-containing intermediate, proceed to afford the $Mo_3S_4^{4+}$ core (*127*).

In a series of very interesting papers Shibahara and co-workers reported on the reactions of the $[Mo_3S_4(H_2O)_9]^{4+}$ ion (*129–137*) with metals under acidic conditions. Heterometallic clusters that contain the Mo_3MS_4 cubane units were obtained with Fe (*131*, *132*), Co (*133*), Ni (*134*), Cu (*135*), Hg (*133*), Sn and Sn^{2+} ion (*136*), and In (*137*).

The mixed chalcogenido $Mo_3O_2S_2]^{4+}$, $[Mo_3O_3S]^{4+}$, and $[Mo_3OS_3]^{4+}$ cores also exist (*130*) in molecules such as $[Mo_3O_2S_2(NCS)_9]^{5-}$ (*138–140*), $[Mo_3O_3S(HNTA)_3]^{2-}$ (*141*), and $[Mo_3OS_3(Dtp)_4(CH_3CN)]$ (*142*).

The syntheses of the aqua ions of these clusters have been described in detail (*130*).

The reactivity of the $[Mo_3E_nS_{4-n}]$ core is under study and the $[(H_2O)_9Mo_3ES_3]^{4+}$ clusters have been reported to react with acetylene to give the $[(H_2O)_9Mo_3(\mu_2\text{-}E)(\mu\text{-}S)(\mu_3\text{-}S_2C_2H_2)]^{4+}$ complexes. The structure of one of these compounds ($E = 0$) has been determined (*143*). Complexes with mixed metal cores such as $[(H_2O)_9Mo_xW_{3-x}S_4]^{4+}$ have been reported (*144*) ($x = 1, 2$) (also $[(HNTA)_3Mo_xW_{3-x}S_4]^{2-}$). The $[Mo_3S_4(Cl)_3(Dmpe)_3]^+$ species has been synthesized and structurally characterized (*145*). The procedure employed in this synthesis gave the cluster directly by a reaction of $MoCl_3(THF)_3$ with NaSH in THF followed by addition of Dmpe.

New clusters with the Mo_3S_4 core and Et_3P, $Et_2HP{=}O$, and halide ligands have been synthesized (*146*) using the polymeric trimers $Mo_3S_7X_y$ (*147*). These compounds are considered excellent starting materials for the synthesis of complexes that contain the Mo_3S_4 core.

The synthesis (*128*, *148*) and characterization of the $[Mo_4S_4(H_2O)_{12}]^{4+}$ cubane has been described. The $[Mo_4S_4(CN)_{12}]^{8-}$ cluster contains the $[Mo_4S_4]^{4+}$ unit (*149*). The same unit in oxidized forms is found in $[Mo_4S_4(^iPr\text{-}Cp)_4]^{+,2+}$ (*150*) and also in $[Mo_4S_4(NO)_4(CN)_8]^{8-}$ (*151*). The synthesis (*152*) and solution chemistry (*153*) of the oxidized $[Mo_4S_4(H_2O)_{12}]^{5+}$ cluster have been reported. The structure of $Cs_3[Mo_4S_4(EDTA)_2]\cdot 28H_2O$ containing the oxidized $[Mo_4S_4]^{5+}$ (*154*) core and the structure of the $[Mo_4S_4]^{6+}$ core (*155*) have been determined.

IV. Reactions of Oxo/thiometallates. Functional Group Chemistry

A. Bonding and Characteristic Reactivity of the Mo–S_x Groups

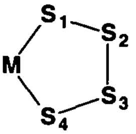
In the rich chemistry of the $Mo(S)(S_x)$ and $Mo(O)(S_x)$ "functional groups" (Fig. 3; $x = 1$, 2, and 4), the nucleophilic character of the S_x^{2-} ligands plays an important role in reactions toward alkynes, heteroallenes, and SO_2. In tetrahedral Mo, thio and oxothio anions in the presence of a $Mo{=}E$ "spectator" group (*vide infra*), adjacent to the site of attack by an electrophile, greatly facilitate electrophilic addition reactions. This applies not only to the $(L)_2Mo(E)_2$ units but also to the $(L)_2Mo(E)(S_2)$ complexes. In the latter the span of the S_2^{2-} ligand at ~2.0 Å is too small to accommodate two coordination sites, and the coordination geometry of the $(L)_2Mo(E)(S_2)$ unit can be described as pseudotetrahedral, with the centroid of the S_2^{2-} ligand occupying one coordination site. In situations wherein both a Mo=O and a Mo–S_x ligand (x = 1, 2) are bound to the same tetrahedrally coordinated Mo atom, the Mo=O group serves as a spectator, and the site of reactivity without exception is the "softer" Mo–S_x chromophore. Apparently the strength of the Mo=O bond precludes the reactivity expected on the basis of the greater polarity of the Mo=O group.

An analysis of the structural and reactivity data available for the various $[(L)(Mo_2^{V}E_2S_2)(L')]^{n-}$ and $[E{=}Mo^{IV}(L)(L')]^{n-}$ thiomolybdate complexes (E = O^{2-} or S^{2-}, L, L′ = O^{2-}, S^{2-}, S_2^{2-}, Cp^-, CS_4^{2-}, or S_4^{2-}) reveals trends that can be attributed to distal or proximal electronic effects associated with the axial (E) and equatorial (L, L′) ligands. The chemistry of the Mo–η^2-S_4^{2-} group, in most cases, can be attributed to the presence of the Mo–η^2-S_2^{2-} group (*28b*) that emerges as the "activated" S_4^{2-} ligand dissociates S_2. Direct evidence for a Mo–η^2-S_4^{2-}/Mo–η^2-S_2^{2-} equilibrium has been obtained unequivocally by ^1H NMR spectroscopic studies in CH_3CN solutions of $[(Cp)(Mo_2^{V}O_2S_2)(S_2)]^-$ and elemental sulfur (*28b*) (*vide infra*). The activation of the coordinated S_4^{2-} ligand and the subsequent dissociation of S_2 seems to be a consequence of both distal and proximal electronic effects. In the $[(L)(Mo_2^{V}E_2S_2)(L')]^{n-}$ complexes, the π-donor ligands S_4^{2-} and Cp^- on one side of the dimeric complexes can affect the reactivity of the ligands on the opposite side of the $(Mo_2^{V}E_2S_2)^{2+}$ unit. This is illustrated in the ready dissociation of S_2 from the $[(S_4)(Mo_2E_2S_2)(S_4)]^{2-}$ and $[(S_4)(Mo_2E_2S_2)(Cp)]^-$ complexes (*28b*). Similarly, dissociation of CS_2 readily occurs in analogous complexes where the S_4^{2-} ligands have been replaced by CS_4^{2-} (*28a*) (*vide infra*). In contrast, no dissociation of S_2 is observed in solutions of the $[(S_4)(Mo_2E_2S_2)(S_2)]^{2-}$ complexes, where the η^2-S_2^{2-} ligand, a weaker π donor, is not affecting the distant S_4^{2-} ligand. The propagation of electronic effects across the length of these molecules could be rationalized in terms of extensive delocalization of electron density within the "out-of-plane" π system that involves the d_{xz} and d_{yz} orbitals on the Mo^{V} atoms and "out-of-plane" p orbitals on the sulfur ligands. As a consequence of these effects, conversion of an η^2-S_2^{2-} ligand in the $[(S_2)(Mo_2E_2S_2)(S_4)]^{2-}$ complexes to a dithiolene, vinyl disulfide, or CS_4^{2-} promotes the dissociation of S_2 from the distant η^2-S_4 ligand, with generation of another η^2-S_2^{2-} ligand that further reacts with electrophilic reagents.

Proximal effects also are important in activation of the coordinated η^2-S_4^{2-} and η^2-CS_4^{2-} ligands in the $[(L)(Mo_2E_2S_2)(L)]^{2-}$ complexes (L = CS_4^{2-}, S_4^{2-}). In general, η^2-S_4^{2-} ligands proximal to oxo-axial ligands do not dissociate S_2 readily and are less reactive than those proximal to sulfido-axial ligands. The *p* orbitals of the axial E groups (E = O, S) overlap and form two π bonds with the Mo d_{xz} and d_{yz} orbitals, which also have the proper symmetry to *p* bond with the *3p* orbitals of the S donor atoms in equatorial L, L′ ligands. The strongly electron-withdrawing oxo group apparently is more effective than a terminal sulfido group in weakening the Mo–S (out of plane) π bonding and indirectly strengthens the $p\pi$–$p\pi$ interactions in the S/S bonds directly adjacent to the Mo–S bonds. Crystallographic data, available for the $[E{=}Mo(S_4)_2]^{2-}$ complexes, support the previous arguments regarding the effects of neighboring axial ligands (*vide infra*). The effects of $d\pi$–$p\pi$ Mo–S bonding in the $p\pi$–$p\pi$ interactions within the S–S bonds are evident in the S–S bond lengths of the Mo-coordinated S_4^{2-} ligands. A significant elongation of the S–S bonds directly adjacent to the Mo atom correlates directly with a shortening of the corresponding Mo–S bonds (Table XI) and suggests that bonding electrons from the S–S bond are transferred to Mo–S bonding orbitals.

TABLE XI

M—S AND S—S DISTANCES OF MO-COORDINATED S_4^{2-} LIGANDS



Compound[a]	S(1)—S(2) (Å)	S(2)—S(3) (Å)	S(3)—S(4) (Å)	M—S(1) (Å)	M—S(4) (Å)	Reference
$[Zn(S_4)_2]^{2-}$	2.045(4)	2.044(5)	2.062(5)	2.376(3)	2.331(3)	98
	2.034(5)	2.032(5)	2.056(5)	2.343(2)	2.354(3)	
$[Ni(S_4)_2]^{2-}$	2.073(2)	2.037(4)	2.073(2)	2.185(2)	2.185(2)	*98, 156*
$(Ph_3P)_2Pt(S_4)$	2.024(8)	2.022(10)	2.081(10)	2.360(6)	2.366(5)	*157*
$[(S_2)(Mo_2S_4)(S_4)]^{2-}$[b]	2.093(4)	2.018(4)	2.053(3)	2.399(2)	2.427(2)	*24a*
$[(S_2)(Mo_2S_4)(S_4)]^{2-}$[c]	2.019(5)	1.970(6)	2.115(5)	2.409(2)	2.403(3)	*24b*
$[S{=}Mo(S_4)_2]^{2-}$	2.107(1)	2.012(1)	2.166(1)	2.387(1)	2.331(1)	*24a*
$[O{=}Mo(S_4)_2]^{2-}$	2.120(3)	2.008(3)	2.159(3)	2.395(2)	2.363(2)	*24a*
$[(\eta^5\text{-}Cp)_2Mo(S_4)]$	2.081(8)	2.018(9)	2.085(7)	—	—	*158*
$[(\eta^5\text{-}Cp)_2W(S_4)]$	2.105(7)	2.016(8)	2.116(9)	—	—	*159*
$[(\eta^5\text{-}Cp)Mo(S_4)_2]^-$	2.141(2)[d]	2.031(2)	2.061(2)	2.305(2)	2.446(2)	*116a*
	2.124(2)	2.022(2)	2.073(2)	2.336(2)	2.430(2)	

[a] The $[Zn(S_4)_2]^{2-}$ anion contains two crystallographically independent S_4^{2-} ligands.

[b] Ph_4P^+ salt; data for the S_4^{2-} ligand not subject to disorder.

[c] Ph_4As^+ salt; data for the S_4^{2-} major component in a disordered structure.

