

SEVEN COORDINATION IN MOLYBDENUM CHEMISTRY: ANALYSIS OF OLIGONUCLEAR STRUCTURES

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ABBREVIATIONS

bipy 2,2'-bipyridyl
t-BuHNCCNH-t-Bu (*N,N'*-di-tert-butylamino)acetylene

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$o\text{-C}_6\text{H}_4(\text{AsMePh})_2$	<i>o</i> -phenylenebis(methylphenylarsine)
$\text{C}_6\text{H}_{10}\text{Si}_2\text{F}_4$	1,1,4,4,-tetrafluoro-2-tert-butyl-1,4-disila-but-2-ene
$\text{C}_6\text{H}_{11}\text{CN}$	cyclohexyl isocyanide
CN-t-Bu	tert-butyl isocyanide
CNPh	phenyl isocyanide
C_2O_4	oxalate
dbd	dibenzoyldiarene
diars	<i>o</i> -phenylenebis(dimethylarsine)
dml	(<i>s</i>)- <i>N,N</i> -dimethylactamide
dpam	bis(diphenylarsino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dta	ditoluoylacetylene
L_{ax}	axial ligand
L_{c}	capped ligand
L_{cf}	capped face ligand
L_{e}	capped edge ligand
L_{eq}	equatorial ligand
L_{qf}	capped quadrilateral face ligand
L_{tab}	tetragonal base ligand
L_{tib}	trigonal base ligand
L_{uf}	uncapped face ligand
$(\text{NEt}_4)^+$	tetraethylammonium
N-NEt(Ph)	<i>N</i> -ethyl- <i>N</i> -phenylhydrazide
N_2Ph	phenyldiazenide
PEt_3	triethylphosphine
phen	1,10-phenanthroline
$(\text{PH}_3\text{B})_2\text{CN}$	cyano-bis(triphenylboron)
3-Ph(NO ₂)	3-nitrophenyldiazenide
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	ethylenediphosphine tetraphenyl
PMe_3	trimethylphosphine
PMeCl_2	dichloro(methyl)phosphine
PMe_2Ph	dimethylphenylphosphine
$\text{P}(\text{OCH}_3)_3$	trimethoxyphosphine
PPh_3	triphenylphosphine
$(\text{PPh}_4)^+$	tetraphenylphosphonium
py	pyridine
pydca	pyridine-2,6-dicarboxylate
pyH	pyridinium
S_2CNBu_2	<i>N,N</i> -dibutyldithiocarbamate
$\text{S}_2\text{CN}(\text{CH}_2)_5$	<i>N,N</i> -pentamethylenedithiocarbamate
S_2CNEt_2	<i>N,N</i> -diethyldithiocarbamate

S_2CNMe_2	<i>N,N</i> -dimethyldithiocarbamate
S_2CNPt_2	<i>N,N</i> -dipropyldithiocarbamate
SPh_2	sulphide-diphenylphosphine
tcne	tetracyanoethylene

A. INTRODUCTION

Systematic studies in the field of stereoselectivity of coordination compounds in the last two decades have rapidly found wide interest. The problem of stereoselectivity in coordination compounds is very often related to the well-known stereochemical specificity of biological systems, catalysis and the stereochemical effect in technical processes, etc.

Molybdenum is one of the most important transition metals to function in redox enzymes. Important new texts have been published concerned with the biochemistry and related chemistry of molybdenum [1,2] and the chemistry and uses of this element [3]. From the transition metal point of view, coordination number seven dominates much of the coordination chemistry of molybdenum [4,5].

Seven coordination is possibly the most complicated subject in the structural and dynamic stereochemical aspects of coordination chemistry [5]. These aspects are of considerable importance to an understanding of associative and dissociative reactions of six and eight coordinate compounds, respectively [6]. Only a more extensive set of structural and stereochemical studies can yield a thorough understanding of seven coordination.

This review represents a brief survey of the structural data of seven coordinated molybdenum compounds. The material included was obtained from reports published in primary journals to the end of 1983 or to volume 99 of Chemical Abstracts. The aim of the following presentation is to discuss the factors leading to a better understanding of the stereochemical interactions in the seven coordination sphere of molybdenum compounds. We report the first overview of seven coordination for molybdenum.

The systems to be discussed include; (Section B) a series of molybdenum compounds with a pentagonal bipyramidal geometry; (Section C) a series of molybdenum compounds with a capped octahedral geometry; (Section D) a series of molybdenum compounds with a capped trigonal prism geometry; and (Section E) a series of molybdenum compounds with a square antiprism geometry (the 4:3 geometry).

The reasons for the geometry adopted in seven coordination are not well understood and therefore more structure determinations are important. We also describe here the crystal and molecular structure of the seven coordinate molybdenum(II) compounds, $[HMo(CO)_2(PMe)_4]PF_6$, $[Mo(CO)_2(PMe)_3(F_3CCOO)_2]$ and $[Mo(CO)_2\{\mu-(O)(P)(OMe)_2\}(F_3CCOO)]_2$, which are not yet published.

B. X-RAY DATA FOR MOLYBDENUM COMPOUNDS WITH A PENTAGONAL BIPYRAMIDAL GEOMETRY

(i) Mononuclear compounds

In Table 1 are collected structural data for mononuclear molybdenum compounds with a pentagonal bipyramidal geometry (Fig. 1). The structures are tabulated by increasing number of different coordinated atoms (ligands). Figure 1 shows that the axial sites are the least crowded while equatorial sites are among the most crowded in the ideal polyhedra. From the dentate ligand point of view, of the compounds summarised in Table 1, only $[\text{MoO}(\text{O}_2)(\text{pydca})\text{F}]\text{NH}_4$ [29] contains a tridentate ligand. There are three examples with equivalent unidentate ligands and no examples of tetra- or multi-bonded ligands.

Figure 2 illustrates, as a representative example, the structure of the $[\text{Mo}(\text{NO})\{\text{OCN}(\text{CH}_3)_2\}(\text{NCS})_4]^{2-}$ ion [30]. The molybdenum is surrounded by six ligands (five unidentate and one bidentate) in the form of a distorted pentagonal bipyramid, the equatorial plane of which consists of the three NCS groups ($\text{Mo}-\text{N} = 2.114(6) \text{ \AA}$) and a carbamido moiety, $\{\text{OCN}(\text{CH}_3)_2\}$, bound by an oxygen atom ($\text{Mo}-\text{O} = 2.078 \text{ \AA}$) and a carbon atom ($\text{Mo}-\text{C} = 2.029 \text{ \AA}$). The apical positions are occupied by NO and the remaining NCS group. The apical $\text{Mo}-\text{N}$ bond distances are $1.767(6)$ and $2.188(6) \text{ \AA}$, respectively.

The decreasing order of occurrence of the oxidation number of the central atoms is (Table 1): six > two > four > three. Inspection of the data in Table 1 reveals that most examples have $\text{Mo}-\text{L}_{\text{ax}}$ bond distances shorter than the $\text{Mo}-\text{L}_{\text{eq}}$ bond distances by approximately $0.20 \text{ \AA}$, ranging from 0.004 to

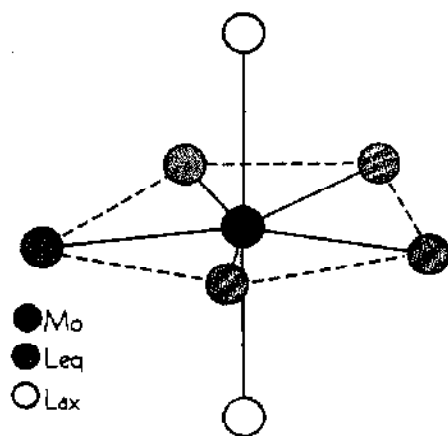


Fig. 1. A schematic view of a pentagonal bipyramid.

TABLE 1

Structural data for mononuclear molybdenum compounds with a pentagonal bipyramidal geometry ^a

Compound	Space group	Z	Chromophore	Mo-L _{ax} Mo-L _{eq} (Å)	L _{ax} -Mo-L _{ax} L _{ax} -Mo-L _{eq} (°)	L _{eq} -Mo-L _{eq} <i>cis</i> (°) <i>trans</i> (°)	Ref.
Na ₃ [Mo ^{II} (CN) ₇]·10H ₂ O	<i>P</i> $\bar{1}$	2	MoC ₇	2.129(11), 2.125(10) 2.153(7)	169.7(3) 89.5(3)	72.0(3) 143.9(3)	7
K ₅ [Mo ^{II} (CN) ₇]·H ₂ O	<i>I</i> 1	2	MoC ₇	2.13(3), 2.16(3) 2.14(3)	170.1(10) 90.6(10)	72.9(10) 142.3(11)	7
NaK ₃ [Mo ^{III} (CN) ₇]·2H ₂ O	<i>P</i> 2 ₁ / <i>m</i>	2	MoC ₇	2.160(3) ^c		72.3(1)	8
K ₂ [Mo ^{VI} O(O ₂) ₂ (C ₂ O ₄)]	<i>P</i> 2 ₁ / <i>n</i>	4	MoO ₇	1.678(14), 2.259(11) 1.972(15)	170.0(6) 90.47(6)	70.6(6) 136.1(6)	9
[Mo ^{VI} O(O ₂) ₂ (dmf)]	<i>P</i> 2 ₁ 2 ₁ 2 ₁	4	MoO ₇	1.671(5), 2.357(4) 1.950(5)	165.4(2) 92.5(2)	70.5(2) 135.7(2)	10
[Mo ^{VI} O(O ₂) ₂ (hmp)(H ₂ O)]	<i>P</i> 2 ₁ / <i>c</i>	4	MoO ₇	1.662(5), 2.347(5) 1.965(5)	173.90(21) 90.08(22)	70.85(22)	11, 12
[Mo ^{VI} O(O ₂) ₂ (hmp)(py)]	<i>P</i> 6 ₃	8	MoO ₆ N	O ^b 1.658(12), N ^b 2.450(11) 1.948(12)	172.68(34) 90.27(15)	70.53(42)	11, 12
K ₃ [Mo ^{III} (NO)(C ₂ O ₄) ₃]·4H ₂ O	<i>C</i> 2	4	MoO ₆ N	N 1.780(5), O 2.09 2.11	173.3(2)		13
[Mo ^{II} (NO)(H ₂ NO)(N ₃) ₄][C ₆ H ₅] ₄ PI ₂ ·H ₂ O	<i>P</i> $\bar{1}$	2	MoN ₆ O	N 1.761(8), N 2.211(10) 2.138(5)	175.5(2) 90.0(3)	71.8(2) 144.6(2)	14
[Mo(NO){OCN(CH ₃) ₂ }(NCS) ₄](PPh ₃) ₂	<i>P</i> $\bar{1}$	2	MoN ₆ O	N 1.770(9), N 2.192(9) N 2.107(8), O 2.090(6)	178.3(4) 90.3(3)	71.6(3) 142.8(3)	15
[Mo ^{IV} (NO)(H ₂ NO)(phen) ₂][I ₂ (phen)·H ₂ O]	<i>P</i> 2 ₁ / <i>n</i>	4	MoN ₆ O	N 1.69(3), N 2.18(2) 2.12(2)	172.0(1) 90.0(1)	71.0(1)	16
[Mo ^{VI} {S ₂ CN(CH ₂) ₅ }(N-NEt(ph))](BPh ₄)	<i>P</i> 2 ₁	2	MoS ₈ N	N 1.72, S 2.55 2.50			17
[Mo ^{VI} N(S ₂ CNEt ₂) ₃]	<i>P</i> 2 ₁ / <i>c</i>	4	MoS ₈ N	N 1.641(9), S 2.852(3) 2.522(3)	164.1(3) 91.9(3)	70.6(1)	18
[Mo(NS)(S ₂ CNMe ₂) ₃]	<i>P</i> $\bar{1}$	2	MoS ₈ N	N 1.738(11), S 2.602(4) 2.515(4)	165.7(3) 90.8(3)	71.2(1)	18

TABLE 1 (continued)

