Syntheses of sulphur-bridged molybdenum and tungsten coordination compounds

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ABBREVIATIONS

Ligands

H_2abt	*o*-aminobenzenethiol
[9]aneN_3	1,4,7-triazacyclononane, $\{NH(CH_2CH_2)\}_3$
bipy	2,2'-bipyridyl, $(C_5H_4N)_2$
$HBpz_3$	tris-pyrazoborate ion, $BH(C_3H_3N_2)_3^-$
Bu	butyl, C_4H_9
BzSSSBz	dibenzyl trisulphide, $C_6H_5CH_2SSSCH_2C_6H_5$
H_2cat	catechol, $C_6H_4(OH)_2$
chs	cyclehexensulphide, $C_6H_{10}S$
cod	1,5-cyclooctadiene, C_8H_{12}
Cp	cyclopentadienyl, C_5H_5
Cp*	pentamethylcyclopentadienyl, $C_5(CH_3)_5$
H_2cys	L-cysteine, $HSCH_2CH(NH_2)CO_2H$
HcysMe	L-cysteine methylester, $HSCH_2CH(NH_2)CO_2CH_3$
dba	dibenzoyl acetylene, $C_6H_5COC{\equiv}CCOC_6H_5$
H_3dba	3,4-dihydroxybenzoic acid, $C_6H_3(OH)_2COOH$
depe	1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$
diglyme	diethyleneglycol dimethyl ether, $(CH_3OCH_2CH_2O)_2O$
dioxane	dioxacyclohexane, $C_4H_8O_2$
dmac, dma	dicarbomethoxyacetylene, $MeOC(O)C{\equiv}CC(O)OMe$
dmad	1,2-dicarbomethoxy-1,2-ethylenedithiolate, $S_2C_2(CO_2Me)_2^{2-}$, prefixes (S,C- and S,S-) of dmad, see text
H_2dme	1,2-dimercaptoethane, $HSCH_2CH_2SH$
H_2dmpn	*N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptoethyl)-1,3-propanediamine, $HSCH_2CH_2N(CH_3)CH_2CH_2N(CH_3CH_2CH_2)SH$
dmf	dimethylformamide, $HCON(CH_3)_2$
dmmpH	4,6-dimethyl-2-mercaptopyrimidine, $(CH_3)_2C_4N_2SH$
dmpe	1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
H_4dsa	*meso*-2,3-dimercaptosuccinic acid, $C_4H_6O_4S_2$
R_2dtc$^-$	*N*,*N*-dialkyl dithiocarbamate ion, $R_2NCS_2^-$
R_2dtp$^-$	dialkyl dithiophosphate ion, $(RO)_2PS_2^-$
H_2edt	1,2-ethanedithiol, $S_2C_2H_6$
H_4edta	ethylenediaminetetraacetic acid, $(HO_2C)_2N(CH_2)_2N(CO_2H)_2$
Et	ethyl, CH_3CH_2
Hhis	L-histidine, $HOOCC(NH_2)HCH_2(C_3N_2H_3)$
H_2ida	iminodiacetic acid, $NH(CO_2H)_2$
Him	imidazole, $HC_3H_4N_2$
H_2mba	*o*-mercaptobenzoic acid, $C_7H_6O_2S$
Me	methyl, CH_3
H_2mida	methyliminodiacetic acid, $NCH_3(CO_2H)_2$

mnt	1,2-dicyanoethylene-2,2-dithiolate, $S_2C_2(CN)_2^{2-}$
H_3msa	2-mercaptosuccinic acid, $C_4H_6O_4S$
H_3nta	nitrilotriacetic acid, $N(CH_2CO_2H)_3$
ox	oxalate ion, $C_2O_4^{2-}$
oxaz	oxazole, C_3H_3NO
Hoxq	8-hydroxyquinoline, C_9H_7NO
HX_2oxq	5,7-dihalogeno-8-quinolinol $C_9H_5NOX_2$
H_4pdta	R-propylenediaminetetraacetic acid, $(HO_2C)_2NCH(CH_3)CH_2N(CO_2H)_2$
PEt_3	triethylphosphine, $P(CH_3CH_2)_3$
PPh_3	triphenylphosphine, $P(C_6H_5)_3$
PPN	bis(triphenylphosphoranylidene)ammonium, $(PPh_3)_2NH_2^+$
Pr	propyl, $CH_3CH_2CH_2$
Hpts	*p*-toluensulphonic acid, $CH_3C_6H_4SO_3H$
py	pyrizine, C_5H_5N
Hpz	pyrazole, $C_3H_4N_2$
$HS_2P(O^iPr)_2$	diisopropylphosphorodithioic acid, $HS_2P(OC_3H_7)_2$
tetds	tetraethylthiuram disulphide, $[Et_2NC(S)S-]_2$
tht	tetrahydrothiophene, C_4H_8S
tol	tolyl, $CH_3C_6H_4$
Htpy	2-thiopyridine, $C_6H_4N(SH)$
tpy_2	2,2′-dithio-dipyridine, $C_5H_4NS-SC_5H_4N$
xan	xanthate, S_2COR^- (R = alkyl)

Solvents

Ac_2O	acetic anhydride, $(CH_3CO)_2O$
ACET	acetone, CH_3COCH_3
AN	acetonitrile, CH_3CN
AQ	water, H_2O
BZ	benzene, C_6H_6
CBZ	chlorobenzene, C_6H_5Cl
CDS	carbon disulphide, CS_2
CF	chloroform, $CHCl_3$
DBM	dibromomethane, CH_2Br_2
DCE	dichloroethane, $C_2H_4Cl_2$
DCM	dichloromethane, CH_2Cl_2
DMAM	dimethylacetamide, $CH_3CON(CH_3)_2$
DME	1,2-dimethoxyethane, $CH_3OCH_2CH_2OCH_3$
DMF	dimethylformamide, $HCON(CH_3)_2$
DOX	dioxane, $C_4H_8O_2$
EtOH	ethanol, C_2H_5OH
HOAc	acetic acid, CH_3COOH

HX	hexane, C_6H_{14}
IF	iodoform, CHI_3
MeOH	methanol, CH_3OH
TCM	tetrachloromethane, CCl_4
THF	tetrahydrofurane, C_4H_8O
TL	toluene, $C_6H_5CH_3$
TMPH	1,2,5-trimethylbenzene, $C_6H_3(CH_3)_3$
XY	xylene, $C_6H_4(CH_3)_2$

A. INTRODUCTION

Molybdenum is one of the essential trace elements for many organisms, including human, and almost all molybdenum enzymes contain sulphur atoms [1]. Many molybdenum–sulphur compounds have been synthesized and the structures determined. Many sulphur-bridged tungsten, a congener of molybdenum, compounds are also known.

In order to introduce sulphur atom(s) to di- or polynuclear compounds, many combinations of molybdenum (or tungsten) compounds and sulphur-containing compounds (or S_8) have been employed.

This review covers the synthetic aspects of sulphur bridged molybdenum and/or tungsten compounds. Emphasis is placed on sulphide (S^{2-}) and disulphide (S_2^{2-})-bridged compounds. Some of organometallic sulphur compounds containing SH or SR bridged are also described. Although the final products described here are limited to molecular or non-polymeric compounds, the synthetic methods described involve not only techniques of solution chemistry but also those of solid-state chemistry. Compounds with sulphur-bridged Mo_6 cores are not included. A review of this latter group was published recently by Spink [2].

Several types of sulphur bridge are shown in Fig. 1. Disulphur also acts as a bridging group. Roughly speaking, there are two bridging modes: one is side-on and the other is end-on or bridging, and these are shown in Fig. 2. Almost all sulphur bridges described here are of the type μ_2-S and μ_3-S.

Previous reviews [3–10] focus on synthetic aspects of metal–sulphur compounds (including molybdenum and/or tungsten). Very recently, Coucouvanis et al. reviewed the synthesis and reactivity of dinuclear Mo/S and Mo/S/O compounds [11], and Lee and Holm emphasized cluster excision from non-molecular metal chalcogenide/halide solids [12].

Other topics on molybdenum and/or tungsten have also been reviewed: electrochemistry by Zanello [13], structure and/or bonding by Dance [14], Cotton [15], and Harris (especially on cubane-type mixed-metal clusters) [16]; chemical and physical properties by Cannon and White [17]; and solution chemistry of compounds with $M_3O_xS_{4-x}$ (M = Mo, W) cores by Ooi [18]. A review by Stiefel [19] also described syntheses of molybdenum compounds with sulphur bridge(s). A recent

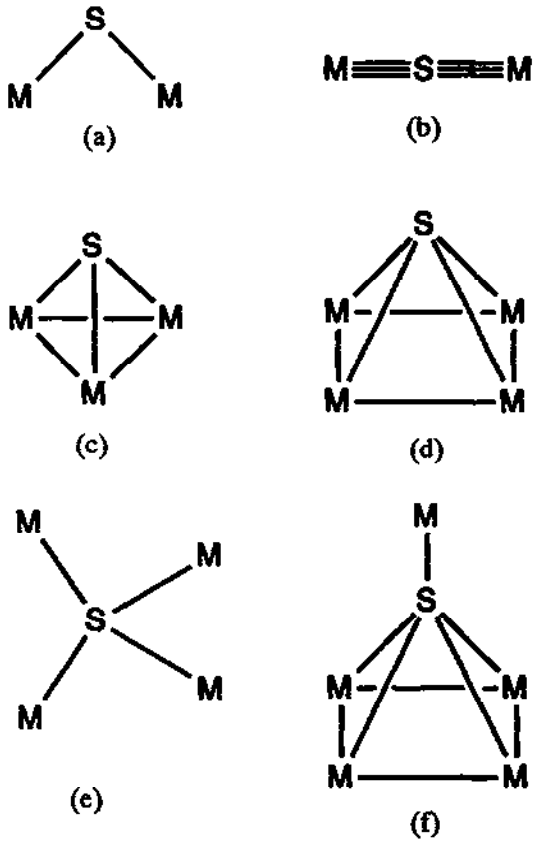


Fig. 1. Types of sulphur bridge.

review by the present author, focused on X-ray structure with brief notes on synthetic procedures [20].

This review is based on the literature that appeared through the end of 1991.

B. SYNTHESES OF DINUCLEAR MOLYBDENUM COMPOUNDS

(i) $Mo_2O_{4-n}S_n$ cores ($n = 1$–4)

Compounds containing $Mo_2O_{4-n}S_n$ cores ($n = 1$–4) have either planar or bent MoX_2Mo (X = O, S) structures with terminal oxo (O_t) or sulphido (S_t) ligands. *Syn/anti* isomers are different in the position of terminal oxo or sulphido ligands with double bond character as shown in Fig. 3. The term "*syn*" will not be appended to the *syn* compounds except where it is unclear without it. No compounds with *anti*-$Mo_2S_2(\mu\text{-O})(\mu\text{-S})$ or *syn/anti*-$Mo_2S_2(\mu\text{-O})(\mu\text{-S})$ cores have been reported to our knowledge. Compounds with Mo_2O_4 cores will not be included here.

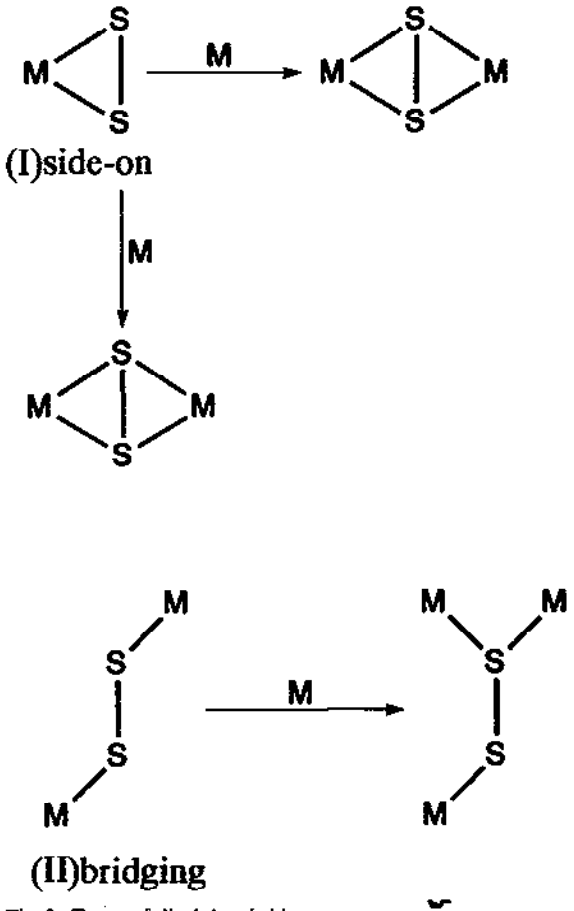


Fig. 2. Types of disulphur bridge.

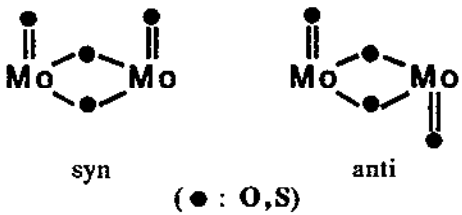


Fig. 3. Molybdenum dinuclear compounds with *syn*- and *anti*-$Mo_2O_{4-n}S_n$ cores.

(a) Syn- and anti-$Mo_2(O_t)_2(\mu\text{-}S)_2$ cores

Molybdenum dinuclear compounds with *syn*- (Fig. 4(a)) and *anti*-$Mo_2O_2(\mu\text{-}S)_2$ cores are summarized in Table 1 [21–60], where molybdenum- and sulphur-containing starting materials are listed.

The main synthetic routes to compounds with *syn*-$Mo_2O_2(\mu\text{-}S)_2$ cores are:

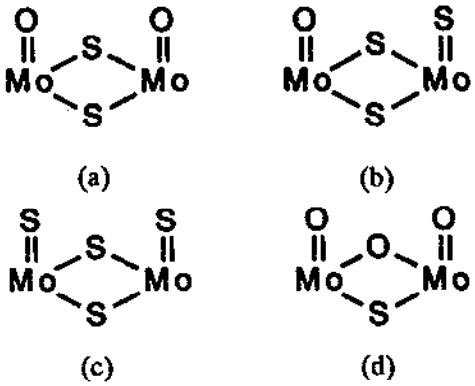


Fig. 4. Molybdenum dinuclear compounds with (a) $Mo_2(O_t)_2(\mu\text{-}S)_2$, (b) $Mo_2(O_t)(S_t)(\mu\text{-}S)_2$, (c) $Mo_2(S_t)_2(\mu\text{-}S)_2$, or (d) $Mo_2(O_t)_2(\mu\text{-}S)(\mu\text{-}O)$ cores.

(1) bubbling H_2S gas through a solution of the molybdate, MoO_4^{2-} (or isopolymolybdate, $Mo_7O_{24}^{6-}$) in water followed by the addition of an appropriate ligand to the solution; (2) bubling H_2S gas through an aqueous solution containing di-oxo-bridged compounds. This replaces two oxo-bridges with two sulphido-bridges; (3) replacement of ligands of compounds with $Mo_2O_2S_2$ cores. This route includes the reaction of ligand in the source material; (4) formation of compounds with these cores from compounds with other cores. In addition to the methods described, a facile synthetic method for $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$ has recently been developed, using solid sodium sulphide instead of hydrogen sulphide gas [22(a),22(b)].

As mononuclear molybdenum sources, thio derivatives of the molybdate, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$, and MoS_4^{2-}, have also been used. In addition to hydrogen sulphide and sodium sulphide, dithiocarbamates, elemental sulphur, and thiomolybdates can be sources for the bridging sulphur.

Halbert et al. [46] reported the insertion reaction of acetylene derivatives, dmac, to Mo–S bonds of the terminal disulphides of $(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$ to give $(Et_4N)_2[Mo_2O_2S_2(S,S\text{-dmad})_2]$, and Coucouvanis et al. [61] found a reaction of dmac with $(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]$ to give $[Et_4N]_2[Mo_2O_2S_2(S,S\text{-dmad})_2]$. (Note: S,C- and S,S-dmad indicate that the ligating atoms of the ligand dmad to molybdenum are sulphur and carbon, and sulphur and sulphur, respectively.) Two types of isomerization reaction have also been reported: (a) S,C- to S,S-dmad compound, and (b) *anti* to *syn* compound [47].

In addition to the compounds listed in Table 1, many dinuclear compounds with sulphur ligands may be converted to compounds with $Mo_2O_2S_2$ cores. These include $[(MeCp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$, $[(MeCp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$, $[(MeCp)_2Mo_2(O)(S)(\mu\text{-}S)_2]$, and *syn*-$[(MeCp)_2Mo_2(O)(S)(\mu\text{-}S)_2]$ [48].

The aqua ion, $Mo_2O_2S_2^{2+}(aq)$, is easily obtained by aquation of the corresponding cysteinato compound [22(a),22(b),39], and is a good starting material for other

TABLE 1

Compounds with *syn*- and *anti*-$Mo_2(O_t)_2(\mu\text{-}S)_2$ cores[a]

Compound	Source	Solvent	Ref.
$Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$	$Na_2MoO_4\cdot 2H_2O$, H_2S, L-H_2cys · HCl	AQ	21
$Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$	$Na_2MoO_4\cdot 2H_2O$, $Na_2S\cdot 9H_2O$, L-H_2cys · HCl	AQ	22
$Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$	$Na_2[Mo_2O_2(\mu\text{-}O)_2(cys)_2]\cdot 4H_2O$, H_2S, NaOH	AQ	23,24
$[Mo_2O_2S_2(Mecys)_2]$	$Na_2MoO_4\cdot 2H_2O$, H_2S, L-HcysMe · HCl	AQ	24–26
$[Mo_2O_2S_2(Mecys)_2]$	$[Mo_2O_2(\mu\text{-}O)(Mecys)_4]$, H_2S	EtOH	25
$[Mo_2O_2S_2(hist)_2]\cdot 2H_2O$	$Na_2MoO_4\cdot 2H_2O$, H_2S, Hhist	AQ	23,24,27
$Na_2[Mo_2O_2S_2(edta)]\cdot 4H_2O$	$Na_2MoO_4\cdot 2H_2O$, H_2S, Na_2H_2edta · $2H_2O$	AQ	21
$Na_2[Mo_2O_2S_2(edta)]\cdot 4H_2O$	$Na_2MoO_4\cdot 2H_2O$, $Na_2S\cdot 9H_2O$, Na_2H_2edta · $2H_2O$	AQ	22
$Cs_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$	$Cs_4[(MoO_3)_2(edta)]$, H_2S	AQ	28
$Na_2[Mo_2O_2S_2(pdta)]\cdot 3H_2O$	$Na_2MoO_4\cdot 2H_2O$, H_2S, pdta	AQ	24
$[Mo_2O_2S_2(X_2oxq)_2]$	$Na_2MoO_4\cdot 2H_2O$, $Na_2S_2O_4$, H_2S, HX_2oxq (X = Cl, Br, I)	AQ	29
$[Mo_2O_2S_2\{O_2CN(C_6H_{11})_2\}_2]$	$Na_2MoO_4\cdot 2H_2O$, H_2S, $(C_6H_{11})_2NCO_2K$	AQ	30
$[Mo_2O_2S_2\{O_2CN(CH_3)(C_6H_{11})\}_2]$	$Na_2MoO_4\cdot 2H_2O$, H_2S, $(CH_3)(C_6H_{11})NCO_2K$	AQ	30
$[Mo_2O_2S_2\{O_2CN(C_5H_{10})\}_2]$	$Na_2MoO_4\cdot 2H_2O$, H_2S, ppc[b]	AQ	31
$[Mo_2O_2S_2(H_2dtc)_2]\cdot 2CH_3CN$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $NH_4(NH_2CS_2)$	AQ	32
$[Mo_2O_2S_2(Et_2dtc)_2]$	$(NH_4)_2MoO_2S_2$, $Na(Et_2dtc)$	AQ	33
$[Mo_2O_2S_2(Et_2dtc)_2]$	$[Mo_2O_4(Et_2dtc)_2]$, H_2S	CF	34,35
$[Mo_2O_2S_2(Pr_2dtc)_2]$	$MoO_2(Pr_2dtc)_2$, H_2S	ACET/DCM	36
$[Mo_2O_2S_2(R_2dtc)_2]$ (R = Et, cyclohexyl, Pr^i)	$Na_2MoO_4\cdot 2H_2O$, H_2S, NaR_2dtc	AQ	37
$[Mo_2O_2S_2((neo\text{-}Men)(H)dtc)_2]$[c]	$Na_2MoO_4\cdot 2H_2O$, H_2S, Na(neo-Men(H)-dtc), $Na_2S_2O_4$	AQ	37
$K_2[Mo_2O_2S_2(i\text{-}mnt)_2]\cdot H_2O$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, K_2(i-mnt)	AQ	35,38
$Mo_2O_2S_2^{2+}$(aq)	$Na_2[Mo_2O_2S_2(cys)_2]$, HCl	AQ	22,39
$[Mo_2O_2S_2(dmf)_6]^{2+}$	$[Mo_2O_2(\mu\text{-}S)_2(S_2)(dmf)_3]$, I_2	DMF	40
$Cs_2[Mo_2O_2S_2(ox)_2(H_2O)_2]\cdot 2H_2O$	$Mo_2O_2S_2^{2+}$(aq), H_2Ox	AQ	41,42
$(Et_4N)_2[Mo_2O_2S_2(dmpn)_2]$	$(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$, H_2dmpn	AN	43
$[Mo_2O_2S_2(Rxan)]$ (R = Me, Et, Pr^i, Bu^n, Bu^i)	$[Mo_2O_3(Rxan)_4]$, H_2S	CF	44

$Na_2[Mo_2O_2S_2(C_4H_8O_2S_2)_2]$ ($C_4H_{10}O_2S_2$ = dithiothreitol)	$Na_2[Mo_2O_4(C_4H_8O_2S_2)_2]$, H_2S	AQ	45
$(Et_4N)_2[Mo_2O_2S_2(S,C\text{-dmad})_2]$	$(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S)_2]$, dmac	AN	46
$(Et_4N)_2[Mo_2O_2S_2(S,S\text{-dmad})_2]$	$(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]$, dmac	AN	47
$[Mo_2O_2S_2Cp_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp_2]$, air	DCM	48
$(pyH)_4[Mo_2O_2S_2(NCS)_6]$	$Mo_2O_2S_2^{2+}$ (aq), KSCN	AQ	49
$[Mo_2O_2S_2Br_4][Bu_3P(CH_2)_4P(^nBu)_3]$	$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4]$, Bu_3P	THF	50
$(Me_4N)_2[Mo_2O_2S_2(S_2)_2]$	$(NH_4)_2MoO_2S_2$, NaOH, Me_4NCl	AQ	33,51
$(Me_4N)_2[Mo_2O_2S_2(S_2)_2]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, NH_3aq	AQ	52
$R_2[Mo_2O_2S_2(S_2)(S_4)]$ (R = Me_4N, Et_4N, PPh_4)	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, NH_3aq, $(NH_4)_2S_x$, RCl	AQ	53
$(PPh_4)_2[Mo_2O_2S_2(S_2)(S_3O_2)]$	$(PPh_4)_2MoOS_3$, S_8, O_2	AN	54,55
$(PPh_4)_2[Mo_2O_2S_2(S_2)(S_3O_2)]$	$(PPh_4)_2MoS_4$, O_2	DMF	54,55
$(Et_4N)[Mo_2O_2S_2(S_2)Cp]$	$[(dmf)_3Mo(O_t)(\mu\text{-}S)_2Mo(O_t)(S_2)]$, NaCp	DMF	56
$[Mo_2O_2S_2(S_2)(dmf)_3]$	$(Et_4N)_2[Mo_2(O_t)_2(\mu\text{-}S)_2(S_2)(S_4)]$, I_2	DMF	40,56
$(Et_4N)_2[Mo_2O_2S_2(S_4)(S,C\text{-dmad})]$	$(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]$, dmac	AN	47
anti-$(Et_4N)_2[Mo_2O_2S_2(dmad)_2]$	*anti*-$(Et_4N)_2[(Mo_2O_2(\mu\text{-}S)(S_2)_4)]$, dmac	AN	47
anti-$[Mo_2O_2S_2Cp_2]$	$[Mo_2(Cp)_2(CO)_6]$, chs	BZ	57,58
anti-$[Mo_2O_2S_2Cp_2]$	$[Mo_2(Cp)_2(CO)_6]$, SO_2(liquid), light	THF	59
anti-$[Mo_2O_2S_2Cp_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp_2]$	DCM	48
anti-$[Mo_2O_2S_2Cp^*_2]$	*anti*-$[Mo_2(S_t)_2(\mu\text{-}S)_2Cp^*_2]$, air	CF	60
anti-$[Mo_2O_2S_2(MeCp)_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(MeCp)_2]$	DCM	48

[a] Anti isomers have the prefix *anti*, whereas syn isomers do not have the prefix *syn*.
[b] ppc = potassium piperidine carbamate.
[c] (neo-Men)(H)-dtc = neomethyldithiocarbamate.

compounds with $Mo_2O_2S_2$ cores. Raman and resonance Raman spectra of cysteinato and related thiolato compounds with $Mo_2O_2S_2$ cores have been reported [62(a)]. Electrochemical data for the compounds $[Mo_2O_{4-n}S_n(LL)_2]$ (LL = dtcEt$_2$, $S_2P^iPr_2$, i-mnt) have been reported [35]. Synthesis and vibration studies of the ^{34}S isotope compounds, $[Mo(Ot)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ and $[Mo_2(\mu\text{-}S_2)_2Br_8]^{2-}$ have been reported [62(b)].

