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Invited review

A new approach to the formal classification of covalent compounds of the elements

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Abstract

A new approach to the classification of covalent compounds of the transition metals is presented. The classification introduces the concepts of valency number and ligand bond number as alternatives to the concepts of formal oxidation state and coordination number. Population density maps (MLX plots) which represent the covalent compounds of an element as a function of all the known ligands are exemplified for chromium; molybdenum and tungsten; and nickel, palladium and platinum. These plots are used to identify the major characteristic chemical properties of the elements including reactivity trends and reaction mechanisms.

Keywords: Molybdenum; Covalent bond classification

1. Introduction

This article describes and illustrates a new method for the formal classification of the covalent compounds of the elements called the Covalent Bond Classification (C.B.C.).

The C.B.C. method is concerned only with those compounds which are well described by the covalent model, including the infinite lattice compounds which may be described as covalent polymers, and it applies to the covalent compounds of all elements. In this article the development and use of the new classification is illustrated by reference, primarily, to molybdenum chemistry. The choice of molybdenum was made since this element has an exceptionally rich and varied chemistry.

The new method of classification differs in important respects from the customary approach used in organising inorganic compounds. Thus, the concept of formal oxidation state, (O.S.) (or oxidation number) is abandoned, and while the coordination number (C.N) is retained as the "number of atoms of the ligands which are attached to the central atom", the C.N. of a compound is not used for the organisation of compounds in the C.B.C. method.

The need for a new approach to the formal classification arises since the use of O.S. as a general classifying principle presents several difficulties in the discussion of the chemistry of an element, especially one as complex as that of molybdenum. Thus, in assigning the formal oxidation state of a compound any homopolar bonds present are neglected (by definition) and, further, there is confusion and debate about the inclusion of many other bonds in the determination of O.S., especially in organometallic compounds. This point is illustrated by the series of compounds $[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}R]]$, {where R = Cl, Br, H, CH_3, SiR_3, $HgCH_3$ and Mo(or W)$(CO)_3(\eta\text{-}C_5H_5)$; and the O.S. of Mo is +2, +2, +2, ? + 2, ? + 2, ? + 1, and + 1, respectively (by definition)}, and also by the series of manganese compounds given in Table 10 in Section A.7.

Within the last twenty-five years very many transition metal compounds with homopolar metal–metal bonds have been identified. Similarly, there are many transition metal compounds which have strong covalent bonds to other elements which are defined as metals. The O.S. principle is not useful for the classification of these compounds anymore than it is for the classification of most organic compounds, and for this reason "formal oxidation states" are not used in this manner in organic chemistry. Thus, consider the series CCl_4 (4), $CCl_3\text{–}CCl_3$ (3), $CCl_2(CCl_3)_2$ (2) and the (hypothetical) $C(CCl_3)_4$ (0!). The O.S. for the identified carbon *C* in these compounds is given in parenthesis. In the formal definition of O.S. homopolar metal–metal bonds are simply not counted, even though a metal–

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metal bond is not fundamentally different from any other covalent bond between the metal and another atom.

Likewise, the concept of C.N. becomes confusing for compounds in which there are ligands which do not bond in a simple "two electrons per bond" manner. The coordination number of an atom in a molecule is defined as the number of other atoms bonding to the choosen atom. For example, in the series of compounds $Mo(CO)_6$. $Mo(\eta\text{-}C_6H_6)(CO)_3$ and $Mo(\eta\text{-}C_6H_6)_2$ the molybdenum atom has the coordination number 6, 9, and 12, respectively. However, the η^6-benzene ring is often referred to as a "pseudo three coordinate" ligand so that each of these three compounds is often described as "six-coordinate". The $\eta^5\text{-}C_5H_5(\eta^5$-cyclopentadienyl) ligand is also referred to as "pseudo three coordinate", even when the ligand clearly has five carbon atoms bonding equally to a metal centre. There are many compounds of an element which are chemically very similar but where the coordination numbers do not relate in a simple manner (see Table 10, Section A.7). Further comments on the limitations of the classification by O.S. are published elsewhere [1].

The concepts of O.S. and C.N. have been central to the organisation of inorganic compounds since the earliest days when the ionic nature of the bonding in simple salts was first recognised. The concepts remained useful during the early development of coordination chemistry since initially most ligands were relatively simple, e.g. the halogens, CN, O, OH, H_2O, NH_3, etc. In short, the first classifications of inorganic compounds where made on the basis that all compounds could be described as ionic, i.e. as a form of sodium chloride.

For the reasons given above it seems that a new method of formal classification which would apply to all molecular compounds and covalent polymers would be more appropriate than the conventional ionic model. The new C.B.C. approach is a method for the formal classification and organisation of molybdenum compounds made on the basis that all the compounds can be described as being essentially covalent, i.e. as a form of methane. A further aspect of the classification reflects the increasing recognition that in many of the diverse ligand environments of transition metal compounds the 18-electron rule is obeyed. This was not apparent for the historically early ligand environments. In order to