[d] The complex contains two crystallographically independent S_4^{2-} ligands.

The alternation of S–S bonds is not observed in the S_4^{2-} ligands of the tetrahedral $[Zn(S_4)_2]^{2-}$ complex that contains the d^{10} Zn^{II} ion. The transfer of bonding S–S electrons to Mo–S bonding orbitals also is apparent in the structural features of the Mo–CS_4 complexes (Table XII). Here again the Mo–S bond directly adjacent to the lengthened S–S bond of the CS_4^{2-} ligand always is shorter than the Mo–S bond with the thiolate sulfur of the ligand. Such differences in M–S bonding are not observed in the structure of the $[Ni(CS_4)_2]^{2-}$ complex (*98*).

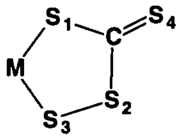
Based on the previous discussion and the nature of the Mo–η^2-S_4 chromophore, the reactions of the thio- and oxo/thiometallates mainly involve the Mo=S and Mo–S_2 groups and include (Figs. 20 and 21) sulfur addition reactions, sulfur abstraction reactions, addition of electrophilic molecules such as CS_2 and DMA, Mo=S dimerization reactions, and abstraction of S^{2-} by thiophilic metal ions.

The addition of sulfur to terminal sulfido ligands very likely is the end result of electrophilic attack on the Mo^{n+}=S (n = 4, 5, 6) sulfur by the $S^+(S)_xS^-$ products of heterolytically cleaved S_8 molecules, and accounts for the synthesis of the $[E{=}Mo^{IV}(S_4)_2]^{2-}$ anions (*24a*) (E = S, O) and various members of the $[(S_x)(Mo_2^VS_4)(S_y)]^{2-}$ (*82*), $[(S_x)(Mo_2^VO_2S_2)(S_y)]^{2-}$ (*104*, *106*), and $[(S_x)(Mo_2^VOS_3)(S_y)]^{2-}$ (*73*) series (Figs. 11, 13, and 14).

In the $[(S_4)(Mo_2E_2S_2)(S_2)]^{2-}$ complexes, the easily polarizable η^2-S_2^{2-} ligands also react readily with nucleophiles such as trialkyl or triaryl phosphines and are more reactive than the η^2-S_4^{2-} ligands. The abstraction of S with Ph_3P, from the $(S_2)Mo{=}S$ and $(S_2)Mo{=}O$ units

TABLE XII

M–S AND S–S DISTANCES OF M-COORDINATED $(CS_4)^{2-}$ LIGANDS



Compound	S(2)–S(3) (Å)	S(1)–C (Å)	S(2)–C (Å)	M–S(1) (Å)	M–S(3) (Å)	Reference
$[Ni(CS_4)_2]^{2-}$	2.064(2)	1.707(4)	1.711(5)	2.174(2)	2.165(2)	*98*
$[S{=}Mo(CS_4)_2]^{2-}$	2.102(5)	1.735(12)	1.719(12)	2.386(3)	2.320(3)	*160, 161*
(trans)[a]	2.100(5)	1.739(12)	1.709(12)	2.380(3)	2.333(3)	
$[S{=}Mo(CS_4)_2]^{2-}$	2.105(4)	1.756(10)	1.726(11)	2.376(3)	2.320(3)	*161*

[a] Contains two symmetry-independent $(CS_4)^{2-}$ ligands.

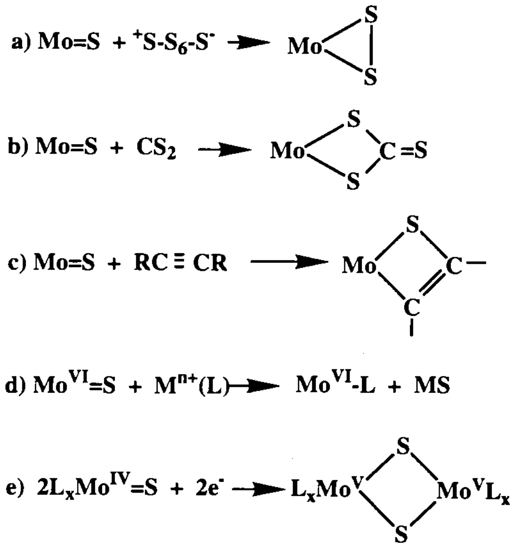


FIG. 20. Reactions of the Mo=S chromophore.

in these complexes, occurs at ambient temperature and results in the formation of the $[(E{=}Mo(S_4)(MoS_3E)]^{2-}$ complexes (*82*, *103*). The η^2-S_4^{2-} ligands do not react further with Ph_3P unless heated to 80°C for extended periods of time. With transition metal ions, the thiomolyb-

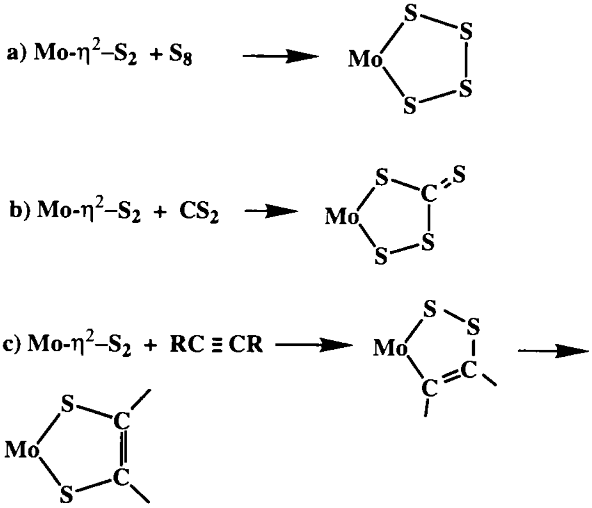


FIG. 21. Reactions of the Mo—η^2-S_2 chromophore.

denyl groups can serve either as electron pair donors or as a source of sulfide ions for the eventual formation of highly insoluble, thermodynamically stable, transition metal sulfides. The former course of reactivity is represented in the multitude of heterometallic complexes wherein the $(MoS_4)^{2-}$ anion serves as a ligand for transition metal ions (*52–54*). The irreversible removal of sulfide ions from Mo=S units by the formation of insoluble transition metal sulfides allows for the introduction of nonsulfur terminal ligands in the thiomolybdate ions by metathetical reactions. An example of this reaction is available in the synthesis of the $\{[O{=}Mo^{VI}(S_2)_2]_2X\}^-$ anions from the reaction of NiX_2 (X = Cl, I) with an isomeric form of the $\{[(\eta^2\text{-}S_2)_2Mo(O)]_2(\mu\text{-}S)\}^{2-}$ anion (*83*, *106*).

B. The Spectator Group Effect

The industrially important olefin metathesis reaction is a reaction that involves the simultaneous cleavage of two olefin double bonds followed by the formation of the alternate double bonds [Eq. (4)]:

$$C{=}C + C^*{=}{}^*C \rightarrow 2{}^*C{=}C. \tag{4}$$

At present it is accepted that the catalyst is a metal alkylidene complex that reacts with an olefin to form a metallacyclobutane intermediate (Fig. 22) that decomposes to give the product olefin (*162*). The metal alkylidene complex is formed from the $Mo(O)_2Cl_2$ catalyst and olefin with elimination of an organic carbonyl compound. In these reactions the Mo=O and $Mo{=}CH_2$ groups are proposed to be activated by the Mo=O spectator groups and as a result readily add an olefin. These additions result in a change in the coordination geometry of the Mo atoms from four-coordinate tetrahedral to five-coordinate square pyramidal. Associated with this change is a large negative free energy that is attributed mainly to the transformation of the bond order of the Mo=O spectator group from double to triple (*162*) (Fig. 22).

C. Addition of Electrophiles to the $Mo{-}S_x$ Groups

1. Addition of CS_2; Trithio- and Perthiocarbonate Complexes

The generation of the perthiocarbonate anion, $(CS_4)^{2-}$, generally is accomplished by the addition of a polysulfide or disulfide dianion to CS_2. The associated counterions include Na^+, K^+, Cs^+, Sn^{2+}, and NH_4^+ (*15*). The $[M(CS_4)_2]^{2-}$ complexes can be generated in the

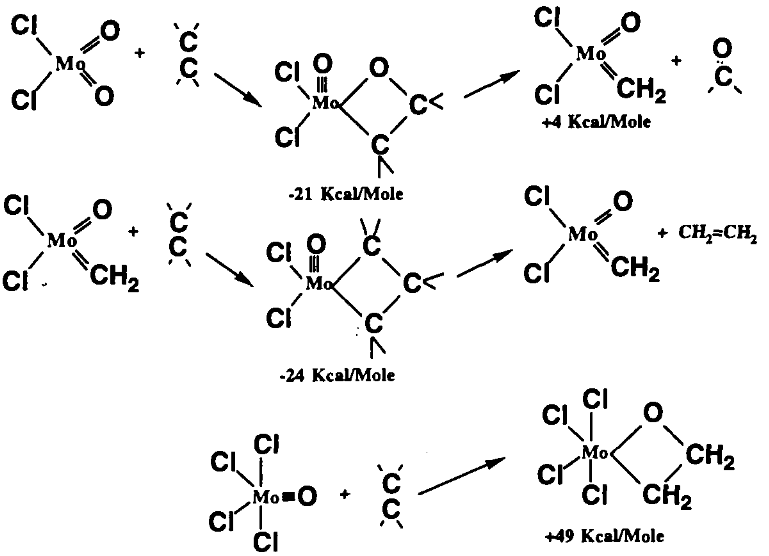


FIG. 22. A minimal mechanism for the olefin metathesis reaction (Data from Ref. *162a*).

$[M(CS_3)_2]^{2-}$ complexes (M = Ni, Pt) by either I_2 oxidation or sulfur addition reactions (*16*).

Addition of CS_2 to DMF solutions of $[Ph_4P]_2[S{=}Mo(\eta^2\text{-}S_4)_2]$ and $[Ph_4P]_2[(S_4)Mo_2S_4)(S_2)]^{2-}$ results in the formation of perthiocarbonate derivative complexes (*160*) (Fig. 23; Table XIII). The illustrated pathways are based on CS_2 addition mechanisms involving the $Mo{-}\eta^2\text{-}S_2$ units. It should be noted that addition to the Mo=S unit, followed by intramolecular S transfer, also is a possible pathway to $(CS_4)^{2-}$. Both cis and trans isomers of the $[S{=}Mo(\eta^2\text{-}CS_4)_2]^{2-}$ anion have been isolated (*161*). The $[O{=}Mo^{IV}(S_4)_2]^{2-}$ complex is unreactive toward CS_2 unless activated by Ph_3P (*73b*).

Presumably, Ph_3P "activation" involves the generation of reactive $\eta^2\text{-}S_2$ or Mo=S units from the Mo-coordinated $\eta^2\text{-}S_4$ ligands. These observations also suggest that the lack of reactivity of the $[O{=}Mo^{IV}(S_4)_2]^{2-}$ complex toward CS_2 is due either to the absence of a reactive Mo=S functional group or to the inability of the $Mo{-}\eta^2\text{-}S_4$ unit in $[O{=}Mo^{IV}(S_4)_2]^{2-}$ to dissociate S_2 and generate the reactive $Mo{-}\eta^2\text{-}S_2$ group.