The compound *anti*-$[Cp_2Mo_2O_2S_2]$ was separated chromatographically as early as 1966 by Treichel and Wilkes from the reaction mixture of $[CpMo(CO)_3]_2$ and cyclohexenesulphide, $C_6H_{10}S$ [57]. Compounds with both *syn*- and *anti*-$Mo_2O_2S_2$ cores are prepared from compounds with $Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ or $Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ cores [48]. *Anti*-$(Et_4N)_2[Mo_2O_2S_2(dmad)_2]$ is the only compound that does not contain Cp or its derivatives [47]. A Mo(IV) trimer can also be the source of dinuclear Mo(V) compounds [50].

(b) Syn- and anti-$Mo_2(O_t)(S_t)(\mu\text{-}S)_2$ cores

Compounds with *syn*- (Fig. 4(b)) and *anti*-$Mo_2OS(\mu\text{-}S)_2$ cores are listed in Table 2 [35,36,48,63–68]. Only a few compounds containing both Mo=S and M=O units with di-μ-sulphido bridges have been reported. The MoS_4^{2-} anion is a convenient starting material for compounds with $Mo_2OS(\mu\text{-}S)_2$ cores [63,65–67]. The organic trisulphide BzSSSBz serves as both oxidizing and sulphur-transfer agent for the $[(PhS)_2Mo(O)(MoS_4)]^{2-}$ anion, which can be synthesized from MoS_4^{2-} (see Table 3). The compound Ph_3P removes a sulphur atom from terminal S_2 or S_4 groups. Both *syn*- and *anti*-$[(MeCp)_2Mo_2OS_3]$ have been isolated and characterized by spectroscopic methods [48].

(c) Syn- and anti-$Mo_2(S_t)_2(\mu\text{-}S)_2$ cores

Compounds with *syn*- (Fig. 4(c)) and *anti*-$Mo_2S_2(\mu\text{-}S)_2$ cores are listed in Table 3 [34–36, 43,48,60,68-86]. The first example of a compound with an Mo_2S_4 core, $[Mo_2S_4(R_2dtc)_2]$ (R = ethyl, iso-propyl, butyl, and iso-butyl), was obtained by P_4S_{10} treatment of a xylene solution of sulphurized molybdenum dialkyldithiocarbamate obtained from MoO_3, HNR_2, and CS_2 [79]. $(NH_4)_2MoS_4$ is the most easily obtainable source for the synthesis of compounds with Mo_2S_4 cores. $(NH_4)_2(Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$ is another useful source. The reagent P_4S_{10} replaces both terminal and bridging oxygen atoms, while bubbling H_2S only replaces oxo bridges as described in Table 1. $(NEt_4)_2[Mo_2S_2(\mu\text{-}S)_2(S_4)_2]$ reacts with PPh_3 in CH_3CN to give $(NEt_4)_2[Mo_2S_4(S_2)_2]$, the two terminal S_2 groups being replaced by the addition of $Na^iBu_2dtc\cdot 3H_2O$ to give $[Mo_2S_4(^iBu_2dtc)_2]$ [78].

The two isomers, *syn*- and *anti*-$(Et_4N)_2[Mo_2S_4(dme)_2]$, were obtained through variation of the reagent ratio [70]. Detailed structures of both the *syn* and *anti* compounds have been reported [71]. Compounds with *anti*-Mo_2S_4 cores can be synthesized directly from the mononuclear molybdenum compound $[Cp^*Mo(CO)_3H]$, which is obtained from $Mo(CO)_6$ and LiCp* in THF [60]. The reaction

TABLE 2

Compounds with *syn*- and *anti*-$Mo_2(O_t)(S_t)(\mu\text{-}S)_2$ cores[a]

Compound	Source	Solvent	Ref.
$[Mo_2OS_3(Et_2dtc)_2]$	K_2MoS_4, $NaEt_2dtc \cdot 2H_2O$, $Na_2S_2O_4$	AQ/DCM	63
$[Mo_2OS_3(Pr_2dtc)_2]$	$MoO_2(Pr_2dtc)_2$, H_2S	ACET/DCM	36
$[Mo_2OS_3(Et_2dtc)_2]$	$[Mo_2O_3(Et_2dtc)_4]$, H_2S	DCM	35
$(Bu_4N)_2[Mo_2OS_3(mnt)_2]$	$[Mo_2(O_2CMe)_4]$, Na_2mnt, Bu_4NBr	MeOH	64
$(Bu_4N)_2[Mo_2OS_3(S_2)_2]$	$(NH_4)_2MoS_4$, HClaq, Bu_4NBr	AQ	65
$(Bu_4N)_2[Mo_2OS_3(S_2)_2]$	$(Bu_4N)_2MoS_4$	EtOH	66
$(Ph_4P)_2[Mo_2OS_3(S_2)_2]$	$(Ph_4P)_2[Mo_2(O_t)(S_t)(\mu\text{-}S)_2(S_2)(S_4)]$, Ph_3P	DMF	67
$(Ph_4P)_2[Mo_2OS_3(S_2)_2]$	$(Ph_4P)_2[(PhS)_2Mo(O_t)(MoS_4)]$, BzSSSBz	DMF	67
$(Ph_4P)_2[Mo_2OS_3(S_2)(S_4)]$	$(Ph_4P)_2[(PhS)_2Mo(O_t)(MoS_4)]$, BzSSSBz	DMF	67
$[Mo_2OS_3(MeCp)_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(MeCp)_2]$, C_2H_4	DCM	48
anti-$[Mo_2OS_3(MeCp)_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(MeCp)_2]$, C_2H_4	DCM	48
$[Mo_2OS_3Cp_2]$	$[Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2Cp_2]$	TL	68

[a]Anti isomers have the prefix *anti*, whereas syn isomers do not have the prefix *syn*.

TABLE 3

Compounds with *syn*- and *anti*-$Mo_2(S_t)_2(\mu\text{-}S)_2$ cores[a]

Compound	Source	Solvent	Ref.
$(Et_4N)_2[Mo_2S_4(edt)_2]$	$(NH_4)_2MoS_4$, $edtH_2$	DMF	69
$(Et_4N)_2[Mo_2S_4(abt)_2]$	$(NH_4)_2MoS_4$, $abtH_2$	DMF	69
syn/anti-$(Et_4N)_2[Mo_2S_4(dme)_2]$	$MoCl_3$, NaHS, $NaOCH_3$, H_2dme	MeOH	70,71
$(Et_4N)_2[Mo_2S_4(dme)_2]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, Na_2dme	MeOH	72
$(Et_4N)_2[Mo_2S_4(SPh)_4]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, NaSPh	AN	72
$[Mo_2S_4(C_6H_4SNH_2)_2]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, $C_6H_4(SH)(NH_2)$	EtOH	72
$(Bu_4N)_2[Mo_2S_4(dmpn)_2]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, H_2dmpn	AN	43
$(Ph_4P)_2[Mo_2S_4(CS_4)_2]\cdot 0.5DMF$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(S_2)(S_4)]$, CS_2	DMF	73
$[Mo_2S_4(Et_2dtc)\{HB(Me_2Pz)_3\}]$	$[\{HB(Me_2Pz)_3\}MoO(Et_2dtc)]$, B_2S_3	DCM	74,75
$[Mo_2S_4(Et_2dtc)_2]$	$[Mo_2(O_t)_2(\mu\text{-}O)_2(Et_2dtc)_2]$, P_4S_{10}	XY	34,35
$[Mo_2S_4(Et_2dtc)_2]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$, $NaEt_2dtc$	EtOH	72,76
$[Mo_2S_4(Pr_2dtc)_2]$	$MoO_2(Pr_2dtc)_2$, H_2S	ACET/DCM	36
$[Mo_2S_4(Bu_2dtc)_2]$	$[Mo_2O_2(\mu\text{-}S)_2(Bu_2dtc)_2]$, P_4S_{10}	XY	77
$[Mo_2S_4(^iBu_2dtc)_2]$	$(NEt_4)_2[Mo_2S_2(\mu\text{-}S)_2(S_4)_2$, Ph_3P, $Na^iBu_2dtc\cdot 3H_2O$	AN	78
$[Mo_2S_4(R_2dtc)_2]$	MoO_3, HNR_2, CS_2, P_4S_{10} (R = Et, ^{i}Pr, Bu, ^{i}Bu)	XY	79
$(Ph_4P)_2[Mo_2S_4(S_2)_2]$	$(Ph_4P)_2[Mo(S_t)_2(MoS_4)]$, Bz_2S_3	DMF	80
$(Ph_4P)_2[Mo_2S_4(S_2)_2]$	$(Ph_4P)_2[Mo(S_t)(S_2)(MoS_4)]$, Bz_2S_3	DMF	80
$(Ph_4P)_2[Mo_2S_4(S_2)_2]$	$(NH_4)_2MoS_4$, RSSR	DMF	81
$(NEt_4)_2[Mo_2S_4(S_2)_2]$	$(NEt_4)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(S_4)_2]$, Ph_3P	AN	78
$(NEt_4)_2[Mo_2S_4(S_4)_2]$	$(NH_4)_2MoS_4$, S_8	DMF	78
$(Ph_4P)_2[Mo_2S_4(S_4)_2]\cdot 0.5DMF$	$(Ph_4P)_2MoS_4$, BzSSSBz	DMF	82
$(AsPh_4)_2[Mo_2S_4(S_2)(S_4)]$	$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]$, Na, $AsPh_4Cl$, C_6H_5SH	MeOH/DMSO	83
$(Ph_4P)_2[Mo_2S_4(S_2/S_4)(S_4)]\cdot 0.5DMF$	$(Ph_4P)_2[Mo(S_t)(S_2/S_4)(MoS_4)]$, Bz_2S_3	DMF	80
$(Ph_4P)_2[Mo_2S_4(S_2/S_4)(S_4)]\cdot 0.5DMF$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S_2)(S_2)_2]$, Bz_2S_3	DMF	80
anti-$[Mo_2S_4Cp_2]$	$[MoCp(CO)_3H]$, C_3H_6S (1:3)	DCM	84,85
syn/anti-$[Mo_2S_4MeCp_2]$	*syn/anti*-$[Mo_2(O_t)_2(\mu\text{-}S)_2(MeCp)_2]$, $(Me_3Si)_2S$	DCM	48

anti-$[Mo_2S_4MeCp_2]$	$[Mo_2MeCp_2(CO)_6]$, S_8	BZ	60
syn/*anti*-$[Mo_2S_4Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp^*_2]$	DCM	86
anti-$[Mo_2S_4Cp^*_2]$	$[Mo_2Cp^*_2(CO)_4]$, S_8	TL	68
anti-$[Mo_2S_4Cp^*_2]$	$[MoCp^*(CO)_3H]$, S_8	THF	60

[a]Anti isomers have the prefix *anti*, whereas syn isomers do not have the prefix *syn*.

of $[(Cp^*)_2Mo_2(CO)_4]$ with elemental sulphur results in the formation of three different isomers of $[(Cp^*)_2Mo_2S_4]$: *syn*- and *anti*-$[(Cp^*)_2Mo_2S_4]$, and $[(Cp^*)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$ [68].

(d) Syn-$Mo_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ cores

Compounds with *syn*-$Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)$ cores are listed in Table 4 [21,22(b),24,29–31,34–36,49,87–93]. Water-soluble dimeric molybdenum(V) compounds with this core (Fig. 4(d)) were first prepared by Schultz and co-workers [21]. Studies on these cores using organic solvents have also been developed [34,88–90,92]. A very facile method for synthesizing $Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$ was reported recently. This uses the easily obtainable sodium molybdate and hydrazine-hydrochloride, instead of molybdenum pentachloride, and sodium sulphide instead of bubbling H_2S gas [22(b),87]. The corresponding edta and aqua compounds can easily be obtained via reaction with this compound [21,22(b),87]. The X-ray structure of $[Mo_2O_3S(cys)_2]^{2-}$ has been determined [94]. In the preparations of $[Mo_2O_3S(S_2P(O^iPr)_2)_2]$ and $[Mo_2O_3S(dmmp)_2(MeOH)]$, neither H_2S gas nor other sources of sulphur were used; decomposition of the starting materials, H^iPr_2dtp or dmmpH was presumably the origin of the sulphur [88,91].

The reaction of $[Mo_2O_3S(S_2P(O^iPr)_2)_2]$ with pyridine or pyridazine gives rise to 1:1 adducts where pyridine and pyridazine bridge the metal atoms [92,95].

^{18}O-enriched compounds $[Mo_2O_3S(dtc)_2]$ and $[Mo_2O_3S(S_2P(i\text{-}Pr)_2)_2]$ have been prepared by bubbling H_2S into dichloroethane solution of $[Mo_2O_4(dtc)_2]$ and $[Mo_2O_4((S_2P(i\text{-}Pr)_2)_2]$, respectively [89,96(a),96(b)].

(ii) $Mo_2(\mu\text{-}S)_2$, $Mo_2(\mu\text{-}O)(\mu\text{-}S)$, $Mo_2(\mu\text{-}S)$, $Mo_2(O_t)_2(\mu\text{-}S)$, and $Mo_2(S_t)_2(\mu\text{-}S)$ cores

The compounds collected in Table 5 [47,52,61,97–115] contain one of the following cores: $Mo_2(\mu\text{-}S)_2$ (Fig. 5(a)), $Mo_2(O_t)(\mu\text{-}S)_2$ (Fig. 5(b)), $Mo_2(\mu\text{-}O)(\mu\text{-}S)$ (Fig. 5(c)), $Mo_2(\mu\text{-}S)$ (Fig. 5(d)), $Mo_2(O_t)_2(\mu\text{-}S)$ (Fig. 5(e)), or $Mo_2(S_t)_2(\mu\text{-}S)$ (Fig. 5(f)). The compound *anti*-$[CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp]$ has an *anti* configuration on the two Cps (Fig. 5(b)).

Some compounds in this group do not have terminal oxygen or sulphur atoms. In the absence of oxygen, the reaction between MoO_3 (or MoO_4^{2-}), H_2S, and CN^- yields the double sulphur-bridged compound $[Mo_2S_2(CN)_8]^{6-}$, and in the presence of oxygen the single sulphur-bridged compound $[Mo_2S(CN)_{12}]^{6-}$ [100,107]. The anion $[Mo_2(\mu\text{-}S)(CN)_{12}]^{6-}$ is the first X-ray-structure-determined molybdenum compound with a single sulphide bridge. A short Mo–S distance and a nearly linear Mo–S–Mo arrangement (Mo–S = 2.173(1) Å, Mo–S–Mo = 169.5(2)°) were observed in $K_6[Mo_2(\mu\text{-}S)(CN)_{12}]\cdot 4H_2O$ [100,109]. The formation of $[S_3Mo{-}S{-}MoS_3]^{2-}$ had been reported through pH and conductometric measurements of the acidification

TABLE 4

Compounds with *syn*-$Mo_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ cores

Compound	Source	Solvent	Ref.
$Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$	$MoCl_5$, L-H_2cys · HCl, H_2S	AQ	21
$Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$	$Na_2MoO_4\cdot 2H_2O$, $Na_2S\cdot 9H_2O$, $N_2H_4\cdot 2HCl$, L-H_2cys · HCl	AQ	87,22b
$Mo_2O_3S^{2+}$(aq)	$Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$, HCl	AQ	21,87
$Na_2[Mo_2O_3S(R\text{-}pdta)]\cdot 4H_2O$	$MoCl_5$, R-pdta, H_2S, NaOH	AQ	24
$[Mo_2O_3S(S\text{-}hist)_2]\cdot 3H_2O$	$MoCl_5$, Hhist, H_2S	AQ	24
$[Mo_2O_3S(X_2oxq)_2]$ (X = Cl, Br, I)	$Na_2MoO_4\cdot 2H_2O$, HX_2oxq, H_2S	AQ	29
$[Mo_2O_3S(mcc)_2]$[a]	$Na_2MoO_4\cdot 2H_2O$, Kmcc, H_2S	AQ	30
$[Mo_2O_3S(pc)_2]$[b]	$Na_2MoO_4\cdot 2H_2O$, Kpc, H_2S	AQ	31
$[Mo_2O_3S(dmmp)_2(MeOH)]$	$[MoO_2(acac)_2]$, dmmpH	MeOH	88
$[Mo_2O_3S(Et_2dtc)_2]$	$[Mo_2O_4(Et_2dtc)_2]$, H_2S	DCM	34,35,89
$[Mo_2O_3S(Pr_2dtc)_2]$	$[MoO_2(Pr_2dtc)_2]$, P_4S_{10}	ACET	36,90
$[Mo_2O_3S(^iPr_2dtp)_2]$	$Na_2MoO_4\cdot 2H_2O$, H^iPr_2dtp	AQ	91
$[Mo_2O_3S(^iPr_2dtp)_2(\mu\text{-py})]$	$[Mo_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)(^iPr_2dtp)_2]$, py	TL	92
$[Mo_2O_3S(S_2P^iPr_2)_2]$	$[Mo_2(O_t)_2(\mu\text{-}O)_2(S_2P^iPr_2)_2]$, H_2S	DCM	35,89
$(pyH)_4[Mo_2O_3S(NCS)_6]\cdot 2H_2O$	$Mo_2O_3S^{2+}$(aq), KSCN	AQ	49
$K_6[\{Mo_2O_3S(ox)_2\}_2(ox)]\cdot 10H_2O$	$Mo_2O_3S^{2+}$(aq), H_2ox	AQ	93

[a] Kmcc = potassium *N*-methyl-*N*-cyclohexyl carbamate.

[b] Kpc = potassium piperidine carbamate.

TABLE 5

Compounds with $Mo_2(\mu\text{-}S)_2$, $Mo_2(\mu\text{-}S)$, $Mo_2(\mu\text{-}O)(\mu\text{-}S)$, $Mo_2(O_t)_2(\mu\text{-}S)$, or $Mo_2(S_t)_2(\mu\text{-}S)$ cores

Compound	Source	Solvent	Ref.
$Mo_2(\mu\text{-}S)_2$ core			
$(Ph_4P)_2[Mo_2S_2(dmad)_4]$	$(Ph_4P)_2[Mo(S)(S_4)_2]$, dma	AN	47
$(Ph_4P)_2[Mo_2S_2(dmad)_4]$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(S_4)(S_2/S_4)]\cdot 0.5DMF$, dma	AN	61
$(Ph_4P)_2[Mo_2S_2(dmad)_4]$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(CS_4)_2]\cdot 0.5DMF$, dma	AN	61
$(Ph_4P)_2[Mo_2S_2(dmad)_4]\cdot 2CH_2Cl_2$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(CS_4)_2]\cdot 0.5DMF$, dma	AN	47
$(Ph_4P)_2[Mo_2S_2(dmad)_4]\cdot 2CH_2Cl_2$	$(Ph_4P)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(S_4)(S_2/S_4)]$, dma	AN	47
$[Mo_2S_2(Cp)_2(S_2CC_6H_5)_2]$	$[Cp_2Mo_2(CO)_6]$, $Zn(S_3CC_6H_5)_2$	BZ	97
$[Mo_2S_2(^tBuS)_4(PMe_2Ph)_2]$	$[Mo(^tBuS)_4]$, PMe_2Ph	TL	98
$[Mo_2S_2(^tBuS)_4(HNMe_2)_2]$	$[Mo_2(NMe_2)_6]$, ^tBuSH	HX	99
$K_6[Mo_2S_2(CN)_8]\cdot 4H_2O$	MoO_3, KCN, KOH, H_2S	AQ	100
$K_6[Mo_2S_2(CN)_8]\cdot 4H_2O$	$(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$, KCN	AQ	52
$(Ph_4P)_4[Mo_2(\mu\text{-}S)_2(CN)_8]\cdot 2H_2O$	$K_6[Mo_2S_2(CN)_8]\cdot 4H_2O$, Ph_4PCl	AQ	101
$[Mo_2S_2(SCNPr_2)_2(Pr_2dtc)_2]$	$Mo_2(MeCO_2)_4$, $(NH_4)Pr_2dtc$	EtOH	102,103
$[Mo_2S_2(Cp)_2(NCMe_3)_2]$	$[Mo_2Cp_2(CO)_6$, $(Me_3CN)_2S$	BZ	104
anti-$[CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp]$[a]	$[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, C_2Ph_2	DCM	105
$Mo_2(\mu\text{-}O)(\mu\text{-}S)$ core			
$[Mo_2(\mu\text{-}O)(\mu\text{-}S)(RCO_2)_2]$ (R = *n*-hexyl, *n*-pentyl, *n*-heptyl, cyclohexyl, iso-octyl, phenyl)	$Na_2MoO_4\cdot 2H_2O$, H_2S, $KRCO_2$	AQ	106
$Mo_2(\mu\text{-}S)$ core			
$K_6[Mo_2(S)(CN)_{12}]\cdot 4H_2O$	MoO_3, KCN, KOH, H_2S	AQ	107
$K_6[Mo_2(S)(CN)_{12}]\cdot 0.5K_2MoO_4\cdot 5H_2O$	MoO_3, KCN, KOH, H_2S	AQ	100
$K_6[Mo_2(S)(CN)_{12}]\cdot 4H_2O$	$K_6[Mo_2(\mu\text{-}S)_2(CN)_8]\cdot 4H_2O$, KCN	AQ	108
$K_6[Mo_2(S)(CN)_{12}]\cdot 4H_2O$	MoO_3, KCN, KOH, H_2S	AQ	109
$[(HB(Pz)_3)_2Mo_2(S)(CO)_4]$	$[(HB(Pz)_3)Mo(CO)_3H]$, S_8	TL	110
$[Mo_2(S)(dtc)_6]\cdot C_6H_5CH_3$	$[Mo_2(dtc)_6]$, aeration	TL	111

$Mo_2(O_t)_2(\mu\text{-}S)$ core			
$(Et_4N)_2[Mo_2(O_t)_2(S)(S_2)_4]$	$(Et_4N)_2[MoO(S_4)_2]$, $PF_6[FeCp_2]$	AN	112
$(Me_4N)_2[Mo_2(O_t)_2(S)(S_2)_4]\cdot CH_3CN$	$(NH_4)_6Mo_7O_{24}$, $NH_2OH\cdot HCl$, K_2S, Me_4NBr	AQ	113
$(Ph_4As)_2[Mo_2(O_t)_2(S)(S_2)_4]$	$(AsPh_4)_2MoOS_3$, S_8	AN/MeOH	114
$(Et_4N)_2[Mo_2(O_t)_2(\mu\text{-}S/S_2)(S_2)_4]$	$(Et_4N)_2[MoO(S_4)_2]$, I_2	DMF	115
$Mo_2(S_t)_2(\mu\text{-}S)$ core			
$(AsPh_4)_2[Mo_2(S_t)_2(S)(S_2)_4]$	$(AsPh_4)_2MoS_4$, S_8	AN/MeOH	114
$(Et_2NH_2)[Mo_2(S_t)_2(S)(S_2)_4]$	$(Et_2NH_2)_2MoS_4$, S_8	DMF	114

[a]See text.

