UNIQUE REACTIVITY CHARACTERISTICS OF Mo-COORDINATED S_2^{2-} AND S_4^{2-} LIGANDS

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Abstract—The synthesis of the new dithiolene complexes, $[\{(MeOOC)_2C_2S_2\}_2Mo(\mu_2-S)]_2^-$ and $[OMo(S_2C_2(COOMe)_2)_2]^{2-}$, is reported. These complexes are obtained by the reaction of dicarbomethoxyacetylene (DMA) with either $[(S_4)Mo(S)(\mu_2-S)_2Mo(S)(S_4)]^{2-}$ or $[(CS_4)Mo(S)(\mu_2-S)_2Mo(S)(CS_4)]^{2-}$ and $[OMo(S_4)_2]^{2-}$, respectively. The reaction of $[(S_4)Mo(O)(\mu_2-S)_2Mo(O)(S_2)]^{2-}$ with DMA results in the new dithiolene complex $[\{(MeOOC)_2C_2S_2\}Mo(O)(\mu_2-S)]_2^-$, which is the isomeric form of the vinyl disulfide complex obtained in the reaction of the $[(S_2)Mo(O)(\mu_2-S)_2Mo(O)(S_2)]^{2-}$ complex with DMA. The difference in reactivity between the two complexes that contain the same $[Mo_2O_2S_2]^{2+}$ core is attributed to the intrinsically different reactivity characteristics of the S_4^{2-} and S_2^{2-} ligands. As a result of Mo–S $d_\pi-p_\pi$ bonding an alternation in the S—S bond lengths is observed in virtually all of the structurally characterized Mo-S_4 units. The consequent weakening of the S—S bonds adjacent to the Mo—S bonds allows for the ready dissociation of S_2^0 from the Mo-coordinated S_4^{2-} ligands. This weakening also accounts for the facile formation of dithiolenes in cycloaddition reactions of alkynes with the Mo-S_4 units. By comparison, the S—S bond in side-on Mo-coordinated S_2^{2-} ligands is strengthened as a result of depopulation of the ligand π^*-orbitals. Reactions of the latter with alkynes do not proceed by cycloaddition. Instead, insertion into the Mo—S bond has been reported for at least one such reaction. The importance of activated polysulfide ligands in the hydrodesulfurization reaction is discussed.

The extensive chemistry of molecular binary molybdenum sulfide compounds presents a unique opportunity for the study of units which may be structurally and electronically similar to the Mo–S active sites in the catalysts employed in the hydrodesulfurization (HDS) reaction.

The wide variety of binary molybdenum sulfides that have emerged in recent years derives primarily from the reactivity of the MoS_4^{2-} dianion toward sulfur reagents. The complex equilibria and interconversions between Mo thioanions that prevail in MoS_4^{2-}–$(NH_4)_2S_x$ or MoS_4^{2-}–S_8 solutions, in aqueous or non-aqueous media, have been described.[1] Depending on the conditions employed and the nature of the counterions salts of thioanions, such as $[Mo_2(S_2)_6]^{2-}$,[2] $(MoS_9)^{2-}$,[1]

$[Mo_2(S)_4(S_2)(S_4)]^{2-}$,[1,3] $[Mo_2(S)_4(S_4)_2]^{2-}$,[1] $[(MoS_4)_2MoS]^{2-}$,[4] $(Mo_3S_{13})^{2-}$[5] and $(Mo_2S_8)^{2-}$,[6] can be isolated from these solutions in crystalline form and their structures have been determined (Fig. 1).

The reaction chemistry of the Mo thioanions with electrophilic reagents is extensive. With electrophiles such as CS_2 and dicarboalcoxyacetylenes the $(MoS_9)^{2-}$ and $[Mo_2(S)_4(S_4)_2]^{2-}$ anions react to form the $[(CS_4)_2MoS]^{2-}$,[7] $[Mo_2(S)_4(CS_4)_2]^{2-}$[7] and $\{Mo[S_2C_2(COOR)_2]_3\}^{2-}$[8] complexes. The CS_4^{2-} and dithiolene ligands in these compounds possibly are generated by cycloaddition reactions to the coordinated S_x^{2-} ligands. The $[Mo_2S_6O_2]^{2-}$ anion displays unique reactivity in its reaction with dicarbomethoxyacetylene and forms the very interesting $\{Mo_2O_2S_2[SSC_2(COOMe)_2]_2\}^{2-}$ complex.[9] In the latter, insertion of the alkyne into the