The $[(CS_4)(Mo_2S_4)(CS_4)]^{2-}$ complex reversibly loses CS_2 to give the known $[(S_2)(Mo_2S_4)(S_2)]^{2-}$ complex (*35*, *79*). The $(CS_4)^{2-}$ ligands in both isomers of $[S{=}Mo(\eta^2\text{-}CS_4)_2]^{2-}$ (Fig. 23, structures 3A and 3B) also readily lose CS_2. One of these products has been spectroscopically

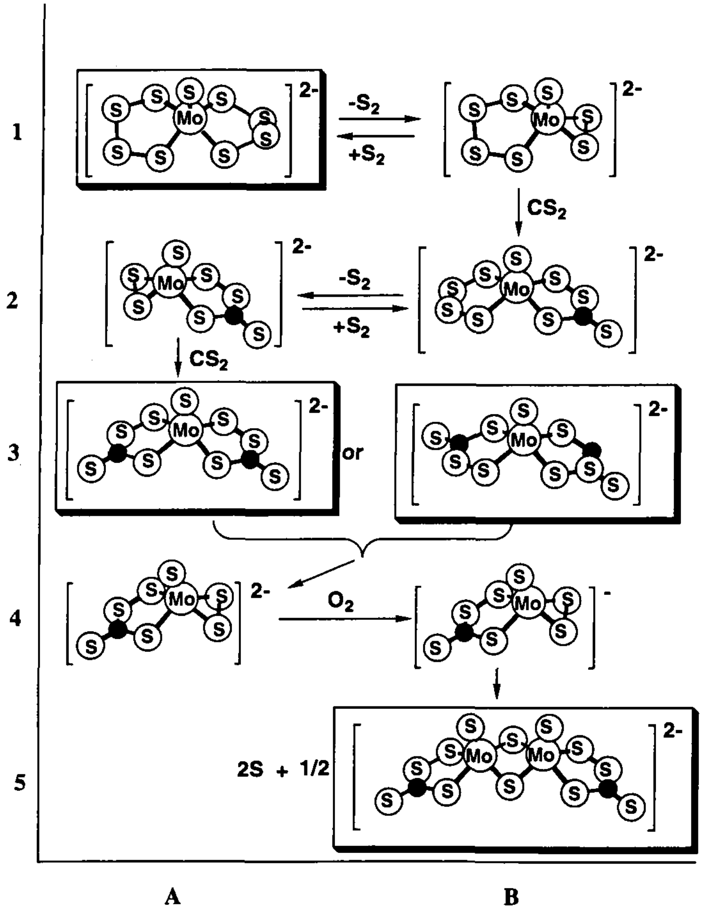


FIG. 23. Synthesis of Mo–thiocarbonate complexes.

examined and postulated to be the $[S{=}Mo(S_2)(CS_4)]^{2-}$ complex (Fig. 23, structure 4A) (*160b*). The formation of $[(CS_4)(Mo_2S_4)(CS_4)]^{2-}$ (Fig. 23, structure 5B) from $[S{=}Mo(\eta^2\text{-}CS_4)_2]^{2-}$ may be due to a solvent-assisted self-coupling reaction of the postulated $[S{=}Mo(S_2)(CS_4)]^{2-}$ intermediate followed by reductive S–S bond cleavage. The $[(\eta^2\text{-}CS_3)(Mo_2S_4)(\eta^2\text{-}CS_3)]^{2-}$ complex has been obtained by the reaction of CS_2 with $(Mo_2S_6)^{2-}$ or the reaction of Ph_3P with the $[(CS_4)(Mo_2S_4)(CS_4)]^{2-}$ anion (*161*). The same anion also can be obtained from $(MoS_4)^{2-}$ (*vide infra*).

The lack of reactivity of the remaining free Mo=S groups in the $(CS_3)^{2-}$ and $(CS_4)^{2-}$ complexes may be due to the stability of the Mo–S

TABLE XIII

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF BINARY AND TERTIARY [(L)(Mo$_2$E$_2$(L′)]$^{2-}$ COMPLEXES[a]

Compound	Infrared absorption (cm^{-1})	λ_{max}
[CS$_4$)(Mo$_2$S$_4$)(CS$_4$)]$^{2-}$	C=S, 982; Mo–S$_b$, 464(2)[b]	314(sh); 365; 470(sh); 610(sh)[c]
[CS$_3$)(Mo$_2$S$_4$)(CS$_3$)]$^{2-}$	C=S, 1052; Mo–S$_b$, 460(w)[b]	344, 444(sh)[c]
[CS$_3$)(Mo$_2$O$_2$S$_2$)(CS$_4$)]$^{2-}$	C=S, 1054; Mo=O, 950(s), 982 (m); Mo–S$_b$, 460(w)[b]	374(sh); 460[c]
[CS$_3$)(Mo$_2$O$_2$S$_2$)(S$_4$)]$^{2-}$	C=S, 1058; Mo=O, 949(vs); Mo–S$_b$, 468(m)[b]	258(sh); 310(sh)[c]
[CS$_3$)(Mo$_2$S$_4$)(S$_2$)]$^{2-}$	C=S, 1051; Mo=O, 952(s); Mo–S$_b$, 479(2)[b]	330(sh); 380(sh), 460[c]
[CS$_3$)(Mo$_2$O$_2$S$_2$)(CS$_3$)]$^{2-}$	C=S, 1046; Mo=O, 947(s), 934; Mo–S$_b$, 470(w)[b]	450[c]

[a] E = S, O; L, L′ = (CS$_4$)$^{2-}$ or (CS$_3$)$^{2-}$, S$_x^{2-}$. Data from Ref. *161*.

[b] In KBr disk.

[c] In DMF.

triple bond in the stable (CS$_4$)$^{2-}$ and (CS$_3$)$^{2-}$ five-coordinate Mo^{V} complexes and/or the weak electrophilic character of CS$_2$. The reactions of (MoS$_4$)$^{2-}$ with CS$_2$ afford the [(CS$_3$)(Mo$_2$S$_4$)(CS$_3$)]$^{2-}$ complex, which has been structurally characterized (Table I). A pathway that leads to this compound has been suggested (*73b*) (Fig. 24). The same molecule has been obtained by addition of CS$_2$ to the [(S)(Mo$_2$O$_2$S$_2$)(S)]$^{2-}$ anion (*113*) (Table III).

The addition of CS$_2$ to the Mo=S and the (Mo–η^2-S$_4$-derived) Mo–η^2-S$_2$ functional groups (*28b*) in [(S)(Mo$_2$O$_2$S$_2$)(S$_4$)]$^{2-}$ [Eqs. (5–7)] also has been described and very likely is influenced by the spectator group effect (*162*).

$$[(S)(Mo_2O_2S_2)(S_4)]^{2-} + CS_2 \rightarrow [(CS_3)(Mo_2O_2S_2)(S_4)]^{2-} \tag{5}$$

$$[(CS_3)(Mo_2O_2S_2)(S_4)]^{2-} = [(CS_3)(Mo_2O_2S_2)(S_2)]^{2-} + \tfrac{1}{4}S_8 \tag{6}$$

$$[(CS_3)(Mo_2O_2S_2)(S_2)]^{2-} + CS_2 \rightarrow [(CS_3)(Mo_2O_2S_2)(CS_4)]^{2-} \tag{7}$$

The importance of this effect also is demonstrated by the synthesis of the [(CS$_3$)(Mo$_2$O$_2$S$_2$)(S$_4$)]$^{2-}$ complex (*161*) from [(S)(Mo$_2$O$_2$S$_2$)(S$_4$)]$^{2-}$ and one equivalent of CS$_2$. The synthesis and structure of the related [(CS$_3$)(Mo$_2$O$_2$S$_2$)(S$_2$)]$^{2-}$ complex (Fig. 25, structure 2A) have been reported (*161b*). The preferential reactivity of the four-coordinate

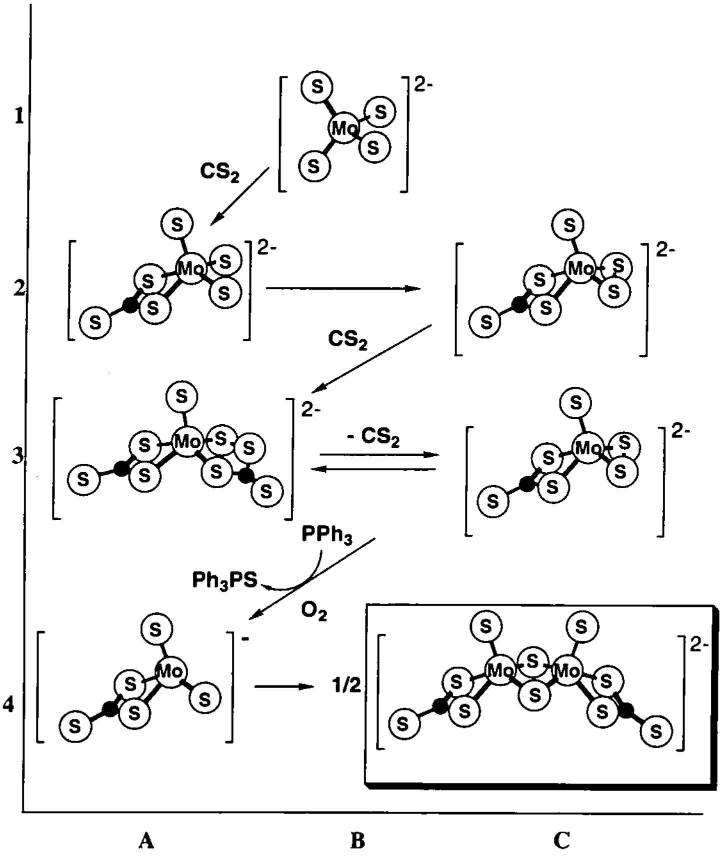


FIG. 24. The reaction of $(MoS_4)^{2-}$ with CS_2.

$(\mu\text{-}S)_2(O)Mo{=}S$ group relative to the five-coordinate $(\mu\text{-}S)_2(O)Mo{-}S_4$ group very likely has its origin in the different bond orders of the $Mo{=}O$ chromophores in the two groups (Fig. 25).

The structures of various $(CS_4)^{2-}$ and $(CS_3)^{2-}$ complexes have been determined (Tables I and III). The vibrational infrared, ^{13}C NMR, and electronic spectra of the Mo–trithio- and perthiocarbonate complexes have been compiled in Table XIII. The energy of the $C{=}S$ vibration of the coordinated $(CS_3)^{2-}$ ligands invariably is lower (~980 cm^{-1}) than that of the $C{=}S$ vibration in the $(CS_4)^{2-}$ complexes (~1050 cm^{-1}) and can be used as a spectroscopic diagnostic criterion for the identification of the ligands with considerable confidence. An additional diagnostic indicator for the $(CS_3)^{2-}$ and $(CS_4)^{2-}$ ligands is the

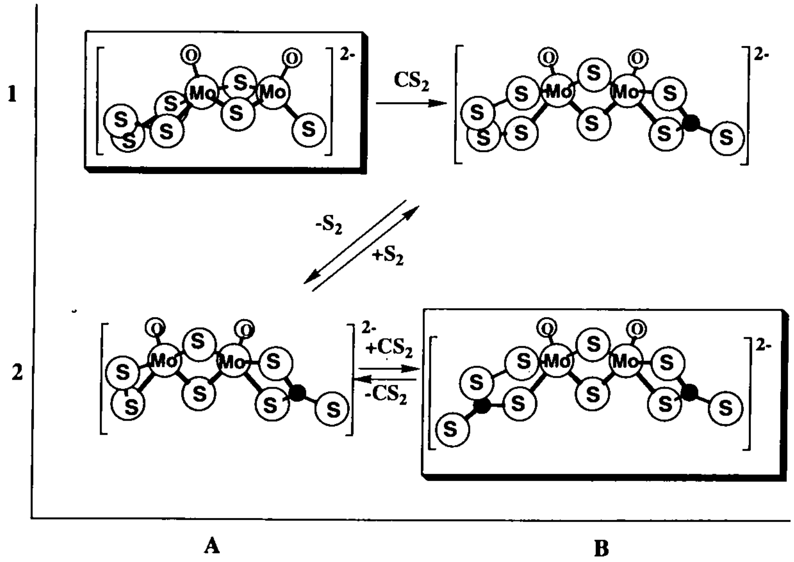


FIG. 25. CS_2 addition to the $[(S_x)(Mo_2O_2S_2)(S_y)]^{2-}$ complexes.

characteristic ^{13}C NMR resonance associated with each of the two ligands. Generally, this resonance is found near 246 ppm for the Mo-coordinated $(CS_4)^{2-}$ ligands and around 253 ppm for the Mo-coordinated $(CS_3)^{2-}$ ligands (*161*).