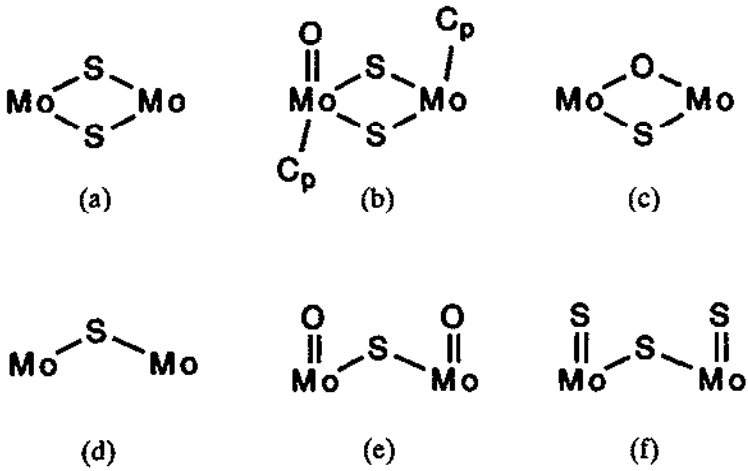


Fig. 5. Molybdenum dinuclear compounds with (a) $Mo_2(\mu\text{-}S)_2$, (b) $Mo_2(O_t)(\mu\text{-}S)_2Cp_2$, (c) $Mo_2(\mu\text{-}O)(\mu\text{-}S)$, (d) $Mo_2(\mu\text{-}S)$, (e) $Mo_2(O_t)_2(\mu\text{-}S)$, or (f) $Mo_2(S_t)_2(\mu\text{-}S)$ cores.

of sodium thiomolybdate with progressive addition of HCl [116]. The anion $[Mo_2(\mu\text{-}S)_2(CN)_8]^{6-}$ was reported as early as 1928 [117].

Monomeric Mo(IV) and Mo(VI) compounds are used for the synthesis of $[Mo_2(X)_2(\mu\text{-}S)(S_2)_4]^{2-}$ (X = O, S) [112–115]. In the reaction of $(Et_4N)_2[MoO(S_4)_2]$ and $[Fe(Cp)_2]PF_6$, the latter works as an oxidizing agent [112], and if I_2 is used as oxidant, a mixture of compounds with μ-S and end-on μ-S_2 is obtained [115].

An oxidative carbon–sulphur bond cleavage of Pr_2dtc^- followed by formation of a molybdenum–carbene bond occurred in the formation of the compound $[Mo_2(\mu\text{-}S)_2(SCNPr_2)_2(S_2CPNr_2)_2]$ [102,103].

The formation of dimers through dissociation or splitting of a tetramer [48,118–122] is not included in Table 5.

(iii) Mo(MoS$_4$) and Mo(MoO$_3$S) cores

Compounds with $Mo(MoS_4)$ or $Mo(MoO_3S)$ cores are collected in Table 6 [67,80,123–126]. In these compounds, the MoS_4^{2-} and $MoOS_3^{2-}$ groups may be regarded as ligands. Four types of core are included here, as shown in Fig. 6.

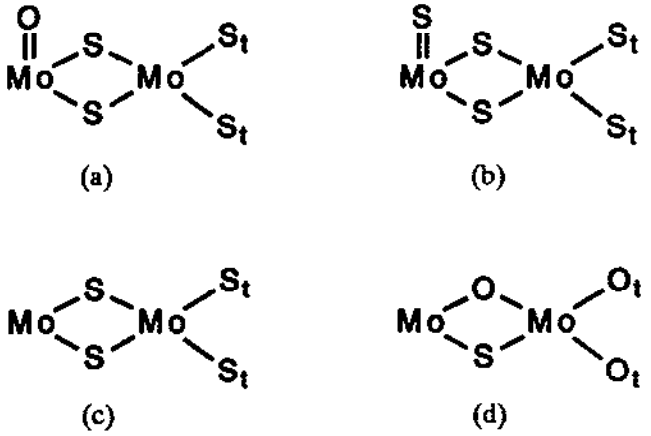
Synthesis of the $[(PhS)_2Mo(O_t)(MoS_4)]^{2-}$ anion is accomplished by the replacement of two of the four thiophenolate ligands in the compound $[(PhS)_4Mo(O)]^-$ with the chelating MoS_4^{2-} ligand, as shown in the equation [67]

$$[(PhS)_4Mo(O)]^- + MoS_4^{2-} \rightarrow [(PhS)_2Mo(O)(MoS_4)]^{2-} + PhS^- + \tfrac{1}{2}PhSSPh \qquad (1)$$

The reagent Ph_3P abstracts one sulphur atom from terminal S_2 in $[Mo_2OS(\mu\text{-}S)_2(S_2)_2]^{2-}$ and $[Mo_2OS(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$ [67], and from S_2 and S_4 in $[Mo_2S_2(\mu\text{-}S)_2(L)_2]^{2-}$ (L = S_2, S_4) [80].

TABLE 6
Compounds with $Mo(MoS_4)$ or $Mo(MoO_3S)$ cores

Compound	Source	Solvent	Ref.
Mo(O)(MoS$_4$) or Mo(S)(MoS$_4$) core			
$(Ph_4P)_2[(PhS)_2Mo(O)(MoS_4)]$	$[(PhS)_4Mo(O)]^-$, MoS_4^{2-}	DMF	67
$(Ph_4P)_2[(S_2)Mo(O)(MoS_4)]$	$(Ph_4P)_2[Mo_2OS(\mu\text{-}S)_2(S_2)_2]$, Ph_3P	DMF	67
$(Ph_4P)_2[(S_4)Mo(O)(MoS_4)]$	$(Ph_4P)_2[Mo_2OS(\mu\text{-}S)_2(S_2)(S_4)]$, Ph_3P	DMF	67
$(Ph_4P)_2[(S_2)Mo(S)(MoS_4)]$	$(Ph_4P)_2[Mo(S)(S_2)(MoS_4)]$, Bz_2S_3	DMF	80
$(Ph_4P)_2[(S_4)Mo(S)(MoS_4)]$	$(Ph_4P)_2[(S_4)Mo(S)(\mu\text{-}S)_2(S)Mo(S_2)]$, $NaBH_4$	DMF	123
$(Ph_4P)_2[(S_4)Mo(S)(MoS_4)]$	$(Ph_4P)_2Mo_2S_{10}/S_{12}\cdot 0.5DMF$, $NaBH_4$	DMF	80
$[(S_2)Mo(S)(MoS_4)]^{2-}$	$(Ph_4P)_2[Mo(S)(MoS_4)(S_4)]$	DMF	123
Mo(MoS$_4$) or Mo(MoO$_3$S) core			
$[(Cp_2Mo(MoS_4)]$	Cp_2MoCl_2, $(NH_4)_2MoS_4$	AQ	124
$[(MeCp)_2Mo(MoS_4)]$	$(NH_4)_2MoS_4$, $Mo(MeCp)_2Cl_2$, H_2S, NH_3	AQ	124
$[(BuCp)_2Mo(MoS_4)]$	$[BuCp_2MoCl_2]$, $(NH_4)_2MoS_4$, NH_3	AQ	124
$(Ph_4P)_2[(S)_2Mo(MoS_4)]$	$(Ph_4P)_2[Mo_2S_2(\mu\text{-}S)_2(S_2/S_4)_2]$, Ph_3P	DMF	80
$[(NNMe_2)_2(PPh_3)Mo(MoS_4)]$	$[MoCl(NNMe_2)_2(PPh_3)_2Cl]$, $(^nBu_4N)_2[M'S_4]$	AN	125
$[Cp'_2Mo(MoS_4)]$ (Cp′ = MeCp, Cp)	$[Cp'MoCl_2]$, Na_2MoS_4	AQ	126
$[(MeCp)_2Mo(MoO_3S)]$	$(MeCp)_2MoCl_2$, Na_2SO_4	AQ	124
$[(BuCp)_2Mo(MoO_3S)]$	$(BuCp)_2MoCl_2$, CH_3COCH_3, Na_2SO_4	AQ	124



(a) (b) (c) (d)

Fig. 6. Molybdenum dinuclear compounds with (a) $Mo(O_t)(MoS_4)$, (b) $Mo(S_t)(MoS_4)$, (c) $Mo(MoS_4)$, or (d) $Mo(MoO_3S)$ cores.

The reactivity of the Mo(O)(S) functional group in $[(L)Mo(O)(\mu\text{-}S)_2Mo(O)(S)]^{n-}$ dimeric thiomolybdate compounds ($L = Cp^-$, $n = 1$; S_4^{2-}, $n = 2$) has been discussed [56]. In addition to the compounds listed in Table 6, several compounds with the Mo(O)(S) group, e.g. $(PH_4P)_2[(S_4)Mo(O_t)(\mu\text{-}S)_2Mo(O_t)(S_t)]$ and $(Et_4N)_4\{[(S_4)Mo(O_t)(\mu\text{-}S)_2Mo(O_t)(S_t)]\}_2$ (linear tetramer), have been synthesized [56].

(iv) $Mo_2(\mu\text{-}S_2)$ cores.

This section collects compounds with at least one $(\mu\text{-}S_2)$, as shown in Table 7 [48,53,60,68,84,86,115,127–146]. The compounds in this group contain one of the following cores: $Mo_2(\mu\text{-}S_2)$ (Fig. 7(a)), $Mo_2(O_t)_2(\mu\text{-}S_2)$ (Fig. 7(b)), $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)$ (Fig. 7(c); X = OH, SO_2, SBu), $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)_2$ (Fig. 7(d); X = Cl, $S_2C_2Ph_2$), $Mo_2(S_t)_2(\mu\text{-}S_2)$ (Fig. 7(e)), $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (Fig. 7(f)), $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_2)$, $Mo_2(\mu\text{-}S_2)_2$ (Fig. 7(g)).

The synthesis [127] and X-ray structure of $[\{Mo(BuCp)Cl_2\}_2(\mu\text{-}S_2)]$, having only a disulphide (S^{2-}) bridge, has been reported [147]. End-on bridging of S_2^{2-} is also known (Fig. 8(a)) [60]. The two Mo atoms in the compound $[Mo_2(\mu\text{-}S_2)\{S_2C_2Ph_2\}_4]\cdot 1.5CH_2Cl_2$ are bridged by four sulphur atoms. Two of the bridging sulphur atoms are supplied by the two bridging dithiolene ligands, and two by the bridging S_2 unit [134].

The disulphide bridge in $[Mo_2(O)_2(\mu\text{-}S_2)(S_2)_3Cl]^-$ [115] can be both end- and side-on, as shown in Fig. 8(b)). A tetrameric compound having both end-on and end/side-on bridges, $[\{Mo_2(O)_2(\mu\text{-}S_2)(S_2)_3\}_2(\mu\text{-}S_2)]^{2-}$, has also been synthesized [115].

An interconversion reaction occurs between the two groups with $Mo_2(S_t)_2$-

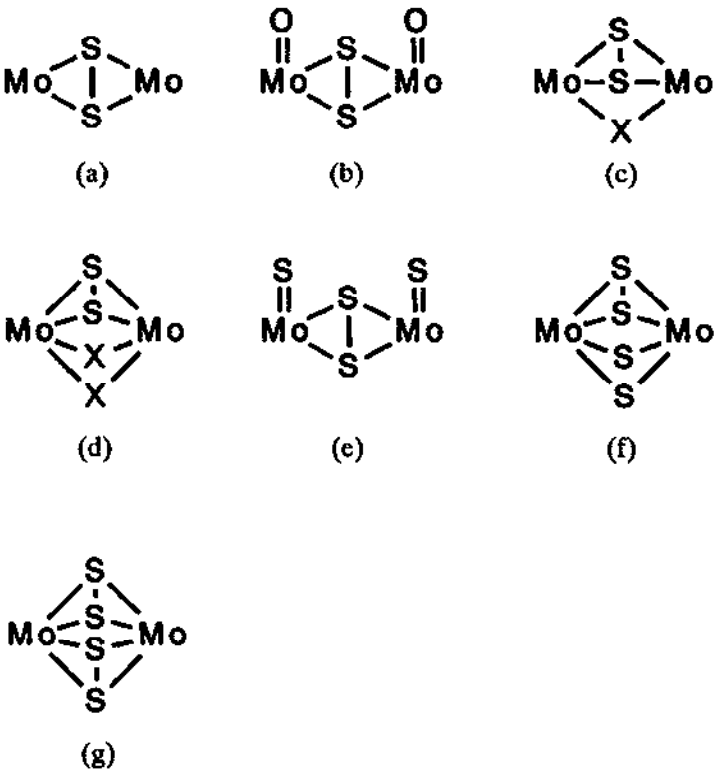


Fig. 7. Molybdenum dinuclear compounds with (a) $Mo_2(\mu\text{-}S_2)$, (b) $Mo_2(O_t)_2(\mu\text{-}S_2)$, (c) $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)$ (X = OH, SO_2, SBu), (d) $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)_2$ (X = Cl, $S_2C_2Ph_2$), (e) $Mo_2(S_t)_2(\mu\text{-}S_2)$, (f) $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, or (g) $Mo_2(\mu\text{-}S_2)_2$ cores.

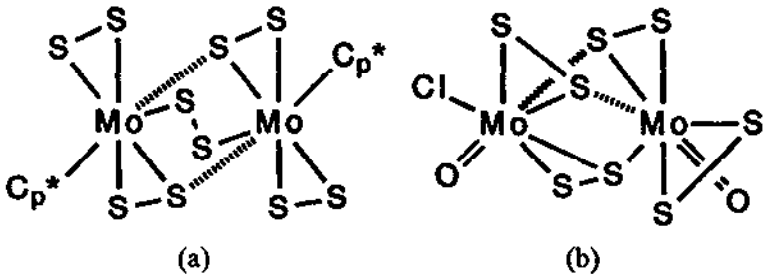


Fig. 8. Structures of (a) $[Mo_2(\mu\text{-}S_2)(S_2)_4Cp^*_2]$ and (b) $[Mo_2(O_t)_2(\mu\text{-}S_2)(S_2)_3Cl]^-$.

$(\mu\text{-}S_2)$ and $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ cores: a cyclic photo isomerization process has been reported [135,148].

$$\begin{array}{l} \textit{anti}\text{-}[Cp^*_2Mo_2(S)_2(\mu\text{-}S)_2](A) \rightarrow [Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2] \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textit{syn}\text{-}[Cp^*_2Mo_2(S)_2(\mu\text{-}S_2)] \rightarrow A \end{array} \qquad (2)$$

TABLE 7

Compounds with $Mo_2(\mu\text{-}S_2)$, $Mo_2(O_t)_2(\mu\text{-}S_2)$, $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)$ (X = OH, SO_2, SBu), $Mo_2(\mu\text{-}S_2)(\mu\text{-}X)_2$ (X = Cl, $S_2C_2Ph_2$), $Mo_2(S_t)_2(\mu\text{-}S_2)$, $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_2)$, or $Mo_2(\mu\text{-}S_2)_2$ cores

Compound	Source	Solvent	Ref.
$Mo_2(\mu\text{-}S_2)$ core			
$[(BuCp)_2Mo_2(S_2)Cl_4]$	$[\{(BuCp)Mo(\mu\text{-}O)O\}_2]$, HCl, H_2S	CBZ/pet.	127
$[Mo_2(\mu\text{-}S_2)(S_2)_4Cp^*_2]$	$[MoCp^*(CO)_3H]$, S_8	THF/CDS	60
$Mo_2(O_t)_2(\mu\text{-}S_2)$ core			
$(Et_4N)[Mo_2(O)_2(\mu\text{-}S_2)(S_2)_3X]$[a] (X = Cl, I)	$(Et_4N)_2[Mo_2O_2(\mu\text{-}S/\mu\text{-}S_2)(X)(S_2)_3]$, NiX_2	AN	115
$Mo_2(\mu\text{-}S_2)(\mu\text{-}X)$ core			
$(NH_4)_3[Mo_2(S_2)(\mu\text{-}OH)(NO)_2(S_2)_3(S_5)OH]\cdot 2H_2O$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, NH_2OH, KSCN, $(NH_4)_2S$, S_8	AQ	128
$K_4[Mo_2(S_2)(\mu_2\text{-}SO_2)(CN)_8]\cdot 2.5H_2O$	$K_6[Mo_2(\mu_2\text{-}S)_2(CN)_8]\cdot 4H_2O$	AQ	129
$K_{4+x}[Mo_2(S_2)(SO_2)(CN)_8]_x\cdot 4H_2O$	$K_6[Mo_2(S)_2(CN)_8]\cdot 4H_2O$, CH_3COOH, O_2	AQ	130
$[Mo_2(S_2)(\mu\text{-}SC_4H_8)Cl_6(C_4H_8S)_2]$	$Mo(CO)_6$, S_2Cl_2	DCM	131
$(PPh_4)_4[Mo_2(\mu\text{-}S_2)(\mu\text{-}SO_2)(CH)_8]\cdot 6H_2O$	$K_6[Mo_2S_2(CH)_8]\cdot 4H_2O$, O_2, PPh_4Cl	AQ	132
$Mo_2(\mu\text{-}S_2)(\mu\text{-}X)_2$ core			
$(Et_4N)_2[Mo_2(S_2)(\mu\text{-}Cl)_2Cl_6]$	$MoCl_5$, NEt_4SH	DCM/TCM	133
$[Mo_2(S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]\cdot 1.5CH_2Cl_2$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $[Ph_2C_2S_2PS_2]_2$	DOX	134
$Mo(S_t)_2(\mu\text{-}S_2)$ core			
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2(CO)_4Cp^*_2]$, S_8	TL	68
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp^*_2]$	TL	68
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp^*_2]$, light	CF	135

Mo(μ-S_2)(μ-S)$_2$ core			
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2(CO)_4Cp^*_2]$, S_8	TL	68
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp^*_2]$, SO_2(gas)	*CBZ/BzOH*	*136*
$[Mo_2(S)_2(S_2)Cp^*_2]$	$[Mo_2S_2(\mu\text{-}S)_2Cp^*_2]$, light	CF	135
$[Mo_2(S)_2(S_2)Cp^*_2]I_2$	$[Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2Cp^*_2]$, I_2	TL	137
$[Mo_2(S_2)(S)_2(MeCp)_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(MeCp)_2]$, $C_{12}H_{10}N_2$	DCM	138
$[Mo_2(S_2)(S)_2(MeCp)_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2(MeCp)_2]$, SO_2	TL	86
$[Mo_2(S_2)(S)_2(MeCp)_2]$	$[Mo_2(O_t)_2(\mu\text{-}S)_2(MeCp)_2]$, $[(CH_3)_3Si]_2S$	CF	48
$[Mo_2(S_2)(S)_2Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$, SO_2	TL	86
Mo(μ-S_2)(μ-S)(μ-SX) core			
$[Mo_2(S_2)(S)(S\cdot SO_2)Cp^*_2]$	$[Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2Cp^*_2]$, SO_2	TL	86
Mo_2(μ-S_2)$_2$ core			
$[Mo_2(S_2)_2Cp_2]$	$[(Cp)Mo(CO)_2(P(OPh)_3)H]$, C_3H_6S	THF	84
$(NH_4)_2[Mo_2(S_2)_2(S_2)_4]\cdot 2H_2O$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2S_x$, NH_3aq, H_2S	AQ	53,139–142
$(NH_4)_2[Mo_2(S_2)_2(S_2)_4]\cdot 2H_2O$	$(NH_4)_2MoO_2S_2$, H_2S, S_8, NH_3aq	AQ	143
$(Ph_4P)_2[Mo_2(S_2)_2Cl_8]\cdot CH_2Cl_2$	$Mo(S_2)Cl_3$, PPh_4Cl	DCM	144
$(Ph_3MeP)_2[Mo_2(S_2)_2Cl_8]\cdot 2CH_2Cl_2$	$Mo(S_2)Cl_3$, PPh_3MeCl	DCM	144
$(Ph_4P)_2[Mo_2(S_2)_2Br_8]\cdot 3CH_2Br_2$	$MoBr_4$, S_7NH	DBM	144
$[Mo_2(S_2)_2(Et_2dtc)_4](BF_4)_2\cdot 2CHBr_3$	$[MoO(Et_2dtc)_3]BF_4$, B_2S_3	DCM	145
$(Ph_3EtP)_2[Mo_2(S_2)_2Cl_8]\cdot 2CH_2Cl_2$	$H_2Mo_2S_4Cl_8\cdot 6H_2O$, $(Ph_3EtP)Br$	BF	144
$(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$	$Mo_2(\mu\text{-}S_2)_2Cl_4Cl_4/2$, $(NH_4)_2S_x$	AQ	146

[a]See text (different bridging modes).

Reaction of SO_2 with solutions of $[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$ initially yields $[Cp^*_2Mo_2(S_2)(S)(S\cdot SO_2)]$ (Fig. 9(a)), which is shown by crystallography to contain an SO_2 weakly bound to a μ-S. SO_2 further reacts quantitatively with $[Cp^*_2Mo_2(S_2)(S)(S\cdot SO_2)]$ to give $[Cp^*_2Mo_2(S_2)(S)(S\cdot SO_3)]$ (Fig. 9(b)), which now contains an SO_3 bound to the μ-S. A μ-S_2O_3 (thiosulphate) ligand is formed by an oxygen-transfer process, and the source of the oxygen is established by ^{18}O labelling as SO_2 [86].

A one-to-three molar ratio reaction of $[(Cp)Mo(CO)_2(P(OPh)_3)H]$ with propylene sulphide affords the di-μ-S_2 compound $[Cp_2Mo_2(S_2)_2]$, while a one-to-one mixture of these compounds gives an incomplete cubane-type trimer $[Mo_3S_4(Cp)_3]$ (see Table 9, Sect. C.(i)) [84].

(v) Miscellaneous

In addition to the compounds described above, there are many other interesting compounds. Some representative compounds are listed in Table 8 [48,60,86, 137,138,149–156]. The core structures are depicted in Fig. 10: $Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2$ (Fig. 10(a); R = H, alkyl), $Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)$ (Fig. 10(b)), $Mo_2(\mu\text{-}S)(\mu\text{-}SX)(\mu\text{-}S_2CH_2)$ (Fig. 10(c); X = H, OH, R), $Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}S_2R)$ (Fig. 10(d)), $Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}SOR)$ (Fig. 10(e)), $Mo_2(\mu\text{-}SH)(\mu\text{-}SR)(\mu\text{-}S_2R)$ (Fig. 10(f)).