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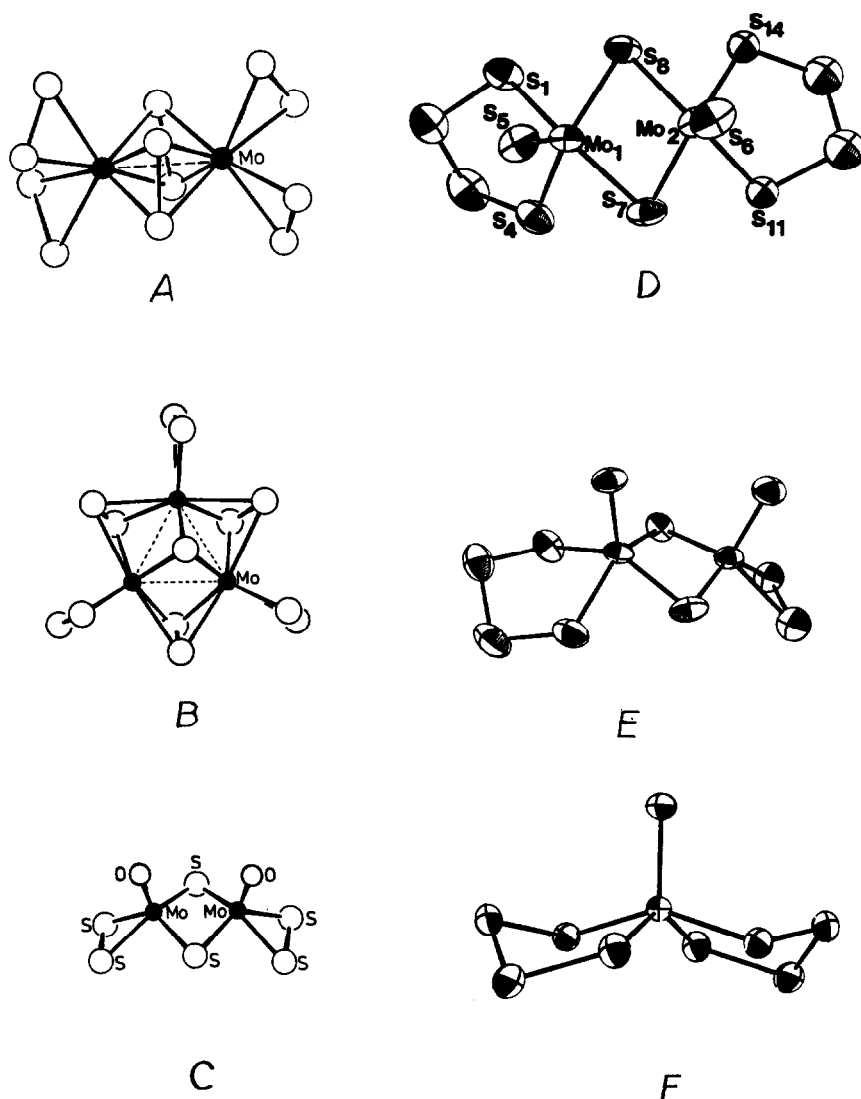
Fig. 1. Structures of: (A) $[Mo_2(S_2)_6]^{2-}$,[2] (B) $(Mo_3S_{13})^{2-}$,[5] (C) $(Mo_2S_8)^{2-}$,[6] (D) $[Mo_2(S)_4(S_4)_2]^{2-}$,[1] (E) $[Mo_2(S)_4(S_2)(S_4)]^{2-}$,[1,3] and (F) $[MoS_9]^{2-}$ and $[MoS_8O]^{2-}$.[1]

Mo—S bond results in the formation of a vinyl disulfide chelate ligand which is S,C bound to the Mo(V) ion.

The reactivity of the Mo thioanions often can be attributed to facile intramolecular charge-transfer or redox processes that activate the Mo–S_x units prior to their reactions with electrophiles.[6] This reactivity depends on the nature of the S_x^{2-} ligand coordinated to the Mo atom and appears to be different for the S_4^{2-} ligands by comparison with the S_2^{2-} ligands. This difference in reactivity reflects the structural and electronic differences between the "side-on" bonded S_2^{2-} ligand and the chelating S_4^{2-} ligands.