Compound	Space group	Z	Chromophore	Mo-L _{ax} Mo-L _{eq} (Å)	L _{ax} -Mo-L _{ax} L _{ax} -Mo-L _{eq} (°)	L _{eq} -Mo-L _{eq} cis (°) trans (°)	Ref.
[Mo(N ₂ Ph)(S ₂ CNMe ₂) ₃]·CH ₂ Cl ₂	P2 ₁ /n	4	MoS ₈ N	N 1.781; S 2.411(1) 2.514			19
[Mo{N ₂ -3-Ph(NO ₂) ₂ }(S ₂ CNMe ₂) ₃]	C2/c	8	MoS ₈ N	N 1.770(6), S 2.574(2) 2.515			19
[Mo ^{II} (NO)(S ₂ CNBU ₂) ₃]	P2 ₁ /c	4	MoS ₈ N	N 1.731(8), S 2.568(4) 2.508(4)	167.9(3) 70.3(2)	71.7(2)	20
[Mo ^{IV} O(S ₂ X)(S ₂ CNPr ₂) ₂]	P2 ₁ /c		MoS ₈ O	O 2.377(7) ^d			21
[Mo ^{VI} O(S ₂ CNEt ₂) ₃]·[Mo ^{VI} O ₄ F ₆]	C2/c	4	MoS ₈ O	O 1.684(6), S 2.630(2) 2.486(2)	161.8(2) 93.9(2)	73.0(1) 139.7(1)	22
[Mo ^{II} (dppm)(CNCH ₃) ₅](PF ₆) ₂	Cc	4	MoC ₅ P ₂	C 2.090(9), C 2.107(10) C 2.135(6), P 2.528(1)	178.2(2) 90.0(2)	72.4(2) 143.2(2)	23
[Mo ^{II} (dppe)(CNCH ₃) ₅](PF ₆) ₂	P $\bar{1}$	2	MoC ₅ P ₂	C 2.101(5), C 2.119(5) C 2.117(6), P 2.535(2)	175.9(2) 90.0(2)	73.8(2) 141.5(2)	23
[Mo ^{II} (CO) ₅ (C ₆ H ₁₀ Si ₂ F ₄)]	P $\bar{1}$	2	MoC ₅ Si ₂	C 2.035(9), C 2.041(10) C 2.042(9), Si 2.605		72.0(3) 150.0(3)	24
[Mo ^{IV} (NO)(H ₂ N) ₂ (bipy)]Cl	Cc	4	MoN ₅ O ₂	N 1.773(4), N 2.217(4) N 2.125(5), O 2.031(5)	169.6(2) 84.8(2)	57.4(2)	25
[Mo ^{VI} O(O ₂)F ₄](NH ₄) ₃ F	P ₃ ca	8	MoF ₄ O ₃	O 1.67(2), F 2.03(1) O 1.91(2), F 1.97(1)	172.1(7) 90.4(7)	71.5(8) 141.0(8)	26
[Mo ^{VI} O(O ₂)F ₄](K ₂ ·H ₂ O)	P2 ₁ /c	1	MoF ₄ O ₃	F 1.998(14), F 2.027(31) O 1.855(25), F 2.006(13)	156.4(7) 89.0(9)	74.7(9) 144.0(1)	27
[Mo ^{VI} O{H(CH ₃)NO} ₂] {HNC(SN(CH ₃)O)}	I4 ₁ /a	16	MoO ₄ N ₃	O 1.677(8), O 2.027(7) O 1.962(8), N 2.084(9)	160.1(4) 91.3(4)	71.5(4) 137.1(4)	28
[Mo ^{VI} O(O ₂)pydca]F[NH ₄]	P ₃ ca	8	MoO ₅ NF	O 1.661(5), F 2.058(4) O 1.985(6), N 2.119(6)	169.1(2) 90.3(3)	71.5(3)	29

$[\text{Mo}^{\text{II}}(\text{NO})\{\text{OCN}(\text{CH}_3)_2\} \cdot (\text{NCS})_4] \cdot [(\text{C}_6\text{H}_5)_4\text{P}]_2$	$P\bar{1}$	2	MoN_3CO	N 1.767(6), N 2.188(6) N 2.114(6), O 2.029 $O_{\text{eq}} = 2.078$	30
$[\text{Mo}^{\text{VI}}\text{O}(\text{H}(\text{CH}_3)\text{NO})\{\text{HNC}(\text{S})\text{N}(\text{CH}_3)\text{O}\} \cdot \{\text{H}_2\text{NC}(\text{S})\text{N}(\text{CH}_3)\text{O}\}] \cdot \text{H}_2\text{O}$	$P2_1/a$	4	$\text{MoO}_4\text{N}_2\text{S}$	O 1.691(3), O 2.114(3) O 1.998(3), N 2.120(4) $S_{\text{eq}} = 2.489(2)$	28
$[\text{Mo}^{\text{III}}\text{H}(\text{CO})_2(\text{dppe})_2]\text{AlCl}_4$			$\text{MoP}_4\text{C}_2\text{H}$		31
$[\text{Mo}^{\text{III}}\text{H}\{\text{P}(\text{OCH}_3)_3\}_4(\text{F}_3\text{CCOO})]$	$P2_1/n$	4	$\text{MoP}_4\text{O}_2\text{H}$	P 2.389(1), P 2.419(1) P 2.322(1), O 2.316(2) $H_{\text{eq}} = 1.59(4)$	32
$[\text{Mo}^{\text{II}}(\text{NO})(\text{S}_2\text{CNEt}_2)_2(\text{diars})]\text{BF}_4$	$I2/a$	8	$\text{MoS}_4\text{As}_2\text{N}$	N 1.78(1), S 2.552(4) S 2.522(4), As 2.630(2) O 1.682(4), S 2.576(2) C 2.285(6), S 2.452(2)	33
$[\text{Mo}^{\text{VI}}\text{O}(\text{tenc})\{\text{S}_2\text{CNPr}_2\}_2]$	$Pbca$	8	$\text{MoS}_4\text{C}_2\text{O}$	O 1.686(2), S 2.696(1) S 2.489(1), C 2.121(4) O 1.701(4), Cl 2.504(1) S 2.498(1), Cl 2.417(1)	34
$[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{CNMe}_2)_2(\text{dta})]$	$P2_1/c$	4	$\text{MoS}_4\text{C}_2\text{O}$	O 1.656(5), Br 2.729(1) S 2.485(2), Br 2.550(1) O 1.685(10), O 2.054(14) S 2.525(13), N 2.119(18)	38
$[\text{Mo}^{\text{VI}}\text{OCl}_2(\text{S}_2\text{CNEt}_2)_2]$	$P2_1/c$	4	$\text{MoS}_4\text{Cl}_2\text{O}$	C 2.007(7), C 2.027(7) S 2.622(2), P 2.441(2)	35
$[\text{Mo}^{\text{VI}}\text{OBr}_2(\text{S}_2\text{CNEt}_2)_2]$	$P\bar{1}$	2	$\text{MoS}_4\text{Br}_2\text{O}$		35
$[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{CNMe}_2)_2(\text{dbd})]$	$P2_1/c$	4	$\text{MoS}_4\text{O}_2\text{N}$	O 1.656(5), Br 2.729(1) S 2.485(2), Br 2.550(1) O 1.685(10), O 2.054(14) S 2.525(13), N 2.119(18)	36
$[\text{Mo}^{\text{II}}(\text{CO})_2(\text{PPh}_3)(\text{SPPH}_2)_2] \cdot \text{CH}_2\text{Cl}_2$	$P\bar{1}$	2	$\text{MoP}_3\text{C}_2\text{S}_2$	C 2.007(7), C 2.027(7) S 2.622(2), P 2.441(2)	37

^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average values for an individual distance or angle. ^b The chemical identity of the coordinated atom is specified in these columns. ^c Only the average value of Mo–L distance was published. ^d The bond distance for the ligands coordinated in the axial position.

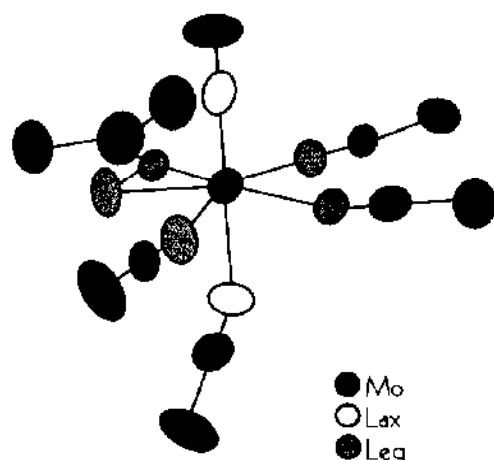


Fig. 2. Molecular structure of $[\text{Mo}(\text{NO})(\text{OCN}(\text{CH}_3)_2)(\text{NCS})_4]^{2-}$ (without H-atoms) [30].

0.496 Å. For example, while the mean value of the Mo–L_{ax} bond distance is 1.968 Å the Mo–L_{eq} distance is only 1.972 Å in $\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$ [9], but the same values in $[\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{SPPH}_2)_2] \cdot \text{CH}_2\text{Cl}_2$ [37] are 1.869 and 2.444 Å, respectively. There are a few examples [7,10–12,27,28], where the Mo–L_{ax} distances are longer than Mo–L_{eq}; for example, in $[\text{MoH}\{\text{P}(\text{OCH}_3)_3\}_4(\text{F}_3\text{CCOO})]$ [32], the average value of the Mo–L_{ax} bond distance is 2.404 Å, while the Mo–L_{eq} is only 2.173 Å, in spite of the fact that the two apical sites of a pentagonal bipyramid are less sterically hindered than the five equatorial sites. These observations indicate that the variation of Mo–L_{ax} and Mo–L_{eq} bond distances is not a simple function of the least/most crowded in the ideal polyhedra. The significance, if any, of this observation cannot be definitively evaluated on the basis of existing experimental data. It does however suggest possible rational directions for further experiments.

There exist different types of ligands which are bound in an axial site and equatorial plane. Examples are known with terminal C, F, N, O, P, NS, OBr, OC, OF, ON, and OS. The mean values of the Mo–L_{ax} and Mo–L_{eq} bond distances increase in the order of coordinated ligands: $\text{F} < \text{O} < \text{N} < \text{C} < \text{Cl} < \text{P} < \text{S} < \text{Br}$, corresponding to increasing van der Waals radii of the atoms in the order given [84].

The mean value 2.05 Å of the Mo–L_{ax} bond distance is smaller than that of 2.25 Å found as the average of the Mo–L_{eq} bond lengths (Table 1). This relatively large difference in general accords with the idea that the two apical sites of a pentagonal bipyramid are less sterically hindered than the five equatorial sites [4–6].

As already noted there is no case with equivalent Mo–L_{ax} bond lengths.

The MoL_5 girdle is distorted in such a way that the central atom is above the equatorial plane toward the apical ligand with a shorter Mo-L_{ax} bond length. It seems there is a correlation between the Mo-L_{ax} bond distances and the movement of the molybdenum atom out of the basal plane. For instance, the Mo-L_{ax} and Mo-basal plane distances are 2.13 and 0.1 Å in $\text{K}_5[\text{Mo}(\text{CN})_7] \cdot \text{H}_2\text{O}$ [7] but in $[\text{MoO}(\text{O}_2)_2(\text{hmp})](\text{H}_2\text{O})$ [11] are 1.67 and 0.40 Å, respectively.

Another factor of interest is the sum of all interatomic distances around molybdenum, the observed values ranging from 13.4 to 17.1 Å with an average value of 15.3 Å. The sum increases from 13.4 Å in $[\text{MoO}(\text{O}_2)\text{F}_4]^{2-}$ [26], through 15 Å in $[\text{Mo}(\text{CN})_7]^{5-}$ [7] to 17.1 Å in $[\text{Mo}(\text{NO})(\text{S}_2\text{CNet}_2)_2(\text{diars})]^+$ [33], which corresponds well with the increasing size of the ligands.

One of the important shape characteristics for describing a pentagonal bipyramidal geometry is the ratio of bond distances $(\text{M-L}_{\text{ax}})/(\text{M-L}_{\text{eq}})$. However, we also note that any distortions from the ideal geometry will also be reflected in the value of the bond angles: $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{eq}}$; $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{ax}}$; $\text{L}_{\text{eq}}-\text{M}-\text{L}_{\text{eq}}$. In the ideal pentagonal bipyramid the values of these angles are: $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{eq}}$ 90°, $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{ax}}$ 180° and $\text{L}_{\text{eq}}-\text{M}-\text{L}_{\text{eq}}$ 72 and 144°, respectively [4,5].

Inspection of the data in Table 1 reveals that the $\text{L}_{\text{eq}}-\text{Mo}-\text{L}_{\text{eq}}$ angles in the pentagonal base differ from the ideal pentagonal angles of 72 and 144°, respectively, by one to three degrees for the former and by six to eight degrees for the latter, the observed values ranging from 70 to 74° with an average value of 71°, and from 136 to 150° with an average value of 142°, respectively. Smaller $\text{L}_{\text{eq}}-\text{Mo}-\text{L}_{\text{eq}}$ angles occur between the intraligand coordinated atoms while the larger ones involve interligand bonded atoms. The average values are identical with those of the ideal bipyramid.