The compound $[(Cp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$ catalyzes HD exchange between H_2 and D_2 as well as between H_2 and D_2O [149]. Formation of $[(MeCp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$ from *syn/anti*-$[(MeCp)_2Mo_2(O_t)(X_t)(\mu\text{-}S)_2]$ (X = O, S) was monitored by NMR [48]. The reaction of $[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$ with H_2 gives $[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$, in contrast to $Cp^*_2Cr_2S_4$, which gives the cubane-type cluster $Cp^*_4Cr_4S_4$ [151]. Conversion of two SH bridges into an S_2CH_2 bridge occurred in $[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)]$. The core structure changed from one in Fig. 10(a) (R = H) to another in Fig. 10(b) [86,154]. The formation of a hydrosulphide bridge from a sulphide bridge by the reaction with molecular hydrogen in $[(MeCp)_2$-

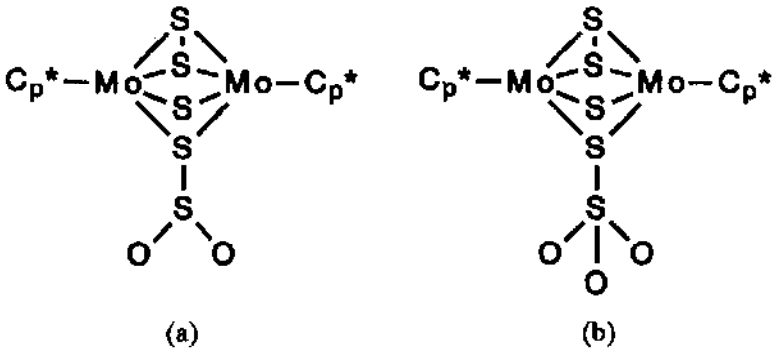
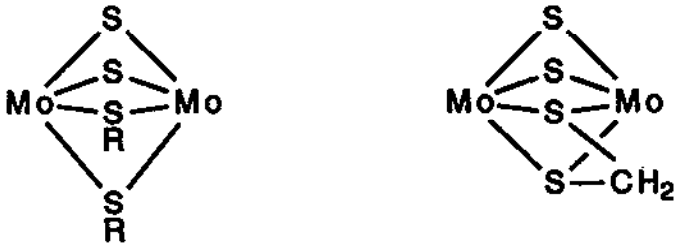
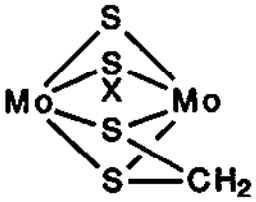


Fig. 9. Structures of (a) $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_2)Cp^*_2]$ and (b) $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}S\cdot SO_3)Cp^*_2]$.

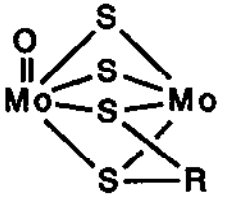


(a)

(b)



(c)



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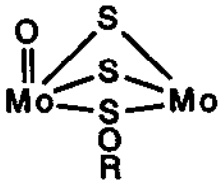
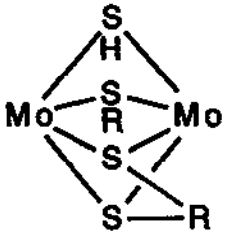


(e)



(f)

Fig. 10. Molybdenum dinuclear compounds with (a) $Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2$ (R = H, alkyl), (b) $Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)$, (c) $Mo_2(\mu\text{-}S)(\mu\text{-}SX)(\mu\text{-}S_2CH_2)$ (X = H, OH, R), (d) $Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}S_2R)$, (e) $Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}SOR)$, or (f) $Mo_2(\mu\text{-}SH)(\mu\text{-}SR)(\mu\text{-}S_2R)$.

$Mo_2(\mu\text{-}S)(\mu\text{-}SCH_3)(\mu\text{-}S_2CH_2)$] has been reported [138,157]. The reaction of $[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)]$ with hydrogen and dichloromethane to give $[Cp^*_2Mo_2(\mu\text{-}S_2CH_2)_2]$ has recently been described [158].

Intermolecular oxo-sulphido transfer is involved in the reaction of *syn*-$[(MeCp)_2Mo_2(O)(S)(\mu\text{-}S)_2]$ with alkynes, resulting in products $[(MeCp)_2Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}XCR{=}C(R)S)]$ (X = O, S) [48].

Reaction of $[Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)]$ (CP' = Cp, MeCp, Cp*) with methyl

TABLE 8

Compounds with miscellaneous cores

Compound	Source	Solvent	Ref.
$Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2$ core			
$[Mo_2(S)_2(SR)_2Cp'_2]^a$ ($Cp' = Cp$, MeCp; R = Me, Et, ^iPr, Ph)	$[Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$, H_2, RSH	CF/TL	149
$[Mo_2(S)_2(SH)_2Cp_2]$	$[CpMoS_x]_y$, H_2	CF	149
$[Mo_2(S)_2(SH)_2Cp^*_2]$	$(Cp^*MoS_x)_n$, H_2, Et_3N	CBZ/EtOH	86
$[Mo_2(S)_2(SH)_2Cp'_2]$	$[Cp'MoS_x]_y$, H_2	CF	60
$[Mo_2(S)_2(SH)_2Cp_2]$	$(CpMo_2S_x)_n$, $LiEt_3BH$	THF	150
$[Mo_2(S)_2(SH)_2Cp^*_2]$	$[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$, H_2	TL	151
$[Mo_2(S)_2(SH)_2(MeCp)_2]$	*anti*-$[MeCp_2Mo_2(O_t)_2(\mu\text{-}S)_2]$	CF	48
$[Mo_2(S)_2(SMe)_2Cp^*_2]$	$[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]I_2$, CH_3Li	THF	137
$[Mo_2(S)_2(SMe)_2Cp_2]$	$[Cp_2Mo_2(\mu\text{-}SMe)_2(CO)_2]$, S_8	THF	152
$Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)$ core			
$[Mo_2(S)_2(\mu\text{-}S_2CH_2)Cp_2]$	$[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_3)(\mu\text{-}S_2CH_2)(Cp)_2]$	THF	153
$[Mo_2(S)_2(\mu\text{-}S_2CH_2)Cp^*_2]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp^*_2]$, CH_2Br_2, NaOMe	MeOH/THF	86,154
$Mo_2(\mu\text{-}S)(\mu\text{-}SX)(\mu\text{-}S_2CH_2)$ core			
$[Mo_2(S)(\mu\text{-}SH)(\mu\text{-}S_2CH_2)MeCp_2](SO_3CF_3)$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)(MeCp)_2]$, HSO_3CF_3	DCM	154
$[Mo_2(S)(\mu\text{-}SCH_3)S_2CH_2Cp_2]^-$	$[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2Cp_2]I$	IF/THF	153
$Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}S_2R)$ core			
$[Mo_2(O_t)(S)_2(\mu\text{-}SCH{=}CHS)MeCp_2]$	$[Mo_2(O)(S)(\mu\text{-}S)_2MeCp_2]$, C_2H_2	DCM	48
$Mo_2(O_t)(\mu\text{-}S)_2(\mu\text{-}SOR)$ core			
$[Mo_2O(S)_2(SC_2H_2O)MeCp_2]$	$[Mo_2(O)(S)(\mu\text{-}S)_2MeCp_2]$, C_2H_2	DCM	48

$Mo_2(\mu\text{-}SH)(\mu\text{-}SR)(\mu\text{-}S_2R)$ core			
$[Mo_2(\mu\text{-}SH)(\mu\text{-}SCH_3)(\mu\text{-}S_2CH_2)MeCp_2]$	$[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_3)(\mu\text{-}S_2CH_2)(MeCp)_2]$, H_2	THF	138
$Mo_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2$, $Mo_2(\mu\text{-}S)_2$, $Mo_2(\mu\text{-}S_2)_2$ core			
$(Et_4N)_3[Mo_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2Cl_6]Cl \cdot CH_2Cl_2$	$MoCl_5$, Et_4NHS	DCM	155
$[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5]$	$MoCl_2(PMe_3)_4$, $SPMe_3$	TL	156

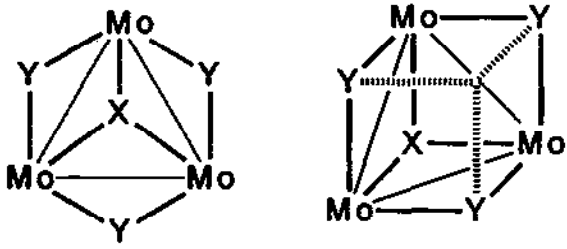
iodide or methyl fluorosulphate leads to formation of the cationic dimer $[Cp'_2Mo_2(\mu\text{-}S)(\mu\text{-}SX)(\mu\text{-}S_2CH_2)]^+$ (X = H, OH, CH_3, C_2H_5) [153,154].

The polymeric species molybdenum dithiotrichloride, $Mo_2(\mu\text{-}S_2)_2Cl_4Cl_{4/2}$, reacts with ammonium polysulphide to give $(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$ [146]. Another polymeric species, molybdenum dithiodichloride $Mo_2(\mu\text{-}S_2)_2Cl_8/2$ also gave $(NH_4)_2[Mo_2(\mu\text{-}S_2)_2(S_2)_4]\cdot 2H_2O$ [146].

Labile and coordinatively unsaturated molybdenum(III)-μ-sulphido dimers $[Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4(L)]$ (L = PMe_3, MeCN, vacant) are formed by sulphur atom abstraction from $SPMe_3$ [156].

C. SYNTHESES OF TRINUCLEAR MOLYBDENUM COMPOUNDS

Two types of trinuclear molybdenum compound exist: triangular and non-triangular (or linear). The cores of the triangular compounds described here are limited to those of $Mo_3(\mu_3\text{-}X)(\mu\text{-}Y)_3$ (Fig. 11(a); X, Y = O, S) and $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ (Fig. 11(c)). The former is of an incomplete cubane-type (Fig. 11(b)). Emphasis is laid



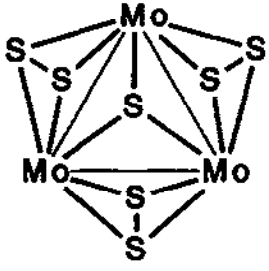


Fig. 11. Molybdenum trinuclear compounds with (a), (b) $Mo_3(\mu_3\text{-}X)(\mu\text{-}Y)_3$ (X, Y = O, S) or (c) $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$.

on the triangular compounds and only a few non-triangular compounds are listed in this review. The sulphido- and carbonyl-bridged clusters such as $[Mo_3(\mu_3\text{-}S)(\mu\text{-}CO)_3(CO)_9]$ [159] are not included here.

(i) $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores

Many compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores have been reported, and are collected in Table 9 [22(a),84,101,160–189]. The cyclopentadienyl compound $[Mo_3S_4Cp_3][Sn(CH_3)_3Cl_2]$ was the first reported to have the triangular molybdenum core $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ [175]. It was obtained as one of the products from the reaction of $Mo(Cp)(CO)_3Cl$ in 1,2-dimethoxyethane with a tin compound, $[Sn(CH_3)_2]_2S$ [175]. Subsequently, many compounds with this core have been reported (Table 9).

Many starting materials for compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores have been reported. Mononuclear and dinuclear molybdenum compounds used so far for such syntheses include $[MoCl_3(H_2O)_3]$, $[MoCl_3(thf)_3]$, $[Mo(CO)_6]$, $[Mo(Cp)(CO)_3Cl]$, $(NH_4)_2MoS_4$, $[Mo_2O_2S_2(cys)_2]^{2-}$, $Mo_2O_2S_2^{2+}(aq)$, and $[Mo_2O_4(cys)_2]^{2-}$. Metallic molybdenum as well as trinuclear molybdenum compounds, and polymeric compounds have also been used as source materials. The oxidation states of molybdenum in the starting compounds were in the range 0–VI. Sources of sulphur include P_2S_5, H_2S, NaHS, $[Sn(CH_3)_2]_2S$, and $(NH_4)_2MoS_4$. The oxidation state of molybdenum with the Mo_3S_4 core described in this section is IV except for a few exceptions: $[Mo_3(III,IV,IV)S_4Cp'_3]$ (Cp' = Cp, Cp*).

The aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ has attracted much attention. It was synthesized by Cotton et al. [160], by Sykes and co-workers [166,167] and by the author's group [161,162] independently. Several synthetic methods for the aqua ion have been reported and the very facile method [163] reported recently is included in the table. Crystallization of the aqua ion was successful and the structure has been determined [168].

The water ligand in $[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$ can readily be replaced by other ligands to give many derivatives [170–173]. The reaction of MoS_3 obtained from $(NH_4)_2MoS_4$ with KCN in water gave $K_5[Mo_3S_4(CN)_9]\cdot 2H_2O$ [101].

Compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores can also be obtained from polymeric or discrete compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores. There are two types of cluster with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores: one has the formula $Mo_3S_7X_2X_{4/2}$ (X = Cl, Br), and the other the formula $M^I_2[Mo_3S_7X_6]$ (M^I = monovalent cation). The former is polymeric and has two terminal and four bridging X atoms, giving an infinite chain structure as shown in Fig. 12(a) and the latter has a discrete structure (Fig. 12(b)). Removal of one sulphur atom from each bridging S_2 group results in the formation of three single sulphur bridges.

The compounds with PEt_3, $[Mo_3S_4Cl_4(PEt_3)_3(H_2O)_2]\cdot OPEt_3$ and $[Mo_3S_4Br_4(PEt_3)_3(OPEt_2H)(H_2O)]\cdot 2thf$, were synthesized by treatment of a thf

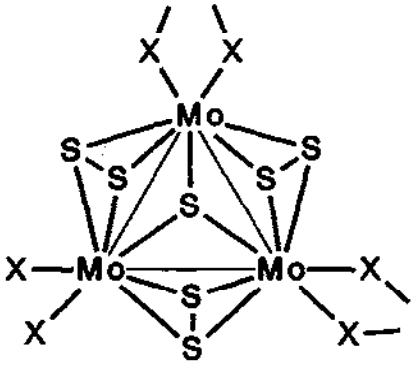
TABLE 9

Compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores

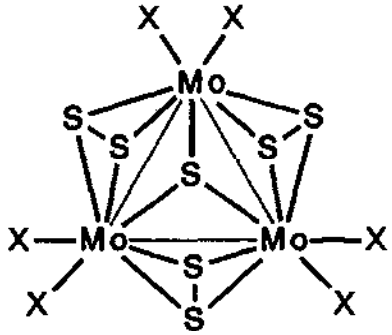
Compound	Source	Solvent	Ref.
$[Mo_3S_4(H_2O)_9]^{4+}$	$Mo(CO)_6$, Na_2S	Ac_2O	160
$[Mo_3S_4(H_2O)_9]^{4+}$	$[Mo_2(O_t)_2(\mu\text{-}S)_2(cys)_2]^{2-}$, $NaBH_4$	AQ	22(a),161–164
$[Mo_3S_4(H_2O)_9]^{4+}$	$[Mo_2(O_t)_2(\mu\text{-}S)_2(cys)_2]^{2-}$, electrolysis	AQ	165–167
$[Mo_3S_4(H_2O)_9]^{4+}$	$Mo_2(O_t)_2(\mu\text{-}S)_2^{2+}$(aq), $[MoCl_6]^{3-}$	AQ	165,166
$[Mo_3S_4(H_2O)_9]^{4+}$	$(NH_4)_2MoS_4$, $NaBH_4$	AQ	163
$[Mo_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Hpts	AQ	168
$[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$	$MoCl_3 \cdot 3H_2O$, HCl gas, P_4S_{10}, H_2S	EtOH	169–171
$[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(oxaz)] \cdot MeCN$	$[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$, oxaz	AN	170
$[Mo_3S_4\{\mu\text{-}(Et_2O)POS\}(Et_2dtp)_3(oxaz)]$	$[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$, oxaz, $Fe(ClO_4)_3$	AN	172
$[Mo_3S_4(\mu\text{-}Et_2dtp)(Et_2dtp)_3(R)]$ (R = EtCN, $PhCH_2SH$, PPh_3, DMF, $PhCH_2CN$, Py, $SC(NH_2)(NHC_3H_5)$)	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, R	EtOH/ACET	173,171
$[Mo_3S_4(\mu\text{-}O_2CR)(Et_2dtp)_3(Py)]$ (R = H, Me, Et)	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, Py, RCO_2^-	EtOH/ACET	171
$[Mo_3S_4(Et_2dtp)_3(bipy)]^+(Et_2dtp)^-$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, bipy	EtOH/ACET	171
$[Mo_3S_4(Et_2dtp)_3(Him)_3]^+(Et_2dtp)^-$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, Him	AN	171
$Ca_{1.5}[Mo_3S_4(Hnta)_2(nta)] \cdot 13H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, H_3nta	AQ	161
$Ca[Mo_3S_4(ida)_3] \cdot 11.5H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, H_2ida	AQ	162
$(NH_4)_3[Mo_3S_4(Hnta)_2(nta)] \cdot 3EtOH$	$(NH_4)_2[Mo_3S_7(S_2)_3] \cdot 2H_2O$, H_3nta	DMF/AN	174
$Cs_2[Mo_3S_4(ox)_3(H_2O)_3] \cdot 3H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, H_2ox	AQ	160
$[Mo_3S_4Cp_3][Sn(Me)_3Cl_2]$	$Mo(Cp)(CO)_3Cl$, $[Sn(Me)_2]_2S$	DME	175
$[Mo_3S_4Cp_3^*]$	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp_2^*]$, $[Mo_2Cp_2^*(CO)_4]$	TL	176
$[Mo_3S_4Cp_3]$	$[Mo(H)(CO)_2(P(OPh)_3)Cp]$, $C_3H_6S^a$ (1:1)	THF	84
$K_5[Mo_3S_4(CN)_9] \cdot 2H_2O$	$(NH_4)_2MoS_4$, KCN	AQ	101
$K_5[Mo_3S_4(CN)_9] \cdot 3KCN \cdot 4H_2O$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$, KCN	AQ	177
$K_5[Mo_3S_4(CN)_9] \cdot 7H_2O$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$, KCN	AQ	178
$[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$	$[Mo_3S_4(H_2O)_9]^{4+}$ (dried), PEt_3	MeOH	179
$[Mo_3S_4Cl_4(PEt_3)_{3+x}(MeOH)_{2-x}]$ ($x = 0, 1$)	$Mo_3S_7Cl_4$, PEt_3	MeOH	179

$[Mo_3S_4Cl_4(PEt_3)_3(H_2O)_2]\cdot OPEt_3$	$Mo_3S_7Cl_4$, PEt_3	THF	180
$[Mo_3S_4Br_4(PEt_3)_3(OPEt_2H)(H_2O)]\cdot 2THF$	$Mo_3S_7Br_4$, PEt_3	THF	180
$[Mo_3S_4Cl_3(dmpe)_3]PF_6\cdot MeOH$	$[MoCl_3(thf)_3]$, NaHS, dmpe, MeOH	THF	181,182
$[Mo_3S_4X_4(L)_3]$ (X = Cl, Br; L = PPh_3, dppe)	$(R_4N)_2Mo_3S_7X_6$, L (R = Me, Et)	MeOH	183
$[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]\cdot 3THF$	$Mo_3S_7Cl_4$, PPh_3	THF	184
$(Et_4N)_2[Mo_3S_4(SCH_2CH_2S)_3]$	$(NH_4)_2[Mo_3S_7(S_2)_3]$, Et_4NBr, $Na_2(SCH_2CH_2S)$	AN	185
$[Mo_3S_4(\mu\text{-}Et_2PS_2)(Et_2PS_2)_3]$	$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(Et_2PS_2)_3]^+[Et_2PS_2]^-$, Ph_3P	DCM	186
$[Mo_3S_4(Et_2dtc)_4(dmf)]\cdot EtOH$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, Et_2dtc^-	DMF	187
$[Mo_3S_4(HBpz_3)_2]_2(\mu\text{-}O)(\mu\text{-}pz)_2\cdot 2THF$	$[Mo_3S_4(H_2O)_9]^{4+}$, Hpz, $K[HBpz_3]$, THF	MeOH	188
$[Mo_3S_4([9]aneN_3)_3](ZnCl_4)(ZnCl_3OH_2)_2\cdot 3H_2O$	$[Mo_4(\mu_3\text{-}S)_4(NCS)_{12}]^{6-}$, amine, $ZnCl_2$	AQ	189

[a] Propylenesulphide.



(a)



(b)

Fig. 12. Structures of $Mo_3S_7X_2X_{4/2}$ and $Mo_3S_7X_6$ (X = Cl, Br).

solution of $Mo_3S_7Cl_4$ and $Mo_3S_7Br_4$, respectively, with PEt_3 [180]. If PPh_3 was used instead of PEt_3, $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]\cdot 3thf$ was obtained from $Mo_3S_7Cl_4$ [184]. If MeOH was used as a solvent, $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ and $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$ were obtained from $Mo_3S_7Cl_4$ and PEt_3 [179]. $[Mo_3S_4X_4(dppe)_3]$ and $[Mo_3S_4X_4(PPh)_3]$ (X = Cl, Br) are synthesized by the reaction of $(Me_4N)_2Mo_3S_7X_6$ with dppe and PPh_3, respectively [183]. The compounds $[Mo_3S_4(Et_2PS_2)_4]$ and $[Mo_3S_7(Et_2PS_2)_3](Et_2PS_2)$ can be converted into each other by partial desulphuration with Ph_3P or reaction with S_8 or $Et_2P(S)S_2P(S)Et_2$ [186]. Reaction of $(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$ with H_3nta and $Na_2(SCH_2CH_2)$ gives $(NH_4)_3[Mo_3S_4(Hnta)_2(nta)]\cdot 3EtOH$ [174], and $(Et_4N)_2[Mo_3S_4(SCH_2\text{-}CH_2S)_3]$ [185], respectively.

Ligand substitution is a useful method to apply to the synthesis of clusters with Mo_3S_4 cores. One of the source clusters is $[Mo_3S_4(Et_2dtp)_4(H_2O)]$ [170]. By change of reaction conditions, ligands, and solvents, many clusters with the Mo_3S_4 core have been synthesized. The water molecule in $[Mo_3S_4(Et_2dtp)_4(H_2O)]$ is always replaced by other ligands, and, in a few cases, one of four Et_2dtp groups is also replaced. Another source cluster for substitution reaction is $[Mo_3S_4(H_2O)_9]^{4+}$, where all or some of the water molecules can be substituted. $[Mo_3S_4(HBpz_3)_2]_2$-$(\mu$-O$)(\mu$-pz$)_2 \cdot 2$thf and $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ were obtained by the treatment of a methanol solution of $[Mo_3S_4(H_2O)_9]^{4+}$ with Hpz and $KHBpz_3$ [188], and PEt_3 [179], respectively.

(ii) $Mo_3(\mu_3$-S$)(\mu$-O$)_{3-n}(\mu$-S$)_n$ $(n = 0–3)$ and $Mo_3(\mu_3$-O$)(\mu$-S$)_3$ cores

Compounds with $Mo_3(\mu_3$-S$)(\mu$-O$)_3$, $Mo_3(\mu_3$-S$)(\mu$-O$)_2(\mu$-S), $Mo_3(\mu_3$-S$)(\mu$-O$)$-$(\mu$-S$)_2$, and $Mo_3(\mu_3$-O$)(\mu$-S$)_3$ cores are listed in Table 10 [87,164,170,171,190–192].