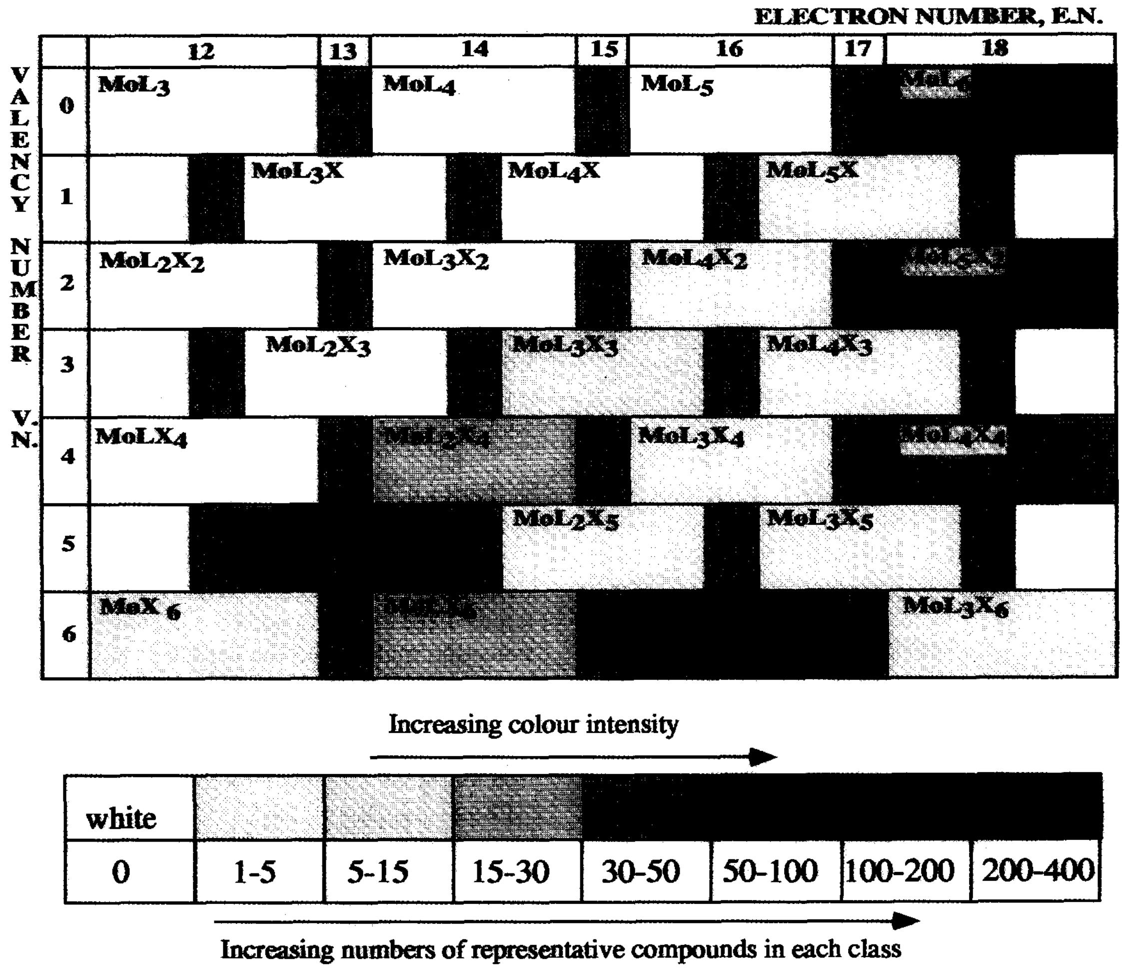

Fig. 1. The MLX plot for molybdenum. The population density for each ML_lX_x class is shown by colour intensity scale.

gain a broad overview of the dominant features of chemistry of any particular element a diagram called the **MLX** plot is been developed for the element in question. A typical **MLX** plot is shown in Fig. 1 and in this instance the element chosen is molybdenum.

This **MLX** plot shows the abundance (population densities) of different molybdenum compounds which are classified according to the nature of the ligand environment about the molybdenum. The relationship between colour intensity and the numbers of compounds is given below the **MLX** plot. Before consideration of the implications of this diagram it is necessary to explain how the covalent compounds are classified and organised and how the **MLX** plot is constructed.

2. Covalent bonding classification and definitions

2.1. Covalent compound classification

In the new C.B.C. approach the covalent compounds of any element (designated as **M**) are classified as follows: (a) According to the total number of electrons (E.N.) involved in primary bonding in the valence shell of the element **M**. Thus, E.N. is the number of electrons in the valency shell of the element **M** plus the total number of electrons (**e**) contributed by the bonding of the ligands to **M**. (N.B. do not confuse the designation E.N. with electronegativity.) (b) According to the number of electrons required by the ligands in the formation of the ligand bonds to **M**.

A general classification of many atoms and molecular groups which are known to bond as ligands to the d-block transition metals is shown in Table 1. The classification shows the number of electrons required by each ligand (denoted as x) together with the total number of electrons donated to the **M** atom by the ligand (denoted as the ligand number, L.N.).

The Table 1 also assigns the class of each ligand (Table 1, column 3). The class of a ligand is defined in terms of the different bonding functions of the ligand, as described below. The identification of the ligand class is crucial to the C.B.C. method. For many ligands the nature of the primary metal–ligand bonding is well understood. For other ligands there may be ambiguities and these, as for the O.S. formalism, expose the limitations of the C.B.C. formalism. Examples of ambiguous (or non-innocent) ligands are discussed in Section 2.4.

2.2. Definition of ligand class

The atoms of a ligand which are directly involved in primary bonding to the metal centre are denoted as the "ligating atoms". There are three possible bonding

Table 1

Typical ligands found in molybdenum chemistry classified according to the number of electrons required for bonding (x), the number of electrons donated to the molybdenum (L.N.) and the $L_lX_xZ_z$ class of the ligands [a]

x	L.N.	Class	Examples
2	0	Z	BH_3, BF_3, BCl_3, BR_3, $B(C_6F_5)_3$, $AlMe_3$, SiF_4, (generally Lewis acids)
1	1	X	H
1	1		CR_3, $-CR{=}CR_2$, $-C{\equiv}CR$, $-COR$, $-C_6H_5$, η^1-$CH_2CH{=}CH_2$, η^1-C_5H_5, CF_3, C_6F_5, CH_2CMe_3, CH_2SiMe_3, CH_2CMe_2Ph
1	1		NR_2, OR, $-OOR$, F
1	1		SiR_3, $-PR_2$, SR, Cl
1	1		GeR_3, AsR_2, SeR, Br
1	1		SnR_3, I
1	1		CN, SCN, NCS, N_3, OCN, NCO, OSO_2R, ONO, ONO_2, $OClO_3$, $OSiR_3$
1	1		$Mn(CO)_5$, $Fe(\eta$-$C_5H_5)(CO)_2$, $Mo(\eta$-$C_5H_5)(CO)_3$, $Au(PPh_3)$, HgCl
2	2	X_2	bidentate with mono-functional ligating atoms, -SCH_2CH_2S-, oxalato, *o*-quinones, $-(S)_2$-, SO_4, CO_3, $-(O)_2$-, metallacycles-$(CH_2)_n$-, where $n = 2$ [b], 3 or 4
2	2	$\bar{X}_2$ [c]	monodentate with poly-functional ligating atoms, $=CR_2$, $=NR$ [c] (bent), $=O$ [b], $=S$, $=C{=}CR_2$
0	2	L	NH_3, NR_3, OH_2, OR_2, PR_3, $P(OR)_3$, SR_2, SeR_2, AsR_3
0	2		CO, $H_2C{=}CH_2$, $R_2C{=}CR_2$, $RC{=}CR$, $S{=}CR_2$, N_2, PF_3
0	2		THF, Et_2O, DMSO, RCN, RNC, py
0	2		L-function of X-μ-L-ligands, e.g. in bridging Cl. Also the half-arrow function of agostic hydrogen, see Fig. 3(i)
3	3	X_3	tridentate with 3 monofunctional X-ligating atoms. None known
3	3	$\bar{X}_3$ [c]	monodentate with one tri-X-functional ligating atom, $\equiv CR$, $\equiv N$
1	3	LX	η-C_3H_5 (generally η-allylic systems,) acac, dmg, η^2-acetato, η-O_2CR, η-S_2CR, η-S_2CNR_2, η-S_2PR_2, $NH_2CH_2CO_2$- (amino acids), BF_4. BH_4
1	3	$L\bar{X}$ [c]	NO, NR_2 (in planar MNR_2 amido systems)
4	4	X_4	$\equiv MoX_2L_2$, e.g. in $[Mo_2Cl_8]^{4-}$
2	4	LX_2	η-C_4H_4, (generally η-cyclobutadiene derivatives)
2	4	LX_2	NR (linear imido ligands)
0	4	L_2	η-C_4H_6, (dienes generally) [b], bipyridyl, o-phenanthroline ethylenediamine $RS(CH)_2SR$, diphosphines, e.g. $Ph_2PCH_2CH_2PPh_2$ (dppe)
3	5	LX_3	$N(CH_2COO)_3$
1	5	L_2X	η^5-C_5H_5, dienyls generally
2	6	L_2X_2	1,5,-diazacyclooctane-N,N′-diacetate (dacoda)
0	6	L_3	η^6-benzene, (η^6-arenes generally), η^6-C_7H_8, η^6-COT, $RSi(CH_2PMe_2)_3$
1	7	L_3X	none known
3	7	L_2X_3	η-C_7H_7
4	8	L_2X_4	EDTA
2	8	L_3X_2	η^8-COT, η^5-$C_5H_4(CH_2)_3NR$
3	9	L_3X_3	η-$C_5H_4(CH_2)_3N{=}$ (linear imido)
0	12	L_6	$(FB(ONCHC_5H_3)_3P)$, $P(bipy)_3$