2. Reactions of Activated Alkynes with the Mo–η^2-S_4^{2-}, Mo–η^2-S_2^{2-}, Mo=O, and Mo=S Functional Groups; Dithiolene Complexes

The addition of alkynes to transition metal sulfide complexes is a well-known reaction and examples include the synthesis of $(R\text{-}Cp)_2Ti(DMAD)$ from $(R\text{-}Cp)_2TiS_5$ and DMA (*165a,b*), of $(R\text{-}Cp)V(DMAD)_2$ from $(R\text{-}Cp)_2V_2S_5$ and DMA (*165d*), of $(R\text{-}Cp)_2V_2(S)_2(DMAD)$ from $(R\text{-}Cp)_2V_2S_4$ and DMA (*165d*), of $(R_n\text{-}Cp)_2Mo_2(S_2C_2R_2)_2$ from $(R_n\text{-}Cp)_2Mo_2S_4$ and R_2C_2 (*19a*), of $Fe_2(DMAD)(CO)_6$ from $Fe_2S_2(CO)_6$ and DMA (*165e*), of $[Ni(DMAD)_2]^{2-}$ from $[Ni(S_4)_2]^{2-}$ and DMA (*98*), of $(Et\text{-}Me_4\text{-}Cp)_4Ru_2S_2C_2R_2$ from $(Et\text{-}Me_4\text{-}Cp)_4Ru_2S_4$ and R_2C_2 (*165f*), and of $[Fe(DMAD)_2]_2^{2-}$ from $[Fe_2S_{12}]^{2-}$ (*166*) and DMA (*167*). Reactions of dicarbomethoxy acetylene (DMA) with the binary and tertiary molybdenum sulfides also give dicarbomethoxy dithiolene (DMAD) complexes (Table XIV). A possible mechanism suggested for these reactions (*28a*) involves cycloaddition of the electrophilic alkyne to the coordinated S_x^{2-} chelate ligand. Precedence

TABLE XIV

DISTANCES AND ANGLES IN SELECTED DITHIOLENE Mo COMPLEXES[a]

Compound	Mo=S (Å)	Mo=S (Å)	C−S (Å)	S−Mo−S[b] (°)	S−Mo−S[c] (°)	S−Mo=O (°)	Reference
$[Mo(DMAD)_3^{2-}$	2.393(5)		1.74(2)	80.7(2)	82.9(10)	—	*25*
$[Mo_2(\mu\text{-}S)_2(DMAD)_4]^{2-}$[d]	2.383[3]		1.732[e]	80.1	84.1	—	*25*
	2.459[f]		1.697[f]				
$[O{=}Mo(DMAD)_2]^{2-}$	2.380(4)	1.686(6)	1.758(9)	83.1	84.8	108.9(5)	*25*
$[O{=}Mo(Bdt)_2]^{2-}$	2.388(2)	1.699(6)	1.767(6)	83.1(1)	85.8(1)	—	*171c*
	2.38(3)	1.665(5)	1.75(1)			107.5(6)	*170c*
$[O{=}Mo^{V}(Bdt)_2]^{-}$	2.377(1)	1.668(3)	1.763(4)	84.4(1)	84.6(1)	—	*171c*
$[O{=}Mo(Ph_3Si\text{-}Bdt)_2]^{2-}$	2.39(2)	1.677(4)	1.763(6)	—	—	108.6(14)	*170c*
$[O{=}Mo^{IV}(Tdt)_2]^{2-}$	2.388(5)	1.700(9)	1.77(1)	—	—	108.2(17)	*170c*
$[O)_2Mo^{VI}(MNT)_2]^{2-}$	2.42[g]	1.69(1)	1.77(1)	—	—	—	*171b*
	2.59[h]	1.73(1)					

[a] See footnote *a*, Table I.
[b] Intraligand.
[c] Interligand.
[d] Mo–Mo distance, 2.938(1) Å.
[e] Distances cis to a bridging sulfide.
[f] Distances trans to a bridging sulfide.
[g] Cis to an oxo ligand.
[h] Trans to an oxo ligand.

for this type of interaction can be found in the reactions of dithiolene complexes (*168*).

In the thiomolybdate complexes both the Mo–η^2-S_x and Mo=S groups are nucleophilic enough to undergo attack by dicarbomethoxy acetylene. When both are present within a molecule the Mo=S serves as the spectator group. This is apparent in the reaction of the $[S{=}Mo(S_4)_2]^{2-}$ anion with DMA (Fig. 26). It is proposed that the chromophores that first undergo nucleophilic attack are the Mo–S_2 groups that emerge as the Mo–η^2-S_4 units dissociate S_2. The vinyl disulfide complexes, $[S{=}Mo(VDS)_2]^{2-}$, that may form initially have not been detected but very likely are the species that undergo a sulfur-catalyzed isomerization reaction to give the corresponding dithiolenes, DMAD. On occasion the vinyl disulfide (VDS) formed by addition of DMA to the Mo–S_2 group can be isolated (*vide infra*). The question still remains whether S_x^{2-} ligands bound to metals other than Mo undergo $S_{x\text{-}2}$ dissociation. If this dissociation indeed takes place then alkyne addition to the M–S_2 unit and VDS formation may also occur with metals other than Mo. The DMA addition to the $(R\text{-}Cp)_2TiS_5$ complex that leads to $(R\text{-}Cp)_2Ti(DMAD)$ is reported to initially give a vinyl disulfide complex that eventually rearranges to the dithiolene (*165a*).

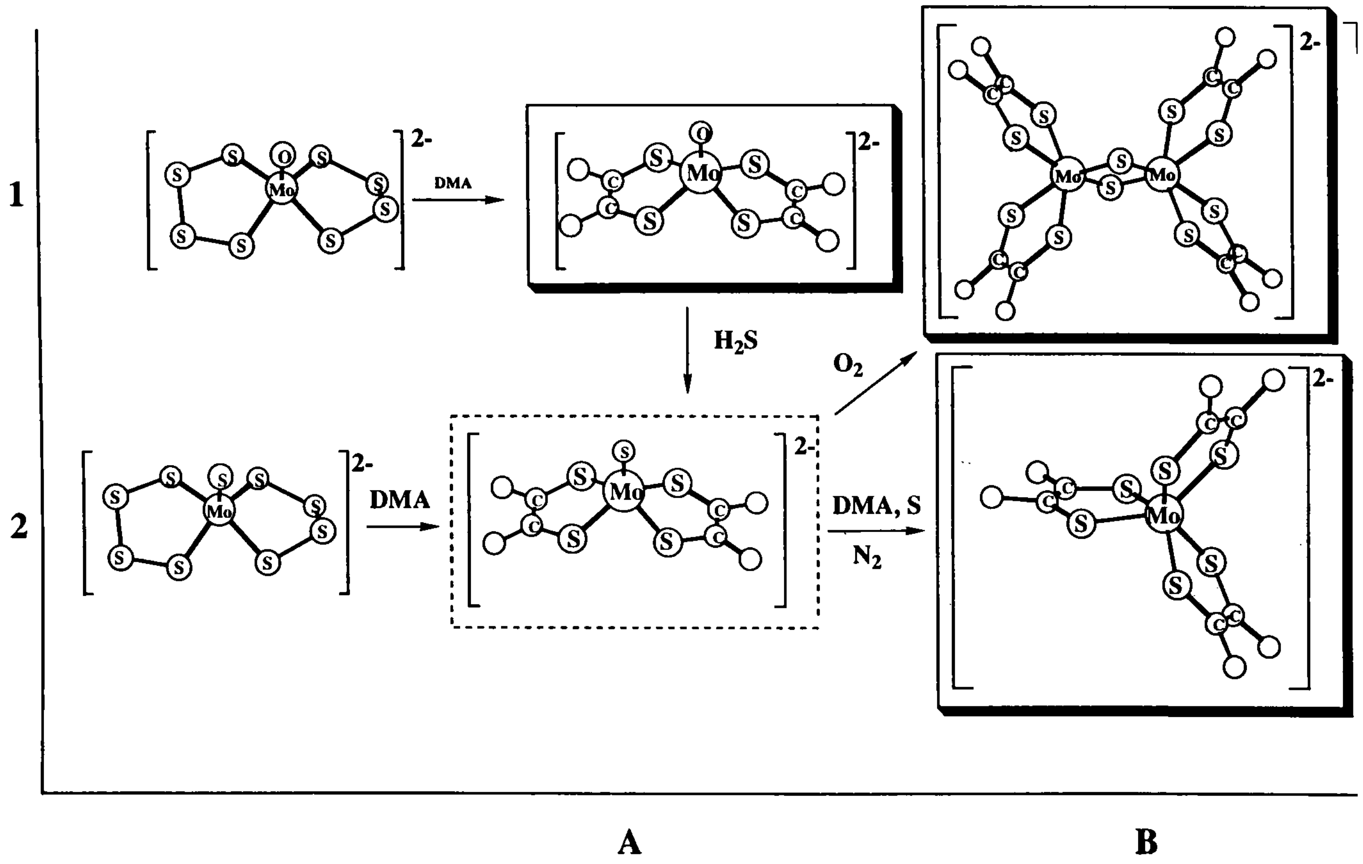


FIG. 26. Reactions of binary Mo/S complexes with DMA.

The reaction of the $[S{=}Mo(S_4)_2]^{2-}$ and $[(S_4)(Mo_2S_4)(S_2)]^{2-}$ complexes with DMA (Fig. 26) proceed until all S_x^{2-} ligands (with the exception of the μ-S^{2-} sulfido ligands) are converted into the DMAD ligands. The type of DMAD complex that forms depends on the synthetic conditions. The $[Mo^{IV}(DMAD)_3]^{2-}$ complex (Fig. 26, structure 2B; Table XIV) is the final product obtained when the reaction of $[S{=}Mo(S_4)_2]^{2-}$ with DMA is carried out under anaerobic conditions. In the presence of oxygen, the same reaction affords the oxidized $[(DMAD)_2Mo^V(\mu\text{-}S)_2Mo^V(DMAD)_2]^{2-}$ complex (*25*, *28b*) (Fig. 26, structure 1B). The same compound also has been obtained by the reaction of either $[(S_4)(Mo_2S_4)(S_2)]^{2-}$ or $[(S_2)(Mo_2S_4)(S_2)]^{2-}$ with DMA. It has been suggested (*28b*) that the dithiolene ligands form (1) as a result of S addition to the vinyl sulfide ligands initially obtained by addition of DMA to the Mo=S group or (2) by isomerization of the vinyl disulfides that form by addition of DMA to the $Mo{-}S_2$ group.