The oxo/sulphido mixed-bridged aqua cluster $[Mo_3(\mu_3$-S$)(\mu$-O$)_3(H_2O)_9]^{4+}$ may be synthesized by treatment of $Mg[Mo_2O_3S(edta)] \cdot 6H_2O$ with K_2CO_3 in alkaline solution [190] or by the reduction of $[Mo_2O_3S(H_2O)_6]^{2+}$ with $NaBH_4$ [87,164]. The latter method gives a higher yield (ca. 70%). The derivative clusters, $Ba[Mo_3O_3S(Hnta)_3] \cdot 10H_2O$ [87,190] and $K_2[Mo_3O_3S(cys)_3] \cdot 6H_2O$ [87], are also known and the X-ray structures determined. The other aqua clusters, $[Mo_3$-$(\mu_3$-S$)(\mu$-O$)_2(\mu$-S$)(H_2O)_9]^{4+}$ [164,191], and $[Mo_3(\mu_3$-S$)(\mu$-O$)(\mu$-S$)_2(H_2O)_9]^{4+}$ [164,192] were synthesized by the reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ with $NaBH_4$ followed by Sephadex G-10 separation. The derivative clusters $(pyH)_5[Mo_3$-$O_2S_2(NCS)_9] \cdot 2H_2O$ [191] and $Ba[Mo_3OS_3(ida)_3] \cdot 7H_2O$ [192] were synthesized from the corresponding aqua clusters and the X-ray structures were determined. Triangular oxo/sulphido aqua compounds were also synthesized by electrochemical reduction of pairs of $Mo(V)_2$ compounds from $[Mo_2O_4(cys)_2]^{2-}$, $[Mo_2O_3S$-$(cys)_2]^{2-}$, and $[Mo_2O_2S_2(cys)_2]^{2-}$ in equimolar amounts [167].

A compound with μ_3-O, $[Mo_3(\mu_3$-O$)(\mu$-S$)_3(Et_2dtp)_4(oxaz)]$ [171] was synthesized by a similar method to $[Mo_3(\mu_3$-S$)(\mu$-S$)_3(Et_2dtp)_4(oxaz)]$ with H_2S bubbling [170]. Refluxing $[Mo_3S_4(Et_2dtp)_4(H_2O)]$ in an acid for a long time gave $[Mo_3(\mu_3$-O$)(\mu$-S$)_3(Et_2dtp)_4(H_2O)]$ [171]. $[Mo_3(\mu_3$-O$)(\mu$-S$)_3(Et_2dtp)_4(im)]$ is also known [171,193].

(iii) Triangular $Mo_3(\mu_3$-S$)(\mu$-$S_2)_3$ cores

A group of compounds with another triangular core, $Mo(\mu_3$-S$)(\mu$-$S_2)_3$ is collected in Table 11 [5,141,143,146,155,171,183,184,186,194–208]. Metallic molybdenum, and mononuclear, dinuclear, and trinuclear molybdenum compounds have been used as starting materials. Several sulphur sources, such as S_8, H_2S, S_2Cl_2, $R_2P(S)$–S_2–$P(S)R_2$ (R = Et, Pr), have been used.

TABLE 10

Compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_{3-n}(\mu\text{-}S)_n$ ($n = 0$–2) or $Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3$ cores

Compound	Source	Solvent	Ref.
$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_{3-n}(\mu\text{-}S)_n$ ($n = 0$–2) cores			
$Mo_3O_3S^{4+}$(aq)	$Mg[Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(edta)]\cdot 6H_2O$, K_2CO_3	AQ	190
$Mo_3O_3S^{4+}$(aq)	$Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)^{2+}$(aq), $NaBH_4$	AQ	87,164
$Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$	$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$(aq), H_3nta	AQ	87,190
$K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$	$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$(aq), L-cys · HCl · $2H_2O$	AQ	87
$Mo_3O_2S_2^{4+}$(aq)	$Mo_2O_2(\mu\text{-}S)_2^{2+}$(aq), $NaBH_4$	AQ	164,191
$Mo_3O_2S_2^{4+}$(aq)	$Mo_2O_2(\mu\text{-}S)_2^{2+}$(aq), $K_3[MoCl_6]$	AQ	191
$(PyH)_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$	$Mo_3O_2S_2^{4+}$(aq), KSCN, py	AQ	191
$Mo_3OS_3^{4+}$(aq)	$Mo_2O_2(\mu\text{-}S)_2^{2+}$(aq), $NaBH_4$	AQ	164,192
$Ba[Mo_3OS_3(ida)_3]\cdot 7H_2O$	$Mo_3OS_3^{4+}$(aq), H_2ida, $BaCl_2$	AQ	192
$Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3$ cores			
$[Mo_3OS_3(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$	$MoCl_3\cdot 3H_2O$, P_4S_{10}, H_2S	EtOH	170,171
$[Mo_3OS_3(\mu\text{-}Et_2dtp)(Et_2dtp)_3(oxaz)]$	$[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(\mu\text{-}Et_2dtp)(Et_2dtp)_3(H_2O)]$, oxaz	AN	170

The polymerized species $Mo_3S_7X_4$ ($Mo_3S_7X_{4/2}X_2$; X = Cl, Br; Fig. 12(a)) can be synthesized at high temperatures (400–450°C) in sealed tubes. Four different methods have been employed:

(1) molybdenum halides and elemental sulphur [5,194,195,197]. The corresponding selenium compound $Mo_3Se_7Cl_4$ was synthesized by a similar method at 400°C [194]

$$MoX_3 + S_8 \rightarrow Mo_3S_7X_4$$

(2) molybdenum metal, elemental sulphur and bromine [184, 196]

$$Mo + S_8 + Br_2 \rightarrow Mo_3S_7Br_4$$

(3) molybdenum sulphide and bromine [196]

$$3MoS_3 + 3Br_2 \rightarrow Mo_3S_7Br_4 + S_2Br_2$$

(4) molybdenum, elemental sulphur, and disulphur dichloride [196]

$$Mo + S_8 + S_2Cl_2 \rightarrow Mo_3S_7Br_4$$

$[Mo_6Br_8]Br_4$ can also be the source of $Mo_3S_7Br_4$ [198]. Polymeric $Mo_3S_7X_4$ (X = Cl, Br) reacts with PPh_3 or PEt_3 in organic solvents to give clusters with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores (see Sect. C.(i)).

Many compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores have been reported. $[Mo_3S_7(R_2PS_2)_3]^+[R_2PS_2]^-$ (R = Et, Pr) are synthesized by heating a mixture of $Mo(CO)_6$ and $R_2P(S)\text{–}S_2\text{–}P(S)R_2$ in toulene [207]. $MoCl_5$ and Et_4NHS in CH_2Cl_2 gave $(Et_4N)_3[Mo_3S_7Cl_6]Cl \cdot CH_2Cl_2$ via an intermediate whose composition is $(Et_4N)_2Mo_2S_3Cl_9$ [155], $(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$ was obtained by the reaction of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with $(NH_4)_2S_2$ [141,199(a),199(b),200].

Incomplete cubane-type compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores can also be starting materials for compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores. By the addition of H_2S and appropriate reagents to $[Mo_3S_4(Et_2dtp)_4(H_2O)]$, clusters with the formula $[Mo_3S_7(Et_2dtp)_3X]$ (X = Cl, I) were obtained [171,206].

Ligand replacement is a convenient method. The terminal ligand X (X = Cl, Br) in $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_6]^{2-}$ is replaced by SCN, Hmsa, or mba to give the corresponding compounds [200,204]. In addition, the mba compound $(HNEt_3)_2$-$[Mo_3S_7(mba)_3]$, Hdsa and H_2dsa mixed ligand cluster with the core has been synthesized and electrochemical reduction of the clusters with the core in aqueous solution has been reported [203]. $(NH_4)_2Mo_3S_{13}$ may also be used to prepare $(Et_4N)_2Mo_3S_7Br_6$ [183,200].

Using KSeCN instead of KSCN leads to some interesting reactions [204]. Selenium atoms are incorporated as a μ-SeS bridge

$$Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3 \xrightarrow{KSeCN} Mo_3(\mu_3\text{-}S)(\mu\text{-}SeS)_3L_x \qquad (3)$$

TABLE 11

Compounds with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores

Compound	Source	Solvent	Ref.
$Mo_3S_7Cl_4$	$MoCl_3$, S (1:10–30) at 450°C 20–24 h	None	194
$Mo_3S_7Cl_4$	$MoCl_3$, S, S_2Cl_2 at ca. 450°C	None	195
$Mo_3S_7Cl_4$	Mo, S, S_2Cl_2 in a sealed tube at 425°C	None	184
$Mo_3S_7Cl_4$	Mo, S, S_2Cl_2 at 420°C	None	196
$Mo_3S_7Br_4$	Mo, S, Br_2 in a sealed tube at 425°C	None	184
$Mo_3S_7Br_4$	3Mo, 7S, $2Br_2$ at 400–420°C	None	196
$Mo_3S_7Br_4$	$3MoS_3$, $3Br_2$ at 400°C for 30 h	None	196
$Mo_3S_7Br_4$	$[Mo_6Br_8]Br_4$, S at 420°C for 10 h	None	197
$Mo_3S_7X_4$ (X = Cl, Br)	MoX_3, S_8	None	5,197
$Mo_3S_7Br_4$	$[Mo_6Br_8]Br_4$, S_8 at 420°C for 10 h	None	198
$(NH_4)_2[Mo_3S_7(S_2)_3]\cdot 0.5H_2O$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $NH_2OH\cdot HCl$, $(NH_4)_2S_x$	AQ	199a,199b
$(NH_4)_2[Mo_3S_7(S_2)_3]$	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2S_2$aq	AQ	141,200
$(NH_4)_2[Mo_3S_7(S_2)_3]\cdot 2H_2O$	$Mo_3S_7Cl_4$, $(NH_4)_2S_x$	AQ	146
$(NH_4)_2[Mo_3S_7(S_2)_3]\cdot nH_2O$ (n = 0–2)	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, H_2S, S_8, NH_3aq	AQ	143
$[Mo_3S_7X_4(PPh_3)_2]$	$Mo_3S_7X_4$, PPh_3 (X = Cl, Br) (in an evacuated sealed ampoule, 80°C 10 h)	AN	201
$(Et_4N)_3[Mo_3S_7Cl_6]Cl\cdot CH_2Cl_2$	$MoCl_5$, Et_4NHS, Et_4NCl	DCM	155
$(PPh_4)_2Mo_3S_7Br_6$	$(NH_4)_2[Mo_3S_{13}]\cdot 2H_2O$, HBr, PPh_4Br	AN	183
$(Et_4N)_2Mo_3S_7Br_6\cdot \frac{1}{3}CH_3CN$	$(NH_4)_2Mo_3S_{13}$, HBr	AN	200
$[Mo_3S_7(oxq)_3]Br$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, Hoxq, NEt_3	AN	202
$(PPh_4)_2[Mo_3S_7(cat)_3]$	$(PPh_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, H_2cat	AN	202
$(Et_4N)_2[Mo_3S_7(R')_3]$ (R′ = Hmsa, Hmba)	$(Et_4N)_2[Mo_3S_7Br_6]\cdot \frac{1}{3}CH_3CN$, R (R = H_3msa, H_2mba)	AN	200
$(HNEt_3)_2[Mo_3S_7(mba)_3]$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, H_2mba, Et_3N	AN	203
$(Et_4N)_2[Mo_3S_7(NCS)_6]$	$(Et_4N)_2[Mo_3S_7Cl_6]$, KSCN	AN	204
$(Et_4N)_2[Mo_3S_4Se_3(NCS)_6]$	$(Et_4N)_2[Mo_3S_7(NCS)_6]$, KSeCN (or Ph_3PSe)	AN	204

$(Et_4N)_2[Mo_3S_4Se_3(NCS)_6]$	$(Et_4N)_2[Mo_3S_4Se_3Cl_6^-]$, KSCN	AN	204
$(Et_4N)_2[Mo_3S_4Se_3Cl_6]$	$(Et_4N)_2[Mo_3S_4Se_3(NCS)_6]$, HClaq	EtOH/AQ	204
$(PPh_3Et)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}SSe)_3Cl_6]$	$(PPh_3Et)_3Mo_2S_7Cl_6$, $SePPh_3$	AN	205
$[Mo_3S_7(tpy)_3]I \cdot CH_2Cl_2$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$, tpy_2, NaI	DMF	202
$[Mo_3S_7(Et_2dtc)(tpy)_2]I$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$, tpy_2, Et_2dtc_2, NaI	DMF	202
$[Mo_3S_7(Et_2dtc)_3]I$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$, Et_2dtc_2, NaI	DMF	202
$[Mo_3S_7(Et_2dtc)_3]I$	$(NH_4)_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, $NaEt_2dtc$, NaI	DMF	202
$[Mo_3S_7(Et_2dtp)_3(I)]$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, H_2S, I_2	HCl/EtOH	171
$[Mo_3S_7(Et_2dtp)_3(I)]$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, P_2S_5, H_2S, I_2	HCl/EtOH	206
$[Mo_3S_7(Et_2dtp)_3(Cl)]$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, H_2S, HCl	AQ	171
$[Mo_3S_7(Et_2dtp)_3]_2Cl \cdot FeCl_4$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, H_2S, H_2O_2, $FeCl_3$	HCl/EtOH	171
$[Mo_3S_7(R_2PS_2)_3]^+[R_2PS_2]^-$ (R = Et, ^{n}Pr)	$Mo(CO)_6$, $Et_2P(S)\text{–}S_2\text{–}P(S)Et_2$ (reflux)	TL	186,207
$[Mo_3S_7X(R_2PS_2)_3]$ (X = Cl, Br, I; R = Et, Pr, Bu)	$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(R_2PS_2)_3](Et_2PS_2)$, EtX (or Et_4NX)	DCM	208

The discrete $[Mo_3S_7X_4(PPh_3)_2]$ (X = Cl, Br) clusters were obtained by boiling $Mo_3S_7X_4$ (X = Cl, Br) with PPh_3 in MeCN. The bridging S_2 groups remain intact [201]: $[Mo_3S_7(dtc)_3]I$ can be synthesized from $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]^{2-}$ or $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]^{2-}$ and the corresponding bromide can also be obtained [202].

Bonds exist between halogen and one of the sulphur atoms of each disulphido bridge in the compounds $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X(R_2PS_2)_3]$ (X = Cl, Br, I; R = Et, Pr, Bu). Thus, X is incorporated into the cluster core leading to a cubane-type structure [208]. The thermal decomposition of $(NH_4)_2[Mo_3S(S_2)_6]\cdot nH_2O$ has been reported [209,210].

(iv) Non-triangular Mo_3 cores

Several non-triangular trinuclear molybdenum clusters are listed in Table 12 [75,171,211–215]. A non-triangular molybdenum compound has two Mo–Mo bonds, while triangular molybdenum compounds have three. Long exposure of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(Et_2dtp)_4(H_2O)]$ solution to air gave $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2(O)_2(Et_2\text{-}dtp)_3(OSP(OEt)_2)]$ through loss of one μ-S and gain of two Mo=O bonds [171]. The core structure of $Mo_3(O_t)_2(\mu_3\text{-}S)(\mu\text{-}S)_2$ is shown in Fig. 13. The formal oxidation state of molybdenum in the compound is 4.67. The oxidation states of molybdenum in $[(MoS_4)Mo(S_t)(MoS_4)]^{2-}$ (Fig. 14) are formulated as VI, IV, and VI, respectively [214].

The cluster $(PPh_4)_2[Mo_3O_{1.9}S_{8.1}]$ has an $M^{VI}(\mu\text{-}S)_2Mo^{IV}(O_t)(\mu\text{-}S)_2M^{VI}$ core [215] and the mixed-metal cluster $(PPh_4)_2[Mo_{1.4}W_{1.6}O_{1.3}S_{8.3}]$ obtained from $(PPh_4)_2WS_4$ and $MoO_2(acac)_2$ has a similar core structure to those of $M^{VI}\text{-}(\mu\text{-}S)_2Mo^{IV}(O_t)(\mu\text{-}S)_2M^{VI}$ cores (M = Mo, W) [215].

D. SYNTHESES OF TETRANUCLEAR MOLYBDENUM COMPOUNDS

Cubane-type molybdenum compounds with Mo_4S_4 (Fig. 15(a)) or Mo_4OS_3 (Fig. 15(b)) cores are collected in Table 13 [75,101,118,122,140,164,166,191,216–239]. Some non-cubane-type sulphur-bridged tetranuclear molybdenum compounds are included here, and such compounds as (a) tetrahedral molybdenum clusters, e.g. $Al_xMo_2S_4$ and $Ga_xMo_2S_4$ ($x \approx 0.5$) [240] and (b) a dimer composed of dimers, e.g. $[Mo_2(NAr)_2(Et_2dtp)_2S_2(O_2CR)]_2$ [241] are not included in the table.

The existence of the cubane-type Mo_4S_4 core was first recognized in 1975 through a single-crystal X-ray structure analysis of the polymeric species MoSBr [235]. In the same year, the formation of discrete cubane-type clusters, $[Mo_4\text{-}(\mu_3\text{-}S)_4O_4(dtc)_4]^{1-/2-}$, was proposed through the application of electrochemistry [242]. Edelblut and Wentworth isolated the first discrete compound with a Mo_4S_4 core, $[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$, in 1980 [216]. The oxidation state of molybdenum

TABLE 12

Compounds with non-triangular Mo_3 cores

Compound	Source	Solvent	Ref.
$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2(O)_2(Et_2dtp)_3(OSP(OEt)_2)]$	$[Mo_3S(\mu_3\text{-}S)(\mu\text{-}S)_3(Et_2dtp)_4(H_2O)]$, O_2	HCl/EtOH	171
$(Bu_4N)_2[(MoS_4)Mo(O_t)(\mu\text{-}S)_2Mo(O_t)(S_2)]$	$(NH_4)_2MoO_2S_2$, Bu_4NBr	MeOH	211
$(Bu_4N)_2[(MoS_4)Mo(O_t)(\mu\text{-}S)_2Mo(O_t)(S_2)]$	$(Bu_4N)_2MoOS_3$, MeCOOH	MeOH	211
$(PPh_4)_2[(MoS_4)Mo(Me_2NN)_2(\mu\text{-}S)_2Mo(St)_2]$	$[(S_t)_2Mo(\mu\text{-}S)_2Mo(Me_2NN)_2(PPh_3)]$, LiSPh	AN	212
$(Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$	α-$(Bu_4N)_4[Mo_8O_{26}]$, $(Me_3Si)_2S$	DMF	213
$[\{HB(Me_2Pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$	$\{HB(Me_2Pz)_3\}MoOCl_2$, $NH_4[S_2P(OEt)_2]$	DMAM	75
$R_2[Mo_3S_9]$ ($R = Et_4N$, PPh_4)	$(NH_4)_2MoS_4$, RX($= Et_4NBr$, PPh_4Cl), C_6H_5SH	DMF	214
$(PPh_4)_2[Mo_3O_{1.9}S_{8.1}]$	$(PPh_4)_2MoS_4$, $MoO_2(acac)_2$	AN	215

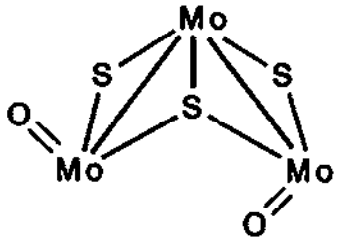


Fig. 13. Structure of the $Mo_3(O_t)_2(\mu_3\text{-}S)(\mu\text{-}S)_2$ core.

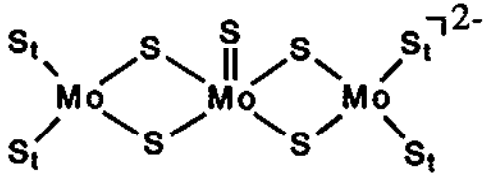


Fig. 14. Structure of $[Mo(S_t)(MoS_4)_2]^{2-}$.

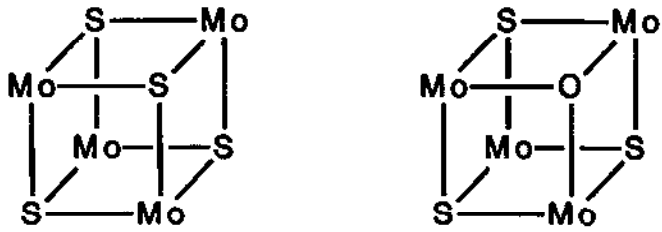


Fig. 15. Cubane-type molybdenum compounds with (a) Mo_4S_4 or (b) Mo_4OS_3 cores.

varies from V to III in cubane-type clusters with Mo_4S_4 cores, and the total oxidation number of four molybdenum atoms (Mo_4) varies from 20 to 12.

The number of oxo-sulphido mixed-bridged cubane-type clusters reported is very limited compared with those of sulphur-bridged clusters; the total oxidation numbers of Mo_4 therein is limited to 14 and 13.

(i) Cubane-type $Mo_4(\mu_3\text{-}S)_4$ and $Mo_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3$ cores

The reaction of $[Mo(Ntol)(Et_2dtp)_3]$, which has been prepared from $Mo(CO)_4Cl_2$, NH_4Et_2dtp, and *p*-tolyl azide ($CH_3C_6H_4N_3$), with H_2S in methanol gave $[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$, the structure of which has been determined by X-ray structure analysis [217]. An improved preparative method of this cubane-type compound has been reported [218]. The tetramer (T) dissociates into two dimers (D): The equilibrium constant ($2D \rightleftharpoons T$) was found to be about 10^4 in CH_2Cl_2. Acid

hydrolysis of $[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$ in a mixture of THF and hydrochloric acid gave $[Mo_4S_4(O)_2(NC_6H_5)_2(Et_2dtp)_4]$ [122]. The reaction of $[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$ with Na^iBu_2dtc in THF gave $[Mo_4S_4(Ntol)_4(^iBu_2dtc)_4]$ [118]. Reaction of MoS_3 obtained by acid hydrolysis of $(NH_4)_2MoS_4$ with aqueous KCN solution gave $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$ [101,219(a),219(b)], which was studied by cyclic voltammetry [243].

The reaction of the tetranuclear planar compound $[Mo_4(NO)_4(\mu\text{-}S_2)_6O]^{2-}$ [239], which had been prepared from MoO_4^{2-}, $NH_2OH\cdot HCl$, and H_2S, with KCN in H_2O gave $K_8[Mo_4S_4S_4(NO)_4(CN)_8]\cdot 4H_2O$ (Mo_4, +12 or +20) [220]. (Total oxidation number in parentheses.)

Reaction of the dimer $[Mo_2(\mu\text{-}Cl)_4(Pr^iCp)_2]$ with lithium hydrosulphide gave $[Mo_4S_4(Pr^iCp)_4]$ [221]. Treatment of the compound with dilute aqueous acid causes oxidation to the cation $[Mo_4S_4(Pr^iCp)_4]^+$, which was isolated as the BF_4^- salt [221]. Addition of iodine to a toluene solution of $[Mo_4S_4(Pr^iCp)_4]$ results in a two-electron oxidation, giving $[Mo_4S_4(Pr^iCp)_4]^{2+}$ as the bis(tri-iodine) salt [221]. X-ray structures of all three compounds have been determined [221]. The study on $[Mo_4S_4(Pr^iCp)_4]^n$ ($n = 0, 1, 2$) was extended and the corresponding selenium clusters reported [244].

Reduction of $[Mo_2(O_t)_2(\mu\text{-}S)_2(edta)_2]^{2-}$ (see Sect. B.(i)) with $NaBH_4$ followed by air oxidation gave a water-soluble green compound $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ (Mo_4, +13) whose cyclic voltammogram indicated the existence of both the one-electron oxidant, $[Mo_4S_4(edta)_2]^{2-}$, and the one-electron reductant, $[Mo_4S_4(edta)_2]^{4-}$ [222]. Both the oxidant and the reductant were isolated, and X-ray structure analyses of these three compounds determined [222,223]. While the volume of Mo_4 in $[Mo_4S_4(Pr^iCp)_4]$ increases as the oxidation number of molybdenum decreases; that of Mo_4 in $[Mo_4S_4(edta)_2]^{4-}$ decreases. Kinetic and electrochemical data for $[Mo_4S_4(edta)_2]^{3-}$ have been reported [245–248].