[a] Comments on the form of this table are given in Section A.6

[b] Ambiguities may arise, see Fig. 5.

[c] For the significance of the bar notation, see Section A.5.

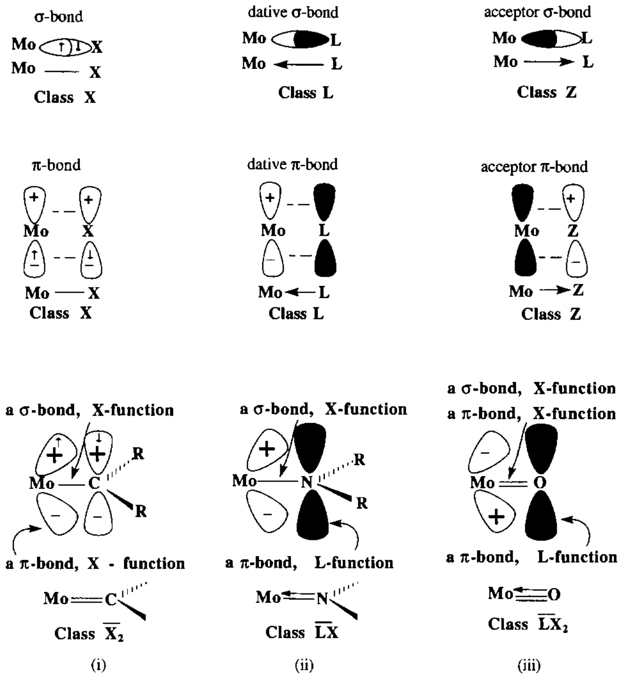

Fig. 2. Showing the relationship between the nature of the primary molybdenum–ligand bonding and the class of the ligand. All these examples are for monodentate ligands which use only a single ligating atom. The first two rows are examples of monofunctional ligating atoms. The third row shows examples of polyfunctional ligating atoms. For polyfunctional ligands a bar is drawn over the ligand class in order to draw attention to the polyfunctional nature of the ligating atom (the occasional need and use of the bar notation in determining the equivalent neutral class of anions is discussed in the Appendix, Section A5). (i) Only the orbitals for the p_π-X-function are shown. (ii) Only the orbitals for the p_π-L-functions are shown. (iii) Only the orbitals for the p_π-Z-function are shown. The shading of orbitals indicates that they are occupied by two electrons. The +/− symbols indicate the phase of the p_π-or d_π-orbitals. Orbitals which are occupied by only a single electron are indicated by the small arrows. Those orbitals which are both unshaded and which have no small arrows are empty. A valence bond representation of the bonding is given under the orbital representation.

functions for ligating atom(s) of a ligand and these are designated the X-function, the L-function and the Z-function.

2.2.1. The X-function

This is a singly occupied orbital on the ligand which requires one electron from the element M centre to form a two-electron covalent bond. The local symmetry of the orbital may be σ, π or δ. The number x of X-functions on a ligand is represented by X_x. Normally the subscript when $x = 1$ is treated as default, i.e. the hydrogen ligand is a monofunctional X ligand. A ligand which has two singly occupied orbitals, i.e. two X-functions, is designated as X_2; an example is the carbene ligand$=CR_2$ (see Fig. 2). The X-ligand function most commonly occurs with σ-symmetry (local symmetry). However, π-symmetry X-functions are found, e.g. in the linear NR ligand, in the terminal oxo ligand, and in the singly occupied HOMO of the η-cyclopentadienyl ligand (see Fig. 4).

2.2.2. The L-function

This is a ligand based orbital filled with two electrons which are donated to an empty orbital on the M centre. The number l of L-functions on the ligand is represented by L_l. A ligand with a single L-function (often described as a lone-pair) is represented as L (subscript $l = 1$ is taken as default). A ligand with two L-functions, e.g. $Me_2PCH_2CH_2PMe_2$ is designated as L_2, etc., see Fig. 3. An L-function can occur with local σ-symmetry (e.g. NH_3), or with π-symmetry (e.g. in the linear imido NR ligand (see Fig. 2), the planar NR_2 ligand and the two degenerate HOMOs in the η-benzene ligand (see Fig. 4).

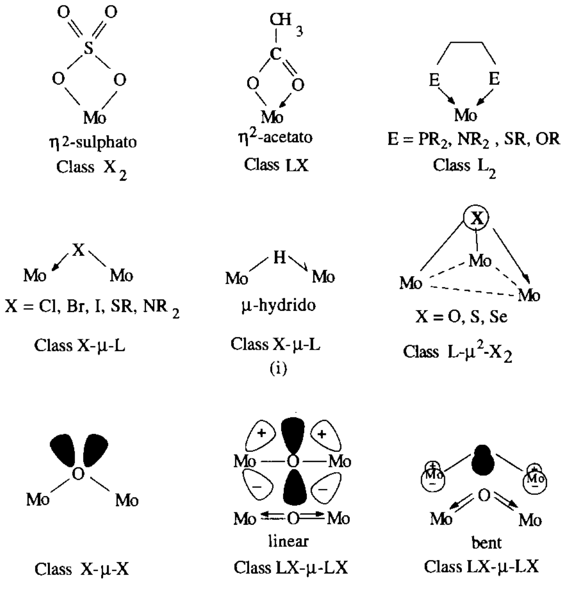

Fig. 3. Illustrations of the classification of some polydentate ligands (not to be confused with polyfunctional ligand (ligating) atoms). (i) The half-arrow indicates this is a two-electron, three-centred σ-bond and for the purposes of electron counting the 'half-arrow' end of the bridging ligand formally donates two electrons to the molybdenum centre. The electron count for the bridging hydrogen system is the same as if the bridging hydrogen were replaced by Cl, SR (sp^3) or NR_2. (ii) The shaded orbitals indicates they are occupied by a pair of electrons. The +/− signs indicate the phase for the bonding combination of the p_π-bonds in the classes LX-μ-LX (linear) and LX-μ-LX (bent): both these have two-electron, three-centre π-bonds. (iii) Normally there is no evidence to distinguish between bent bridging X-μ-X oxo and the bent bridging LX-μ-LX oxo. It is usually assumed that the class X-μ-X is the most appropriate description since bent μ-oxo systems are found more commonly, for example in H_2O. When the Mo–O–Mo bond is linear then this is taken as a clear indication that the p_π-orbitals on the bridging sp-hybridised oxygen are donating to the empty d_π-orbitals on the molybdenum: hence the class is given as LX-μ-LX.