Interestingly also, the average value of 90° found for $\text{L}_{\text{ax}}-\text{Mo}-\text{L}_{\text{eq}}$ angles (Table I) is exactly the theoretical one. The $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{ax}}$ angle in the ideal pentagonal dipyrmaid is 180°, the observed values ranging from 156 to 178° with an average value of 170°. These smaller angles reflect significant deviation from the ideal pentagonal bipyramidal geometry.

(ii) Binuclear compounds

Binuclear molybdenum compounds with a pentagonal bipyramidal arrangement have not been studied as extensively as the mononuclear ones, but a few examples exist and are gathered in Table 2.

From the bridge point of view, the molybdenum compounds summarised in Table 2 can be divided into three groups. In the structures of $[\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}_2\text{O}]_2(\text{pyH})_2$, $[\text{MoO}(\text{O}_2)_2\text{OOH}]_2(\text{pyH})_2$, $\text{K}_2[\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}_2\text{O}](\text{H}_2\text{O})_2$ and $[\{\text{MoO}(\text{O}_2)(\text{pydca})\}_2\text{F}][\text{Net}_4]$ the two

TABLE 2

Structural data for binuclear molybdenum compounds with a pentagonal bipyramidal geometry ^a

Compound	Space group (Z)	Chromophore	Mo-L _{ax} Mo-L _{eq} Mo-basal plane (Å)	L _{ax} -Mo-L _{ax} L _{ax} -Mo-L _{eq} (°)	L _{eq} -Mo-L _{eq} <i>cis</i> <i>trans</i> (°)	Mo-L-Mo' (°)	Ref.
[{Mo ^{VI} O(O ₂) ₂ (H ₂ O)} ₂ O] ₂ (pyH) ₂	Cc, C2/c (4)	MoO ₇	1.674(7), 2.445(7) 1.954(7) 0.38	177.03(22) 89.91(22)	70.47(22)	O ^b 148.55(17)	39
[Mo ^{VI} O(O ₂) ₂ OOH] ₂ (pyH) ₂	P $\bar{1}$ (1)	MoO ₇	1.669(6), 2.391(6) 1.955(6) 0.44	168.59(14) 90.34(16)	71.01(16)	O 110.15(12)	39
K ₂ [(Mo ^{VI} O(O ₂) ₂ (H ₂ O)} ₂ O](H ₂ O) ₂	P $\bar{1}$ (2)	MoO ₇	1.664(12), 2.420(9) 1.959(10) 0.38	178.6(4) 90.0(4)	70.4(4) 135.7(4)	O 136.1(4)	40
		Mo'O ₇	1.662(10), 2.470(9) 1.955(10) 0.38	178.5(4) 90.0(4)	70.3(4) 134.9(4)		
[{Mo ^{VI} O(O ₂) ₂ (pydca)} ₂ F][NEt ₄]	C2/c (2)	MoO ₅ NF	O 1.659(3), F 2.135(1) O 1.977(4), N 2.129(3) 0.30	170.2(2) 90.3(2)	71.1(2)	F	41
[Mo ^{III} (S ₂)(SO ₂)(CN) ₈] ·[(PPh ₄) ₄]-6H ₂ O	P $\bar{1}$ (2)	MoC ₄ S ₃ Mo'C ₄ S ₃	C 2.16(3), S 2.369(8) C 2.19(3), S 2.430(7) C 2.16(3), S 2.363(8) C 2.15(3), S 2.436(7)			3S	42
[Mo ⁰ (CO) ₂ (py)(PPh ₃)(SO ₂) ₂]	P $\bar{1}$ (1)	MoC ₂ O ₂ NPS	C 1.991(7), N 2.283(4) C 1.889(6), S _e 2.419 (2) O _e 2.231(4), P _e 2.531(2)	170.6(2) 90.9(2)	81.4(2) 132.7(2)	S, O	43

^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average values for an individual distance or angle. ^b The chemical identity of the bridged atom is specified in the column.

molybdenum atoms of the binuclear anion are linked by a single non-linear oxygen bridge in the first three and by a fluorine in the last. In the structure of $[\text{Mo}_2(\text{S}_2)(\text{SO}_2)(\text{CN})_8] \cdot [(\text{PPh}_4)_4] \cdot 6\text{H}_2\text{O}$ the molybdenum(III) atoms are triply bridged by a disulphur S_2^{2-} ligand and by a bridging SO_2 molecule through an S atom.

The structure of $[\text{Mo}(\text{CO})_2(\text{py})(\text{PPh}_3)(\mu\text{-SO}_2)]_2$ [43] is shown in Fig. 3, as a representative example. The two molybdenum(0) atoms are doubly bridged by two molecules of SO_2 in which all three atoms of SO_2 are metal coordinated. Each molybdenum(0) has a 1,5,1-pentagonal bipyramidal environment, the equatorial plane of which consists of a phosphorus atom (PPh_3) ($\text{Mo-P} = 2.531(3) \text{ \AA}$), one of the carbon atoms (CO) ($\text{Mo-C} = 1.889(6) \text{ \AA}$), one of the oxygen atoms (SO_2) ($\text{Mo-O} = 2.243(3) \text{ \AA}$); and two atoms of the remaining SO_2 ($\text{Mo-O} = 2.188(4) \text{ \AA}$; ($\text{Mo-S} = 2.419(2) \text{ \AA}$); one nitrogen atom (py) ($\text{Mo-N} = 2.283(4) \text{ \AA}$) and a carbon atom of the remaining CO ($\text{Mo-C} = 1.991(7) \text{ \AA}$) form the apices. The two types of Mo-C bonds differ in length by $0.102 \text{ \AA}$, the longest bond being to C_{ax} . This lengthening of the Mo-C_{ax} bond can be attributed primarily to the competition between CO and the $\eta^2\text{SO}_2$ for π electrons [43].

Note the trend here (Table 2) i.e. movement of the metal atom from the basal plane toward the apical ligand with shorter Mo-L_{ax} bond distances, similar to the case of mononuclear molybdenum compounds.

In the case of doubly and triply bridged binuclear compounds the Mo-L_{ax} bond distances are smaller than those of Mo-L_{eq} , in accord with one of the shape characteristics of a pentagonal bipyramidal geometry [4,5]. On the contrary in the case of mono-bridged binuclears, the average value for the Mo-L_{eq} bond is smaller than that for Mo-L_{ax} (Table 2). This is a reflection on the value of the sum of all interatomic distances around the

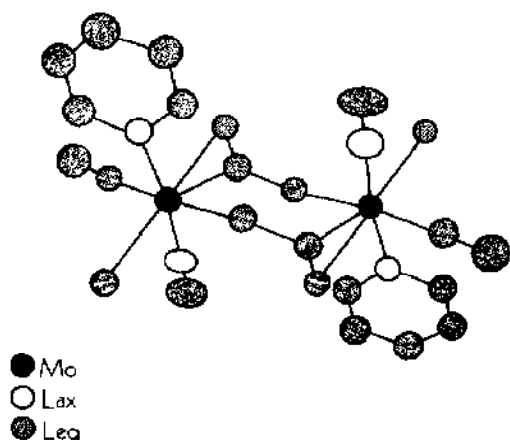


Fig. 3. Molecular structure of $[\text{Mo}(\text{CO})_2(\text{py})(\text{PPh}_3)(\mu\text{-SO}_2)]_2$ (without benzene rings) [43].

central atom where the average value is 13.9 Å in the case of mono-bridged compounds, but 15.8 Å in the others. The significance, if any, of this observation cannot be definitively evaluated on the basis of existing experimental data.

Examination of the bond angles listed in Table 2 shows that the $L_{ax}-Mo-L_{eq}$ angles range from 90 to 91° with an average value of 90° which is equal to the theoretical. The $L_{ax}-Mo-L_{ax}$ angle ranges from 169 to 179° with an average value of 174°, which is smaller than those in the ideal pentagonal bipyramid. The average values of 74 and 134°, were found in the case of $L_{eq}-Mo-L_{eq}$ angles. While the first is equal to the theoretical value, the second differs from the ideal of 142° by eight degrees.

(iii) *Tri-, tetra- and polynuclear compounds*

Bishop et al. [44] have studied the crystal structure of $[(Et_2NCS_2)_3MoN]_2Mo(S_2CNEt_2)_3(PF_6)_3$. This complex is the first example of a trinuclear structure. The crystal contains two kinds of central atoms. As can be seen in Fig. 4, two tris(diethyldithiocarbamato)molybdenum nitride molecules, with pentagonal bipyramidal geometry, coordinate to a central [tris(diethyldithiocarbamato)molybdenum] group, in which the Mo atom has dodecahedral geometry. The central atoms of the trinuclear cation are linked

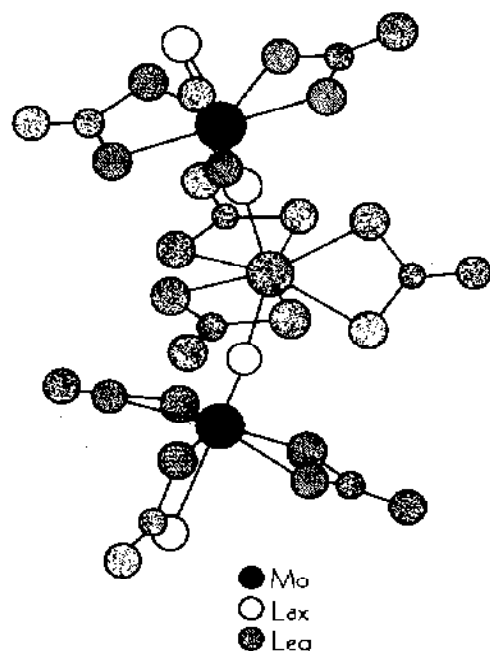


Fig. 4. Molecular structure of $[(Et_2NCS_2)_3MoN]_2Mo(S_2CNEt_2)_3^{3+}$ (without carbon atoms of the ethyl groups) [44].

together by nitride ligands ($\text{Mo-N} = 1.65$ and $1.66(1)$ Å) in the axial position. The remaining axial coordination sites with pentagonal bipyramidal geometry are occupied by diethyldithiocarbamate sulphur atoms. The equatorial plane around each Mo atom is built up by sulphur atoms of bidentate Et_2NCS_2 ligands. The Mo-S distances are in the range 2.49–2.74 Å with those *trans* to the nitride being the longest.

The orange-red crystalline compound $(\text{NH}_4)_4[\text{Mo}_4(\text{NO})_4\text{S}_{13}] \cdot 2\text{H}_2\text{O}$ has been prepared and its X-ray structural analysis has been reported [45]. The compound consists of discrete tetranuclear units well separated from one another with a Mo-Mo distance of $3.372(2)$ Å and an angle between triangular arrays of 127.59° . There are two equilateral triangular arrays of Mo atoms "joined" by a common edge with two triply bonded sulphur atoms normal to each Mo-triangle ($\text{Mo-S} = 2.501(5)$ Å) and one further sulphur atom bonded to each Mo atom ($\text{Mo-S} = 2.616(5)$ Å) and situated on the other side of the triangular arrays. Four of the total of five S_2^{2-} ligands function as unsymmetrical bridges between two Mo atoms, one S atom being bound to only one Mo center ($\text{Mo-S} = 2.465(5)$ Å), and the other to both Mo centers ($\text{Mo-S} = 2.492(5)$ Å). The NO ligands are coordinated through the nitrogen atom ($\text{Mo-N} = 1.742(16)$ Å).

The crystal and molecular structure of potassium diperoxoheptamolybdate(VI) octahydrate, $\text{K}_6\text{Mo}_7\text{O}_{22}(\text{O}_2) \cdot 8\text{H}_2\text{O}$ [46] reveals that the compound consists of a heptanuclear $[\text{Mo}_7\text{O}_{22}(\text{O}_2)_2]^{6-}$ anion, potassium ions, and lattice water molecules. The structure of the diperoxoheptamolybdate(VI) ion is built up from five octahedra and two pentagonal bipyramids. The equatorial plane of the bipyramid contains five oxygen atoms, two of which belong to a peroxo group ($\text{Mo-O} = 1.86\text{--}2.08$ Å). The apical positions are occupied by one double-bonded oxygen atom ($\text{Mo-O} = 1.64$ Å) and one weakly bonded oxygen atom ($\text{Mo-O} = 2.49$ Å). The average value (2.07 Å) for the axially bonded oxygen atoms is greater than that for the equatorially bonded oxygen atoms (1.97 Å). This observation again indicates that factors other than steric play a role. Molybdenum is displaced 0.31 Å out of the plane towards the double-bonded oxygen atom and the Mo-Mo distances range from 3.21 to 3.47 Å. A similar displacement of the central atom from the equatorial plane has been observed in a number of seven-coordinate molybdenum compounds (Table 2).