Four methods have been reported for the syntheses of $Mo_4S_4^{n+}(aq)$ ($n = 4, 5, 6$): (1) reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ or $Mo_2O_2S_2^{2+}(aq)$ in dilute HCl with $NaBH_4$ [164,191,226]; (2) aquation of $[Mo_4S_4(edta)_2]^{3-}$ in concentrated HCl [223]; (3) electrolytic reduction of $[Mo_2O_2S_2(cys)_2]^{2-}$ in 2M HCl [164,224]; and (4) refluxing a mixture of $Mo(CO)_6$ and Na_2S in acetic anhydride [225]. $Mo_4S_4^{6+}(aq)$ is unstable. The aqua ion $Mo_4S_4^{5+}(aq)$ was crystallized as $[Mo_4S_4(H_2O)_{12}](pts)_5\cdot 14H_2O$ and X-ray structure analysis confirmed the cubane-type Mo_4S_4 core [228]. Controlled potential electrolysis of $[Mo_4S_4(H_2O)_{12}]^{5+}$ revealed the existence of $[Mo_4S_4(H_2O)_{12}]^{4+}$ and the instability of $[Mo_4S_4(H_2O)_{12}]^{6+}$ [223]. Kinetic and electrochemical data for $[Mo_4S_4(H_2O)_{12}]^{5+}$ have also been reported [227]. Addition of NCS^- to $[Mo_4S_4(H_2O)_{12}]^{5+}$ in air gives $[Mo_4S_4(NCS)_{12}]^{6-}$ [223,225]. Addition of concentrated ammonia–water to the aqua ion $[Mo_4S_4(H_2O)_{12}]^{5+}$ gave $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$, the structure of which has been determined [226].

Electrolytic reduction of $Mo_2O_2S_2(dtc)_2$ obtained from $Mo_2O_3(dtc)$ and H_2S

TABLE 13

Compounds with cubane-type $Mo_4(\mu_3\text{-}S)_4$, $Mo_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3$, and non-cubane-type Mo_4 cores

Compound	Source	Solvent	Ref.
$Mo_4(\mu_3\text{-}S)_4$ core			
$[Mo_4S_4(Ntol)_4(Et_2dtp)_4](+20)$	$[Mo(CO)_4Cl_2]$, NH_4Et_2dtp, N_3tol, H_2S	MeOH	216,217
$[Mo_4S_4(Ntol)_4(Et_2dtp)_4](+20)$	$[Mo(CO)_6]$, N_3tol, S_8, HEt_2dtp, reflux (N_2)	THF	218
$[Mo_4S_4(O)_2(Ntol)_2(Et_2dtp)_4](+20)$	$[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$, HCl	THF/AQ	122
$[Mo_4S_4(Ntol)_4(^iBu_2dtc)_4](+20)$	$[Mo_4S_4(Ntol)_4(Et_2dtp)_4]$, Na^iBu_2dtc	THF	118
$K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O(+12)$	$(NH_4)_2MoS_4$, KCN	AQ	101,219(a),219(b)
$K_8[Mo_4S_4(NO)_4(CN)_8]\cdot 4H_2O(+12/+20)$	$(NH_4)K[Mo_4(NO)_4(S_2)_6O]\cdot 2H_2O$, KCN	AQ	220
$[Mo_4S_4(Pr^iCp)_4](+12)$	$[Mo_2(\mu\text{-}Cl)_4(Pr^iCp)_2]$, LiHS	AQ	221
$[Mo_4S_4(Pr^iCp)_4]\ BF_4\ (+13)$	$[Mo_4S_4(Pr^iC_p)_4]$, acid, BF_4^-	AQ	221
$[Mo_4S_4(Pr^iCp)_4](I_3^{-1})_2(+14)$	$[Mo_4S_4(Pr^iCp)_4]$, I_2	TL	221
$Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O(+13)$	$Na_2[Mo_2O_2S_2(edta)_2]\cdot 2H_2O$, $NaBH_4$, air	AQ	222
$Na_2[Mo_4S_4(edta)_2]\cdot 6.5H_2O(+14)$	$[Mo_4S_4(edta)_2]^{3-}$, Br_2	AQ	223
$Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O(+12)$	$[Mo_4S_4(edta)_2]^{3-}$, $NaBH_4$	AQ	223
$[Mo_4S_4(H_2O)_{12}]^{5+}(+5)$	Electrolysis of $Na_2[Mo_2O_2S_2(cys)_2]\cdot 3H_2O$	AQ	166,224
$[Mo_4S_4(H_2O)_{12}]^{5+}(+5)$	$[Mo_4S_4(edta)_2]^{3-}$, aquation	AQ	223
$[Mo_4S_4(H_2O)_{12}]^{5+}(+5)^a$	$Mo(CO)_6$, Na_2S	Ac_2O	225
$[Mo_4S_4(H_2O)_{12}]^{5+}(+5)$	$Mo_2O_2S_2^{2+}$(aq), $NaBH_4$	AQ	164
$[Mo_4S_4(H_2O)_{12}]^{5+}(+5)$	$Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$, $NaBH_4$	AQ	191,226
$[Mo_4S_4(H_2O)_{12}]^{4+}(+4)$	Electrolysis of $[Mo_4S_4(H_2O)_{12}]^{5+}$	AQ	223,227
$[Mo_4S_4(H_2O)_{12}](pts)_5\cdot 14H_2O(+13)$	$[Mo_4S_4(H_2O)_{12}]^{5+}$, Hpts	AQ	228
$[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O(+12)$	$[Mo_4S_4(H_2O)_{12}]^{5+}$, NH_3aq	AQ	226
$(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O(+14)$	$[Mo_4S_4(H_2O)_{12}]^{5+a}$, NCS^-, air	AQ	225
$[Mo_4S_4(Et_2dtc)_6]\cdot 2CHCl_3(+14)$	Reflux of $Mo_2(dtc)_6$	TL	229,230
$[Mo_4S_4(R_2PS_2)_6](+14)$ (R = Et, Pr)	$[Mo_3S_4(R_2PS_2)_4]$, $Mo(CO)_6$, $R_2P(S)S_2P(S)R_2$	TL	231
$[Mo_4S_4(\mu\text{-}OAc)_2(Et_2dtp)_4\cdot H](CH_3)_2CO(+13)$	$[Mo_3S_4(Et_2dtp)_4(H_2O)]$, $[Mo(CO)_6]$	HOAc/Ac_2O	232
$[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9](pts)_8\cdot 18H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Mg	AQ	233

$MoSX(+12)$ ($X = Cl, Br, I$)	MoX_2, Mo, 2S at 1000°C	None	234,235
$Mo_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3$ core			
$[Mo_4OS_3(Et_2dtp)_6] \cdot 3CH_3CN(+14)$	$MoCl_3 \cdot 3H_2O$, P_4S_{10}	EtOH	236
$[Mo_4OS_3(Et_2dtp)_6](+14)$	$MoCl_3 \cdot 3H_2O$, HCl gas, P_4S_{10}	EtOH	237
$[Mo_4OS_3(H_2O)_{12}](pts)_5 \cdot 14H_2O(+13)$	$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2$, Fe	AQ	228
Non-cubane-type Mo_4 core			
$(NH_4)_4[Mo_4(NO)_4S_3(S_2)_5] \cdot 2H_2O$ (planar)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)SCN$, $NH_2OH \cdot HCl$, $(NH_4)_2S_x$	AQ	140,238
$(NH_4)_2[Mo_4(NO)_4(S_2)_6O]$ (planar)	$Na_2MoO_4 \cdot 2H_2O$, $NH_2OH \cdot HCl$, H_2S	AQ	239
$[\{HB(Me_2Pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (linear)	$[(HB(Pz)_3)Mo(CO)_3H]$, S_8	DCE	75

[a] See ref, 223.

gave the proposed compound $[Mo_4(\mu_3\text{-}S)_4O_4(dtc)_4]^{1-/2-}$ [242]. The dimer $Mo_2(dtc)_6$ used for the synthesis of $[Mo_4S_4(Et_2dtc)_6]\cdot 2CHCl_3$ was prepared from $Mo(CO)_6$ and tetraethylthiuram disulphide, $Et_2NC(S)\text{—}S\text{—}S\text{—}C(S)NEt_2$ [229,230]. An equimolar amount of $Mo_3S_4(Et_2PS_2)_4$, $Mo(CO)_6$ and $Et_2P(S)\text{—}S\text{—}S\text{—}P(S)Et_2$ gave $[Mo_4S_4(Et_2Et_2dtp)_6]$ [231]. The hydrogen atom in the cluster $[Mo_4S_4(\mu\text{-}OAc)_2(Et_2dtp)_4\cdot H]\cdot(CH_3)_2CO$ exists in SH or OH [232]. Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with magnesium in 6M HCl gave $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$, which was crystallized as its pts^- salt: $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9](pts)_8\cdot 18H_2O$ [233]. X-ray structure analysis revealed that two incomplete cubane-type cores, Mo_3S_4s, are bridged by a molybdenum atom that lies on a centre of symmetry.

The polymeric species MoSX (X = Cl, Br, I) were obtained by heating a stoichiometric amount of MoX_2, Mo, and S at 1000°C [234,235]. A single-crystal X-ray structure of the species MoSBr revealed the existence of the Mo_4S_4 structure [235]. Mo_4 cores also exist in $Ga(orAl)_xMo_2S_4$ ($x \approx 0.5$) [240,249].

(ii) Non-cubane-type Mo_4 cores

From $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)SCN$, $NH_2OH\cdot HCl$, and $(NH_4)_2S_x$ (ammonium polysulphide) in water, a planar compound $(NH_4)[Mo_4(NO)_4(\mu_4\text{-}S)(\mu_3\text{-}S)_2(S\text{-}\mu\text{-}S)_4(S_2)]\cdot 2H_2O$ was obtained [238] (Fig. 16). Introduction of H_2S to the reaction product of $Na_2MoO_4\cdot 2H_2O$ with $NH_2OH\cdot HCl$ gave $[Mo_4(NO)_4(S_2)_6O]^{2-}$ (Fig. 17) as its ammonium or ammonium–potassium salt [239]. The X-ray structures of these compounds have been determined. The linear compound $[\{HB(Me_2Pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (core structure: Fig. 18) was obtained as a by-product in the formation of $[(HB(Pz)_3)_2Mo_2(S)(CO)_4]$ [75,110] (see Table 5).

E. SYNTHESES OF DINUCLEAR TUNGSTEN COMPOUNDS

(i) $W_2O_{4-n}S_n$ cores ($n = 1$–4)

The tungsten dinuclear compounds with *syn*- and *anti*-$W_2O_2(\mu\text{-}S)_2$, *syn*- and *anti*-$W_2(O_t)(S_t)(\mu\text{-}S)_2$, *syn*-$W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$, and *syn*- and *anti*-$W_2(S_t)_2(\mu\text{-}S)_2$ cores are summarized in Table 14 [53,59,68,69,78,84,85,204,250–274] (see the corresponding figures for molybdenum compounds: Figs. 3 and 4). Compounds with W_2O_4 cores will not be included here. No compounds with *anti*-$W_2O_2(\mu\text{-}O)(\mu\text{-}S)$ and *syn*/*anti*-$W_2S_2(\mu\text{-}O)(\mu\text{-}S)$ cores have been reported to our knowledge. The compounds containing $W_2O_{4-n}S_n$ cores ($n = 1$–4) have either planar or bent WX_2W (X = O, S) bridges with terminal oxo (O_t) or sulphido (S_t) bridges. *Syn* and *anti* isomers are different in the position of terminal oxo or sulphido ligand with double bond character (see Fig. 3). The term "*syn*" will not be indicated except when it is unclear

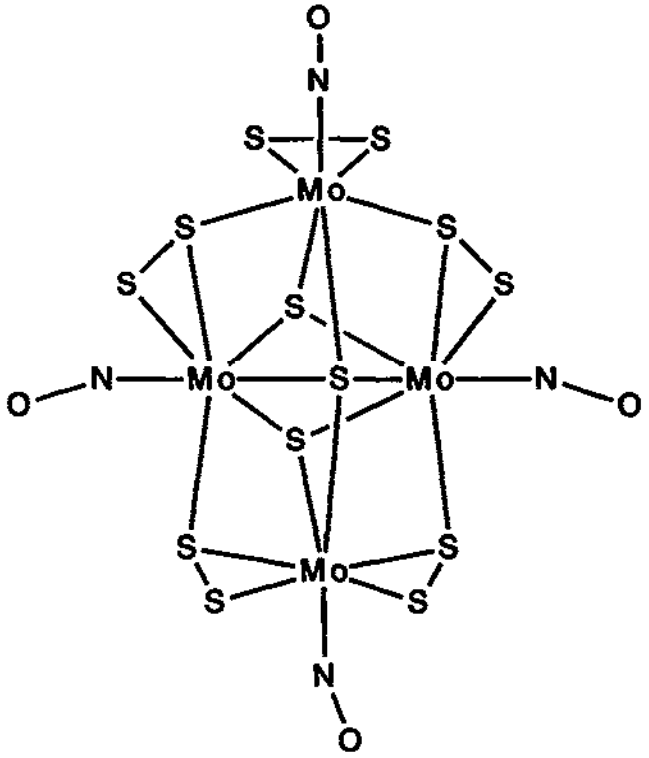


Fig. 16. Structure of $[Mo_4(NO)_4(S)_3(S_2)_5]^{4-}$.

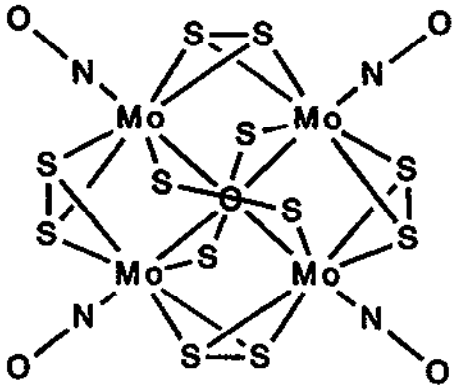


Fig. 17. Structure of $[Mo_4(NO)_4(S_2)_6O]^{2-}$.

without it. The oxidation state of tungsten in all the dimers listed here is V, while those of the tungsten compound sources vary from 0 to 6. The use of organic solvents is inevitable for the syntheses of compounds with W_2S_4 or W_2OS_3 cores.

Lozano et al. [250,251] and Drew et al. [254] were the first to report indepen-

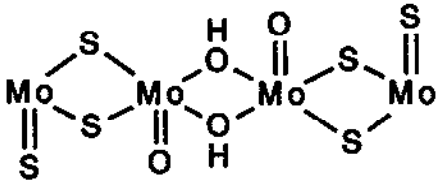


Fig. 18. Structure of the $(Mo(S_t)(\mu\text{-}S)_2Mo(O_t)(\mu\text{-}OH))_2$ core.

dently $[W_2O_2S_2(Rdtc)_2]$ and $(Ph_4As)_2[W_2O_2S_2Cl_4]$, respectively, compounds with $W_2(O_t)_2(\mu\text{-}S)_2$ cores (see Fig. 4(a)). The X-ray structure of the latter has been determined. Lozano et al. also synthesized compounds with $W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ cores (see Fig. 4(d)) [250,251]. There are three different procedures in the syntheses of compounds with $W_2(O_t)_2(\mu\text{-}S)_2$ and $W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ cores: (1) when H_2S gas is passed, the pH of the solution is lower in compounds with the latter cores; (2) ligands are added to the solution after the passage of H_2S gas for the compounds with the latter cores and before the passage of H_2S gas for the compounds with the former cores; and (3) cooling is required only for the syntheses of compounds with the former cores.

A compound with the *anti*-core structure, *anti*-$[Cp_2W_2O_2S_2]$, was synthesized in 1980 for the first time by Wojcicki and co-workers [59] and only few compounds with *syn*- or *anti*-$W_2(O_t)(S_t)(\mu\text{-}S)_2$ cores (see Fig. 4(b)) have been reported. In 1985, Cohen and Stiefel synthesized $W_2OS_3[S_2CN(i\text{-}Bu)_2]_2$ with *syn*-$W_2(O_t)(S_t)(\mu\text{-}S)_2$ core for the first time from $(Et_4N)_2W_2S_2(\mu\text{-}S)_2(S_4)_2$ and Na^tBu_2dtc [78]. The core structures of *anti*-$Cp_2W_2(O_t)_2(\mu\text{-}S)_2$ and *anti*-$Cp_2W_2(O_t)(S_t)(\mu\text{-}S)_2$ were determined by IR spectroscopy [263].

Sarkar and co-workers reported that reaction of $[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ with an acetylene derivative, DBA, gave a dithiolene compound retcinins the core [260,262]. Molybdenum compounds with similar ligands have also been reported [46,47].

Much attention has been paid to the synthesis, structure, and characterization of the cysteinato molybdenum(V) dimer $[Mo_2(O_t)_2(\mu\text{-}S)_2(cys)_2]^{2-}$ (see Sect. B.(i)). The corresponding cysteinato tungsten(V) and the tungsten(V) aqua dimer $W_2O_2S_2^{2+}(aq)$ have also been synthesized [255].

X-Ray structures of the following compounds have been determined: $(PPh_4)_2W_2O_2S_{10}\cdot 0.5DMF$ [261], $K_2[W_2O_2S_2(cys)_2]\cdot 5H_2O$ [255], and $(Ph_4As)_2[W_2O_2S_2Cl_4]$ [254]. The barium salt $Ba[W_2O_3S(edta)]\cdot 6.5H_2O$, obtained from $Na_2[W_2O_3S(edta)]$, is the only X-ray-analyzed compound to have a $W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ core [265].

In 1981, Wunderlich and co-workers reported the first compound with a $W_2(S_t)_2(\mu\text{-}S)_2$ core, $[W_2S_4(Et_2dtp)_2]$ [207]. Many routes to the compound $[W_2S_4(dtcEt_2)_2]$ were reported: tungsten sources used so far are $W(CO)_6$ [267], WS_4^{2-} [264], $[W_2(O_t)_2(\mu\text{-}S)_2(dtcEt_2)_2]$ [268], $[W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)(dtcEt_2)_2]$ [268],

TABLE 14

Compounds with *syn/anti*-$W_2(O_t)_2(\mu\text{-}S)_2$, *syn/anti*-$W_2(O_t)(S_t)(\mu\text{-}S)_2$, *syn*-$W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$, and *syn/anti*-$W_2(S_t)_2(\mu\text{-}S)_2$ cores[a]

Compound	Source	Solvent	Ref.
syn/anti-$W_2(O_t)_2(\mu$-S)$_2$ core			
$[W_2O_2S_2(Rdtc)_2]$	$Na_2WO_4 \cdot 2H_2O$, H_2S, Rdtc[b]	AQ	250–252
$[W_2O_2S_2(Et_2dtc)_2]$	$(NH_4)_2WO_2S_2$, TETDS	DMF	253
$[W_2O_2S_2(Et_2dtc)_2]$	$(Et_2NH_2)_2WOS_3$, CS_2, 2-PrOH, ether	DMF	253
$[W_2O_2S_2(Et_2dtc)_2]$	$Na_2WO_4 \cdot 2H_2O$, NH_4SCN, $(NH_4)_2S_x$, $NaEt_2dtc$	AQ	53
$(Ph_4As)_2[W_2O_2S_2Cl_4]$	WCl_2OS, $(Ph_4As)Cl$	DCM	254
$K_2[W_2O_2S_2(cys)_2] \cdot 5H_2O$	$(NH_4)_2WS_4$, L-cys · HCl · H_2O, KCl	AQ	255
$W_2O_2S_2^{2+}$(aq)	$(NH_4)_2WS_4$, HCl	AQ	255
$W_2O_2S_2^{2+}$(aq)	$[W_2O_2S_2(cys)_2]^{2-}$, aquation	AQ	255
$[W_2O_2S_2(X_2oxq)_2]$	$Na_2WO_4 \cdot 2H_2O$, H_2S, HX_2oxq (X = Cl, Br, I)	AQ	256
$[W_2O_2S_2(oxq)_2]$	$Na_2WO_4 \cdot 2H_2O$, $Na_2S_2O_4$, H_2S, Hoxq	AQ	257
$[W_2O_2S_2(C_2H_5OCS_2)_2]$	$Na_2WO_4 \cdot 2H_2O$, $Na_2S_2O_4$, H_2S, KEtXan	AQ	258
$(Et_4N)_2[W_2O_2S_2(S_2)_2]$	$(NH_4)_2WOS_3$, $(NH_4)_2S_2O_8$ (or I_2), Et_4NBr	AQ	259,260
$(Et_4N)_2[W_2O_2S_2(S_2)_2]$	$(NH_4)_2WOS_3$, Et_4NBr, PhSSPh (or PhOOPh)	DMF	259,260
$(PPh_4)_2[W_2O_2S_{10}] \cdot 0.5DMF$	$(PPh_4)_2WS_4$, S_8	DMF/AN/DCM	261
$R_2[W_2O_2S_2(S_2)(S_4)] \cdot Me_2CO$ (R = Me_4N, Et_4N, Ph_4P)	$Na_2WO_4 \cdot 2H_2O$, NH_4SCN, HCl, $(NH_4)_2S_x$, RCl	AQ	53
$(Et_4N)_2[W_2O_2S_2(S,S\text{-}S_2C_2(COPh)_2)_2]$	$(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$, dba	AN	260,262
$K_4[W_2O_2S_2(CN)_6] \cdot 3H_2O$	$(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$, KCN	AQ	260
anti-$[Cp_2W_2S_2O_2]$	$Na[(Cp)W(CO)_3]$, SO_2	THF	59
anti-$[Cp_2W_2S_2O_2]$	$[Cp_2W_2(CO)_6]$, SO_2	THF	59
anti-$[Cp_2W_2S_2O_2]$	$[Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2]$, dil. acid	AQ	263
syn/anti-$W_2(O_t)(S_t)(\mu$-S)$_2$ core			
$[W_2OS_3(Et_2dtc)_2]$	$(Et_2NH_2)_2WS_4$, CS_2	DMF	264
$[W_2OS_3(Et_2dtc)_2]$	$(NH_4)_2WS_4$, tetds	DMF	264
$[W_2OS_3(^iBu_2dtc)_2]$	$(Et_4N)_2[W_2S_2(\mu\text{-}S)_2(S_4)_2]$, Na^iBu_2dtc	AN	78

TABLE 14 (*continued*)

Compound	Source	Solvent	Ref.
anti-$[Cp_2W_2OS_3]$	$[Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)(S)]$	DCM	263
syn-$W_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ core			
$[W_2O_3S(Rdtc)_2]$	$Na_2WO_4 \cdot 2H_2O$, H_2S, Rdtc[b]	AQ	250–252
$[W_2O_3S(L)_2]$ (L = Q, MQ, X_2Q; X = Cl, Br, I)	$Na_2WO_4 \cdot 2H_2O$, H_2S, L	AQ	256,257
$[W_2O_3S(C_2H_5OCS_2)_2]$	$Na_2WO_4 \cdot 2H_2O$, $Na_2S_2O_4$, H_2S, KEtXan	AQ	258
$[Na_2[W_2O_3S(edta)]$	$(NH_4)_2[WOCl_5]$, Na_2edta, H_2S, Na_2CO_3	AQ	265
syn/anti-$W_2(S_t)_2(\mu\text{-}S)_2$ core			
$[R_2[W_2S_4(L)_2]$ (R = Et_4N, Ph_4P; $H_2L = H_2$edt, H_2abt)	$(NH_4)_2WS_4$, $(Et_4N)Br$, RBr, L	DMF	69
$(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$	$(PPh_4)_2WS_4$, C_4S_5O (or C_6S_{10})	AN	266
$[W_2S_4(Et_2dtc)_2]$	$W(CO)_6$, tetds	TMPH[c]	267
$[W_2S_4(Et_2dtc)_2]$	$(Et_2NH_2)_2WS_4$, CS_2, 2-PrOH, ether	DMF	264
$[W_2S_4(Et_2dtc)_2]$	$(NH_4)_2WS_4$; tetds	DMF	264
$[W_2S_4(R_2dtc)_2]$ (R = ^{i}Bu, Et)	$(Et_4N)_2[W_2S_2(\mu\text{-}S)_2(S_4)_2]$, $dtcR_2$	AN	78
$[W_2S_4(Et_2dtc)_2]$	$[W_2S_4(Et_2dtp)_2]$, Et_2dtc	THF	267
$[W_2S_4(R_2dtc)_2]$	$[W_2O_2(\mu\text{-}S)(\mu\text{-}X)(R_2dtc)]$, P_4S_{10} (X = O, S; R = Et, ^{i}Bu)	XY	268
$[W_2S_4(Et_2dtc)_2py^*_2]$[c]	$[W_2S_4(Et_2dtc)_2]$, py*	EtOH	269
$W_2S_4(Rdtc)_2$ (R = C_4H_8O, C_5H_{10}, C_8H_{10} or C_7H_{14})	$[W_2O_2(\mu\text{-}S)_2(Rdtc)_2]$, P_4S_{10}	XY	270
$[W_2S_4(Et_2dtp)_2]$	$[W(CO)_6]$, $Et_2P(S)\text{–}S_2\text{–}P(S)Et_2$	TMPH	204,271
$[W_2S_4(Et_2dtp)_2]$	WS_2Cl_2, NH_4Et_2dtp	DCM	267
$[W_2S_4(Et_2dtp)_2]$	$(Me_4N)_2WS_4$, HEt_2dtp	AN	267
anti-$[W_2S_4Cp_2]$	[CpW(CO)$_3$H], propylensulphide	TL	84,85
anti-$[W_2S_4MeCp_2]$	$[MeCp_2W_2(CO)_2S_3]$, S_8	TL	68

$(PPh_4)_2[W_2S_4(S_2)(S_4)]\cdot 0.5DMF$	$(PPh_4)_2WS_4$, S_8	DMF	261
$(PPh_4)_2[W_2S_4(S_4)_2]\cdot 0.5DMF$	$(NH_4)_2WS_4$, CH_3NO_2	DMF	261
$(Et_4N)_2[W_2S_4(S_4)_2]$	$(NH_4)_2WS_4$, S_8, Et_4NBr	DMF	78
$(Et_4N)_2[W_2S_4X_4]$	$(Et_4N)_2WS_4$, X_2 (X = Cl, Br)	DCM	272
$[W_2S_4Br_2(PPh_3)_2]\cdot C_6H_6$	$(Et_4N)_2W_2S_4Br_4$, PPh_3, C_6H_6	AN	273
$[W_2S_4Cl_2(py)_4]\cdot 2py$	WS_2Cl_2, py	py	274

[a] Anti isomers have the prefix *anti*, whereas syn isomers do not have the prefix *syn*.