The reaction of oxo/thiomolybdates with DMA (Fig. 27) occurs exclusively with the $Mo{-}S_x$ group ($x = 1, 2$). Thus the $[O{=}Mo(S_4)_2]^{2-}$ anion affords the $[O{=}Mo(DMAD)_2]^{2-}$ complex (*25*, *28b*) (Fig. 26, structure 2A). In Fig. 27, the $[(S_2)(Mo_2O_2S_2)(S_2)]^{2-}$ complex, structure 3A, forms the bis-vinyl disulfide complex, $[(VDS)(Mo_2O_2S_2)(VDS)]^{2-}$, structure 3B, which has been characterized structurally (*169*).

Subsequently the isomerization of the vinyl disulfide ligand (in the Cp analogue of this complex) to dithiolene was recognized to occur by a process that was proposed to occur either thermally or via sulfur catalysis (*28b*) (Fig. 28). The $[(DMAD)(Mo_2O_2S_2)(DMAD)]^{2-}$ complex (Fig. 27, structure 2C), rather than $[(VDS)(Mo_2O_2S_2)(VDS)]^{2-}$, is isolated following the reaction of $[(S_2)(Mo_2O_2S_2)(S_4)]^{2-}$ with DMA. In this reaction the solution contains sufficient amounts of dissociated sulfur, which in turn catalyzes the rapid isomerization of the vinyl disulfide ligands that undoubtedly form initially.

The addition of CS_2 and DMA to the $[(L)(Mo_2O_2S_2)(S)]^{2-}$ complexes ($L = S_4^{2-}$, η^5-Cp; Figs. 29 and 30) demonstrates the exceptional reactivity of the Mo(O)(S) chromophore, which directly and exclusively involves the Mo=S unit activated by the neighboring spectator Mo=O group (*103*). Mechanistic pathways have been proposed, as shown in Fig. 29, for reactions of the $[(S_4)(Mo_2O_2S_2)(S)]^{2-}$ anion (structure 3B) that lead to the $[(CS_3)(Mo_2O_2S_2)(CS_4)]^{2-}$ or the $[(DMAD)(Mo_2O_2S_2)(DMAD)]^{2-}$ anions (structures 2A and 1C). In the absence of electrophiles structure 3B exists in equilibrium with the dimeric form $\{[(S_4)(Mo_2O_2S_2)(S)]_2\}^{4-}$, structure 5B, which has been isolated and characterized structurally as the Et_4N^+ salt (*103*). The lattice energy of the Ph_4P^+ salt of the same compound is sufficiently different to

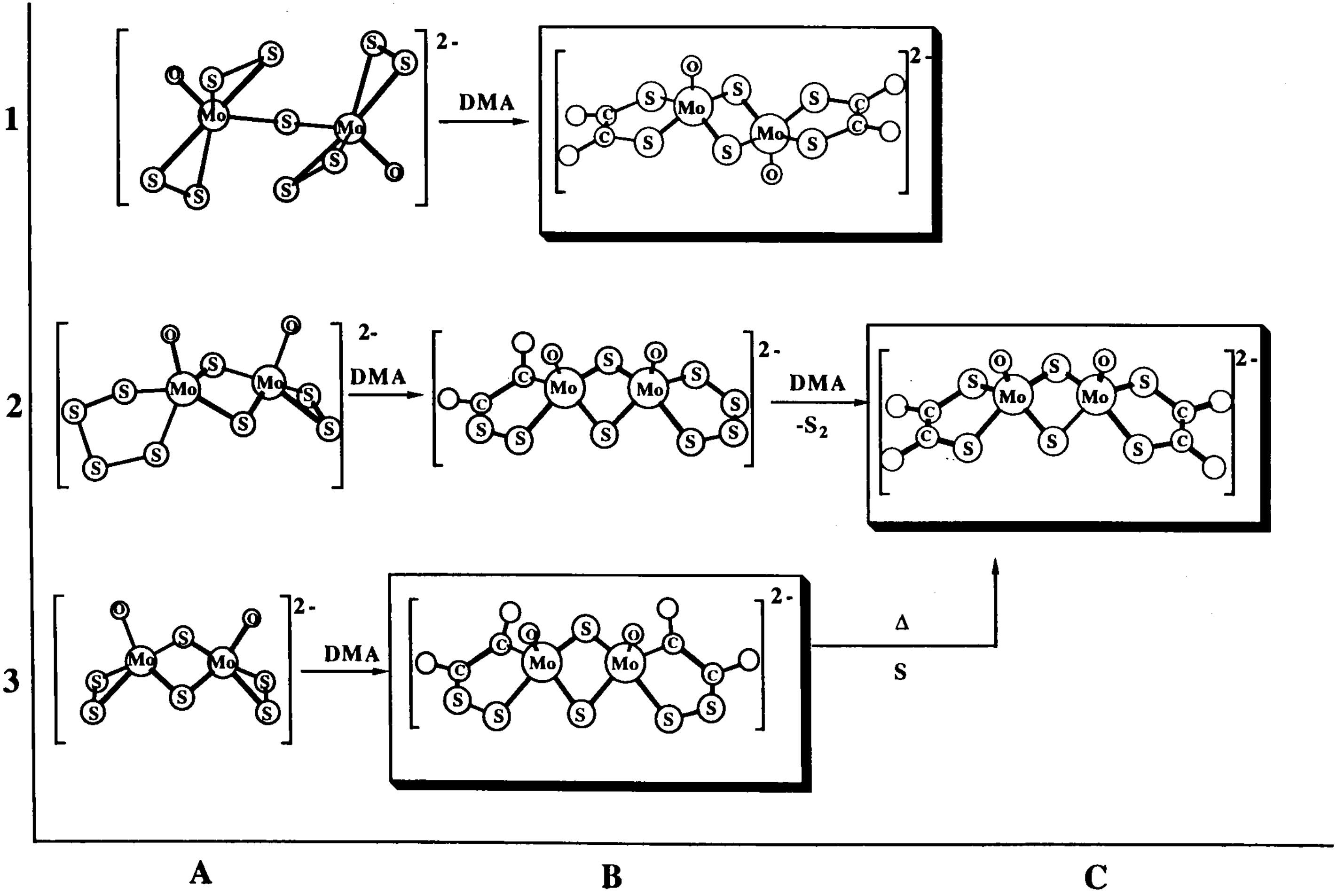


FIG. 27. Reactions of oxo/thiomolybdates with DMA.

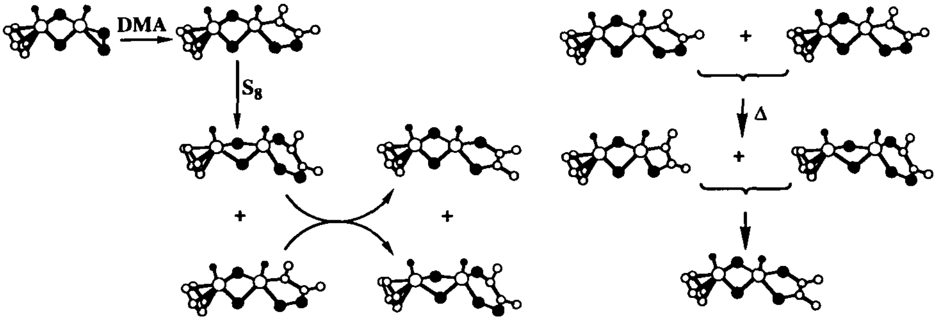


FIG. 28. Proposed mechanism for the sulfur-catalyzed and thermal isomerization of the coordinated vinyl disulfide ligand to 1,2-dithiolene.

stabilize the monomeric form of a compound (structure 3B) that also has been characterized structurally (*103*). The sequence of electrophile additions to structure 3B suggests a reactivity order: Mo=S > Mo–S_2 > Mo–S_4. Similar reactivity patterns have been reported for the $[(\eta^5\text{-Cp})(Mo_2O_2S_2)(S)]^-$ complex (Fig. 30). In the latter, addition of electrophiles such as CS_2 or DMA to the Mo–S_2 group leads to $(CS_4)^{2-}$ and $(VDS)^{2-}$ ligands, which eventually isomerize to dithiolenes. Proposed mechanisms for the thermally and sulfur-catalyzed isomerization reactions have been advanced (Fig. 28) on the basis of NMR data that show ^1H resonances assigned to vinyl sulfide, vinyl disulfide, and dithiolene complexes.

The sulfur-rich dithiolene persulfide ligand SDMAD in the structurally characterized $[(\eta^5\text{-Cp})_2Mo(SDMAD)]$ complex is obtained (*169b*) by the reaction of $(\eta^5\text{-Cp})_2MoS_4$ with DMA. This compound undergoes sulfur abstraction by Ph_3P to give the $[(\eta^5\text{-Cp})_2Mo(DMDA)]$ dithiolene complex. Its existence justifies earlier postulates (*28b*) of the possible involvement of a perthiolene intermediate in the vinyl disulfide-to-dithiolene isomerization process (Fig. 28). The lack of evidence for the formation of a vinyl disulfide ligand in the reactions of DMA with any of the $[(S_x)(Mo_2S_4)(S_y)]^{2-}$ complexes has been noted (*28b*). It is suggested that the exceptionally reactive Mo=S group initially affords a vinyl sulfide ligand that rapidly abstracts sulfur from the neighboring S_x^{2-} ligands to form the stable dithiolene.

Interest in the molybdenum oxidoreductases and recognition of the importance of the molybdopyranopterin cofactor (Fig. 1) in the active sites of these enzymes have led to the synthesis of $[(L)_2Mo^{IV}{=}O]^{2-}$ [L = MNT (*170a,b*), Bdt (*170c*, *171c*), Tdt (*170c*)], $[(L)_2Mo^{VI}(O)_2]^{2-}$ [L = Bdt (*171c*), MNT (*171b*, *170e*), Tdt (*170d,e*)], and $[(L)_2Mo^{V}(O)_2]^-$

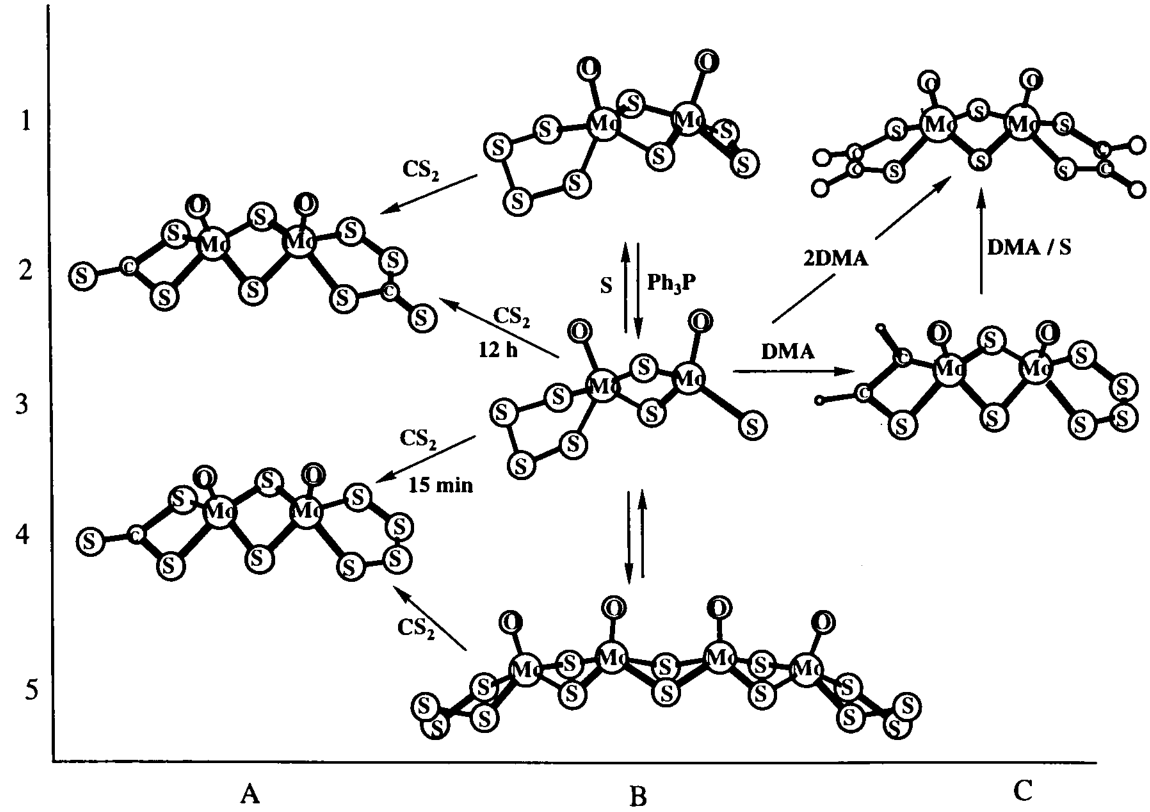


FIG. 29. The chemistry of the Mo(O)(S) unit in the $[(S_4)(Mo_2O_2S_2)(S)]^{2-}$ complex.