2.2.3. The Z-function

This is a ligand orbital which is empty and which accepts the donation of an electron pair from the metal. The number z of Z-functions is represented by Z_z. The Lewis acid molecule BR_3 has one Z-function. Compounds of transition metals containing σ-bonding Z_z ligands are rare and will not be further discussed in this article. Many ligands have an empty orbital normally of π- or δ-symmetry which can act as an acceptor for a filled orbital of appropriate symmetry on the **M** centre.

Table 2
Examples of typical molybdenum compounds classified according to their MLX class [a]

Class	Examples
MoL_6	Many examples, $Mo(CO)_6$, $Mo(\eta\text{-arene})_2$, $Mo(\eta\text{-arene})(CO)_3$, $Mo(dpme)_3$, $Mo(\eta\text{-arene})(PR_3)_3$, $Mo(P(OMe)_3)_6$, $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$, $Mo(triene)(CO)_3$, $Mo(CO)_nL_{n-6}$, where $L = PR_3$ ($n = 1–3$), $Mo(N_2)_2(depe)_2$, $Mo(PMe_3)_6$, $Mo(butadiene)_3$, $[Mo(\eta\text{-lutadine})_2]$, $[Mo(PMe_3)_4(\eta\text{-}C_2H_4)_2]$, $Mo(CNR)_6$
MoL_5	$Mo(CO)_5$ in an argon matrix
MoL_5X	$Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)$, $[Mo(\eta\text{-}C_6H_6)_2]^+$
MoL_5X_2	Many examples, $Mo(\eta\text{-}C_5H_5)(CO)_3X$, where X = alkyl, Cl, Br, Cl, H; $[Mo(\eta\text{-}C_5H_5)(CO)_4]^+$, $Mo(CO)_3L_2X_2$, where $L = PR_3$, L_2 = diars, $RS(CH)_2SR$, and X = halogen; $Mo(\eta\text{-arene})$ $(\eta\text{-allyl})(O_2CMe)$, $Mo(\eta\text{-arene})(dmpe)H_2$, $[Mo(\eta\text{-arene})(\eta\text{-allyl})L_2]^+$, where L = dmpe, diphos, butadiene; $Mo(\eta\text{-}C_5H_5)_2CO$, $Mo(\eta\text{-}C_5H_5)_2(\eta\text{-olefin})$, $MoH(O_2COEt)(dppe)_2$ $[Mo(CO)_5]^{2-}$, $[Mo(CNR)_7]^{2+}$, $[Mo(CN)_7]^{5-}$, $[Mo(CN)_5(NO)]^{4-}$
MoL_4X_2	$Mo(dppe)_2I_2$, $[Mo(\eta\text{-}C_5H_5)_2$ in a matrix, $Mo(CO)_4I_2$, $Mo(diars)_2X_2$, $[Mo(CN)_6]^{4-}$, $[Mo(CO)_4Br_2]$
MoL_4X_3	$[Mo(diars)(CO)_3Br]^+Br^-$, $[Mo(CN)_7]^{4-}$, $[Mo(CO)_2(diars)I_3]$ ($gm_{eff} = 1.40$ B.M.)
MoL_3X_3	$[Cl_2MoL_2(\mu\text{-}Cl)_2L_2MoCl_2]$ (L = MeCN, py, L_2 = dppe); $K_3[Mo(CN)_6]$, $[MoX_3]_n$, X = Cl, Br; $Mo_2Cl_4(OR)_2(ROH)_4$, $Mo(acac)_3$, $[Mo(NCS)_6]^{3-}$, $Mopy_3Cl_3$, $Mo(THF)_3Cl_3$, $Mo(PR_3)_3Cl_3$, $[MoCl_4(dipy)]^-$, $[MoX_6]^{3-}$ (X = Cl, Br, F), $[Mo(S_2C_2R_2)_3]^{3-}$, $[MoCl_2(dipy)_2)]^+$
MoL_4X_4	$K_4[Mo(CN)_8]$, $K_4[MoF_8]$, $Mo(PR_3)_4H_4$, $Mo(\eta\text{-}C_5H_5)_2X_2$ (X = H, alkyl, Cl, Br, I, SH, SR, C≡CR, =O, N_3), $[Mo(\eta\text{-}C_5H_5)_2LX]^+$ (LX = $(PR_3)H$, (CO)H, (CO)Me, $(R_2S)Br$, etc), $[Mo(\eta\text{-}C_5H_5)_2L_2]^{2+}$ (L_2 = dmpe, $(NH_3)_2$), $Mo(NR_2)_4$, $Mo(\eta\text{-allyl})_4$, $Mo(S_2CNMe_2)_4$, $Mo(NO)_4$, $[Mo(\eta\text{-}C_5H_5)(NO)_2Cl]$,
MoL_4X_4	$[Mo(\eta\text{-}C_6H_6)(\eta\text{-}C_7H_7)]^+$, $[Mo(\eta\text{-}C_5H_5)(NO)Cl(\mu\text{-}Cl)]_2$ $[Mo(\eta\text{-}C_5H_5)(CO)_2Cl_3]$, $Mo(R_3P)_4H_4$, $[Mo(dmpe)_3H_2]^{2+}$, $[Mo(O)_2(CN)_4]^{4-}$, $[Mo(\eta\text{-}C_4Ph_4)_2(CO)_2]$, $[Mo(\eta\text{-}C_5H_5)(NR)(PR_3)Cl]$
MoL_3X_4	$MoCl_4(PMe_2Ph)_3$, $[Mo(O)Cl(MeNC)_4]^+I_3^-$
MoL_2X_4	$[MoCl_6]^{2-}$, $MoCl_4L_2$ (L = MeCN, py, PMe_2Ph, R_2O, R_2S; L_2 = dppe, diars, bipy; typical $\mu_{eff} = 2.3–2.5$ B.M.), $[MoI_6]^{2-}$, $[MoBr_6]^{2-}$, $[Mo(NCS)_6]^{2-}$, $Mo(R_3P)_2(O)Cl_2$, $[MoO_2(CN)_4]^{4-}$
MoL_3X_5	$K_3[MoF_8]$, $K_3[Mo(CN)_8]$, $[Mo(\eta\text{-}C_5H_5)_2X_2]^+$ (X = Cl, Br, Me) $[Mo(\eta\text{-}C_5H_5)(NR)Cl_2]$
MoL_2X_5	$[MoOCl_3]_n$, $[MoOCl_4L]^-$ (1 = MeoH, MeCN, Ph_3AsO), $[MoO(LX)_2]_2(\mu\text{-}O)$, (LX = acac, oxine, dtc), $[MoO(NCS)_5]^{2-}$
$MoLX_5$	$[MoX_5]_2$, X = Cl, Br; $[MoF_4(\mu\text{-}F)]_4$, $K[MoF_6]$, ;MoF_5L, L = Et_2O MeCN, py, $[MoCl_4(OMe)_2]^-$, $MoOCl_3L$ (L = R_3PO, Ph_3P, R_2O, R_2S, $\mu_{eff} = 1.64–1.75$ B.M.), $[MoOCl_5]^{2-}$, $[Mo(O)Cl_4]^-$
MoX_5	MoF_5 vapour (decomp. at 60°C to $[MoF_4]_n$ and MoF_6)
MoL_3X_6	$MoH_6(PMe_2Ph)_3$, $[Mo(\eta\text{-}C_5H_5)_2H_3]^{3+}$, $[Cl_3Mo(\mu\text{-}Cl)_3MoCl_3]^{3-}$, $[MoOCl_2]_n$, $Li_2[Mo(NBu^t)_4]$, $(Me_2N)_3Mo{\equiv}Mo(NMe_2)_3$, $Mo(NR_2)_6$, MoO_2Cl_2 (vapour), $\{[(\eta\text{-}C_5H_5)Mo(O)_2]_2(\mu\text{-}O)\}$, $Mo(terpy)(O)_3$, $[MoO_4]^{2-}$ (see Section A.5)
MoL_2X_6	$MoOCl_4L_2$, L = MeCN, Ph_3O, H_2O, L_2 = bipy, *o*-phen; *cis*-$[MoO_2X_4]^{2-}$, X = F, Cl; $[cis\text{-}MoO_2F_3(H_2O)]^-$; $[MoO_2Cl_2]_n$ (isomers), $[MoO_2X_2]_n$, X = Br, I; $Mo(O)Cl_2(S_2CNEt_2)_2$, $Mo(O)(NTs)(S_2CNEt_2)$, $[MoF_8]^{2-}$, $MoO_2Br_2(dipy)$, $[cis\text{-}MoO_2Cl_4]^{2-}$, $[Mo_2Cl_8]^{4-}$, $[Mo(\mu\text{-}OAc)_4Mo]$, $[Mo(O)(O_2)_2F_2]^{2-}$, $Mo_2(X\text{-}\mu\text{-}L)_4$, where $X\text{-}\mu\text{-}L = O_2CR$.
$MoLX_6$	$[MoOF_4]_4$, $[MoOX_4]_n$, X = Cl, Br; $MoOCl_4L$, L = Et_2O, THF, Me_2O, Me; $[MoOX_5]^-$, X = Cl, Br, $[MoF_7]^-$, $[Mo_2O_4(EDTA)]^{4-}$
MoX_6	MoX_6 (X = F, Cl, Br, Me, OPh, NCS; $X_6 = F_5Cl$, Cl_3F_3, $F_5(OMe)$, MoO_2Cl_2 vapour, Mo_2Me_6, $MoCl_4$ vapour, $(RO)_3Mo{\equiv}Mo(OR)_3$, $[Mo_6Cl_{12}]$, $[Mo_6Cl_{14}]^{2-}$