The S—S bond in the "side-on" coordinated S_2^{2-} ligand in the Mo–S_2 units is longer than the S—S bond in S_2^0 but shorter than the S–S single bond in S_2^{2-}. By contrast a pronounced lengthening of the S—S bonds adjacent to the Mo atom in the Mo–CS_4 and Mo–S_4 units is readily apparent in virtually all of the structurally characterized complexes that contain these units. This structural effect has been attributed previously to significant S—Mo p_π–d_π bonding[1] and results in an alternation of the S—S bonds lengths within the Mo-coordinated S_4^{2-} ligand.

Recently we have been exploring the comparative reaction chemistry of the Mo–S_2 and Mo–S_4 units. In this paper we present evidence for the difference in the reactivity characteristics of the Mo–S_4 and Mo–S_2 units.

EXPERIMENTAL

Synthesis

The chemicals in this research were used as purchased. Acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and diethyl ether were distilled over calcium hydride. Dimethyl acetylene dicarboxylate (DMA) was distilled under reduced pressure at $\sim 50°C$. All syntheses were carried out under a dinitrogen atmosphere.

Physical methods

Visible and UV spectra were obtained on Cary Model 118 and 219 spectrophotometers. A Debye–Scherrer camera with nickel-filtered copper radiation was utilized to obtain X-ray powder diffraction patterns.

Electrochemical measurements were performed with a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 universal programmer. The electrochemical cell used had platinum working and auxiliary electrodes. As the reference electrode a saturated calomel electrode was used. All solvents used in the electrochemical measurements were properly dried and distilled, and tetra-n-butylammonium perchlorate was used as the supporting electrolyte. Normal concentrations used were ~ 0.001 M in the electroanalyte and 0.1 M in the supporting electrolyte. Purified dinitrogen was used to purge the solutions prior to the electrochemical measurements.

Preparation of compounds

Bis(tetraphenylphosphonium)bis(μ - thio)(bis - [bis(1, 2 - dimethylcarboxylate)dithioethylene) molybdate(V)] ($(Ph_4P)_2[Mo_2S_2(S_2C_2(COOMe)_2)_4]$). *Method A.* To a solution of $(Ph_4P)_2Mo_2S_{10}/S_{12} \cdot \frac{1}{2}$ DMF^1 (0.52 g, 0.42 mmol) in 300 cm^3 of CH_3CN was added with stirring 0.21 cm^3 (1.67 mmol) of freshly distilled DMA. The ensuing brown solution was refluxed for *ca* 30 min. The color of the solution changed to violet and then to a final green color. Upon cooling to ambient temperature and removing the solvent *in vacuo*, a green residue was obtained. The residue was washed with a 30-cm^3 portion of

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* A detailed description of the structures of

$$\{Mo_2S_2[S_2C_2(COOMe)_2]_4\}^{2-}$$

and

$$[OMo(S_2C_2COOMe)_2]^{2-}$$

will be published elsewhere.

CH_2Cl_2 and the remaining solid was dissolved in the minimum amount of a $DMF-CH_2Cl_2$ (6 : 1) mixture. The slow diffusion of diethyl ether resulted in the formation of green crystals. The yield after drying was 0.22 g (26%).

Method B. To a solution of 0.26 g (0.21 mmol) of $(Ph_4P)_2Mo_2S_4(CS_4)_2 \cdot \frac{1}{2}DMF^7$ in the minimum amount of CH_3CN was added 0.10 cm^3 (0.80 mmol) of freshly distilled DMA. After refluxing for *ca* 30 min. the dark solution was allowed to cool to ambient temperature and the solvent was removed under vacuum. A workup procedure similar to the one described in Method A above yielded 0.10 g of product (26% yield). The X-ray powder pattern, electrochemistry and electronic spectrum of this material was identical to the product obtained by Method A. The X-ray powder pattern of the crystalline product is identical to the pattern calculated on the basis of the single-crystal X-ray diffraction data.*

Electronic spectrum

680 nm ($\varepsilon = 10,600$); 582 nm ($\varepsilon = 14,600$); 430 nm (sh) and 380 nm ($\varepsilon = 20,000$).

IR spectrum (selected characteristic vibrations)

$\nu(C\!=\!O)$: 1705(s), 1675(s) and 1650 cm^{-1}; 1220 cm^{-1} (v.s. broad absorption).

Electrochemical data

The cyclic voltammogram (in CH_3CN) of this material shows a quasireversible reduction at -0.67 V and an irreversible oxidation at $+0.85$ V (vs SCE).