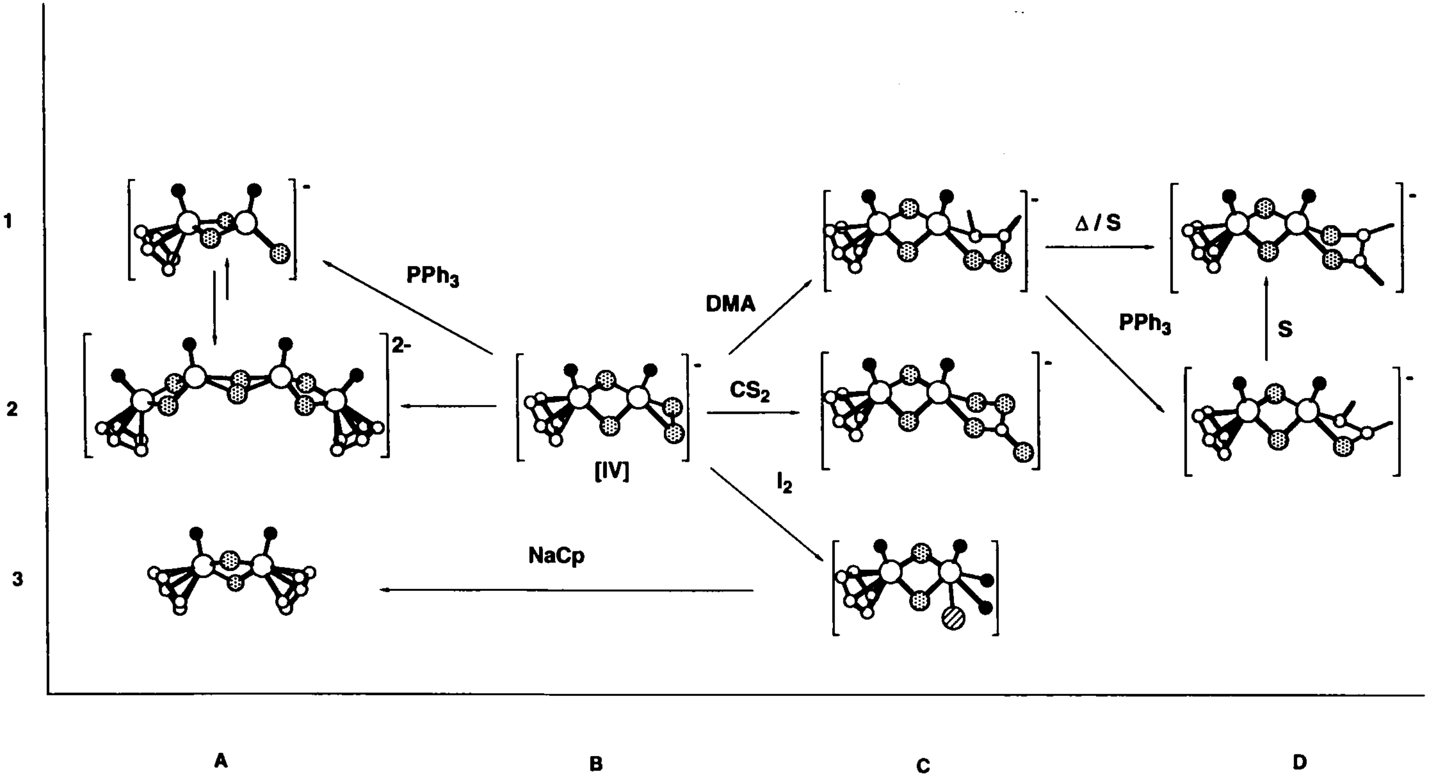


FIG. 30. The chemistry of the Mo(O)(S) unit in the $[(Cp)(Mo_2O_2S_2)(S)]^-$ complex.

complexes (Table XV) (*171c*), which together with analogous DMA complexes can be considered as partial structural analogues for the Mo oxidoreductase cofactor. The resonance Raman spectra of some of these molecules (*171d*) and particularly vibrations associated with the dithiolene functionality are similar to those observed in the molybdoenzymes and are thought to be associated with the dithiolene-functionalized pterin unit. Some of these complexes can be prepared (*173*) conveniently by the reaction of alkynes with the Mo–S_x chromophore (*172*). The $[(Bdt)_2Mo^{VI}(O)_2]^{2-}$ complex has been obtained by the reaction of Me_3NO with the $[O{=}Mo^{IV}(Bdt)_2]^{2-}$ complex (*170c*). The dioxo-Mo^{VI} dithiolene complexes serve as oxo-transfer agents (*171b*) and the $[Mo^{VI}(O)_2(MNT)_2]^{2-}$ complex has been reported to oxidize HSO_3^- to HSO_4^- as it is reduced to $[Mo^{IV}O(MNT)_2]^{2-}$. The reaction obeys saturation kinetics with $K_m = 0.010(1)\ M$ and a K_{obs} (at substrate saturation concentration) of 0.87(4) sec^{-1}. Similarly, the catalytic oxidation of benzoin by air or pyridine N-oxide has been reported with $[O{=}Mo(Bdt)_2]^{2-}$ used as a catalyst (*170g,h*).

TABLE XV

CHARACTERISTIC ELECTRONIC AND INFRARED ABSORPTION SPECTROSCOPIC DATA OF SELECTED DITHIOLENE Mo COMPLEXES

Compound	Infrared absorption (cm^{-1})	λ_{max}	Reference
$[Mo(DMAD)_3]^{2-}$ [a]	C=O, 1730(br); C=O (DMF of solvation, 1710(s); C–O, 1200(s)[b]	356; 450(sh); 650[c]	*25, 160b*
$[Mo_2(\mu{-}S)_2(DMAD)_4]^{2-}$	C=O, 1730(br); C=O (DMF of solvation, 1710(s); C–O, 1200(s)[b]	380; 430(sh); 582; 680[c]	*25*
$[O{=}Mo(DMAD)_2]^{2-}$	Mo=O, 914(s); Mo–S, 388(w), 348(w)[b]	360; 460(sh); 550[c]	*25*
$[O{=}Mo^{V}(Bdt)_2]^-$	944[b]		*171c*
$[O{=}Mo^{IV}(pH_3Si{-}Bdt)_2]^{2-}$	Mo=O, 910; Mo–S, 365[b]	359(13.0); 445(1.3)[c]	*170c*
$[O{=}Mo^{IV}(Bdt)_2]^{2-}$	Mo=O, 905[b]	—	*171*
	Mo=O, 902; Mo–S, 356[b]	328(12.0); 385(0.98); 452(0.47)[c]	*170c*
$[(O)_2Mo^{VI}Bdt)_2]^{2-}$	Mo=O, 858, 829; Mo–S, 356, 322[b]	—	*170d*
$[(O{=}Mo^{IV}(Tdt)_2]^{2-}$	Mo=O, 905; Mo–S, 357[b]	331(11.0); 380(0.7); 454(0.37)[c]	*170c*
$[(O)_2Mo^{VI}(Tdt)_2]^{2-}$	Mo=O, 863, 835; Mo–S, 381, 358, 329, 318[b]	—	*170d*
$[(O)_2Mo^{VI}(MNT)_2]^{2-}$	Mo=O, 885, 851; Mo–S, 354, 330, 313; C=C, 1472[b]	—	*170a*
	Mo=O, 890, 855[b]	365(6.2); 425(6.9); 525(1.62)[c]	*171b*

[a] The cyclic voltammetry of the complex (obtained on a Pt electrode) shows two reversible waves at +0.020 and +0.420 V vs. Ag/AgCl in CH_3CN solution.

[b] In KBr disk.

[c] In CH_3CN solution.

A report of a new strategy for the synthesis of ene-1,2-dithiolate complexes has appeared (*173b*) [Eq. (8)]:

$$(\mathrm{L})_x\mathrm{M}^n(\mathrm{S})_2 + \mathrm{R}(\mathrm{C}_2)\mathrm{R} \rightarrow (\mathrm{L})_x\mathrm{M}^{n-2}(\mathrm{dithiolene}) \qquad (8)$$

where $(\mathrm{L})_x\mathrm{M} = \{\mathrm{HB(Me_2pz)_3}\}\mathrm{WX}$. The reaction of $\{[\mathrm{O{=}Mo}(\eta^2\cdot\mathrm{S_2})_2]_2(\mu\text{-S})\}^{2-}$ with DMA affords a mixture of products with infrared spectra (Table VIII) that suggest the presence of both the anti and syn isomers of $[(\mathrm{DMAD})(\mathrm{Mo_2O_2S_2})(\mathrm{DMAD})]^{2-}$. The structures of both of these isomers have been determined (*25*) (Table VI). The anti geometry is rarely found with the $(\mathrm{Mo_2O_2S_2})^{2+}$ unit. A change of the Mo oxidation state, from +6 in $\{[(\eta^2\text{-S}_2)_2\mathrm{Mo(O)}]_2(\mu\text{-S})\}^{2-}$ to +5 in the DMAD products, suggests that internal electron transfer has taken place with oxidation of a S_x^{2-} ligand to elemental sulfur.

3. *Addition of SO_2 to the Thiomolybdate Complexes*

The Mo–S_x bonds (x = 1, 2, 4) within the $\mathrm{Mo(O)(S}_x)$ units react readily with $\mathrm{SO_2}$ to give various products that contain thiosulfite, thiosulfate, sulfite, or sulfate ligands (Tables V and VI). These reactions are best described as electrophilic additions to the Mo–S_x bond and in many instances may be subject to the effects of the spectator Mo=O group (see Section III,B).