[a] Some structures and further examples are given in Ref. [3].

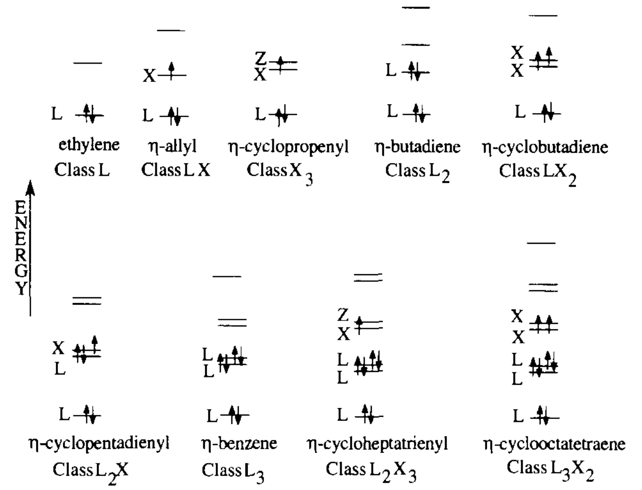

Fig. 4. Showing the classification of representative unsaturated hydrocarbon ligands. The Hückel MOs of each ligand are given on an arbitrary energy scale. A MO of a ligand which is filled (by two electrons) acts as a two-electron donor to the metal centre and is, therefore, an L-function orbital. An orbital which contains only one electron (half-filled) acts as a one-electron donor and requires one electron from an appropriate orbital of the metal centre: therefore it is an X-function orbital. The η-cyclopropenyl and η-cycloheptatrienyl ligands have a doubly degenerate set of orbitals in which there is only one electron. Application of the rule $LZ \rightarrow X_2$, which is discussed in Section 2.2.3., leads to the classification of these ligands as having the classes X_3 and L_2X_3, respectively, i.e. for the cycloheptatrienyl ligand, η-C_7H_7, the apparent class L_3XZ reverts to L_2X_3, and for η-cyclopropenyl $LXZ \rightarrow X_3$.

Examples are the carbon monoxide ligand (the p_π^*-orbitals) or, for the η-benzene ligand, the doubly degenerate, empty δ-symmetry molecular orbitals. If this "back-donation" is thought to contribute a sufficient energy to the metal ligand bond then the ligand orbital should be deemed to be acting as a Z-function. However, such back-donation interactions are not normally regarded as taking part in primary bonding and are ignored in the C.B.C. classification. In the very large majority of cases compounds which appear to contain a Z-ligand also contain an L-ligand. In these cases the class of the compound is defined using the rule $LZ \rightarrow X_2$. For example, the fragment $H_3N \rightarrow \mathbf{M} \rightarrow BR_3$ appears to merit the classification LMZ. However, the correct electron distribution is better represented by H_3N^+–M–B^-R_3, and, therefore, the class of the **M** centre is XMX.