Bis(tetraethylammonium)bis(1,2 - dimethyl - carboxylate)dithioethylene oxomolybdate(IV) ($(Et_4N)_2MoO(S_2C_2COOMe)_2)_2$. To a solution of 2.0 g (3.18 mmol) of recrystallized $(Et_4N)_2MoO(S_4)_2$ in *ca* 350 cm^3 of CH_3CN was added 0.9 cm^3 (7.32 mmol) of DMA. The reaction mixture was stirred for 10 min and an orange red solution was obtained. The solution was concentrated to 30 cm^3, by evaporation of the solvent *in vacuo*, and then filtered. To the filtrate was added 100 cm^3 of tetrahydrofuran (THF). Upon standing, a solid deposited, was isolated and washed with three 30-cm^3 portions of THF. The crude product was recrystallized from a concentrated CH_3CN solution upon addition of THF and standing at ambient temperature for *ca* 10 h. Brown red needles formed and were isolated. The yield after drying was 1.20 g (48.1%). The powder pattern of this compound was identical to the pattern calculated on the basis of single-crystal X-ray diffraction data.[10]
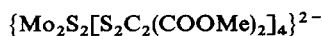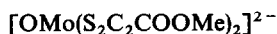
RESULTS AND DISCUSSION

Synthetic studies

Our studies of the reactions of the $(MoS_9)^{2-}$, $(Mo_2S_{10})^{2-}$ and $(Mo_2S_{12})^{2-}$ complexes thus far have shown that these anions readily react with CS_2. The crystalline $[(CS_4)_2MoS]^{2-}$, *(cis* or *trans)* and $[(CS_4)_2Mo_2S_4]^{2-}$ anions contain the S–S chelating perthiocarbonate ligand[7] (Fig. 2). The reaction of $(MoS_9)^{2-}$ with 2-butynedimethanoate (DMA) also proceeds smoothly and the $\{Mo[S_2C_2(COOCH_3)_2]_3\}^{2-}$ anion contains the bidentate $[S_2C_2(COOCH_3)]^{2-}$ ligands and a nearly trigonal prismatic MoS_6 core[8] (Fig. 3B). Under the assumption that the $\{Mo[S_2C_2(COOCH_3)_2]_3\}^{2-}$ complex was a final product of a series of intermediate Mo–sulfido-dithiolene complexes we proceeded with a detailed study of the reactions of the Mo thioanions with DMA. The $[(CS_4)_2Mo_2S_4]^{2-}$ and $[(S_4)_2Mo_2S_4]^{2-}$ anions react with DMA in a 1:4 molar ratio to afford in modest yields the $\{Mo_2S_2[S_2C_2(COOMe)_2]_4\}^{2-}$ anion[10] (1) (Fig. 3A). The synthesis of 1 can also be accomplished by the reaction of $(MoS_9)^{2-}$ with DMA under *aerobic* conditions. The same reaction under a N_2 atmosphere affords the $\{Mo[S_2C_2(COOCH_3)_2]_3\}^{2-}$ complex. A clue regarding the possible reaction pathway toward the synthesis of 1 from $(MoS_9)^{2-}$ is provided by the corresponding reaction of $[MoS_8O]^{2-}$
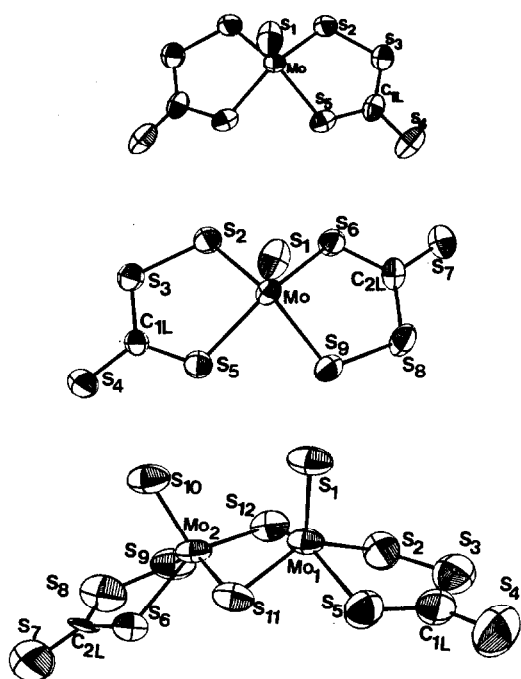
with DMA. In the latter reaction, the $\{OMo[S_2C_2(COOMe)_2]\}^{2-}$ complex is obtained[10] (Fig. 3C) and contains five-coordinate Mo(IV). By analogy, it is reasonable to assume that the MoS_9^{2-} anion reacts with DMA initially to form the $\{SMo[S_2C_2(COOMe)_2]\}^{2-}$ complex. Oxidation
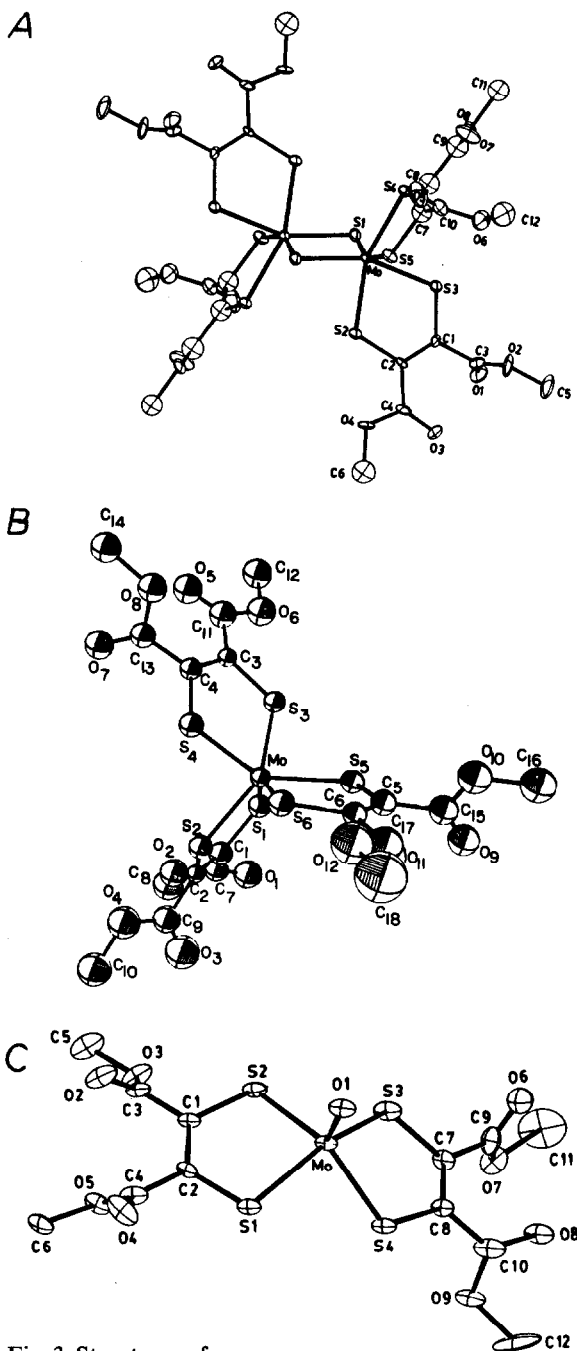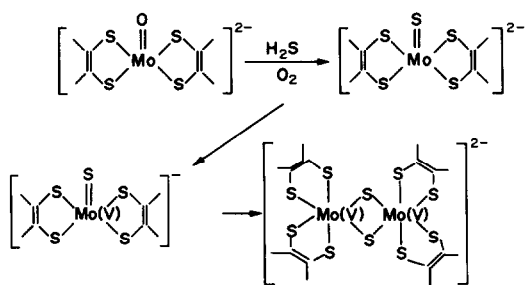
Fig. 3. Structures of:

(A) $\{Mo_2S_2[S_2C_2COOMe)_2]_4\}^{2-}$,[10]

(B) $\{Mo[S_2C_2(COOMe)_2]_3\}^{2-}$,[8]

and

(C) $\{OMo[S_2C_2(COOMe)_2]\}^{2-}$.[10]

Fig. 2. Structures of *cis*- and *trans*-$[(CS_4)_2MoS]^{2-}$ and of $[(CS_4)_2Mo_2S_4]^{2-}$.[7,19]

Fig. 4. Reaction of $\{OMo[S_2C_2(COOMe)_2]\}^{2-}$ with H_2S.

of this complex to the monoanion followed by dimerization will result in the formation of **1**. This assumption is supported by the reaction of $\{OMo[S_2C_2(COOMe)_2]\}^{2-}$ with H_2S. The only product that can be isolated from this reaction (Fig. 4) is I.