Kihlberg [47,48] has studied the crystal structure of $\text{Mo}_{17}\text{O}_{47}$. To our knowledge, this complex is the first example of a molybdenum compound with a pentagonal bipyramid structure characterized by X-ray methods. Crystals of the compound crystallise in the orthorhombic system in space group *Pba2* with 4 formula units in the unit cell. The structure is built up from MoO_6 octahedra and pentagonal MoO_7 bipyramids. The distances to the apical oxygen atoms of the pentagonal bipyramids are 1.75 and 2.21(4)

Å. The distances to the remaining five oxygen atoms situated at the corners of the pentagon are in the range 1.94 to 2.03(3) Å. The corresponding five O–Mo–O angles subtended at the molybdenum atom by neighbouring oxygen atoms range from 70.0 to 73.1° (1.2°). The Mo–Mo distances in the polynuclear structure range from 3.25 to 3.95(3) Å with one value of 2.626(7) Å. This last value should be compared with the interatomic distance of 2.725 Å found in the pure metal. Again in this case the average value of 1.98 Å found for the Mo–L_{ax} bond distance is somewhat shorter than the value of 2.00 Å found for that of Mo–L_{eq}.

C. X-RAY DATA FOR MOLYBDENUM COMPOUNDS WITH A CAPPED OCTAHEDRAL GEOMETRY

(i) Mononuclear compounds

In spite of the fact that the pentagonal bipyramid is the most commonly found polyhedron in monomers and dimers of seven coordinate molybdenum compounds (see Section B), almost twenty examples exist where the polyhedron around molybdenum has the geometry of a capped octahedron. Figure 5 provides a schematic view of an "ideal" capped octahedron. It can be seen in the Figure that in capped octahedra three of the atoms occupy an uncapped face, three others a capped face, leaving one unique, capping position. In the ideal capped octahedral structure the L_{cf}–M–L_{cf} as well as L_{uf}–M–L_{uf} angles within each set should be equal. Another criterion of the symmetry required for the capped octahedral structure is that the angles from the capping atom to the other six atoms should form two sets. Within these the three angles are equal.

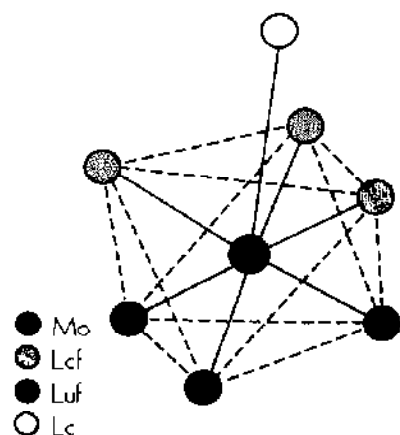


Fig. 5. A schematic view of a capped octahedron.

X-ray data for mononuclear molybdenum compounds with a capped octahedral geometry are collected in Table 3. In Fig. 6 we illustrate, as a representative example, the structure of $[\text{HMo}(\text{CO})_2\{\text{P}(\text{CH}_3)_3\}_4]\text{PF}_6$ [64]. Because the structure of the compound was not published, we discuss it here in more detail.

The compound crystallises in the monoclinic crystal system in space group $P2_1/c$ with 4 molecules per unit cell and with unit-cell dimensions: $a = 14.993(1)$; $b = 10.820(1)$, $c = 17.796(1)$ Å and $\beta = 112.49(1)^\circ$. The crystal structure consists of $[\text{HMo}(\text{CO})_2\{\text{P}(\text{CH}_3)_3\}_4]^+$ cations and PF_6^- anions. The coordination polyhedron around molybdenum can be described as a distorted capped octahedron, with the capped face formed by the three phosphorus atoms and the uncapped face formed by the fourth phosphorus atom and by the two carbon atoms of carbonyl molecules; the hydrogen atom occupies the unique capping position. The Mo–P bond lengths are 2.416(2), 2.565(1) and 2.570(1) Å for the capped face; for the uncapped face the Mo–P bond length is 2.564(2) and those for Mo–C are 1.986(6) and 1.989(7) Å; Mo–H = 1.897(70) Å for the unique capping position. The mean Mo(II)–P distance (2.53 Å) is less than the value predicted from the sum of single bond radii (2.71 Å, taking r_{Mo} as 1.61, [85] and r_{P} 1.10 Å [84]). It can be concluded that Mo–P bonds have some double-bond character presumably through back-donation ($d_\pi \rightarrow d_\pi$) from the central atom. The Mo–C distances are long (because of competition by the carbonyl groups for metal d_π electron density) but are in the range of values previously reported (1.97–2.02 Å) [56,60].

The angles for $[\text{HMo}(\text{CO})_2\{\text{P}(\text{CH}_3)_3\}_4]^+$ cation are: H–Mo–P_{cf} 50.7, 72.6

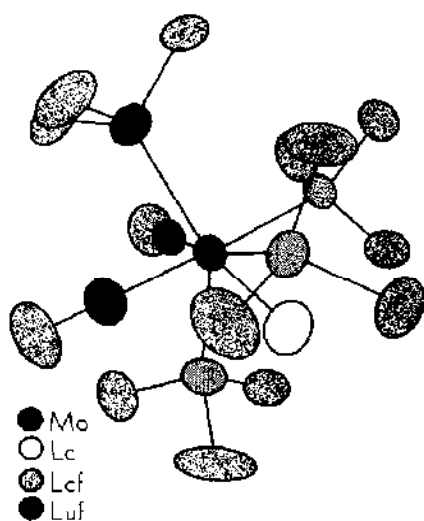


Fig. 6. Molecular structure of $[\text{HMo}(\text{CO})_2\{\text{P}(\text{CH}_3)_3\}_4]^+$ [64].

TABLE 3

Structural data for mononuclear molybdenum compounds with a capped octahedral geometry ^a

Compound	Space group	Z	Chromophore	Mo-L _{uf} Mo-L _{cf} (Å)	Mo-L _c (Å)	L _c -Mo-L _{cf} L _c -Mo-L _{uf} (°)	L _{cf} -Mo-L _{cf} L _{uf} -Mo-L _{uf} (°)	L _{cf} -Mo-L _{uf} cis (°) trans (°)	Ref.
[Mo ^{II} (CNC ₆ H ₁₁) ₇](PF ₆) ₂	P3/c	2	MoC ₇	C ^b 2.143(7) C 2.089(8)	C ^b 2.049(29)	73.2(18) 127.5(7)	111.8(3) 86.0(3)	78.7(3) 159.0(3)	49
[Mo ^{II} (CNCH ₃) ₇](BF ₄) ₂	Pbcn	8	MoC ₇	C 2.147(9) C 2.089(9)	C 2.038(9)	73.5(3) 128.2(3)	112.0(3) 85.9(3)	78.8(3) 158.1(3)	50
[Mo ^{IV} (SnCl ₃)(CN-t-Bu) ₆] ·[Ph ₃ B] ₂ CN]	Pbcm	4	MoC ₆ Sn	C 2.138(10) C 2.071(10)	Sn 2.663(1)	71.4(3) 122.1(3)	112.8(4) 87.1(4)	79.3(3) 166.0(3)	51
[Mo ^{IV} Cl ₄ (PMeCl ₂) ₃].0.33CS ₂	R3c	12	MoCl ₄ P ₃	Cl 2.401(3) P 2.555(3)	Cl 2.354(4)	76.7(1) 125.3(1)	114.8(2) 90.0(1)	74.6(1) 158.0(1)	52
[Mo ^{IV} Cl ₄ (PMe ₂ Ph) ₃].C ₂ H ₅ OH	P2 ₁ /c	4	MoCl ₄ P ₃	Cl 2.447(4) P 2.575(4)	Cl 2.399(3)	74.6(1) 127.3(1)	113.2(1) 87.2(1)	74.8(1) 158.1(1)	53-54
[Mo ^{IV} Br ₄ (PMe ₂ Ph) ₃]	P3̄	2	MoBr ₄ P ₃	Br 2.560(7) P 2.580(7)	Br 2.425(7)	74.5(2) 127.4(1)	113.2(2) 86.9(2)	77.2(1) 158.0(2)	55
[Mo ^I (CO) ₄ ddpe(SnCl ₃)] ·[SnCl ₅ (H ₂ O)]	P2 ₁ /c	4	MoC ₄ P ₂ Sn	P _{uf} 2.56(1) C _{uf} 1.97(5) C _{cf} 2.03(4)	Sn 2.729(4)	72.0(1) 126.4(3)	109.0(2) 87.0(1)	79.0(1) 161.0(1)	56
[Mo ^{II} Cl ₂ (CO) ₃ (PEt ₃) ₂]	Iba2	8	MoC ₃ Cl ₂ P ₂	Cl _{uf} 2.507(8) P _{uf} 2.580(9) C _{cf} 1.97(3) P _{cf} 2.556(9)	C 2.00(3)	73.3(12) 126.1(9)	112.1(10) 88.6(3)	77.5(7) 159.8(8)	57

[Mo ^{II} Br ₂ (CO) ₃ (dppe)] ·CH ₃ COCH ₃	<i>P</i> 2 ₁ / <i>c</i> 4 MoC ₃ Br ₂ P ₂	Br _{ur} 2.661(3) C 1.895(19)	73.5(7)	112.4(6)	76.9(4)	58
		P _{ur} 2.618(5)	125.5(6)	89.7(1)	160.5(4)	
		C _{ur} 1.946(21)				
		P _{ef} 2.500(4)				
[Mo ^{II} H(CO) ₂ (P(CH ₃) ₃) ₄]·PF ₆	<i>P</i> 2 ₁ / <i>c</i> 4 MoC ₂ HP ₄	C _{ur} 1.987(6) H 1.897(70)	65.9(2)	102.5(0.5)	85.5(2)	64
		P _{ur} 2.564(2)	127.0(2)	87.2(2)	164.7(2)	
		P _{ef} 2.517(1)				
		As _{ur} 2.681(4) C 1.73(4)	73.3(16)	112.1(8)	76.4(5)	59
[Mo ^{II} Cl ₂ (CO) ₂ (dpam) ₂]	<i>P</i> 2 ₁ 2 ₁ 2 ₁ 4 MoC ₂ Cl ₂ As ₃	Cl _{ur} 2.510(8)	126.8(12)	87.3(2)	159.1(6)	
		C _{ef} 1.83(4)				
		As _{ef} 2.610(4)				
[Mo ^{II} Br ₂ (CO) ₂ (PMe ₂ Ph) ₃] ·CH ₃ COCH ₃	<i>P</i> 2 ₁ 2 MoC ₂ Br ₂ P ₃	Br _{ur} 2.673(2) C 1.900(16)	73.2(4)	111.9(2)	77.4(3)	60
		C _{ur} 2.026(25)	128.2(5)	89.8(5)	160.9(3)	
		P _{ef} 2.536(5)				
[Mo ^{II} Cl ₂ (CO) ₂ (PMe ₂ Ph) ₃] ·CH ₃ OH	<i>P</i> bca 8 MoC ₂ Cl ₂ P ₃	P _u 2.62 C 1.76(5)	71.9(1.8)	110.8(1.4)	79.9(8)	61
		Cl _{ur} 2.523(15)	128.6(1.5)	85.0(5)	158.7(9)	
		C _{ef} 1.97(5)				
		P _{ef} 2.52				
[Mo ^{II} Br ₂ (CO) ₂ (dpam) ₂]	<i>P</i> 2 ₁ / <i>c</i> 4 MoC ₂ Br ₂ As ₃	Br _{ur} 2.662(5) C 1.92(4)	73.0(1)	112.0(1)	78.5(8)	62
		As _{ur} 2.651(5)	128.0(1)	85.8(2)	157.7(8)	
		C _{ef} 1.90(4)				
		As _{ef} 2.600(5)				
MoCl(CO) ₃ (bipy)SnCH ₃ Cl ₂	<i>P</i> 2 ₁ / <i>c</i> 4 MoC ₃ ClN ₂ Sn	C _{ur} 2.01(1) Sn 2.753(3)	68.5(3)	106.9(5)		63
		N _{ur} 2.23(1)		85.0(4)		
		C _{ef} 1.97(2)				
		Cl _{ef} 2.557(6)				

^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average values for an individual distance or angle. ^b The chemical identity of the coordinated atom is specified in these columns.

and $74.5(2)^\circ$; $\text{H-Mo-L}_{\text{uf}}$ 108.6, 111.5 and $160.9(2)^\circ$; $\text{P}_{\text{cf}}\text{-Mo-P}_{\text{cf}}$ 90.9, 106.9 and $109.8(0.05)^\circ$; $\text{L}_{\text{uf}}\text{-Mo-L}_{\text{uf}}$ 79.7, 83.1 and $98.9(2)^\circ$; $\text{P}_{\text{cf}}\text{-Mo-L}_{\text{uf}}$ (*cis*) 77.4, 78.4, 82.5, 87.2, 91.3 and $96.3(2)^\circ$; (*trans*) 147.8, $170.7(2)$ and $175.6(2)^\circ$. The H-Mo-L angles are discordant and indeed practically all of this structure is distorted from the ideal C_{3v} symmetry of the capped octahedral arrangement.