2.2.4. Further comments on ligand class

Many examples of representative ligands and their classification according to the ligand functions X, L and Z are given for mono- and poly-functional ligands in Figs. 2 and 3, and for η-bounded hydrocarbon ligands in Fig. 4. Where a ligating atom has more than one X or L function, for example, ligands in the class X_2, LX or LX_2, they are called polyfunctional ligating atoms. Polyfunctional ligating atoms should not be confused with polyfunctional ligands, i.e. polydentate ligands with more than one ligating atom. It should be noted that many ligands can vary in the manner in which they bond to a metal centre in different molecules. For example, the cyclopentadienyl ligand may bond in either the η^1, η^3 or η^5 modes. The amido ligand NR_2 may be pyramidal, and therefore an X-function ligand, or planar, when it acts as a LX-function ligand. It may be necessary to ascertain the structure of a metal ligand system before allocating a class to the ligand. Indeed, in some cases not only structural data but magnetic, spectroscopic or other physical data may be required to unambiguously identify a ligand class. Even then uncertainties may remain. For example, when is an η-olefin a X_2 or L ligand? (Examples of the variety of ligand classes formed by O, OH and H_2O are given in Appendix A, Fig. 12.)

2.3. Definition of the class of a compound

A general representation of all neutral covalent compounds is $\mathbf{M}L_lX_xZ_z$, where l, x and z are the number (including zero) of L, X and Z functions of the ligands attached to the element **M**. The class of a particular compound is said to be defined when the values of l, x and z are specified.

A selection of molybdenum compounds is listed in Table 2, where they are organised according to their **MLX** class, e.g. MoL_6 (i.e. $MoL_6X_0Z_0$), etc. Table 2 also includes cations and anions. The **MLX** class of cations and anions is identified in exactly the same way as for neutral molecules except that for the purposes of inclusion in the **MLX** plots the equivalent neutral class (E.N.C.) must be determined. For many compounds the assignment of the equivalent neutral class can be illustrated simply. Consider the following classes of molybdenum compounds: $[MoL_6]^{3+}$, $[MoL_5X]^{2+}$, $[MoL_4X_2]^+$, $[MoL_3X_3]$, $[MoL_2X_4]^-$, $[MoLX_5]^{2-}$, $[MoX_6]^{3-}$. They all have E.N. = 15 and they all have the value $l + x = 6$. Therefore they must all be equivalent to the neutral class MoL_3X_3. Indeed, inspection of the **MLX** plot given in Fig. 1 shows that compounds with $l + x = 6$ and E.N. = 15 must have V.N. (i.e. x) = 3.

A simple rule which converts most cations to the equivalent neutral **MLX** class is that $L^+ \rightarrow X$. Correspondingly, most simple anions convert to the equivalent neutral class by the rule $X^- \rightarrow L$. For example,

$$[MoL_6]^{3+} = [MoL_3(L^+)_3] \text{ and } L^+ \rightarrow X \text{ gives } [MoL_3X_3]$$

$$[MoX_6]^{3-} = [MoX_3(X^-)_3] \text{ and } X^- \rightarrow L \text{ gives } [MoL_3X_3]$$

There are rare examples of anions which have only L ligands. An other example is $[Mo(CO)_5]^{2-}$. For such anions which have no X-function ligands the rule for reduction to the equivalent neutral class in $L^- \rightarrow LX$. Therefore,

$$[Mo(CO)_5]^{2-} = [Mo(CO)_3(CO^-)_2] = [MoL_3(L^-)_2]$$

$$\text{and } L^- \rightarrow LX \text{ gives } [MoL_5X_2]$$

This rule may seem surprising at first sight. However, consider the fact that CO^- and NO are isoelectronic. Therefore $[Mo(CO)_5]^{2-}$ and $[Mo(CO)_3(NO)_2]$ are isoelectronic. Since NO is a LX ligand the latter dinitrosyl classifies as $[MoL_5X_2]$.

There are no stable cations of molybdenum which have only X-ligands and no L-ligands, i.e. the class $[MX_x]^{n+}$. Rare examples of cations in this class are ammonium cations $[R_4N]^+$, and $[PCl_4]^+$ in $[PCl_4]^+[PCl_6]^-$. The rule for the reduction to the E.N.C. for such L-free cations is $X^+ \rightarrow Z$. Therefore, $[PCl_4]^+ = [PX_3(X^+)] = [PX_3Z]$. A more detailed consideration of the classification of anions and cations by the method of reduction to the equivalent neutral class is given in Section A4.

2.4. Determination of MLX class of a compound containing noninnocent ligands and related aspects

The identification of the MLX class of a compound is normally a straightforward matter of looking up the class of the various ligands in the compound, as listed in the Table 1. However, not all ligands in a compound may be unambiguously classified without a detailed knowledge of the electronic structure of the molecule and this may not be available. Examples where ambiguities arise (for some molybdenum compounds) are shown in the Fig. 5. These include ligands which are noninnocent, also those polynuclear compounds where the degree of metal–metal bonding is unclear, and the widespread problem of deciding whether donor p_π lone pair (L-functions) of ligating atoms do or do not take part in primary metal–ligand bonding. This problem is especially prevalent for ligating oxygen atoms, as is illustrated in Fig. 5. When it is not possible to decide the class of a compound unambiguously then this may be indicated by providing a choice or range of values for x in the ML_lX_x class. For example, consider the binuclear compounds $[M_2Cl_3(\mu-Cl)_3]^{3-}$, where M = Cr, Mo or W, shown in Fig. 5(iii). The chromium compound is paramagnetic corresponding to three unpaired electrons. Therefore, no Cr–Cr bonds are implied and the class of each chromium is CrL_3X_3, i.e. d^3. If the three electrons of the anion are deemed to be located on the three bridging chloro ligands then these become bent L-μ-L ligands (as in bridging R_2S), i.e. the anion may be written as $[X_3Cr(L\text{-}\mu\text{-}L)_3CrX_3]$. The tungsten analogue is diamagnetic due to the presence of a tungsten–tungsten triple bond. Thus, the class of both the tungsten moieties is WL_3X_6. The molybdenum compound is weakly paramagnetic so the Mo–Mo bond order is indeterminate and therefore the class is also indeterminate, e.g. MoL_3X_{4-6}.