The formation of the $[S_2C_2(COOMe)_2]^{2-}$ ligand in the reactions of Mo-coordinated S_4^{2-} ligands with DMA contrasts with the reaction of the coordinated S_2^{2-} ligand in the $[Mo_2S_6O_2]^{2-}$ anion (Fig. 1C). The latter inserts DMA into the Mo—S bond with formation of a product that contains the S–C-coordinated vinyl disulfide ligand[9] (Fig. 5).

The $[(S_4)MoO(\mu\text{-}S)_2Mo(O)(S_2)]^{2-}$ complex reacts with DMA at ambient temperature to give the same vinyl disulfide complex (Fig. 5). The same reaction under reflux conditions affords the $[(L)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^{2-}$ dithiolene isomer,[11(a)] $\{L = [S_2C_2(COOR)_2]^{2-}\}$. Apparently, the $[Mo_2S_6O_2]^{2-}$ anion (Fig. 1C), obtained by dissociation of S_2^0 from the $[(S_4)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2)]^{2-}$ complex, reacts rapidly with DMA
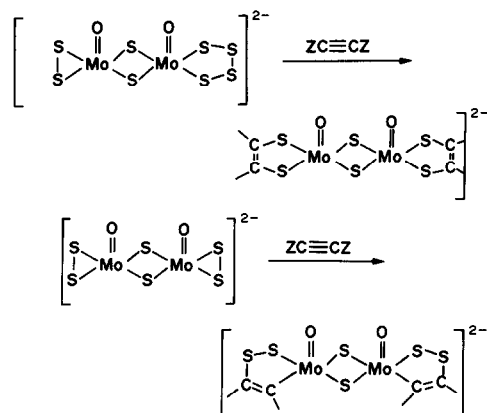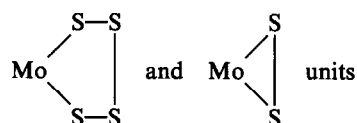

Fig. 5. Reactions of dicarbomethoxyacetylene with the

units

to form the vinyl disulfide complex. The latter, as verified by NMR spectral changes, rearranges thermally to the dithiolene dimer (Fig. 5). A similar thermal rearrangement was observed[11(b)] previously in the formation of the $(Cp)_2Ti[S_2C_2(COOR)_2]$ dithiolene complex from the corresponding vinyl disulfide isomer.

Reactivities of the Mo-coordinated S_4^{2-} and S_2^{2-} ligands

An examination of the structural data available for the Mo-coordinated S_4^{2-} ligands (Table 1) and the

Table 1. Influence of M–S bonding on the S–S bonding of the coordinated S_4^{2-} ligands

| Compound[a]	S(1)—S(2)	S(2)—S(3)	S(3)—S(4)	M—S(1)	M—S(4)	Reference
$(Et_4N)_2Zn(S_4)_2$[b]	2.045(4)	2.044(5)	2.062(5)	2.376(3)	2.331(3)	14
	2.034(5)	2.032(5)	2.056(5)	2.343(2)	2.354(3)	
$(Et_4N)_2Ni(S_4)_2$[c]	2.073(2)	2.037(4)	2.073(2)	2.185(2)	2.185(2)	14, 15
$(Ph_3P)_2PtS_4$	2.024(8)	2.022(10)	2.081(10)	2.360(6)	2.366(5)	16
$(Ph_4P)_2Mo_2S_{10}$[d]	2.093(4)	2.018(4)	2.053(3)	2.399(2)	2.427(2)	1
$(Ph_4As)_2Mo_2S_{10}$[e]	2.019(5)	1.970(6)	2.115(5)	2.409(2)	2.403(3)	3
$(Et_4N)_2MoS_9$	2.107(1)	2.012(1)	2.166(1)	2.387	2.331(1)	1
$(Et_4N)_2MoS_8O$	2.120(3)	2.008(3)	2.159(3)	2.395(2)	2.363(2)	1
$(\eta^5\text{-}C_5H_5)_2Mo(S_4)$	2.081(8)	2.018(9)	2.085(7)			17
$(\eta^5\text{-}C_5H_5)_2W(S_4)$	2.105(7)	2.016(8)	2.116(9)			18

[a] Distances in Å.
[b] The $[Zn(S_4)_2]^{2-}$ anion contains two crystallographically independent S_4^{2-} ligands.
[c] The $[Ni(S_4)_2]^{2-}$ anion possesses D_2-symmetry.
[d] For the S_4^{2-} ligand not subject to disorder.
[e] From the major component in a disordered structure.