Inspection of the composition of the compounds in Table 3 reveals that there are no examples of tri- or higher-dentate ligands in a capped octahedral coordination. In a few examples bidentate ligands occupy the uncapped face [56,63], capped face [59,62] and in one case only the same bidentate ligand occupies one position in the capped face and uncapped face simultaneously [58]. Also it can be seen that the oxidation state of the central atom is most frequently two.

As was shown by Drew [4], the *trans* effect of the M-CO bond is due primarily to the bond lengths to the uncapped face which are generally longer. The mean values calculated from data gathered in Table 3, $\text{Mo-L}_{\text{uf}} = 2.41 \text{ \AA}$; $\text{Mo-L}_{\text{cf}} = 2.28 \text{ \AA}$ and $\text{Mo-L}_{\text{c}} = 2.17 \text{ \AA}$, generally follow this trend. This shows that the capped position is more sterically crowded than the uncapped face. But note that there are a few examples [52–55,60 and 64] where $(\text{Mo-L}_{\text{uf}}) < (\text{Mo-L}_{\text{cf}})$. We can offer no reason for this difference.

Another factor of interest is the sum of all interatomic distances around the central metal. The mean value of $16.3 \text{ \AA}$ (range $14.7\text{--}17.4 \text{ \AA}$) found for mononuclear molybdenum compounds with a capped octahedral structure is greater than that of $15.3 \text{ \AA}$ (range $13.4\text{--}17.1 \text{ \AA}$) for a pentagonal bipyramid, as expected.

A list of individual mean values of $\text{L}_{\text{c}}\text{-Mo-L}_{\text{cf}}$ angles given in Table 3 shows a spread between 65.9 and 76.7° which is larger than that found for $\text{L}_{\text{c}}\text{-Mo-L}_{\text{uf}}$ angles, ranging between $122.1\text{--}128.6^\circ$. In the capped octahedron, the freedom or confinement of the atoms in the uncapped face is usually revealed by the $\text{L}_{\text{uf}}\text{-M-L}$ angles. The average values of the $\text{L}_{\text{uf}}\text{-Mo-L}$ angles, found for the compounds listed in Table 3, are 87.2 , 160 and 126.7° for L_{uf} , L_{cf} , and L_{c} , respectively, and are very near those found in the majority of structures with other central atoms (ca. 90° , 162° , 127°) [4].

(ii) Binuclear compounds

The crystal structure of di- μ -carbonato-bis{carbonyl tris(dimethylphenylphosphine)molybdenum(II)}, $[\{\text{Mo}(\text{CO}_3)(\text{CO})(\text{PMe}_2\text{Ph})_3\}_2]$ [65] reveals that there are two crystallographically independent, structurally identical, centrosymmetric binuclear molecules. The structural scheme of the dimer is shown in Fig. 7. Each molybdenum(II) atom has a capped octahedral configuration with a carbonyl group in the capping position ($\text{Mo-C} =$

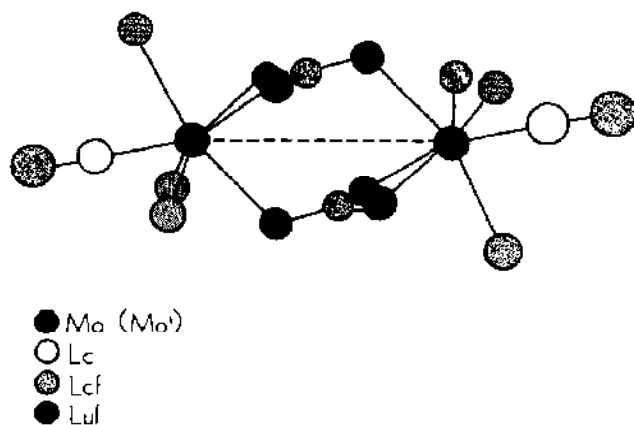


Fig. 7. Molecular structure of $[(\text{Mo}(\text{CO})_3(\text{CO})(\text{PMe}_2\text{Ph})_3)_2]$ (without benzene rings) [65].

1.87(0.10) Å), three phosphorus atoms in the capped face (Mo–P = 2.43 and 2.44 (2x)(1) Å), and three oxygen atoms in the uncapped face (Mo–O = 2.20(2x) and 2.32 (0.1) Å). The molybdenum(II) atoms are bridged by planar carbonate ions each of which acts as a bidentate ligand to one molybdenum atom and as a monodentate ligand to the other (Mo...Mo = 4.950(3) Å).

McDonald [66] studied the crystal structure of cesium [di- μ -sulfido-bis(aqua-oxalato-oxomolybdenum(V) dihydrate)], $\text{Cs}_2[\text{Mo}(\text{S})_2(\text{O})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ and found that the compound exists as a dimer where Mo(V) atoms are bridged by two sulphur atoms (Mo–Mo = 2.822(1) Å). The molybdenum(V) atoms with a 1,3,3-capped octahedral geometry exhibit Mo(1)–S, Mo(1)=O, Mo(1)–OH₂, and Mo(1)–O (oxalate) distances of 2.314(2) (mean value), 1.702(6), 2.229(6) and 2.157(5) Å (mean value); the corresponding values around Mo(2) are 2.314(2) (mean value), 1.692(6), 2.196(7) and 2.165(5) Å, respectively. The S–Mo–S (102.8(1)°) and Mo–S–Mo angles (75.2(1)°) ensure that there is metal–metal bonding in $[\text{Mo}(\text{S})_2(\text{O})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$.

D. X-RAY DATA FOR MOLYBDENUM COMPOUNDS WITH A CAPPED TRIGONAL PRISM GEOMETRY

(i) Mononuclear compounds

The symmetry of the capped trigonal prism requires that the M–L distances should fall into sets of 1, 4 and 2: within the last two the distances should be equal. A schematic view of a capped trigonal prism geometry is illustrated in Fig. 8 [4]. The environment of the central atom is built up by one atom in the unique capping position, four atoms in the capped quadrilateral face, and two atoms making up the remaining edge.

TABLE 4

Structural data for mononuclear molybdenum compounds with a capped trigonal prism geometry ^a

Compound	Space group	Z	Chromophore	Mo-L _{qf} Mo-L _e (Å)	Mo-L _e (Å)	L _c -Mo-L _{qf} L _c -Mo-L _e (°)	L _e -Mo-L _{qf} L _e -Mo-L _e (°)	L _{qf} -Mo-L _{qf} cis (°) trans (°)	Ref.
[Mo ^{II} (CN-t-Bu) ₇](PF ₆) ₂	<i>F</i> 2/ <i>m</i> 4	4	MoC ₇	C ^b 2.133(7) C 2.051(7)	C ^b 2.171(9) 144.2(2)	82.0(3) 144.2(2)	75.1(3), 118.9(3) 71.5(4)	85.5(4) 164.0(2)	67
[Mo ^{II} (CN-t-Bu) ₆ (CN)]·(PF ₆) ₂	<i>Cmca</i> 8	8	MoC ₇	C 2.112(7) C 2.065(10)	C 2.191(9) 144.5(3)	80.9(2) 144.5(3)	75.0(2), 121.1(2) 70.9(3)	90.0(2) 161.8(2)	49
[Mo ^{II} (CN-t-Bu) ₆ Br]·Br	<i>Cmca</i> 8	8	MoC ₆ Br	C 2.116(9) C 2.049(13)	Br 2.673(2) 145.4(4)	81.9(2) 145.4(4)	74.7(3), 120.0(3) 69.2(5)	90.4(4) 163.8(3)	68
[Mo ^{II} (CN-t-Bu) ₆ I]·I	<i>Acam</i> 8	8	MoC ₆ I	C 2.11(2) C 2.06(3)	I 2.862(3) 145.1(6)	81.5(5) 145.1(6)	74.5(6), 120.6(6) 69.7(9)	88.7(7) 163.0(7)	69
[Mo ^{II} (t-BuHNCCNH-t-Bu) (CN-t-Bu) ₄ I]·I	<i>Pbca</i> 8	8	MoC ₆ I	C 2.124(8) C 2.043(8)	I 2.895(1) 160.6	79.7(2) 160.6	86.8(3) 38.5(3)	88.2(3)	70-71
[Mo ^{II} (t-BuHNCCNH-t-Bu) (CN-t-Bu) ₄ I]·PF ₆	<i>Pbca</i> 8	8	MoC ₆ I	C 2.122(8) C 2.026(8)	I 2.893(1) 160.6	79.8(2) 160.6	86.5(3) 39.2(3)	88.2(3)	70-71
[Mo ^{II} (t-BuHNCCNH-t-Bu) (CN-t-Bu) ₄ Br] ₂ ·ZnBr ₄	<i>P</i> 2 ₁ 2 ₁ 2 ₁ 4	4	MoC ₆ Br ^c	C 2.12(2) C 2.03(2) C 2.15(3) C 2.03(2)	Br 2.684(3) 160.7 87.6(9) 160.7	86.2(8) 160.7 87.6(9) 160.7	87.0(9) 38.8(7) 87.8(9) 38.6(7)	88.4(8) 88.1(9)	70
[Mo ^{II} { <i>rac</i> -o-C ₆ H ₄ (AsMePh) ₂ } (CO) ₃ I ₂]·CHCl ₃	<i>P</i> $\bar{1}$ 2	2	MoC ₃ As ₂ I ₂	C _{qf} 2.02(4) As _{qf} 2.633(4) I _{qf} 2.856(3) C _e 1.94(4)	I 2.854(3) 142.7(9)	83.3(5) 142.7(9)	76(1), 115(1) 74(1)	88.9(5) 157(1)	72
[Mo ^{II} { <i>meso</i> -o-C ₆ H ₄ (AsMePh) ₂ } (CO) ₃ I ₂]	<i>P</i> $\bar{1}$ 2	2	MoC ₃ As ₂ I ₂	C _{qf} 2.03(2) As _{qf} 2.620(4) I _{qf} 2.859(4) C _e 1.94(4)	I 2.877(3) 143.9(8)	82.5(3) 143.9(8)	76(1), 116(1) 72(1)	88.7(8) 159.8(4)	72

$[\text{Mo}^{\text{II}}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\} \cdot (\text{CO})_2\text{I}_2]\text{CH}_2\text{Cl}_2$	$P2_1/n$ 4 $\text{MoC}_3\text{P}_2\text{I}_2$	C_{qr} 2.01(1) I_{qr} 2.872(1) P_{qr} 2.511(3) C_e 1.99(1)	P 2.638(3) 84.3(5) 142.7(3)	74.2(3), 118.2(3) 74.6(4)	89.4(4) 161.6(5)	73
$[\text{Mo}^{\text{II}}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\} \cdot (\text{CO})_3\text{I}_2]$	$P2_1/n$ 4 $\text{MoC}_3\text{P}_2\text{I}_2$	C_{qr} 1.99(2) I_{qr} 2.886(2) P_{qr} 2.568(4) C_e 1.97(2)	P 2.631(5) 86.4(1) 142.7(4)	74.5(4), 116.8(4) 74.5(6)	89.7(4) 156.6(3)	73
$[\text{Mo}^{\text{II}}(\text{CO})_2(\text{PMe}_3)_3 (\text{F}_3\text{CCOO})_2]$	$P2_1/c$ 4 $\text{MoC}_2\text{O}_2\text{P}_3$	C_{qr} 2.011(8) P_{qr} 2.544(2) O_{qr} 2.190(5) C_e 1.939(7) P_e 2.476(3)	O 2.179(6) 83.7(2) 144.7(3)	75.3(2), 118.5(3) 70.3(2)	89.5(2) 166.5(2)	74
$[\text{Mo}^{\text{II}}(\text{CO})_2\text{Cl}_2(\text{dppm})_2]$	$P2_1/c$ 4 $\text{MoC}_2\text{Cl}_2\text{P}_3$	C_{qr} 1.82(3) Cl_{qr} 2.554(6) P_{qr} 2.570(6) C_e 1.91(2) P_e 2.484(7)	Cl 2.484(6) 84.7(4) 144.7(5)	79.3(6), 121.3(5) 70.1(7)	89.2(4) 166.7(5)	59
$[\text{Mo}^{\text{II}}(\text{CO})_2\text{Cl}(\text{diars})_2] \cdot \text{I}_3 \cdot (\text{CHCl}_3)_2$	$Pnma$ 4 $\text{MoC}_2\text{ClAs}_4$	As 2.616(5) C 1.89(6)	Cl 2.575(11) 81.7(2) 146.1(17)	77.2(10), 117.5(8) 67.7(24)	93.2(2) 163.4(2)	75
$[\text{Mo}^{\text{II}}(\text{CO})_3(\text{bipy})(\text{HgCl})\text{Cl}]$	$P2_1/c$ 4 $\text{MoC}_3\text{ClHgN}_2$	C_{qr} 1.89(5) N_{qr} 2.28(4) C_e 1.89(5) Hg_e 2.700(7)	Cl 2.51(2) 84.4(20) 148.8(9)	76(2), 114(2) 62.1(12)	90(2) 168(2)	76

^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average values for an individual distance or angle. ^b The chemical identity of the coordinated atom is specified in these columns. ^c The two crystallographically independent cations.