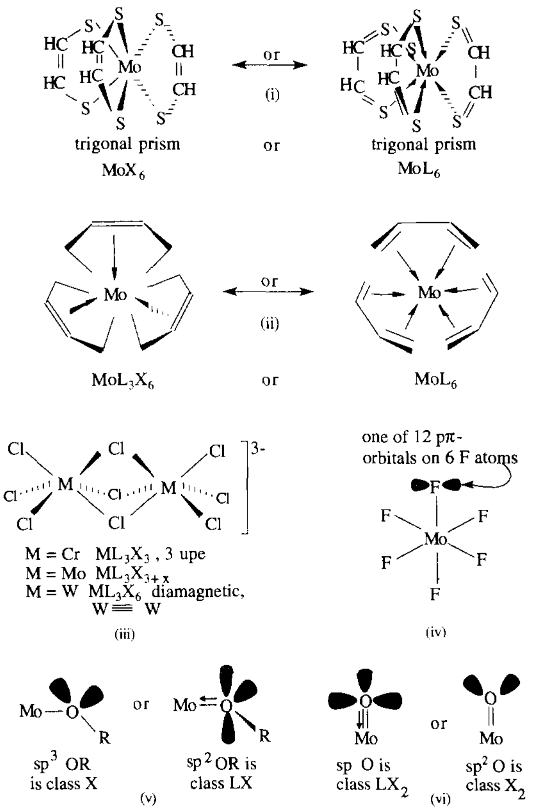

Fig. 5. (i) and (ii) illustrate the noninnocent ligand problem. (iii) See Section 2.4. (iv) There are 12 p_π-orbitals but only those three which have t_{2g} symmetry can bond to the molybdenum d-orbitals. Therefore the class is $MoL_{0\ \text{or}\ 3}X_6$ depending whether the p_π-orbitals are considered to contribute to primary bonding. (v) and (vi) show how the classification depends on the extent of L-function (p_π-lone pair) contribution. However, there are no definitive experimental criterea to decide the extent of contribution of these L-functions. Therefore many molybdenum-oxo compounds have a class with indeterminate values for l.

For most of the compounds in the classes MoL_lX_6 which have oxo ligands the choice of the value of l depends on whether or not it is considered that the "lone pairs" on the oxo ligands contribute to the primary bonding.

2.5. Definition of electron number, valency number, and ligand bond number

We now identify three quantities which are based on the definition of the general class of all compounds as ML_lX_x. (Z_z ligands are neglected since there are few compounds in which their representation is appropriate.)

Table 3
Summary of new definitions for the classification of covalent compounds

Term	Short symbol
A one-electron ligand function	X
Number of X ligands	x
A two-electron ligand function	L
Number of L ligands	l
Electron number of ligand of class L_lX_x	L.N. $= 2l + x$
A monofunctional X_x-ligand-atom	$X_{x=1}$
A polyfunctional X_x-ligand atom	$X_{x>1}$
General representation for the class of a covalent compound	ML_lX_x
Electron number of Mo in MoL_lX_x	E.N. = 6 (for Mo) $+ 2l + x$
Valency number	V.N. $= x$
Ligand bond number	L.B.N. $= l + x$
n of d^n	$n = 6$(for Mo) $- x - (2z)$
Number of electrons in the valency shell of the metal	**Me**
Equivalent neutral class	E.N.C.

(a) Valency number (V.N.) $= x$, where x is the number of X-functions on the ligands.

(b) Ligand bond number (L.B.N.) $= l + x$. This is the sum of the number of L- and X-functions.

(c) Electron Number (E.N.) $=$ **Me** $+ 2l + x$, where **Me** is the number of electrons (**e**) in the valency shell of the element **M**. For the Group 6 element molybdenum **Me** $= 6$. We also define the magnitude of the number n of d^n as $n =$ **Me** $- x(-2z$, where appropriate). A summary of these new definitions is given in Table 3.

For many compounds the magnitude of V.N. is the same as that of the formal O.S. of the metal **M** in the compound. However, they are not always identical, for example the definition of V.N. includes homopolar bonds (e.g. metal–metal bonds). Further, unlike the formal oxidation state, V.N. can not, by definition, be negative. In the rest of this article the value of x for a compound (i.e. the V.N.) will be referred to as the x-valency, for example, a compound where $x = 4$ is referred to as tetravalent.

It can also be seen that the quantity $l + x$ (the L.B.N.) will be identical to the C.N. for those compounds which have as ligands only those which require one or two electrons per ligating atom (monofunctional ligands). However, the L.B.N. of a compound is different from the classic coordination number when the metal ligand bonding is more complex, e.g. for η-hydrocarbon ligands. NO. =(), and, generally, for all polyfunctional ligands.

3. The construction of E.N. vs. V.N. plots (called MLX plots)

The MLX plot for **M** = molybdenum is shown in Fig. 1. The valency number x, the number of electrons required by the ligands, lies along the abscissa (x-axis) and the total number of electrons in the valency shell of the **M** atom (E.N.) lies along the ordinate (y-axis). This gives a matrix of boxes of which half can each be uniquely labelled with a specific MLX class for a molybdenum compound. Thus, when $x = 0$ and E.N. $=$ 18 the compounds must be MoL_6; when $x = 6$ and E.N. $= 12$ the compounds must be MX_6, etc. All possi-

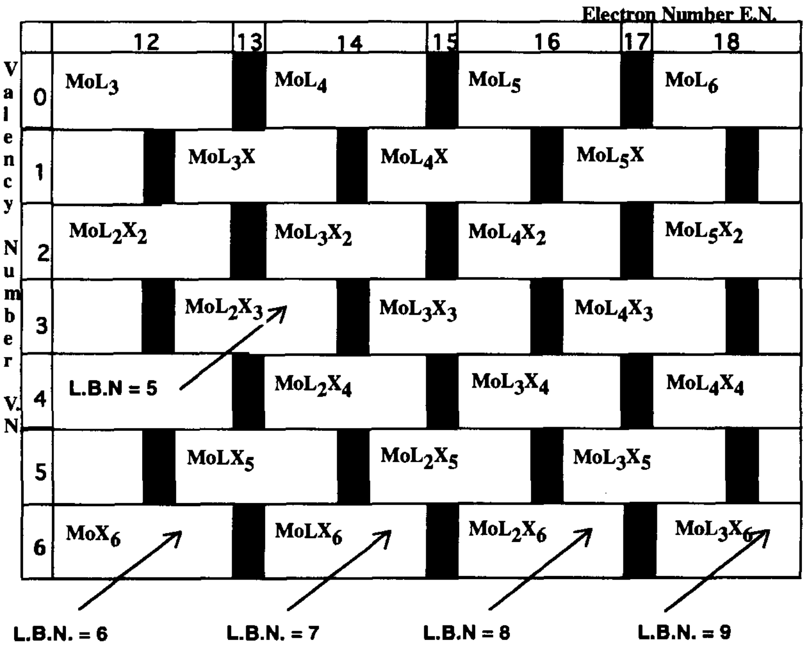

Fig. 6. The general MLX plot for molybdenum showing possible classes for all available V.N. and for values of E.N. from 12 to 18.

ble classes of molybdenum compounds for which x varies from 0–6 and E.N. varies between 12 and 18 are represented in Fig. 6. (An alternative form for MLX plots which emphasises the "no-go" areas is given in Appendix A, Fig. 11.) The grey pillars represent areas for which it is not possible to have a compound class. For example, when V.N. is even ($x = 0$, 2, 4 or 6) and **Me** is even (i.e. 6 for Mo) the E.N. cannot be odd (since E.N. $= 6 + 2l + x$). Likewise, when V.N. is odd ($x = 1$, 3 or 5) then since **Me** = 6 the E.N. must also be odd.