Table 2. Influence of M–S bonding on the structural parameters of the coordinated CS_4^{2-} ligands
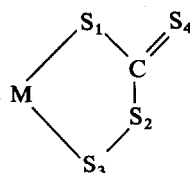
Compound[a]	M—S(1)	M—S(3)	S(2)—S(3)	S(1)—C	S(2)—C	S(4)—C	Reference
$(Ph_4P)_2Ni(CS_4)_2$	2.174(2)	2.165(2)	2.064(2)	1.707(4)	1.711(5)	1.678(4)	14
$(Et_4N)_2Mo(S)(CS_4)_2$ (*trans*)[b]	2.386(3)	2.320(3)	2.102(5)	1.735(12)	1.719(12)	1.640(11)	
	2.380(3)	2.333(3)	2.100(5)	1.739(12)	1.709(12)	1.662(11)	7
$(Ph_4P)_2Mo(S)(CS_4)_2$ (*cis*)	2.376(3)	2.320(3)	2.105(4)	1.756(10)	1.726(11)	1.615(9)	19

[a] Distances in Å.

[b] Contains two symmetry-independent CS_4^{2-} ligands.

S_2^{2-} ligands[12] shows that the effect of coordination is quite different for the two ligands. Thus, the S—S bond length in the "side-on" bound S_2^{2-} ligands ranges[12] from 2.03 to 2.074(5) Å and is slightly longer than the S—S bond in elemental S_8. By contrast, an alternation in the S—S bond lengths is apparent in the bidentate S_4^{2-} ligand in complexes that contain the Mo–S_4 unit. The significant elongation of the S—S bonds directly adjacent to the Mo atom correlates directly with a shortening of the corresponding Mo—S bonds and suggests that bonding electrons from the S—S bond are transferred to Mo–S bonding orbitals. The facile transfer of this type most likely arises as a result of the effective energy matching of the appropriate atomic wavefunctions.*

The ease by which the coordinated S_4^{2-} ligands dissociate S_2^0 following interactions with electrophilic molecules such as CS_2 or DMA very likely is due to the proximal S—S bond activation by the Mo atom. It should be emphasized that the S_4^{2-} ligand in the tetrahedral $[Zn(S_4)_2]^{2-}$ complex anion,[14] which contain the d^{10} Zn(II) ion, does not show an alternation of the S—S bond lengths (Table 1).

A lengthening of the S—S bond adjacent to the Mo atom also is apparent in the structures of both the *cis*- and *trans*-$[(Cs_4)_2MoS]^{2-}$ complex anions (Fig. 2) and in the $[(CS_4)Mo(S)(\mu\text{-}S)_2Mo(S)(CS_4)]^{2-}$ complex (Table 2). As observed with the S_4^{2-} ligands, the Mo—S bond directly adjacent to the lengthened S—S bond of the CS_4^{2-} ligand always is significantly

shorter than the Mo—S bond with the thiolate sulfur of the ligand. Such differences in M–S bonding, or lengthening of the S—S bond are not apparent in the structure of the $[N_1(CS_4)_2]^{2-}$ complex[14] (Table 2).

With the Mo-"side-on"-bound S_2^{2-} ligand, and in the absence of other activating interactions, the transfer of electron density to the Mo—S bonds would originate from the antibonding π^*-orbital and should result in a strengthening of the S—S bond. A bond order >1 for the "side-on"-coordinated S_2^{2-} ligand is evident in the S—S stretching vibrations (500–600 cm^{-1}) and the S—S bond lengths (2.00–2.10 Å) in these species. The corresponding values for the uncoordinated S_2, S_2^- and S_2^{2-} fragments are: S_2^0, 725 cm^{-1}, 1.89 Å; S_2^-, 589 cm^{-1}, 2.00 Å; S_2^{2-}, 446 cm^{-1}, 2.13 Å. A net depopulation of the S_2^{2-} π^*-orbital in the Mo–S_2 complexes and the π^* nature of the LUMO result in a situation where a cycloaddition of an acetylene or olefin to the Mo-"side-on"-bound S_2^{2-} would be a symmetry-forbidden process, it is not surprising therefore that such cycloaddition reactions with "*pure*" Mo–S_2 units are virtually unknown. In the only well-documented reaction of DMA with such a unit [in the $(Mo_2S_6O_2)^{2-}$ complex], the alkyne has inserted into the Mo—S bond.[9]