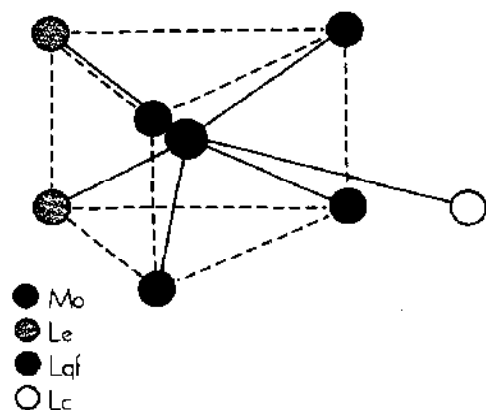


Fig. 8. A schematic view of a capped trigonal prism.

X-ray data for mononuclear molybdenum compounds with the symmetry of a capped trigonal prism are gathered in Table 4. Interestingly, in all cases the central atom is in oxidation state two. The most frequent electronic configuration for molybdenum, in compounds with a capped octahedral symmetry, is d^4 and d^2 . The configurations in the case of pentagonal bipyramid geometry are in the order: $d^0 > d^4 > d^2 > d^3$. Levenson and Towns [86] have pointed out that the d^2 configuration is well suited to the pentagonal bipyramidal symmetry as two electrons are placed in the doubly degenerate d_{xz} , d_{yz} orbitals, and thus the d_{xy} and $d_{x^2-y^2}$ orbitals are effectively antibonding. The data presented do not follow this. It does not appear feasible to decide on theoretical grounds whether electronic factors alone might favor one symmetry or another. Nevertheless, Hoffmann et al. [87] have suggested that the coordination geometry observed may result at least partially from electronic factors. It must, of course, be kept in mind that the compounds contain ligands which have mostly different electronic and steric properties, and that this, too, may be an important though subtle factor in determining their symmetry.

In Fig. 9 we illustrate, as a representative example of mononuclear molybdenum(II) compounds with a capped trigonal prism symmetry, the structure of $[\text{Mo}(\text{CO})_2(\text{PMe}_3)_3(\text{F}_3\text{CCOO})_2]$ [74]. Crystals of the compound crystallise in the monoclinic system in the space group $P2_1/c$ with 4 molecules per unit cell ($Z = 4$). The coordination sphere is built up by the oxygen atom of a monodentate F_3CCOO^- ion in the capping position ($\text{Mo}-\text{O} = 2.179(6) \text{ \AA}$), the quadrilateral face contains two *cis* PMe_3 molecules ($\text{Mo}-\text{P} = 2.479$ and $2.608(2) \text{ \AA}$), one CO ligand ($\text{Mo}-\text{C} = 2.011(8) \text{ \AA}$) and the remaining F_3CCOO^- ion also acting as a monodentate ligand ($\text{Mo}-\text{O} = 2.190(5) \text{ \AA}$), and two atoms, one CO ($\text{Mo}-\text{C} = 1.939(7) \text{ \AA}$) and one PMe_3 ($\text{Mo}-\text{P} = 2.476(3) \text{ \AA}$) making up the remaining edge. The mean $\text{Mo}-\text{P}$

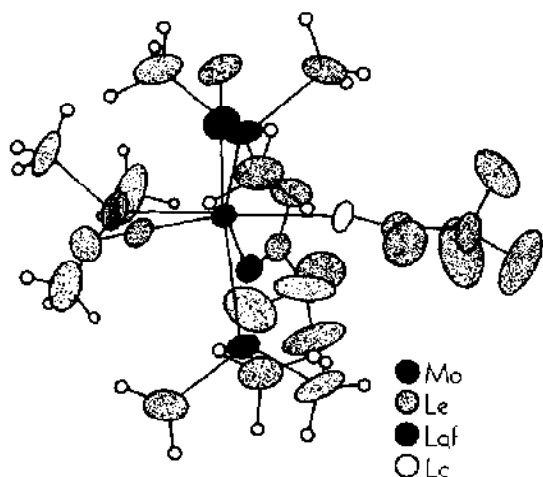


Fig. 9. Molecular structure of $[\text{Mo}(\text{CO})_2(\text{PMe}_3)_3(\text{F}_3\text{CCOO})_2]$ [74].

distance (2.52 Å) is considerably less than the value predicted from the sum of single bond radii (2.71 Å [84,85]), indicating that the bonds have some double-bond character presumably through back-donation ($d_\pi \rightarrow d_\pi$) from the metal. Note also that the Mo–C distances are somewhat shorter than the 2.15 Å predicted on the basis of Slater atomic radii [88] suggesting that the molybdenum–carbon bond orders are greater than one.

The two types of Mo–C bond are different lengths by 0.072 Å, the longest bond being that of C_{qf} . Also the Mo– P_{qf} bond lengths differ by 0.129 Å, this disparity presumably being due to a mutual *trans* influence (the long Mo–C and Mo–P bonds involve ligands *trans* to each other, $\text{C}_{\text{qf}}\text{--Mo--P}_{\text{qf}} = 173.9(2)^\circ$).

From the angles $\text{O}_\text{c}\text{--Mo--C}_\text{e}$, $140.6(3)^\circ$, $\text{O}_\text{c}\text{--Mo--P}_\text{e}$, $148.8(2)^\circ$, $\text{O}_\text{c}\text{--Mo--O}_{\text{qf}}$, $77.1(2)^\circ$, and $\text{O}_\text{c}\text{--Mo--P}_{\text{qf}}$, $82.5(2)^\circ$, it is apparent that the oxygen atom is unsymmetrically placed with respect to both of the distinguishable sets of bonded atoms O_c , P_e , and $\text{P}_{\text{qf}}(2x)$, C_{qf} and O_{qf} .

None of the compounds in Table 4 contain a three- or multiple bond ligand. In $[\text{Mo}(\text{t-BuHNCCNH-t-Bu})(\text{CN-t-Bu})_4\text{I}]^+$ ion [70,71] the coupled ligands is in the unique edge (L_e). A similar situation occurs in the case of $[\text{Mo}(\text{CO})_2\text{Cl}_2(\text{dppm})_2]$ [59], where only one dppm molecule is coupled in the unique edge, while the second one, as a unidentate ligand, is in the quadrilateral capped face. The species $[\text{Mo}(\text{CO})_2\text{Cl}(\text{diars})_2] \cdot \text{I}_3 \cdot (\text{CHCl}_3)_2$ [75] involves both coupled ligands on the quadrilateral capped face, as does $[\text{Mo}\{\text{rac-}o\text{-C}_6\text{H}_4(\text{ASMePh})_2\}(\text{CO})_3\text{I}_2]$ as well as its CHCl_3 adduct [72]. There are also two examples, $[\text{Mo}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{CO})_3\text{I}_2]$ and its CH_2Cl_2 adduct [73], where the coupled ligand is bonded by (a) one donor atom in the unique capping position and (b) through the other donor in the

quadrilateral capped face. The remaining five compounds (Table 4) involve seven unidentate ligands.

Interestingly, the mean value of the sum of all interatomic distances in Mo(II) compounds given in this section, is 15.8 Å, about 0.5 Å greater than the observed average value 15.3 Å for mononuclear Mo compounds with a pentagonal bipyramidal geometry (Section B, (i)), but about 0.5 Å smaller than 16.3 Å found for mononuclear Mo compounds with a capped octahedral geometry (Section C, (i)).

Inspection of the data in Table 4 reveals that the molybdenum–ligand bond distances increase in the order: $(\text{Mo}-\text{L}_e) < (\text{Mo}-\text{L}_{\text{qt}}) < (\text{Mo}-\text{L}_c)$; except $[\text{Mo}(\text{CO})_2(\text{PMe}_3)_3(\text{F}_3\text{CCOO})_2]$ [74], $[\text{Mo}(\text{CO})_2\text{Cl}(\text{diars})_2] \cdot \text{I}_3 \cdot (\text{CHCl}_3)_2$ [75] and $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{HgCl})\text{Cl}]$ [76] where are Mo–L lengths: $\text{L}_{\text{qt}} > \text{L}_e > \text{L}_c$; $\text{L}_{\text{qt}} > \text{L}_c > \text{L}_e$ and $\text{L}_c > \text{L}_e > \text{L}_{\text{qt}}$, respectively. Because of the “exceptions” we cannot offer an argument to explain the observed trends.

Angles are another interesting factor, especially those of $\text{L}_c\text{--Mo--L}_e$ (L_{qt}), which as is well known [4] belong to the shape characteristic for the C_{2v} monocapped trigonal prismatic geometry. The values of 79.4° ($\text{L}_c\text{--Mo--L}_{\text{qt}}$) and 143.3° ($\text{L}_c\text{--Mo--L}_e$), respectively, for the idealised C_{2v} monocapped trigonal prismatic geometry were calculated [89] for a “hard sphere model” based on a choice of 6.0 for the exponent in the potential $E = \sum_{i \neq j} r_{ij}^{-n}$. The mean value 83° found for the $\text{L}_c\text{--Mo--L}_{\text{qt}}$ angle differs from the ideal (79.4°) by four degrees, the observed values ranging from 79.7 to 87.6°, which is equally valid for the capped trigonal prismatic geometry.

The values of the $\text{L}_c\text{--Mo--L}_e$ angles are of two different magnitudes (Table 4), one with a mean value of 144.6°, the observed values ranging from 142.7 to 148.8°, and the other almost constant at 160.6° found in $[\text{Mo}(\text{t-BuHNCCNH-t-Bu})(\text{CN-t-Bu})_4\text{X}]^+$, where $\text{X} = \text{I}$ (two examples) or Br , [70,71]. While the first mean value of 144.6° is quite comparable with the calculated one 143.3° [89], the last one is not. Only in the three cations, $[\text{Mo}(\text{t-BuHNCCNH-t-Bu})(\text{CN-t-Bu})_4\text{X}]^+$, from all those summarised in Table 4, is the coupled ligand in the unique edge and this is the reason why the $\text{L}_c\text{--Mo--L}_e$ angle is more open.

In spite of the fact that the structures of numerous seven coordinate molybdenum compounds have been crystallographically determined, in some cases their geometry cannot yet be exactly predicted. One such example is the structure of tricarbonyl(1,10-phenanthroline)(η^2 -sulphur dioxide) molybdenum(0), $\text{Mo}(\text{CO})_3(\text{phen})(\text{SO}_2)$ [80]. It seems that a capped trigonal prism geometry can be proposed for the mononuclear compound with two bidentate ligands of large bite, with the sulphur atom in the unique capping position (2.532(3) Å), two carbonyl groups (1.958(6)(2x) Å), one nitrogen atom (2.237(4) Å) and one oxygen atom (2.223(5) Å) in the capped quadrilateral face, and the remaining carbonyl group (1.984(9) Å) and nitrogen

atom (2.237(4) Å) making up the remaining edge.

From the angles S_c-Mo-N_e , $114.6(1)^\circ$, S_c-Mo-C_e , $147.3(2)^\circ$; S_c-Mo-C_{qt} , $78.7(2)^\circ$, and S_c-Mo-N_{qt} , $102.4(1)^\circ$, it is apparent that the sulphur atom is unsymmetrically placed with respect to both of the distinguishable sets of bonded atoms.

(ii) Binuclear compounds

The first X-ray analyses of seven coordinate binuclear molybdenum compounds were reported in 1960 [47]. It was not until 1979 that a dimer which contained a capped trigonal prismatic geometry was structurally characterised [78,90].