[b] Abbreviations: Rdtc = diisobutyldithiocarbamate, *N*-ethylanilindithiocarbamate, morpholine dithiocarbamate, piperidine dithiocarbamate, diethyldithiocarbamate.

[c] py* = pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine, 3-aminopyridine or 4-aminopyridine.

$[W_2S_4(Et_2dtp)_2]$ [267], and $(Et_4N)_2[W_2S_2(\mu\text{-}S)_2(S_4)_2]$ [78]. Only two compounds with *anti*-$W_2(S_t)_2(\mu\text{-}S)_2$ cores have been reported.

Stiefel and co-workers determined the X-ray structure of $(Ph_4P)_2[W_2S_4(edt)_2]$ [69]. Since then, X-ray structures of the following compounds have been determined: $[W_2S_4(Et_2dtp)_2]$, $(PPh_4)_2[W_2S_4(S_2)(S_4)]\cdot 0.5dmf$, $(PPh_4)_2[W_2S_4(S_4)_2]\cdot 0.5dmf$, $(Et_4N)_2[W_2S_4(S_4)_2]$, $[W_2S_4(dtcR_2)_2]$ (R = Et), $[W_2S_4Br_2(PPh_3)_2]\cdot C_6H_6$, $[W_2S_4(Et_2dtp)_2]$, $[W_2S_4Cl_2(py)_4]\cdot 2py$.

(ii) $W_2(\mu\text{-}S)_2$ cores

In this section, compounds with $W_2(\mu\text{-}S)_2$ cores (see Fig. 5(a)) are listed in Table 15 [263,275–277]. These compounds have no terminal oxygen or sulphur atom.

The two compounds, $[W_2S_2(Et_2dtc)_2(CH_3O)_4]$ and $[W_2S_2(Et_2dtc)_2(\mu\text{-}Et_2dtc)_2]$, were reported by Cotton and co-workers for the first time in 1978 [275]. The latter compound has two additional bridging Et_2dtc ligands. The W—W distances are 2.791(1) Å in the former compound and 2.530(2) Å in the latter, indicating single and double bond character, respectively. The reaction of WCl_5 with NEt_4SH gives $(NEt_4)_2[W_2S_2Cl_8]$ in a high yield (83%) [277].

Synthetic and vibrational studies of the ^{34}S-isotope compounds $[W_2(St)_2(\mu\text{-}S)_2X_4]^{2-}$ (X = Cl, Br) and $[W_2(\mu\text{-}S_2)_2Br_8]^{2-}$ were recently reported [62(b)].

(iii) $W(\mu_2\text{-}S_2)_2W$, $W(\mu\text{-}S)(\mu\text{-}S_2)W$, and $W(WS_4)$ cores

Compounds with $W(\mu\text{-}S_2)_2W$ (see Fig. 7(g)), $W(\mu\text{-}S)(\mu\text{-}S_2)W$ (see Fig. 7(c); X = S), or $W(WS_4)$ (see Fig. 6(c)) cores are listed in Table 16 [124,272,276,278,279]. Compounds with $W(\mu\text{-}S_2)_2W$ or $W(\mu\text{-}S)(\mu\text{-}S_2)W$ cores have no terminal oxygen or sulphur atoms, and the WS_4^{2-} group in compounds with $W(WS_4)$ cores can be regarded as a bidentate ligand.

The introduction of HX gas to a CH_2Cl_2 solution of $(Et_4N)_2WS_4$ gives both $(Et_4N)_2[W_2S_4X_8]$ (X = Cl, Br) and $(Et_4N)_2[W_2S_3Br_8]$. The former is more soluble in CH_2Cl_2 than the latter, and can be separated by filtration [272]. The X-ray structure of $(Et_4N)_2[W_2S_4Br_8]$ [280] is analogous to that described for the $Mo_2S_4X_8^{2-}$ anions (X = Cl, Br) [144] and the X-ray structure of $(PPh_4)_2[W_2S_3Br_8]\cdot CH_2Cl_2\cdot H_2S$ has been determined [278]. The oxidation state of the tungsten atoms in $[(NNMe_2)_2(PPh_3)W(WS_4)]$ is VI, and $(Et_4N)_2[(OC)_4W(WS_4)]$ is a mixed-valence compound.

(iv) $W(\mu\text{-}S)W$, $(O_t)W(\mu\text{-}S)W(O_t)$, $(S_t)W(\mu\text{-}S)W(S_t)$, and $W(\mu\text{-}S)_2W(S_t)$ cores

Compounds with $W(\mu\text{-}S)W$ (see Fig. 5(d)), $(O_t)W(\mu\text{-}S)W(O_t)$ (see Fig. 5(e)), $(S_t)W(\mu\text{-}S)W(S_t)$ (see Fig. 5(f)), or $W(\mu\text{-}S)_2W(S_t)$ (similar core structure to Fig. 5(b)) cores are listed in Table 17 [68,114,263,281–286].

TABLE 15

Compounds with $W_2(\mu\text{-}S)$ cores

Compound	Source	Solvent	Ref.
$[W_2S_2(Et_2dtc)_2(CH_3O)_4]$	$[W(CO)_3(CH_3CN)_3]$, TETDS	MeOH	275
$[W_2S_2(Et_2dtc)_2(\mu\text{-}Et_2dtc)_2]$	$[W(CO)_3(CH_3CN)_3]$, TETDS	ACET	275
$[W_2S_2(S^tBu)_4(PMe_2Ph)_2]\cdot CH_2Cl_2$	*cis*-$[W(N_2)_2(PMe_2Ph)_4]$, ^tBuSH	THF	276
$[Cp_2W_2S_2(NSiMe_3)_2]$	$[CpW(CO)_3Cl]$, $S(NSiMe_3)_2$	THF	263
$[Cp_2W_2S_2(NSiMe_3)_2]$	$[Cp_2W_2(CO)_6]$, $S(NSiMe_3)_2$	BZ	263
$(NEt_4)_2[W_2S_2Cl_8]$	WCl_5, NEt_4SH	DCM	277
$(NEt_4)_2[W_2S_2Cl_8]$	$WSCl_4$, NEt_4I	DCM	277

TABLE 16

Compounds with $W(\mu\text{-}S_2)_2W$, $W(\mu\text{-}S)(\mu\text{-}S_2)W$, or $W(WS_4)$ cores

Compound	Source	Solvent	Ref.
$W(\mu\text{-}S_2)_2W$ core			
$(Et_4N)_2[W_2S_4X_8]$	$(Et_4N)_2WS_4$, HX gas (X = Cl, Br)	DCM	272
$(Et_4N)_2[W_2S_4Br_8]$	$(Et_4N)_2[W_2(\mu\text{-}S)(\mu\text{-}S_2)Br_8]$, S_8	AN	272
$W(\mu\text{-}S)(\mu\text{-}S_2)W$ core			
$(PPh_4)_2[W_2S_3Br_8]\cdot CH_2Cl_2\cdot H_2S$	WBr_6, H_2S gas, HBr gas, PPh_4Br	AN	278
$(Et_4N)_2[W_2S_3Br_8]$	$(Et_4N)_2WS_4$, HBr gas	AN	272
$(Et_4N)_2[W_2S_3Br_8]$	$[W_2(\mu\text{-}S)(\mu\text{-}S_2)Br_6]\cdot 2CH_3CN$, Et_4NBr	AN	272
$[W_2S_3Br_6]\cdot 2CH_3CN$	$(Et_4N)_2[W_2(\mu\text{-}S)(\mu\text{-}S_2)Br_8]$, HBr gas	AN	272
$[W_2S_3Br_6]\cdot 2CH_3CN$	$(Et_4N)_2[W_2(S_t)_2(\mu\text{-}S)_2Br_4]$, Br_2	AN	272
$W(WS_4)$ core			
$[Cp_2W(WS_4)]$	Cp_2WCl_2, $(NH_4)_2WS_4$	AQ	124
$[(NNMe_2)_2(PPh_3)W(WS_4)]$	$[WCl(NNMe_2)_2(PPh_3)_2]Cl$, $(N^nBu_4)_2WS_4$	AN	276
$(Et_4N)_2[(OC)_4W(WS_4)]$	$(Et_4N)_2WS_4$, $(Et_4N)[W(CO)_4(Et_2dtc)]$	MeOH/EtOH	279

Direct reaction of $[CpW(CO)_3H]$ with SO_2 gave the single sulphur bridged dinuclear compound $[Cp_2W_2(\mu\text{-}S)(CO)_6]$, the structure of which has been determined [282].

Among these three routes to $[Cp_2W_2(\mu\text{-}S)_2(S_t)(NSiMe_3)]$, the reaction of $[CpW(CO)_3SH]$ with Me_3SiN_3 in THF gives the highest yield (11%) [263].

One sulphur atom of the S_2 bridge in the compound $(PPh_4)[(HS)(O)W(\mu\text{-}S)(\mu\text{-}S_2)W(SH)_2(S_2)]$ links with only one of the tungsten atoms [286].

(v) Miscellaneous

Several types of compound having at least one SR bridge are listed in Table 18 [281,287–293]. The symbol R denotes H, C(O)NHMe, Ph, ^{t}Bu, etc. We have not tried to cover all types of compound with SR bridges. The collected types of core are $W(\mu\text{-}SH)W$ (Fig. 19(a)), $W(\mu\text{-}SR)W$ (Fig. 19(b)), $W(\mu\text{-}SR)_2W$ (Fig. 19(c)), and $W(\mu\text{-}S)(\mu\text{-}SR)_2W$ (Fig. 19(d)).

The anion $[W_2(\mu\text{-}S)(CO)_{10}]^{2-}$ was generated by the addition of NaH to $[W_2(\mu\text{-}SH)(CO)_{10}]^-$ in THF. In contrast to the latter, the former is a reactive species toward MeN=C=O [288].

F. TRINUCLEAR TUNGSTEN(IV) COMPOUNDS

Two types of trinuclear tungsten compound (triangular and non-triangular (or linear)) are described here. The cores of the triangular compounds described are limited to those of compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}O)_{3-n}(\mu\text{-}S)_n$ ($n = 0$–3; see Figs. 11(a), (b)), and $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ (see Fig. 11(c)). In addition to linear trinuclear compounds, some linear tetranuclear compounds are also collected here. The sulphido and carbonyl-bridged clusters such as $[W_3(\mu_3\text{-}S)(\mu\text{-}CO)_3(CO)_9]$ [159] were not included.

(i) $W_3(\mu_3\text{-}S)(\mu\text{-}X)_3$ cores ($X = O$, S)

Compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores collected in Table 19 [163,180,181,204,294–303] can be synthesized from mono-, di-, and trinuclear tungsten compounds. Polymeric species can also be source materials.

The first triangular tungsten compound with a sulphur bridge was $[W_3S_4(H_2O)_9]^{4+}$, which was synthesized by the reduction of $(NH_4)_2WS_4$ with $NaBH_4$ in dilute HCl [163,294]. The aqua ion can also be synthesized using a solid-state technique [295,296]. The reaction schemes for both procedures are shown in the reactions

$$H_2WO_4 \xrightarrow{H_2S} WS_4^{2-} \xrightarrow{NaBH_4} [W_3S_4(H_2O)_9]^{4+} \quad (4)$$

$$W\ \text{metal} \xrightarrow[300^\circ C]{S_8, Br_2} W_3S_7Br_4 \xrightarrow{(NH_4)_2S_x} [W_3S_4(S_4)_3(NH_3)_3]^{2-} \xrightarrow{HCl} [W_3S_4(H_2O)_9]^{4+} \quad (5)$$

TABLE 17

Compounds with W(μ-S)W, (O_t)W(μ-S)W(O_t), (S_t)W(μ-S)W(S_t), or W(μ-S)$_2$W(S_t) cores

Compound	Source	Solvent	Ref.
W(μ-S)W core			
$Na(Et_4N)[W_2(\mu\text{-}S)(CO)_{10}]$	$[Et_4N][W_2(\mu\text{-}HS)(CO)_{10}]$, NaH	THF	281
$[Cp_2W_2(\mu\text{-}S)(CO)_6]$	$[CpW(CO)_3H]$, SO_2	AN	282
$[Cp_2W_2(\mu\text{-}S)(CO)_6]$	$[CpW(CO)_3H]$, $S(NMe_2)_2$	Pentane	283
(O_t)W(μ-S)W(O_t) core			
$(AsPh_4)_2[W_2(O_t)_2(\mu\text{-}S)(S_2)_4]$	$(AsPh_4)_2WOS_3$, S_8	AN	114
$(PPh_4)_2[W_2(O_t)_2(\mu\text{-}S)(S_2)_4]$	$(PPh_4)_2WS_4$, $(PPh_4)_2Mn(NCS)_4$	AN	284
(S_t)W(μ-S)W(S_t) core			
$(PPh_4)_2[W_2(S_t)_2(\mu\text{-}S)(S_2)_4]$	$(PPh_4)_2WS_4$, $MnCl_2 \cdot 4H_2O$	AN	285
$(PPh_4)_2[W_2(S_t)_2(\mu\text{-}S)(S_2)_4]$	$(PPh_4)_2WS_4$, $(PPh_4)_2Mn(NCS)_4$	AN	284
$(AsPh_4)_2[W_2(S_t)_2(\mu\text{-}S)(S_2)_4]$	$(AsPh_4)_2WS_4$, S_8, CH_3COOH	AN	114
W(μ-S)$_2$W(S_t) core			
$[Cp^*_2W_2(\mu\text{-}S)_2(S_t)(CO)_2]$	$[Cp^*_2W_2(CO)_4]$, S_8	TL	68
$[Cp_2W_2(\mu\text{-}S)_2(S_t)(NSiMe_3)]$	$[CpW(CO)_3Cl]$, $S(NSiMe_3)_2$	THF	263
$[Cp_2W_2(\mu\text{-}S)_2(S_t)(NSiMe_3)]$	$[Cp_2W_2(CO)_6]$, $S(NSiMe_3)_2$	BZ	263
$[Cp_2W_2(\mu\text{-}S)_2(S_t)(NSiMe_3)]$	$[CpW(CO)_3SH]$, Me_3SiN_3	THF	263
Others			
$(PPh_4)[(HS)(O)W(\mu\text{-}S)(\mu\text{-}S_2)W(SH)_2(S_2)]$	$(PPh_4)_2WS_4$, HCl	AN	286

TABLE 18
Compounds with miscellaneous cores

Compound	Source	Solvent	Ref.
W(μ-SH)W core			
$(Et_4N)[W_2(SH)(CO)_{10}]$	$[W(CO)_6]$, NaSH, diglyme, Et_4NBr	THF	281
$[Na(18\text{-crown-6})][W_2(SH)(CO)_{10}]$	$[W(CO)_6]$, $Na_2S \cdot 9H_2O$, 18-crown-6	EtOH	287
W(μ-SR)W core			
$(Et_4N)[W_2(SC(O)NHMe)(CO)_{10}]$	$Et_4N[W_2(\mu\text{-SH})(CO)_{10}]$, NaH, MeN=C=O, HCl gas	THF	288
W(μ-SR)$_2$W core			
$(Et_4N)_2[W_2(SR)_2(CO)_8]$	$W(CO)_6$, $(Et_4N)(SR)$ (R = Ph, ^{t}Bu)	AN/^{i}PrOH	289
$[W_2(SR)_2(CO)_8]$ (R = Ph, ^{t}Bu)	$(Et_4N)_2[W_2(CO)_8(SR)_2]$, I_2	TL	289
W(μ-S)(μ-SR)$_2$W core			
$[W_2(S)(SEt)_2Cl_4(tht)_2]$	$[WCl_4(tht)_2]$, $SiMe_3(SEt)$	DCM	290
$[W_2(S)(SEt)_2Cl_4(Me_2S)_2]$	$[WCl_4(Me_2S)_2]$, $SiMe_3(SEt)$	DCM	291
$(Ph_4P_2)_2[W_2(S)(SEt)_2Cl_6]$	$[W_2(\mu\text{-S})(\mu\text{-SEt})_2Cl_4(Me_2S)_2]$, Ph_4PCl	DCM	291
$[W_2(S)(SR)_2Cl_4(L)_2]$ (R = Me, Et, ^{i}Bu, CH_2Ph; L = tht, Me_2S)	$WCl_4(L)_2$, Me_2SiSR	DCM	292
$(Et_4N)_2[W_2(S)(SR)_2Cl_6]$ (R = Me, Et; L = tht, Me_2S)	$W_2Cl_4(\mu\text{-SR})_2(\mu\text{-S})(L)_2$, Et_4NCl	DCM	292
$[W_2(S)(SEt)_2Cl_4(L^1)_2]$ (L^1 = MeCN, PPh_3, Py; L = Me_2S, tht)	$[W_2Cl_4(\mu\text{-SEt})_2(\mu\text{-S})(L)_2]$, L^1	DCM	292
$(Me_2SCH_2Ph)_2[W_2(S)(SEt)_2Cl_4Br_2]$	$[W_2Cl_4(\mu\text{-SEt})_2(\mu\text{-S})(Me_2S)_2]$, $PhCH_2Br$	BZ	292
$(M^I)_2[W_2(S)(SEt)_2Cl_6]$ (M^I = Me_2SCH_2Ph, L = $PhCH_2Cl$; M^I = Ph_4P, L = Ph_4PCl)	$[W_2Cl_4(\mu\text{-SEt})_2(\mu\text{-S})(Me_2S)_2]$, L	DCM	292
$[W_2(S)(SEt)_2(SEt)_2(O_t)_2(PMePh)_2]$	*cis*-$[W(N_2)_2(PMe_2Ph)_4]$, EtSH	THF	293

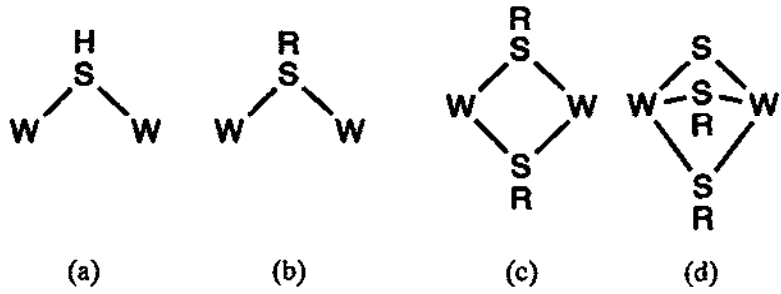


Fig. 19. Tungsten dinuclear compounds with (a) W(μ-SH)W, (b) W(μ-SR)W, (c) W(μ-SR)$_2$W, (d) W(μ-S)(μ-SR)$_2$W.

The reaction of WCl_4 with NaHS in THF and addition of dmpe (or depe), followed by column chromatography gave $[W_3S_4Cl_3(L)_3]^+$ (L = dmpe or depe) [181,298]. By the reaction of polymeric species $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3)Br_4$ with PEt_3 in THF or with $(NH_4)_2S_x$, discrete species $[W_3S_4Br_4(PEt_3)_3(OPEt_2H)(H_2O)]\cdot 2H_2O$ [180] or $(NH_4)(H)(H_2O)_3[W_3S_4(S_4)_3(NH_3)_3]$ [296] were obtained, respectively. Both ligand and bridge replacement occurred when $(Et_4N)_2[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$ was treated with KSCN in boiling CH_3CN to give $(Et_4N)_5[W_3S_4(NCS)_9]$ [204]. Under milder conditions, only replacement of ligand occurred to give $(Et_4N)_2$-$[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(NCS)_6]$ [204].

Treatment of $[W_3S_4(S_4)_3(NH_3)_3]^{2-}$ with boiling concentrated HCl gave $[W_3S_4(H_2O)_9]^{4+}$ [296]. $[W_3S_4(Et_2dtp)_3(\mu\text{-}OAc)py]\cdot 0.5dmf$ was obtained by the reaction of $[W_3S_4(Et_2dtp)_4]\cdot CH_3CN$ with HOAc, Py, and DMF in CH_3CN [299]. The structure of $[W_3S_4(Et_2dtp)_3(\mu_2\text{-}O_2CCH_3)(py)]$ has been determined [304]. $[W_3S_4H_3(R)_3]^+$ (R = dmpe, depe) were synthesized by the reaction of $[W_3S_4Cl_3(R)_3]^+$ with $LiBH_4$ in THF and $NaBH_4$ in MeOH, respectively [181].

Oxo- and sulphido-bridged incomplete cubane-type aqua clusters, $W_3OS_3^{4+}(aq)$, $W_3O_2S_2^{4+}(aq)$, $W_3O_3S^{4+}(aq)$, were synthesized by the reduction of $(NH_4)_2WS_4$ with $NaBH_4$ (or $[W_2Cl_9]^{3-}$) followed by Sephadex column chromatography [301–303]. Reaction of $[W(CO)_6]$ with Na_2S in acetic anhydride also gives a cluster with a W_3O_3S core [300]. No clusters with $W_3(\mu_3\text{-}O)(\mu\text{-}X)_3$ cores (X = O, S) have been reported. The kinetics of 1:1 NCS for H_2O substitution on W(IV) of $W_3S_4^{4+}(aq)$ and $W_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}(aq)$ were reported recently [305].