The reaction of either $[(\mathrm{S_4})(\mathrm{Mo_2O_2S_2})(\mathrm{S_2})]^{2-}$ or $\{[(\mathrm{S_4})(\mathrm{Mo_2O_2S_2})(\mathrm{S})]_2\}^{4-}$ with $\mathrm{SO_2}$ in $\mathrm{CH_3CN}$ solution at ambient temperature affords (Fig. 31), on standing for 12 hr, the $[(\mathrm{S_2O_3})$

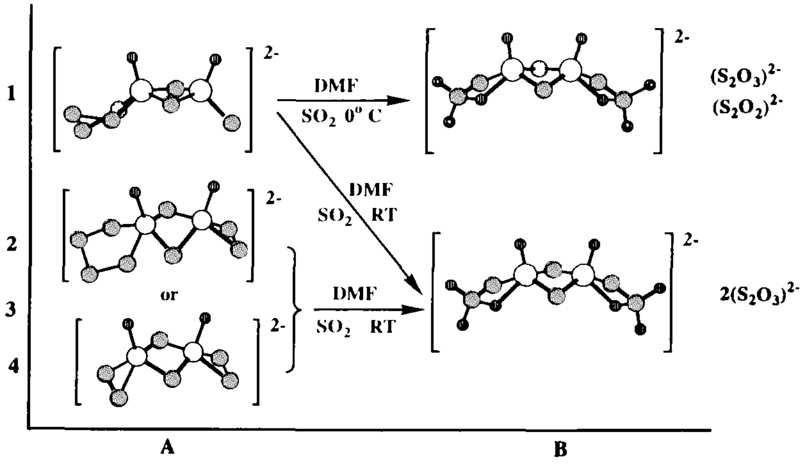


FIG. 31. Addition of $\mathrm{SO_2}$ to tertiary thiomolybdate complexes.

$(Mo_2O_2S_2)(S_2O_3)]^{2-}$ complex (Fig. 31, structure 3B). The same reaction at 0°C results in the $[(S_2O_2)(Mo_2O_2S_2)(S_2O_3)]^{2-}$ complex, where the $S_2O_2^{2-}$ and $S_2O_3^{2-}$ ligands are disordered and distributed equally among the two ligand sites (Fig. 31, structure 1B). In shorter reaction times (~2 hr), at ambient temperature, the $[(S_4)(Mo_2O_2S_2)(S_2O_3)]^{2-}$ complex is obtained. The reaction in DMF solution for ~3 hr also affords the $[(S_2O_3)(Mo_2O_2S_2)(S_2O_3)]^{2-}$ complex (*113*).

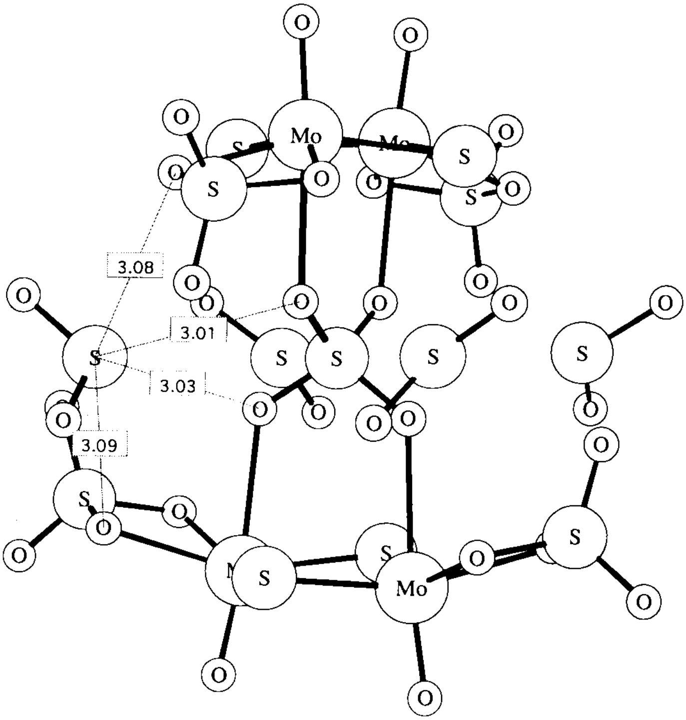
At high temperature (~110°C), in DMF solution, the $[(DMF)_3(Mo_2O_2S_2)(SO_4)]^{2-}$ and $[(SO_4)(Mo_2O_2S_2)(SO_4)]^{2-}$ complexes form from reactions of SO_2 with $[[(S_4)(Mo_2O_2S_2)(S_2)]^{2-}$ or $\{[(S_4)(Mo_2O_2S_2)(S)]_2\}^{4-}$, respectively. The $[(DMF)_3(Mo_2O_2S_2)(SO_4)]^{2-}$ also is obtained by the stoichiometric reaction of $[(DMF)_3(Mo_2O_2S_2)(DMF)_3]^{2+}$ with $(Et_4N)_2SO_4$ in CH_3CN solution. The lability of the SO_4^{2-} ligands in these complexes makes them ideally suited for the synthesis of other complexes that contain the $(Mo_2O_2S_2)^{2+}$ core.

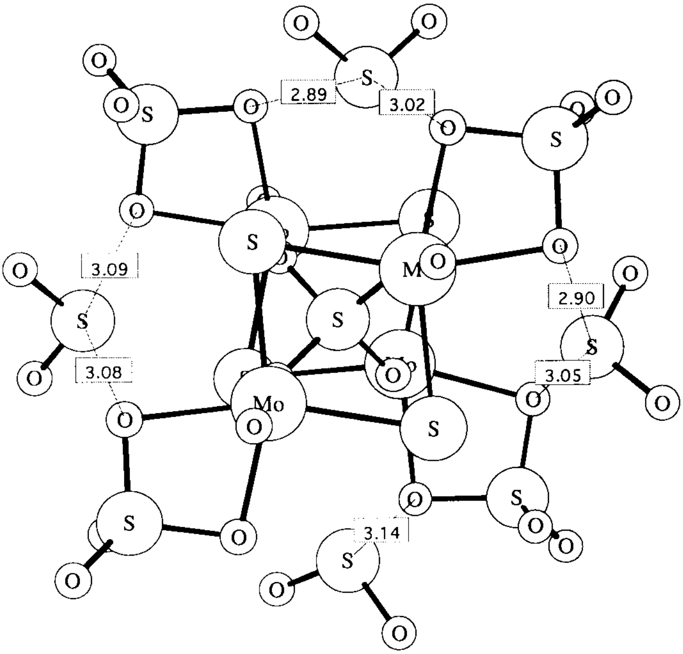
A series of interesting tetrameric molecules is isolated when some of the SO_2 reactions described above are carried out in the presence of the $(CH_3)_2NH_2^+$ cation (*113*, *174*). The $(Et_4N)_x((CH_3)_2NH_2)_{6-x}\{\{[SO_4][Mo_2O_2S_2][SO_4]\}_2\mu_4\text{-}SO_4\}^{6-}$ complexes ($x = 1, 2, 3$) (Fig. 32) contain a central $\mu_4\text{-}SO_4^{2-}$ ligand that is "trapped" by interdimer hydrogen bonds between the $\eta^2\text{-}(SO_4)^{2-}$ ligands and the $(CH_3)_2NH_2^+$ cations.

The reaction of SO_2 with the $[(Cp)(Mo_2O_2S_2)(S_2)]^-$ complex at 0°C in CH_3CN solution gives $[(Cp)(Mo_2O_2S_2)(SO_3)]^-$. At ambient temperature similar reactions between SO_2 and either $[(Cp)(Mo_2O_2S_2)(S_2)]^-$ or $[(Cp)(Mo_2O_2S_2)(S)]^-$ in CH_3CN solution afford $[(Cp)(Mo_2O_2S_2)(S_2O_3)]^-$. At higher temperatures (~100°C) similar reactions in DMF solution give $[(Cp)(Mo_2O_2S_2)(SO_4)]^-$. All three of these complexes have been structurally characterized (Fig. 33) and are shown to contain in the $[Mo_2O_2S_2]^{2-}$ core an η^5-Cp ligand and bidentate $(SO_3)^{2-}$, $(S_2O_3)^{2-}$, and $(SO_4)^{2-}$ ligands.

The reaction of $[(Cp)(Mo_2O_2S_2)(S)]^-$ with SO_2 was monitored by ^1H NMR spectroscopy in an SO_2-saturated $CH_3CN\text{-}d_3$ solution in a sealed NMR tube (*175*). A variety of $[(Cp)(Mo_2O_2S_2)(L)]^-$ products were identified over a period of time by the characteristic resonances of the Cp^- ligand protons. Definite assignments of the $(SO_3)^{2-}$, $(S_2O_3)^{2-}$, and $(SO_4)^{2-}$ products were made by comparison to the NMR resonances of isolated, structurally characterized, "authentic" samples. A correlation between the chemical shift and the sum of the Pauling electronegativities for the atoms in the $(S_xO_y)^{2-}$ ligands was used (*113*) to

FIG. 32. Two orientations of the structure of the $\{\{[SO_4][Mo_2O_2S_2][SO_4]\}_2\mu\text{-}SO_4\}^{6-}$.


3.08
3.01
3.03
3.09
Mo
Mo
Mo
S
O


2.89
3.02
3.09
2.90
3.08
3.05
3.14
Mo
S
O

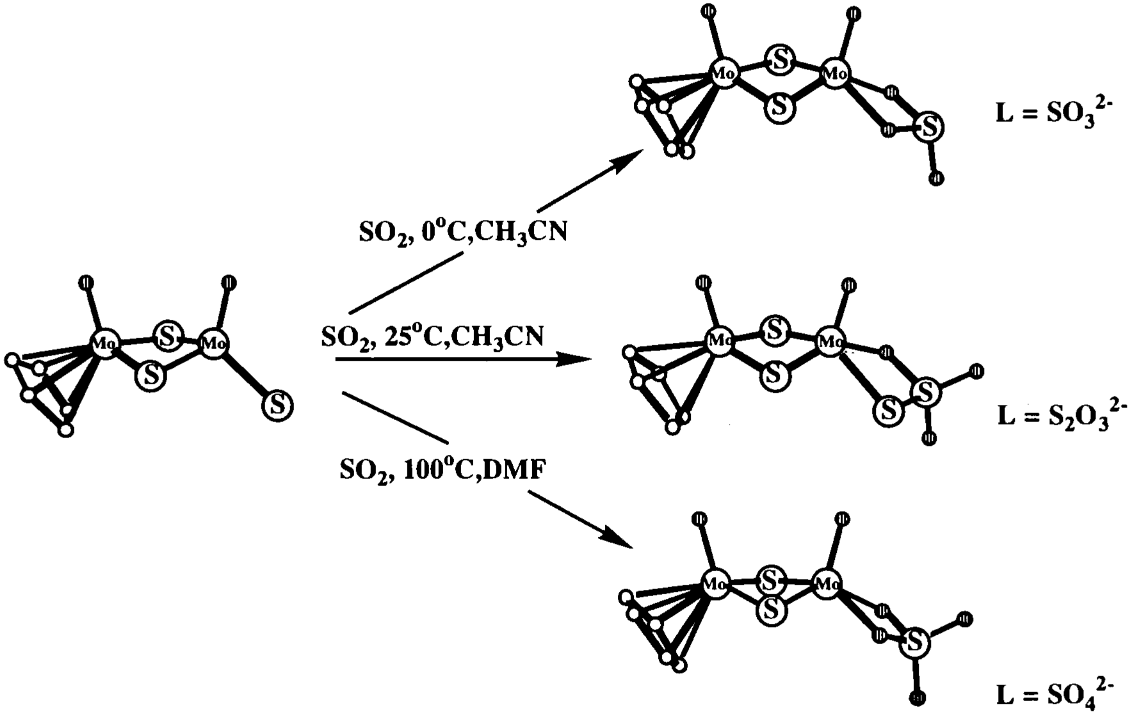


FIG. 33. Addition of SO_2 to the $[(Cp)(Mo_2O_2S_2)(S_x)]^-$ complexes ($x = 1, 2$).

assign resonances for complexes in solution with L = $(S_2O_2)^{2-}$ and $(S_2O)^{2-}$

D. ROLE OF THE Mo=S GROUP IN THE ACTIVE SITE OF XANTHINE OXIDASE

Reactivity studies of the $(O)Mo^{VI}(S)$ groups (*103*) in the oxo/thiomolybdate complexes clearly show the greater comparative reactivity of the $Mo^{VI}{=}S$ group relative to the $Mo^{VI}{=}O$ group. The results of these studies have led to the suggestion (*103*) that the Mo=S group may be a site of exceptional reactivity in the $(O)Mo^{VI}(S)$ chromophore in xanthine oxidase. The presence of the latter in the Mo cofactor has been suggested on the basis of analysis of Mo extended X-ray absorption fine structure (EXAFS) data (*176*). The data (for the reduced form of the cofactor) show that the first coordination sphere around the Mo atom contains the Mo(O)(S) unit (Fig. 34).