The reactions of the Mo-coordinated S_4^{2-} ligands with DMA and the subsequent formation of the dithiolene ligand, are analogous to other reactions of M–S_x units with DMA. Such reactions as the addition of DMA to the Fe–S_5 unit in $(Fe_2S_{12})^{2-}$,[20,21] the addition of DMA to the Ti–S_5 unit in $(Cp)_2TiS_5$ and the V–S_5 unit in $(Cp)_2VS_5$,[22] give rise to dithiolene complexes that contain $M[S_2C_2(COOMe)_2]$ units. An important mechanistic step in these reactions very likely involves the cycloaddition of the electrophilic alkyne to the coordinated S_x^{2-} chelate (Fig. 6). Interactions of the type depicted in Fig. 6 have a precedence in dithiolene chemistry. The addition of alkenes

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*For the neutral free atoms, a compilation of Roothaan–Hartree–Fock atomic wavefunctions show the sulfur $3p$ orbitals with an energy of -0.43694 a.u. and the molybdenum $4d(s^1d^5)$ with an energy of -0.34811 a.u. The localization of partial positive charge on the Mo and partial negative charge on the S is expected to bring these energies even closer together.[13]
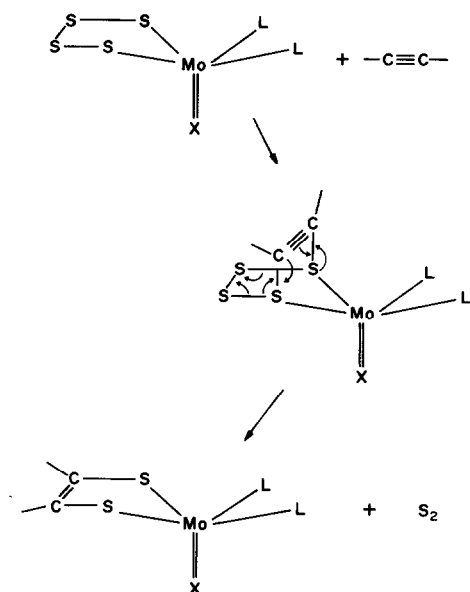
Fig. 6. Cycloaddition of alkynes to the Mo–S_4 unit.

present in the catalyst, may be directly linked with thiophene HDS activity. This suggestion is supported by the pioneering work of Rakowski Dubois, who has demonstrated that appropriately activated S_2^{2-} units in the $(CpMoS_2)_2$ complex are capable of activating H_2[29] and catalyze the reduction of elemental sulfur and the hydrogenation of alkynes.[30] With appropriately activated Mo–S_2 units, in fact, one can envision all of the HDS important reaction steps occurring directly on the S_2 unit (Fig. 7).

across the coordinated S-donor atoms in the $Ni[S_2C_2(Ph)_2]_2$ complexes has been reported by Schrauzer and Mayweg[23] and the norbornadiene adduct of $Ni[S_2C_2(CF_3)_2]_2$ has been obtained and structurally characterized.[24]

The activation, and change in reactivity patterns of the Mo-bound S_2^{2-} ligand, following the addition of elemental sulfur and formation of the Mo–S_4 units, may be of relevance to the HDS reaction. The HDS reaction is important in the catalytic hydrogenolysis of organosulfur compounds, and the heterogeneous catalysts employed in this reaction contain "sulfided" molybdenum and cobalt salts supported on β-alumina.[25] Proposed mechanisms for the HDS reaction[25–27] invariably involve the metals (Mo and Co) directly in the activation of H_2 and the C—S bond cleavage reactions. The suggestion has been advanced[28] that S_2^{2-} pairs,
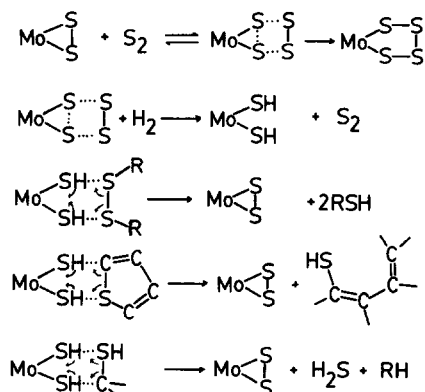

Fig. 7. Possible reactions of the activated S_2^{2-} ligand relevant to the HDS process.

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