Figure 10 provides the molecular structure of $[Mo_2Cl_8H]^{3-}$ [77] and Table 5 contains the X-ray data for such compounds. The ion has C_{2v} (mm) symmetry and one of the mirror planes is rigorously crystallographic, containing the three bridging atoms, hydrogen and two chlorine atoms. The other plane contains two molybdenum atoms, one hydrogen and two chlorine atoms. Thus each molybdenum(III) atom has a 1,4,2-capped trigonal prismatic environment with a chlorine atom in the unique capping position ($Mo(Mo')-Cl = 2.500(3)$ Å), four chlorine atoms in the capped quadrilateral face ($Mo-Cl = 2.465(3)$, $2.466(3)$, $2.393(2)$ and $2.395(2)$), and a hydrogen atom ($Mo(Mo')-H = 1.728(2)$ Å) together with $Mo'(Mo-Mo' = 2.375(2)$ Å) making up the remaining edge. There is a strong *trans* effect due to the $\mu-H$ atom, so that the chlorine atoms (Cl_c) *trans* to $\mu-H$ have $Mo-Cl$ bond distances ca. 0.10 Å greater than those *trans* to $\mu-Cl$ atoms. Indeed, the $Mo-Cl_c$ distances are even greater than the $Mo-(\mu-Cl)$ distances, by ca. 0.03

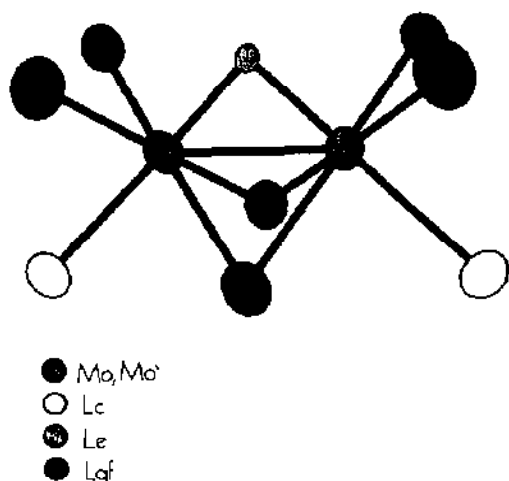


Fig. 10. Molecular structure of $[Mo_2Cl_8H]^{3-}$ [77].

TABLE 5

Structural data for binuclear molybdenum(III) compounds with a capped trigonal prism geometry ^a

Compound	Space group	Mo-L _{qt} Mo-L _c (Å)	Mo-L _c (Å)	Mo-L-Mo' (°)	L _c -Mo-L _{qt} L _c -Mo-L _c (°)	L _c -Mo-L _{qt} L _{qt} -Mo-L _{qt} (°)	Ref.
[Mo ₂ Cl ₈ H][N(C ₂ H ₅) ₄] ₃ ·(H ₃ O ₂)[MoCl ₄ O(H ₂ O)]	<i>Pnma</i>	Cl ^b 2.430(3)	Cl ^b 2.500(3)	Cl(1) ^b 57.58(8)	92.4(1)	89.9(1)	77
	4	H _c 1.728(2)		Cl(2) 57.59(8)	178.8(1) H ^c	90.0(1), 178.5(1)	
	MoCl ₃ HMo'	Mo _c ' 2.375(2)		H 86.8(1)			78
	<i>P</i> $\bar{1}$	Cl 2.439(1)	Cl 2.504(10)	Cl(1) 56.81(2)	91.28(4)	88.7(2)	
[Mo ₂ Cl ₈ H](C ₅ H ₅ NH) ₃	2	H _c 1.742(4)		Cl(2) 56.82(2)	178.5(2) H	89.98(4), 175.45(4)	79
	MoCl ₃ HMo'	Mo _c ' 2.371(1)		H 89.6(2)			
	Mo'Cl ₃ HM	Cl 2.442(1)	Cl 2.474(1)		90.69(4)	89.2(2)	79
	4	H _c 1.620(6)			172.3(2) H	89.98(4), 175.50(4)	
[Mo ₂ Cl ₈ H][N(CH ₃) ₄] ₃	<i>Pnma</i>	Cl 2.443(3)	Cl 2.490(2)	Cl 57.19(2)	90.30(4)	90(1), (89.68(9)) ^d	79
	4	2.445(2) ^d	2.498(3) ^d	56.6(1) ^d	90.37(7) ^d	90.36(5), 179.28(4)	
	MoCl ₃ HM	H _c 1.75(5)		H 86(2)	180(2) H	(90.65(7), 179.2(1)) ^d	79
		1.816(5) ^d		80.6(2) ^d	177.8(2) ^d		
Mo'Cl ₃ HM		Mo _c ' 2.374(1)			133.36(4) Mo'		79
		2.357(3) ^d			132.3(1) ^d		
		Cl 2.434(1)	Cl 2.481(2)		90.77(4)	89(1), (89.7(1)) ^d	79
		2.442(2)	2.481(3) ^d		90.77(7) ^d	90.16(5), 178.34(4)	
H _c 1.73(6)					179(2) H	(90)·63(7), 178.45(9)) ^d	79
		1.829(5) ^d			179.7(2) ^d		
					131.72(5) Mo		79
					130.8(1) ^d		

^a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average values for an individual distance or angle. ^b The chemical identity of the coordinated atom is specified in these columns. ^c The chemical identity of the capped edge atom (ligand) is specified in the column. ^d Neutron diffraction results.

Å. The pairs of distances ($\text{Mo}-\text{Cl}_{\text{qr}} = 2.465$ and $2.466(3)$ Å) and ($\text{Mo}-(\mu-\text{Cl}_{\text{qr}}) = 2.393$ and $2.395(2)$ Å) are virtually identical and the H atom lies in the plane to within the experimental uncertainties [77].

The X-ray analyses of all compounds summarised in Table 5 were performed by Cotton and his co-workers [77–79] and detailed discussions of the crystal structural data of the compounds have been presented and will not be considered here. However, there are two items of interest to compare with other seven coordinate molybdenum compounds. First, the Mo–L bond distances increase in the order: ($\text{Mo}-\text{L}_e$) < ($\text{Mo}-\text{L}_{\text{qr}}$) < ($\text{Mo}-\text{L}_c$), the same trend as found in mononuclear Mo compounds with the same symmetry. The second item of interest is that the sum of all interatomic distances (16.3 Å) is greater than those of 15.8 Å found for mononuclear compounds. However the sum, 16.3 Å, is equal to those found for mononuclear compounds with a capped octahedral environment.

An X-ray investigation of $[\text{Mo}(\text{CO})_2\{\text{P}(\text{OMe})_3\}\{\mu-(\text{O})(\text{P}(\text{OMe})_2)(\text{F}_3\text{CCOO})\}]_2$ [81] shows that the crystals of the binuclear compound crystallise in the orthorhombic system in space group *Pbca* with 4 molecules per unit cell ($Z = 4$). The molybdenum atoms have a 1,4,2-capped trigonal prismatic environment (Fig. 11) and are joined by double oxygen (in the unique capping position, $\text{Mo}-\text{O} = 2.094(3)$ Å) and phosphorus (in the capped quadrilateral face, $\text{Mo}-\text{P} = 2.420(1)$ Å) bridge bonds, each of which is from a different oxydimethoxyphosphine. The remaining three positions in the capped quadrilateral face are occupied by bidentate F_3CCOO^- ion ($\text{Mo}-\text{O} = 2.277(4)$ and $2.306(4)$ Å) and one carbonyl group ($\text{Mo}-\text{C} = 1.942(5)$ Å), while the other carbonyl group ($\text{Mo}-\text{C} = 1.941(5)$ Å) with a phosphorus atom of $\text{P}(\text{OCH}_3)_3$ ($\text{Mo}-\text{P} = 2.402(1)$ Å) makes up the remain-

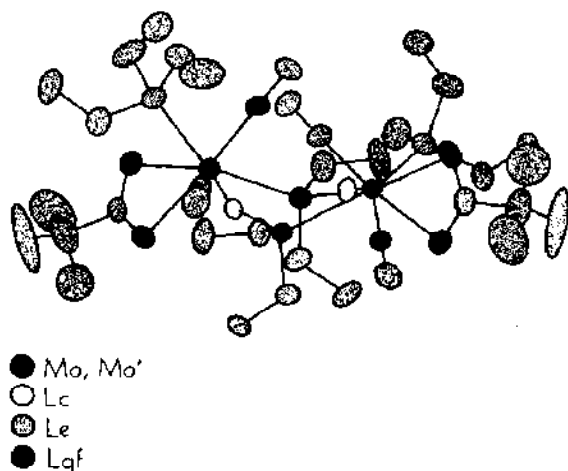


Fig. 11. Molecular structure of $[\text{Mo}(\text{CO})_2\{\text{P}(\text{OCH}_3)_3\}\{\mu-(\text{P}(\text{O})(\text{OCH}_3)_2)(\text{F}_3\text{CCOO})\}]_2$ [81].

$\Sigma(r) (\text{\AA})^c$ 13.43–17.15 (15.34)	13.88–15.96 (14.59)	$\Sigma(r) (\text{\AA})^c$ 14.75–17.46 (16.27)	$\Sigma(r) (\text{\AA})^c$ 14.77–16.90 (15.86)	16.23–16.39 (16.33)
$(\text{Mo}-L_{ax}) < (\text{Mo}-L_{eq})$		$(\text{Mo}-L_o) < (\text{Mo}-L_{cf}) < (\text{Mo}-L_e) < (\text{Mo}-L_{af}) < (\text{Mo}-L_c)$ ($\text{Mo}-L_{uf}$)		
$L_{ax}-\text{Mo}-L_{ax} (^{\circ})$ 156–178 (170) ^a	169–179 (174) ^a	$L_c-\text{Mo}-L_{cf} (^{\circ})$ 66–77 (72.5) ^a	$L_c-\text{Mo}-L_{af} (^{\circ})$ 80–88 (84) ^a	90–92 (91) ^a
$L_{ax}-\text{Mo}-L_{eq} (^{\circ})$ 70–92.5 (90)	90–91 (90)	$L_c-\text{Mo}-L_{uf} (^{\circ})$ 122–129 (127)	$L_c-\text{Mo}-L_e (^{\circ})$ 143–161 (149)	^d H 172–180 (178) Mo' 132–133 (132.5)
$L_{eq}-\text{Mo}-L_{eq} (^{\circ})$ ^e 70–74 (71) ^f 136–150 (142)	70–81 (72) 133–136 (134)	$L_{cf}-\text{Mo}-L_{cf} (^{\circ})$ 102.5–115 (111)	$L_e-\text{Mo}-L_{af} (^{\circ})$ 74–88 (78.5) 114–121 (118)	88.5–90 (89)
	$\text{Mo}-L-\text{Mo}' (^{\circ})$ 110–149 (132)	$L_{uf}-\text{Mo}-L_{uf} (^{\circ})$ 85–90 (87)	$L_e-\text{Mo}-L_e (^{\circ})$ 38.5–75 (62.5)	
		$L_{cf}-\text{Mo}-L_{af} (^{\circ})$ ^e 74.5–85.5 (78) ^f 158–166 (160)	$L_{af}-\text{Mo}-L_{af} (^{\circ})$ ^e 85.5–93 (89) ^f 156.5–168 (163)	175.5–179 (177)
				$\text{Mo}-L-\text{Mo}' (^{\circ})$ H 86–89.5 (87.5) Cl 56.5–57.6 (57)

^a Average values. ^b Total average value. ^c The sum of length is defined as the mean of all seven distances. ^d Chemical identity of the capped edge atom (ligand). ^e *Cis* angles. ^f *Trans* angles.

ing capped face. The P-Mo-O ($81.1(1)^\circ$), Mo-P-O ($116.1(1)^\circ$) and Mo-O-P ($148.1(1)^\circ$) angles ensure that there is no metal-metal bonding, the $\text{Mo} \cdots \text{Mo}$ contact being $4.563(1) \text{ \AA}$.

From the angles $\text{O}_c\text{-Mo-C}_e$, $100.4(1)^\circ$; $\text{O}_c\text{-Mo-P}_e$, $148.2(1)^\circ$; $\text{O}_c\text{-Mo-O}_{qt}$, $77.3(1)^\circ(2x)$; $\text{O}_c\text{-Mo-P}_{qt}$, $81.1(1)^\circ$, and $\text{O}_c\text{-Mo-C}_{qt}$, $136.1(1)^\circ$, it is apparent that the oxygen atom in the unique capping position (O_c) is unsymmetrically placed with respect to both of the distinguishable sets of C_e , P_e atoms and $\text{O}_{qt}(2x)$, P_{qt} , C_{qt} atoms. The angles $\text{P}_e\text{-Mo-C}_e$, $76.5(1)^\circ$; $\text{L}_e\text{-Mo-L}_{qt}$, in the range of $71.9(1)$ to $172.4(1)^\circ$ and $\text{L}_{qt}\text{-Mo-L}_{qt}$, ranging from $57.3(1)$ to $158.1(1)^\circ$, are comparable with those found in other familiar molybdenum compounds (Table 6).