A modification of the first step in the proposed minimal mechanism (*177*) for the oxidation of xanthine to uric acid has been suggested (*103*). In this modification xanthine (RH) initially inserts into the $Mo^{VI}{=}S$ bond by an initial electrophilic attack by the Mo^{VI} at the C-8 position of xanthine. Subsequently the S atom accepts the C-8 proton to form $R\text{-}Mo^{VI}(O)SH$ (Fig. 35). Events that follow include (1) internal $2e^-$ reduction of the Mo and electrophilic attack by R^+ on the Mo=O group and (2) hydroxylation of the Mo^{IV} center to eventually form $RO\text{-}Mo^{IV}(O)SH$ (Fig. 35), as proposed in the original mechanism (*177*).

The reactivity of the Mo=S chromophore in the Mo center of xanthine oxidase also has been revealed in the reaction of this enzyme with bisulfite, which is a competitive inhibitor of xanthine oxidase (*178*). The $(HSO_3)^-$ inhibitor is a protector of the enzyme against cyanolysis and a 1:1 complex of the inhibitor and the enzyme has been isolated. The proposed mode of interaction involves the Mo=S group directly (Fig. 36). The suggestion that the interaction product very

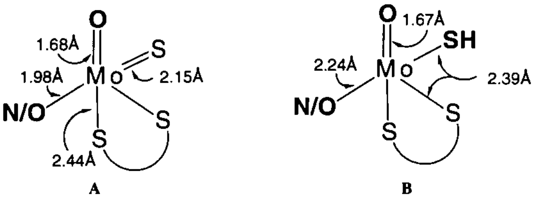


FIG. 34. The Mo coordination spheres in (A) the oxidized and (B) the reduced forms of xanthine oxidase as derived from EXAFS analyses (Data from Ref. *176*).

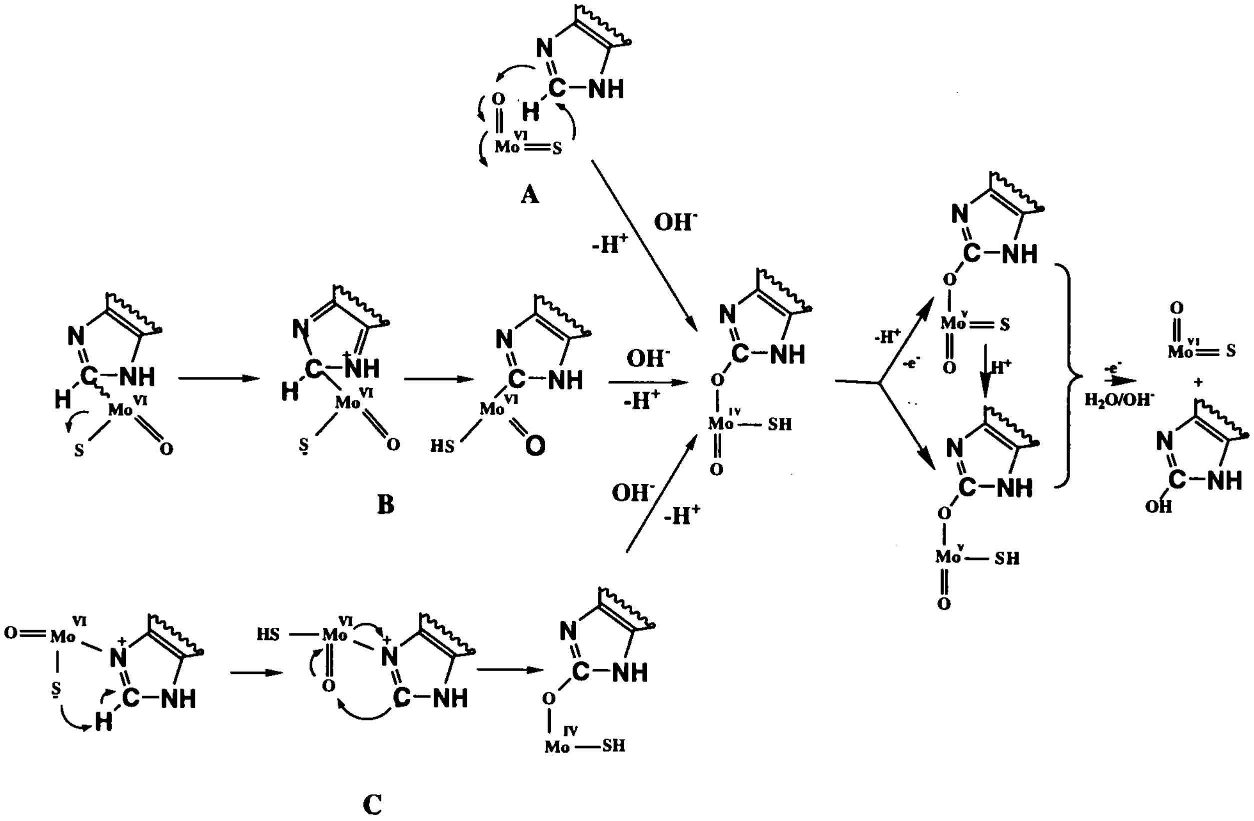


FIG. 35. Possible mechanisms for the action of xanthine oxidase (A, data from Ref. *177;* B, data from Ref. *103*).

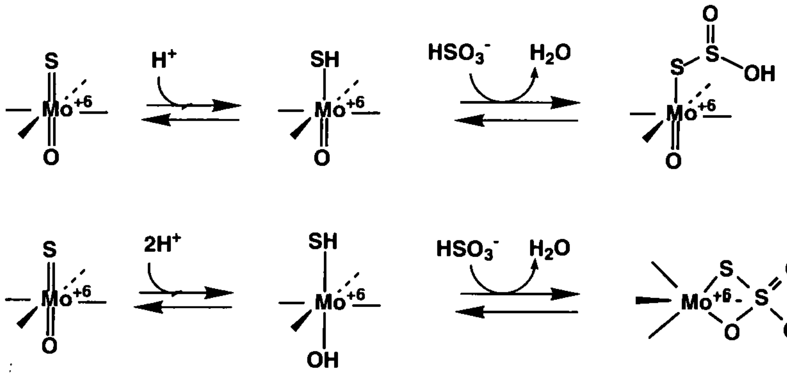


FIG. 36. Proposed mechanism of xanthine oxidase inhibition by $(HSO_3)^{2-}$ (Data from Ref. *178*).

likely contains an Mo-bound protonated thiosulfate ligand is supported by recent work with the $[(S)(Mo_2O_2S_2)(S_4)]^{2-}$ complex (*179*). The latter reacts with HSO_3^- and the isolated and structurally characterized product indeed contains a protonated thiosulfate ligand that presumably forms by insertion of the HSO_3^- anion into the Mo=S bond. The possible involvement of the Mo=S group in xanthine oxidase function also is suggested by recent ^{13}C electron and nuclear double resonance (ENDOR) studies (*180*). These studies show that the (^{13}C-labeled) formaldehyde-inhibited xanthine oxidase center has a carbon bound to the Mo atom at 1.9 Å. The proposed arrangement that places a C atom 1.9 Å from the Mo atom (Fig. 37A) is supported

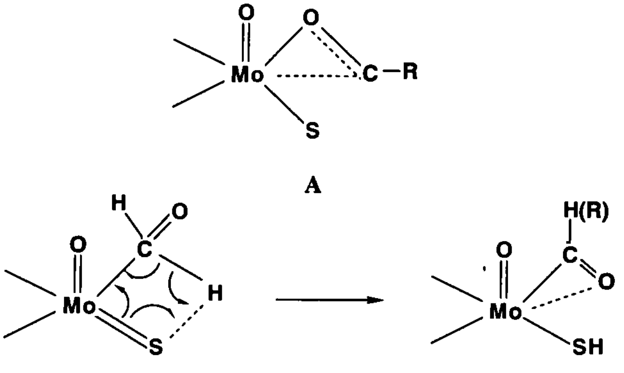


FIG. 37. Proposed modes of interaction of formaldehyde with the Mo cofactor in xanthine oxidase (A, after Ref. *180*).

by EXAFS studies (*181*) and could in fact be the result of a formaldehyde C–H bond addition to the active Mo=S group (Fig. 37B). It is quite clear that enough evidence exists that points to the involvement of the Mo=S group in xanthine oxidase function. Indeed, the reactivity patterns observed with model complexes that contain the Mo(O)(S) group suggest that the Mo=S is a site of preferential reactivity. Very recently ^{17}O and ^{13}C ENDOR measurements and kinetic studies (*182*) on xanthine oxidase have been interpreted in terms of the formal addition of xanthine across the Mo=S bond rather than involving the direct participation of the Mo=O group. These studies are in agreement with the mechanism proposed (*103*) earlier.

V. List of Abbreviations

HDS	Hydrodesulfurization
R_2Dtc	Dialkyldithiocarbamate
Cp	Cyclopentadienyl anion
Me-Cp	Methylcyclopentadienyl anion
Bdt	Benzenedithiolate dianion
PhS	Thiophenolate anion
Tdt	Toluenedithiolate anion
Bipy	2,2-Bipyridine
Phen	1,10-Phenanthroline
CH_3CN	Acetonitrile
Et_4N^+	Tetraethylammonium
DMF	Dimethylformamide
Ph_4P^+	Tetraphenylphosphonium
Ph_4As^+	Tetraphenylarsonium
H_2Salen	Salicylaldimine
NMR	Nuclear magnetic resonance
Ph_3P	Triphenylphosphine
TTN	Trithiacyclononane
^{i}Pr	Isopropyl
^{n}Bu	*n*-Butyl
H_4EDTA	Ethylenediaminetetraacetic acid
H_2Cys	Cysteine
Cp*	Pentamethylcyclopentadienyl anion
Edt	Ethanedithiolate dianion
H_3NTA	Nitrilotriacetic acid
THF	Tetrahydrofuran
DMA	Dicarbomethoxy acetylene
H_2DMAD	1,2-Dicarbomethoxy-2,2-ethylenedithiol

PEt_3	Triethyl phosphine
H_2VDS	1,2-Dicarbomethoxy vinyl disulfide
H_2MNT	1,2-Dicyanoethylene-1,2 ethylenedithiol
Dmpe	Dimethylphosphino ethane
PPh_3	Triphenylphosphine
H_2Dtp	Dithiophosphoric acid

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