(ii) $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores

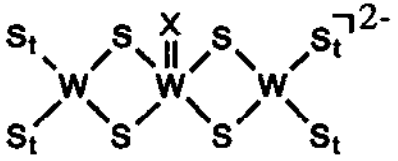
Compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores are listed in Table 20 [184,204,296,306–308].

All procedures so far reported require solid-state techniques: reactions in sealed tubes at high temperature (300–425°C). The polymeric species $W_3S_7Br_4$ was synthe-

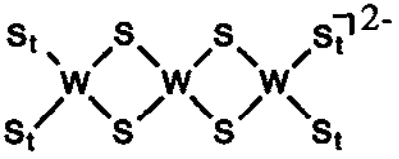
TABLE 19

Compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}X)_3$ cores (X = O or S)

Compound	Source	Solvent	Ref.
$[W_3S_4(H_2O)_9]^{4+}$	$(NH_4)_2WS_4$, $NaBH_4$, HCl	AQ	163,294
$[W_3S_4(H_2O)_9]^{4+}$	W, S, Br_2; $(NH_4)_2S_x$ ($x \approx 2$)	None	295,296
$[W_3S_4(H_2O)_9]^{4+}$	$(NH_4)(H)(H_2O)_3[W_3S_4(S_4)_3(NH_3)_3]$, HCl	AQ	296
$(bpyH)_5[W_3S_4(NCS)_9]\cdot 3H_2O$	$[W_3S_4(H_2O)_9]^{4+}$, KSCN, bpy	AQ	163,293
$[W_3S_4(H_2O)_9](pts)_4\cdot 9H_2O$	$[W_3S_4(H_2O)_9]^{4+}$, Hpts	AQ	163,297
$Na_2[W_3S_4(Hnta)_3]\cdot 5H_2O$	$[W_3S_4(H_2O)_9]^{4+}$, H_3nta, NaOH	AQ	163
$[W_3S_4Cl_3(R)_3]PF_6\cdot H_2O$ (R = dmpe, depe)	WCl_6, NaSH, R	THF	181,298
$[W_3S_4(Et_2dtp)_3(\mu_2\text{-}O_2CCH_3)(py)]\cdot 0.5DMF$	$[W_3S_4(Et_2dtp)_4$, CH_3COOH, py, DMF	AN	299
$(NH_4)(H)(H_2O)_3[W_3S_4(S_4)_3(NH_3)_3]$	$W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_2Br_4$, $(NH_4)_2S_x$	AQ	295,296
$[W_3S_4Cl_3(R)_3]PF_6\cdot nH_2O$ (R = dmpe, $n = 1$; R = depe, $n = 0$)	WCl_4, NaHS, R	THF	181,298
$[W_3S_4Br_4(PEt_3)_3(OPEt_2H)(H_2O)]\cdot 2H_2O$	$W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$, PEt_3	THF	180
$(NH_4)(H)(H_2O)_3[W_3S_4(S_4)_3(NH_3)_3]$	$W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$, $(NH_4)_2S_x$	AQ	296
$(Et_4N)_5[W_3S_4(NCS)_9]$	$(Et_4N)_2[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, KSCN (boiling)	AN	204
$(Et_4N)_2[W_3S_7(NCS)_6]$	$(Et_4N)_2[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, KSCN (r.t.)	AN	204
$[W_3S_4(Et_2dtp)_3(\mu\text{-}OAc)py]\cdot 0.5DMF$	$[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(Et_2dtp)_4]CH_3CN$, HOAc, Py, DMF	AN	299
$[W_3S_4H_3(R)_3]BPh_4$ (R = dmpe, M^I = Li, solv. = THF; R = depe, M^I = Na, solv. = MeOH)	$[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(R)_3]BPh_4$, M^IBH_4		181
$[W_3O_3S(NCS)_9]^{5-}$	$[W(CO_6)]$, Na_2S, NH_4SCN	Ac_2O	300
$W_3O_3S^{4+}$(aq)	$(NH_4)_2WS_4$, $K_3[W_2Cl_9]$	AQ	301
$K_2[W_3O_3S(Hnta)_3]\cdot 9H_2O$	$W_3O_3S^{4+}$(aq), H_3nta	AQ	301
$W_3O_2S_2^{4+}$(aq)	$(NH_4)_2WS_4$, $K_3[W_2Cl_9]$	AQ	302
$Ba[W_3O_2S_2(Hnta)_3]\cdot 9H_2O$	$W_3O_2S_2^{4+}$(aq)	AQ	302
$W_3OS_3^{4+}$(aq)	$(NH_4)_2WS_4$, $NaBH_4$ (or $K_3[W_2Cl_9]$)	AQ	303
$K_2[W_3OS_3(Hnta)_3]\cdot KCl\cdot 7H_2O$	$W_3OS_3^{4+}$(aq), H_3nta	AQ	303



(a)



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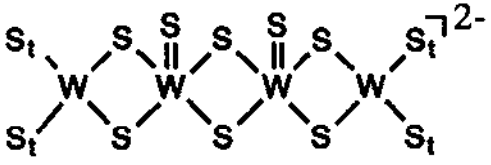

(c)

Fig. 20. Tungsten linear tri- and tetranuclear compounds with (a) $[(WS_4)W(X_t)(WS_4)]^{2-}$ (X = O, S), (b) $[(WS_4)W(WS_4)]^{2-}$, or (c) $[(WS_4)W(S_t)(\mu\text{-}S)_2W(S_t)(WS_4)]^{2-}$.

sized from: (1) tungsten sulphide (WS_3) and bromine [296]; (2) tungsten metal, elemental sulphur, and bromine [184,296]. The homologous compound $W_3S_7Cl_4$ was synthesized from WS_3 and PCl_5 [296]. A discrete compound $(Et_4N)_2W_3S_7Cl_6$ was synthesized from WS_3 and S_2Cl_2 (the solid obtained was treated with $CHCl_3$ and CH_3CN and dried under vacuum; the brown powder was boiled in conc. HCl containing Et_4NBr (red sol.)) [296].

Several triangular tungsten compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores have been synthesized from polymeric and discrete compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores.

The discrete species $(Et_4N)_2W_3S_7Br_6$ was synthesized by reaction of the polymeric species $W_3S_7Br_4$ with Et_4NBr in HBr [296], or with PEt_3 in THF [180]. The interaction of polymeric $W_3S_7Br_4$ with Et_4Br under vibrating mill conditions followed by extraction with acetonitrile resulted in the isolation of the water-

TABLE 20

Compounds with $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ cores

Compound	Source	Solvent	Ref.
$W_3S_7Cl_4$	WS_3, PCl_5 at 300°C	None	296
$W_3S_7Cl_4$	WCl_2 (= W_6Cl_{12}), S_8 at 300°C	None	306
$W_3S_7Br_4$	WS_3, Br_2 at 300°C	None	296
$W_3S_7Br_4$	W, S_8, Br_2 at 300°C	None	296
$W_3S_7Br_4$	W, S_8, Br_2 at 425°C	None	184
$(Et_4N)_2W_3S_7Cl_6$	WS_3, S_2Cl_2, Et_4NBr, HCl	AQ	296
$(Et_4N)_2W_3S_7Br_6$	$W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$, Et_4NBr, HBr	AQ	296
$(Et_4N)_2W_3S_7(NCS)_6$	$(Et_4N)_2[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]$, KSCN	AN	204
$(Et_4N)_2[W_3S_4Se_3X_6]$ (X = Cl, Br)	$(Et_4N)_2[W_3S_7X_6]$, $SePPh_3$	AN	307
$(Et_4N)_2[W_3S_7Br_6]$	$W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$, Et_4NBr (vib. mill)	None	308
$(Et_4N)_2[W_3S_7Cl_6]$	$(Et_4N)_2W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6$, HCl, PPNCl	AQ	308

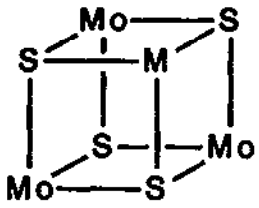

Fig. 21. Structure of cubane-type mixed-metal compounds with Mo_3MS_4 cores (M = metal).

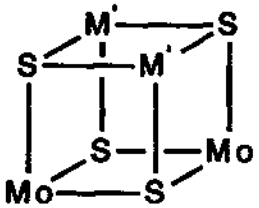

Fig. 22. Structure of cubane-type mixed-metal compounds with $Mo_2M'_2S_4$ cores (M' = metal).

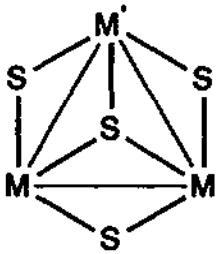

Fig. 23. Structure of incomplete cubane-type mixed-metal compounds with $M_2M'S_4$ cores (M, M' = metal).

soluble cluster $(Et_4N)_2[W_3S_7Br_6]$ [308]. Corresponding selenium clusters were also synthesized.

The bromide ion in $(Et_4N)_2[W_3S_7Br_6]$ may be replaced by SCN^- at room temperature and under more severe conditions, the core W_3S_7 structure changes to give W_3S_4 [204].

Fedin et al. reported the syntheses of $(Et_4N)_2[W_3S_4Se_3X_6]$ (X = Cl, Br), which were obtained by reaction of $(Et_4N)_2[W_3S_7X_6]$ with $SePPh_3$ in CH_3CN [307].

No reports have appeared describing compounds with the formulae $[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]^{2-}$ or $[W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_4)_3]^{2-}$.

TABLE 21

Compounds with linear W_3 or W_4 cores

Compound	Source	Solvent	Ref.
$(Ph_4P)_2[(WS_4)W(O_t)(WS_4)]$	Na_2WO_4, PPh_4Br	DMF	309
$R_2[(WS_4)W(O_t)(WS_4)]\cdot H_2O$	$(NH_4)_2WS_4$, HCl, RCl ($R = Me_4N$, Ph_4P)	AQ	310
$(Bu_4N)_2[(WS_4)W(O_t)(WS_4)]$	$(NH_4)_2WS_4$, HCl, Bu_4NBr	AQ	311
$R_2[(WS_4)W(O_t)(WS_4)]$ ($R = C_5H_5N{-}C_{18}H_{33}$)	$(NH_4)_2WS_4$, HCl, RBr	AQ	311
$(Bu_4N)_2[(WS_4)W(O_t)(WS_4)]$	$[(WS_4)W(S_t)(WS_4)]^{2-}$, air	AQ	312
$Cs_2[(WS_4)W(O_t)(H_2O)(WS_4)]$	$(NH_4)_2WS_4$, HCl, CsCl	AQ	313
$(Bu_4N)_2[(WS_4)W(O_t)(WS_4)]$	$(NH_4)_2WS_4$, HCl, Bu_4NBr	AQ	311
$R_2[(WS_4)W(S_t)(WS_4)]$ ($R = PPh_4$, $AsPh_4$)	$(NH_4)_2WS_4$, HF, RCl	AQ	314
$(PPh_4)_2[(WS_4)W(S_t)(WS_4)]$	$(NH_4)_2WS_4$, PPh_4Cl at 250°C	None	314
$(PPh_4)_2[(WS_4)W(S_t)(WS_4)]$	$(NH_4)_2WS_4$, PPh_4Cl	DMF	313
$(PPN)_2[(WS_4)W(WS_4)]$	$(NH_4)_2WS_4$, H_2SO_4, (PPN)Cl	AQ	315
$(PPh_4)_2[(WS_4)W(S_t)(\mu\text{-}S)_2W(S_t)(WS_4)]$	$(PPh_4)_2WS_4$, CH_3COOH	DCM	316

TABLE 22

Mixed-metal compounds with cubane-type Mo_3MS_4 (M = metal) or $M_2M'_2S_4$ (M = Mo, W; M' = metal) or incomplete cubane-type $M_2M'S_4$ (M = Mo, W; M' = metal) cores

Compound	Source	Solvent	Ref.
Mo_3MS_4 core			
$[Mo_3FeS_4(H_2O)_{10}]^{4+}$	$[Mo_3S_4(H_2O)_9]^{4+}$, Fe	AQ	317
$[Mo_3FeS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$	$[Mo_3FeS_4(H_2O)_{10}]^{4+}$, Hpts	AQ	318
$[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$	$[Mo_3FeS_4(H_2O)_{10}]^{4+}$, NH_3aq	AQ	317
$[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Ni, Hpts	AQ	319,320
$Ca_{2.5}[Mo_3NiS_4(Hnta)_2(nta)Cl] \cdot 14H_2O$	$[Mo_3NiS_4(H_2O)_{10}]^{4+}$, H_3nta, $CaCl_2$	AQ	320
$[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9](pts)_8 \cdot 20H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Cu, Hpts	AQ	321
$[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9](pts)_8 \cdot 18H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Co, Hpts	AQ	322
$[(H_2O)_9Mo_3S_4PdPdS_4Mo_3(H_2O)_9](pts)_8 \cdot 18H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Pd, Hpts	AQ	323
$[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9](pts)_8 \cdot 26H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Sn, Hpts	AQ	324
$[(H_2O)_9Mo_3S_4SbS_4Mo_3(H_2O)_9](pts)_8 \cdot 26H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Sb, Hpts	AQ	325
$[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9](pts)_8 \cdot 20H_2O$	$[Mo_3S_4(H_2O)_9]^{4+}$, Hg, Hpts	AQ	322
$[Mo_3SnS_4(Et_2PS_2)_6]$	$[Mo_3S_4(Et_2PS_2)_4]$, Sn, $[Et_2P(S)S]_2$	TL	326
$[Mo_3CuS_4(Et_2dtp)_3(\mu\text{-}MeCO_2)(I)(dmf)]$	$[Mo_3S_4(Et_2dtp)_4] \cdot H_2O$, CuI, $MeCO_2Et$	DMF	327
$[Mo_3WS_4(Et_2PS_2)_6]$	$[Mo_3S_4(Et_2PS_2)_4]$, $[W(CO)_3(CH_3CN)_3]$, $(Et_2PS)_2S_2$	TL	328
$[Mo_3SbS_4(Et_2dtp)_4(Cl_3)(EtOH)] \cdot EtOH$	$[Mo_3S_4(Et_2dtp)_4] \cdot H_2O$, $SbCl_3$, HCl	EtOH	329
$[Mo_3SbS_4(Et_2dtp)_3(SXP(OEt)_2(Cl_3)(oxaz)]$ (X = 0.5S + 0.5O)	$[Mo_3S_4(Et_2dtp)_4] \cdot$ oxaz, $SbCl_3$	ACET/EtOH	329
$[Mo_3SbS_4(Et_2dtp)_3(SXP(OEt)_2)(Cl_3)(oxaz)]$ (X = 0.5S + 0.5O)	$[Mo_3SbS_4(Et_2dtp)_4(Cl_3)(EtOH)] \cdot EtOH$, $SbCl_3$	ACET/EtOH	329

$[W_3CuS_4(Et_2dtp)_3(I)(\mu\text{-}PhCO_2)(MeCN)]$	$[W_3S_4(Et_2dtp)_4(MeCN)]$, CuI, $PhCO_2H$	AN	330
$[W_3CuS_4(Et_2dtp)_3(I)(\mu\text{-}MeCO_2)(py)]$	$[W_3S_4(Et_2dtp)_4(MeCN)]$, CuI, $MeCO_2H$, py	MeCOOEt	331
$M_2M'_2S_4$ core			
$[Mo_2Fe_2S_4(CO)_2Cp^*_2]$	$[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$, $Fe_2(CO)_9$	THF	332
$[Mo_2Fe_2S_4(NO)_2Cp^*_2]$	$[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$, $(Ph_3PNPPh_3)[Fe(CO)_3NO]$, light	THF	333
$[Mo_2Fe_2S_4(\mu\text{-}Et_2dtc)(Et_2dtc)_4]\cdot MeCN$	$(NH_4)_2MoS_4$, NaS_2CNEt_2, $FeCl_3$	AN/DMF	334
$[Mo_2Co_2S_4(CO)_2Cp^*_2]$	*syn*-$[Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$, $Co_2(CO)_8$	TL	335
$[M_2Co_2S_4(Et_2dtc)_2(MeCN)_2(CO)_2]$ (M = Mo, W)	$[M_2(S_t)_2(\mu\text{-}S)_2(Et_2dtc)_2]$, $Co_2(CO)_8$	AN	336
$[Mo_2Ni_2S_4(CO)_2MeCp_2]$	$[(MeCp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2]$, $Ni(CO)_4$	THF	150,337
$[Mo_2Cu_2S_4(edt)_2(PPh_3)_2]$	$(Et_4N)_2[Mo_2(S_t)_2(\mu\text{-}S)_2(edt)_2]$, $Cu(PPh_3)_3Cl$	AN/DCM	338
$[W_2Cu_2S_4(edt)_2(PPh_3)_2]$	$(Et_4N)_2[W_2(S_t)_2(\mu\text{-}S)_2(edt)_2]$, $CuCl_2\cdot 2H_2O$, PPh_3	EtOH/DCM	338,339
$M_2M'S_4$ core			
$[Mo_2MS_4Cp^*_3]$ (M = W, Cr)	$[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp^*_2]$, $[M_2Cp^*_2(CO)_4]$	THF	176
$[Mo_{3-n}W_nS_4(H_2O)_9](pts)_4\cdot 9H_2O$ (n = 1, 2)	$(NH_4)_2WS_4$, $Na_2[Mo_2(O_t)_2(\mu\text{-}S)_2(cys)_2]\cdot 4H_2O$, $NaBH_4$	AQ	340
$(Et_4N)[M_2CuS_4(edt)_2(PPh_3)]$ (M = Mo, W)	$(Et_4N)[M_2(S_t)_2(\mu\text{-}S)_2(edt)_2]$, $[Cu(PPh_3)_2(Et_2dtp)]$	DCM/AN	341
$(Et_4N)[M_2AgS_4(edt)_2(PPh_3)]\cdot CH_2Cl_2$ (M = Mo, W)	$(Et_4N)[M_2(S_t)_2(\mu\text{-}S)_2(edt)_2]$, $Ag(PPh_3)_3NO_3$	DCM/AN	342
$(Et_4N)[M_2CuS_4(edt)_2(PPh_3)]$ (M = Mo, W)	$(Et_4N)_2[M_2S_4(edt)_2]$, $[Cu(PPh_3)_2(dtp)]$	DCM	343

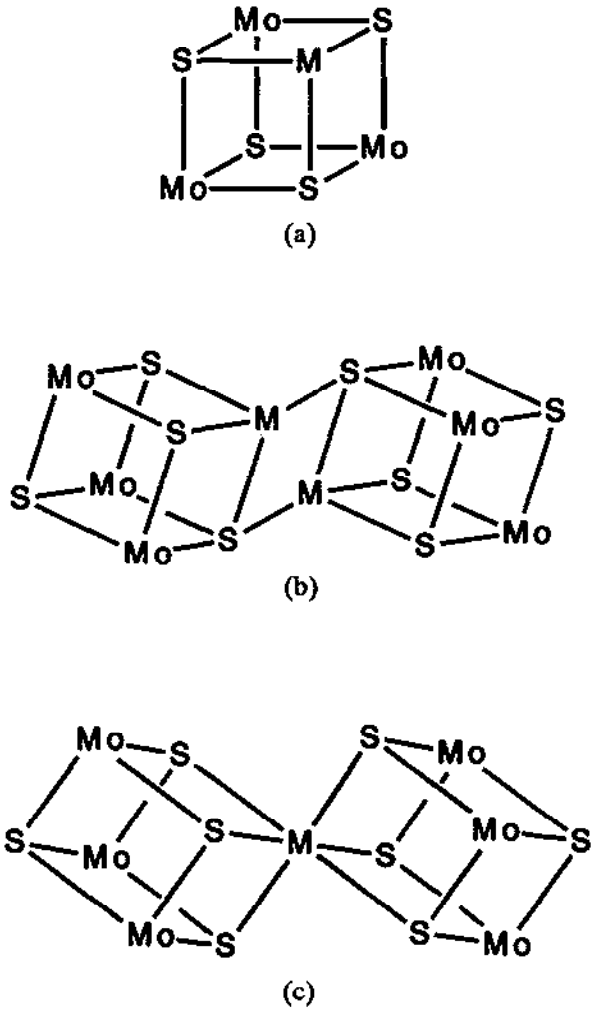

Fig. 24. Three kinds of cubane-type mixed-metal core: (a) single cubane-type, (b) double cubane-type, (c) sandwich cubane-type.

(iii) Linear W_3 or W_4 cores

The linear compounds, $[(WS_4)W(X_t)(WS_4)]^{2-}$ (X = O, S; Fig. 20(a)), $[(WS_4)W(WS_4)]^{2-}$ (Fig. 20(b)), and $[(WS_4)W(S_t)(\mu\text{-}S)_2W(S_t)(WS_4)]^{2-}$ (Fig. 20(c)) are listed in Table 21 [309–316]. WO_4^{2-} and WS_4^{2-} are the tungsten sources.

G. SYNTHESES OF CUBANE-TYPE AND INCOMPLETE CUBANE-TYPE MIXED-METAL COMPOUNDS

Mixed-metal cluster compounds have been extensively studied. Syntheses of cubane-type mixed-metal compounds with Mo_3MS_4 (M = metal; Fig. 21) or

$M_2M'_2S_4$ (M = Mo, W; M′ = metal; Fig. 22) cores or incomplete cubane-type $M_2M'S_4$ (M = Mo, W; M′ = metal; Fig. 23) cores are listed in Table 22 [150,176,317–343]. Dinuclear, linear trinuclear, and other molybdenum/tungsten mixed-metal compounds were not included here.

The incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with metals (Fe [317,318], Co [322], Ni [319,320], Cu [321], Sn [324], Sb [325], Hg [322]) or metal ion (Sn^{2+}) [324] to give mixed-metal cubane-type aqua cluster ions with Mo_3MS_4 cores. Yano et al. also reported reaction of the aqua ion with Pd [323]. There exist three kinds of cubane-type cores (Fig. 24): single cubane-type (Mo_3MS_4, S), double cubane-type ($Mo_3S_4MMS_4Mo_3$, D), and Sandwich cubane-type ($Mo_3S_4MS_4Mo_3$, SW). There are two kinds of driving force for the formation of the cubane-type mixed-metal clusters from the incomplete cubane-type aqua ion and metal or metal ions. One factor is the reducing ability of the metal, and another is the affinity of the metal for the bridging sulphur atom. The reaction of the aqua ion with divalent metal ions in reducing conditions to give the clusters with Mo_3MS_4 cores has also been reported [344,345].

Other routes to Mo_3MS_4 core clusters are: (a) the reaction of $[Mo_3S_4(dtp)_4(L)]$ (L = H_2O, C_3H_3ON) with $SbCl_3$ [329] or CuI [327], and (b) the reaction of $[Mo_3S_4(Et_2PS_2)_4]$ with $[W(CO)_3(CH_3CN)_3]$ and $(Et_2PS)_2S_2$ [328].

Mixed-metal clusters with $M_2M'_2S_4$ (M = Mo, W; M′ = metal) cores have been synthesized from: (a) M_2 dinuclear and M'_2 dinuclear species, and (b) M_2 dinuclear and M′ mononuclear species.

A series of aqua clusters with the Mo_3S_4, Mo_2WS_4, MoW_2S_4, and W_3S_4 cores were synthesized and characterized very recently [340].

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