There is distortion of the trigonal prism, the major cause being the differing ligand types. The molybdenum atom lies $0.488 \text{ \AA}$ away from the center of the quadrilateral face. This dimer type structure is novel in molybdenum structural chemistry, and even dimeric complexes with a capped trigonal prismatic geometry are rare.

E. X-RAY DATA FOR MOLYBDENUM COMPOUNDS WITH A SQUARE ANTI-PRISM GEOMETRY (THE 4:3 GEOMETRY)

(i) Mononuclear compounds

The pentagonal bipyramid is by far the most common structure found in monomers and dimers of molybdenum compounds. The capped octahedron and capped trigonal prism are less common, and examples with square antiprism are much rarer. The square antiprism is shown in Fig. 12. This structural arrangement consists of a quadrilateral face defined by four donor atoms parallel to a trigonal face defined by three donor atoms.

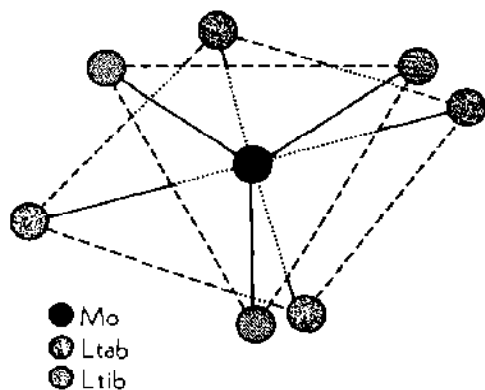


Fig. 12. A schematic view of a square antiprism (the 4:3 geometry).

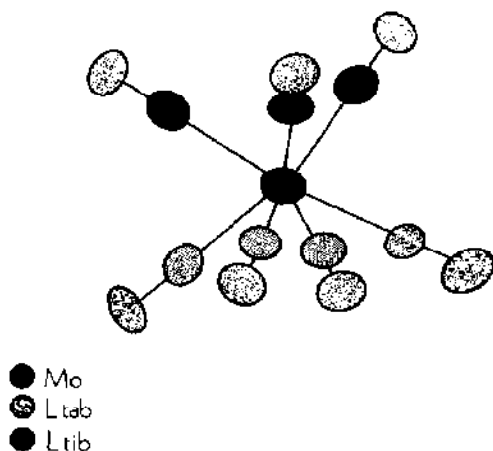


Fig. 13. Molecular structure of $[\text{Mo}(\text{CNPh})_7]^{2+}$ (without benzene rings) [82].

Interestingly, it was only in 1982 that the first mononuclear Mo compound with the 4:3 geometry was structurally characterised, by Dewan and Lippard [82]; the structure of $[\text{Mo}(\text{CNPh})_7](\text{PF}_6)_2$ is depicted in Figure 13. In the quadrilateral face are four carbon atoms bound to the central atom with a mean Mo–C bond length of 2.102 Å and three carbon atoms lie in the trigonal face, Mo–C = 2.151 Å (average). The dihedral angle between the two faces was computed to be 1.04° while that across the diagonal of the quadrilateral face was found to be 2.58° , confirming the 4:3 geometry [82].

(ii) Binuclear compounds

Drew and Wilkins [83] have studied the crystal structure of $[\text{Mo}_2\text{Cl}_3(\text{CO})_4\{\text{P}(\text{OMe})_3\}_4]^{n+}[\text{MoOCl}_4\{\text{OP}(\text{OMe})_2\}]^{n-}$ and found that while the anion is a monomer with an Mo atom in a distorted octahedral environment, the cation is a dimer with Mo...Mo = 3.575 Å. The two molybdenum atoms in the cation are both seven coordinate with 4:3 geometry (Fig. 14) each being bonded to three bridging atoms (trigonal face) (Mo–C = 2.544(6) (mean) Å; Mo'–C = 2.551(6) (mean) Å) and in the quadrilateral face by two carbonyls with the same mean value of 1.92(2) Å for both central atoms, and two phosphorus atoms of $\text{P}(\text{OMe})_3$ (Mo–P = 2.420(7) (mean) Å; Mo'–P = 2.424(6) (mean) Å). Both quadrilateral faces are planar and approximately parallel to the triangular face (angle of intersections 2.3 and 1.1°). The Cl–Mo–Cl (ca. 76°) and Mo–Cl–Mo angles (89°) ensure that there is no metal–metal bond in $[\text{Mo}_2\text{Cl}_3(\text{CO})_4\{\text{P}(\text{OMe})_3\}_4]^{n+}$. The mean Mo–L distance in the quadrilateral face is shorter than that for the trigonal face, as in the case of $[\text{Mo}(\text{CNPh})_7](\text{PF}_6)_2$.

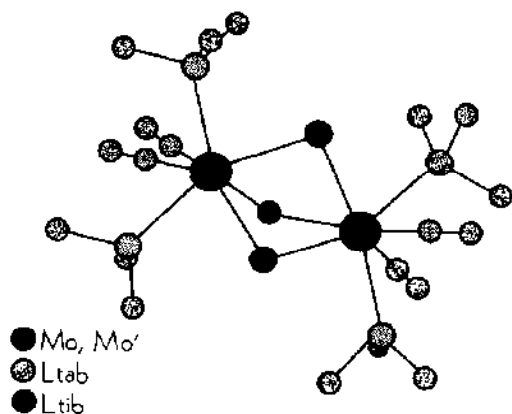


Fig. 14. Molecular structure of $[\text{Mo}_2\text{Cl}_3(\text{CO})_4\{\text{P}(\text{OMe})_3\}_4]^+$ (without methyl groups) [83].

F. CONCLUSIONS

The stereochemistry of seven coordination is complicated for at least two reasons: (a) the geometry of ligands around a central atom is much less symmetric than that of six or eight coordination; (b) these lower symmetry structures are easier to distort which may lead to greater departures from "ideal" structures.

In spite of these inherent difficulties, considerable progress has been made in sorting out the stereochemical problem [4,5]. From 1960, when the first seven coordinate molybdenum compound was characterised by X-ray analysis, to the end of 1983 a few tens (80) of crystals had been prepared and their crystal structures studied. A discussion of the number of isomers possible for seven coordinate systems was published by Drew [4]. For example, for the species MB_5A_2 there are 18 theoretically possible isomers. However no molybdenum isomers of a given structure have yet been demonstrated in the solid state.

The data presented in this review reveal that the number of examples representing the various geometries increases in the order: square antiprism < capped trigonal prism ~ capped octahedron < tetragonal bipyramid. While in the first only two examples exist, half of all the structures presented here belong to the last.

The electronic configuration of molybdenum ranges from d^0 to d^6 ; of these d^1 and d^5 are rare. In the case of the pentagonal bipyramidal geometry the number of examples increases in the order: $d^3 < d^2 < d^4 < d^0$; with capped octahedral geometry: $d^2 < d^4$ and capped trigonal prismatic geometry only d^4 (monomers) and d^3 (dimers).

When the ligand type is considered several trends are noticeable: (a) There is no example with tetra- or even multidentate ligands, and only two

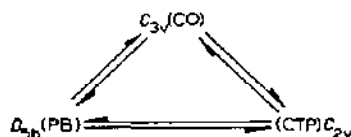
examples with a tridentate ligand (pentagonal bipyramid) where the tridentate ligand is in the equatorial position. (b) The relative rarity of MoL_7 (L = identical unidentate ligand), (three examples of pentagonal bipyramid; two of the capped octahedron and only one of the capped trigonal prismatic geometry). (c) In the pentagonal bipyramid case, $\text{MoL}(\text{L-L})_3$ predominates with two bidentate ligands in the pentagonal plane and the third spanning an axial and an equatorial position. Also, $\text{MoL}_3(\text{L-L})_2$ and $\text{MoL}_5(\text{L-L})$ exist, usually with the chelate bound in the equatorial positions. (d) In the capped octahedron case, MoL_7 exists (L = mostly non-identical ligand) and $\text{MoL}_5(\text{L-L})$ (with chelate in a capped face, or in an uncapped face and in one example even spanning uncapped and capped faces). (e) For the capped trigonal prism geometry, we find MoL_7 (L = non-identical unidentate ligand) and $\text{MoL}_5(\text{L-L})$, with the chelate in an edge, or capped quadrilateral face and in one case even a chelate connecting a capped quadrilateral face with a unique capping position. One example of $\text{MoL}_4(\text{L-L})_2$ has both chelates in the capped quadrilateral face. (f) For the square antiprism geometry only the MoL_7 stoichiometry is known. (g) The molybdenum atom tends to be displaced from the basal plane toward the apical ligand.

A summary of the structural data for seven coordinate molybdenum compounds with different types of geometry is given in Table 6. Inspection of the data in the Table reveals that: (a) In the pentagonal bipyramid case the predominant Mo-L_{ax} bond distance is shorter than that of Mo-L_{eq} . (b) In the capped octahedron case the mean values of bond distances are increased in the order: $(\text{Mo-L}_c) < (\text{Mo-L}_{\text{cf}}) < (\text{Mo-L}_{\text{uf}})$. (c) In the capped trigonal prism case they lie in the order: $(\text{Mo-L}_e) < (\text{Mo-L}_{\text{qt}}) < (\text{Mo-L}_c)$. (d) The mean value of the sum of all interatomic distances in different types of geometry increases in the order: 14.6 Å (binuclear pentagonal bipyramid) < 15.3 Å (mononuclear pentagonal bipyramid) < 15.9 Å (mononuclear capped trigonal prism) < 16.3 Å (mononuclear capped octahedron and binuclear capped trigonal prism).

The fixed values of the $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{eq}}$ (90°), $\text{L}_{\text{ax}}-\text{M}-\text{L}_{\text{ax}}$ (180°) and $\text{L}_{\text{eq}}-\text{M}-\text{L}_{\text{eq}}$ ($72, 144^\circ$) angles in the "ideal" pentagonal bipyramid [4] are comparable to those found as mean values for both mononuclear and binuclear molybdenum compounds with a pentagonal bipyramidal geometry: 90° (for mono- and binuclear), $170, 174^\circ$; $71, 142$ and $72, 134^\circ$. Unlike the pentagonal bipyramid, the L-M-L angles are not fixed for both the capped octahedron and the capped trigonal prism cases and the mean values found in the compounds gathered in this review are shown in Table 6. Observed values are comparable to those found for seven coordinated compounds with other central atoms [4,5].

The choice of an idealized coordination geometry in seven-coordinate compounds is not often simple. One procedure, used in this article, is to

compare the interbond angles at the metal centre with the values compared for various idealised coordination polyhedra. For some seven coordinated molybdenum compounds, no precise conclusion regarding the nature of the geometry type can be drawn. Muetterties and Guggenberger [91] have described the reaction cycle with idealised geometries related by edge stretch-



ing. The closest relationship is between the CO and the CTP [5,6], for example, the geometry of $[\text{Mo}(\text{CO})_2\text{Cl}_2(\text{dppm})_2]$ [59], $[\text{Mo}(\text{CO})_2(\text{PMe}_2\text{Ph})_3\text{Cl}_2] \cdot \text{CH}_3\text{OH}$ [61], and $[\text{Mo}(\text{CO})_3(\text{bipy})(\text{HgCl})\text{Cl}]$ [76] can be considered in terms of either polyhedra.

Relationships between the PB and CO and between the PB and CTP are not so close, but possible pathways can be predicted. An example of a compound with a geometry intermediate between these two polytopes is $[\text{Mo}(\text{CO})_4(\text{dppe})(\text{SnCl}_3)] \cdot [\text{SnCl}_5(\text{H}_2\text{O})]$ [56], whose root mean square deviations are 0.135 Å and 0.199 Å from the CO and PB, respectively. However, since the deviation of 0.135 Å from the idealised capped octahedron geometry is much smaller than that of 0.199 Å from an idealised pentagonal bipyramidal geometry, we have included the complex in Table 3, which represents compounds with a capped octahedral geometry.

The factors that lead to a choice of geometry for a complex are: electronic configuration of the central atom, crystal-packing forces and chelate ligands which are likely to play a dominant role and place substantial constraints on structure, stereochemistry, and dynamic stereochemistry. In the extreme cases, the molecular structure may simply be a minor extension beyond the preferred structure and conformation of the chelate ligand. Detailed theoretical discussions of this phenomenon have been given [4,5].

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