Fig. 6 also shows arrows which are directed along diagonals having constant values for $l + x$. In other words, those compounds which have the same L.B.N. lie on these diagonals. As noted earlier, the L.B.N. corresponds to the C.N. when all the ligands have only monofunctional ligand atoms. It is obvious that the form of the **MLX** plot in Fig. 6 depends only on the possible given values for x of 0–6 and values for E.N. from 12 to 18. Therefore, this plot is equally appropriate for elements which have six valency electrons and nine valency orbitals, i.e. Cr, Mo and W.

3.1. The construction of the MLX plot for molybdenum

The construction of a MLX plot specific to molybdenum proceeds by first identifying the individual $\mathbf{ML}_l\mathbf{X}_x$ class for (in principle) all known compounds of molybdenum which have been prepared and sufficiently well characterised. A selection of molybdenum compounds organised according to their **MLX** class is given in Table 2.

At present there are probably no known isolated compounds of molybdenum which lie outside the limits given in Fig. 6. Thus, it is doubtful that there are any compounds of molybdenum for which it can be argued that the true E.N. is 19 or 20. For example, [Mo(η-C_5H_5)$_2$NR] appears to be a 20-electron compound. However, the evidence indicates that the p_π lone pair on the imido nitrogen makes little contribution to the Mo=N bonding but rather that it slightly destabilises the Mo-η-C_5H_5 bonding [2].

Once a list of all appropriate molybdenum compounds and their **MLX** class has been drawn up, the total number of significantly different compounds in each class is counted and the relative population densities of each class is represented in the **MLX** plot by colour intensity, as shown in Fig. 1. The deeper the red shading the greater the population density. The criterion that compounds be significantly different is made to avoid counting compounds which are different in chemically trivial ways, for example, compounds with different isotopes, compounds with the same molybdenum-containing cation but with different anions, or compounds with apparently very minor changes of ligands, e.g. P(p-C_6H_4R)$_3$, where R = Me or Et. Clearly, some judgement is necessary.

3.2. General comments on the MLX plot for molybdenum

3.2.1. Information provided by the MLX plot

The **MLX** plot represents the relative abundance of the different classes of molybdenum compounds as a function of all the ligand environments known for molybdenum. The pattern of the distribution and relative intensities of the occupations of the various **MLX** boxes is characteristic for molybdenum and differs markedly from the **MLX** plot of all other elements (except for tungsten). The MLX plot for palladium is given in Appendix A to illustrate this point. The **MLX** plot summarises an enormous amount of factual information and in turn reveals the important major characteristics of molybdenum chemistry.

3.2.2. Concerning the stability of compounds forming the MLX plots

It is implicit in the identification of the compounds which are represented in the MLX plot for molybdenum that they are restricted to those which may be described as stable at normal temperatures and pressures, so that they can be isolated and characterised and, normally, stored under inert conditions. Clearly, there are high temperature compounds (e.g. $MoCl_5$ in the vapour, molybdenum-oxide molecules in the vapour of MoO_3) or low temperature matrix-isolated compounds (such as [Mo(CO)$_5$] in an argon matrix). In general then, the **MLX** plot refers to compounds which are "stable to isolation (in an inert bottle) under an inert atmosphere at n.t.p."

There are three "rules" which concern the stability of a compound with respect to its existence at n.t.p. and in the absence of other potential reactants, such as O_2 or H_2O. These rules are:

(a) Filled valency orbitals, e.g. the 18-electron rule in the case of molybdenum.

(b) Steric saturation: steric overcrowding leads to ligand dissociation; steric unsaturation implies there is space to allow access for reactions at the central atom **M**. Thus, steric unsaturation will lead to low energy barriers to pathways for decomposition to more thermodynamically stable products. Very many compounds which can be isolated and stored in bottles are thermodynamically unstable with respect to other combinations of the component atoms and many (especially organometallic compounds) exhibit kinetic stability in air.

The predominance of L.B.N. = 6 (and also C.N. = 6) for transition metal compounds simply reflects the facts that (i) the size of most ligands (as reflected by the cone angle submitted to the metal) is similar, (ii) the sizes of transition metals are quite similar and (iii) the relative sizes of the ligands and the metals M are such that six-coordination leads to comfortable steric saturation.

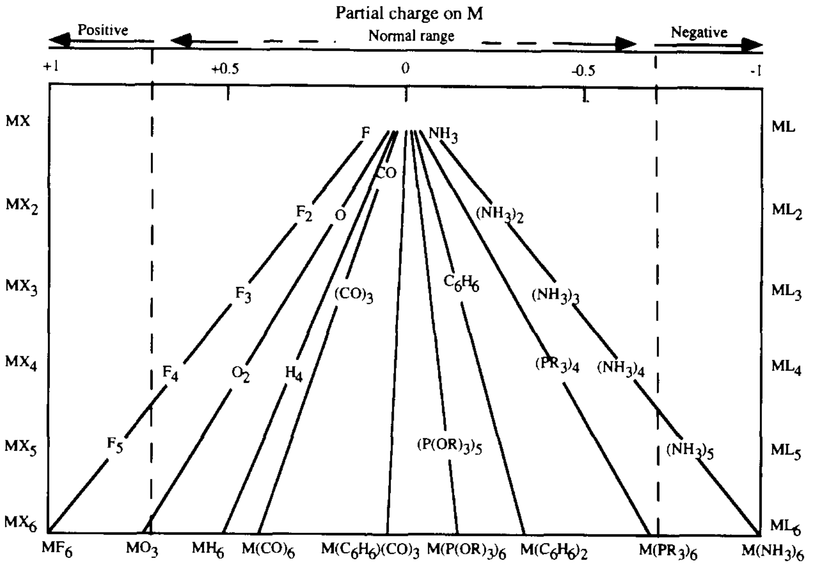

Fig. 7. A qualitative representation of the effect of various ligand environments on the partial charge of the central element **M**.

Contrast that with the situation for the larger lanthanum elements for which L.B.N. = 6 is relatively uncommon and values of 7 or 8 occur frequently.

(c) The Electroneutrality Principle. This principle, first expressed by Pauling, states that within a covalent system there cannot be a charge separation between component atoms of greater than about +1 or −1 electronic charge. The electroneutrality principle explains why compounds which obey the rules (a) and (b) are not stable. For example, consider why the molybdenum compounds $Mo(NH_3)_6$ and $[MoF_6]^{6-}$, which are in the class MoL_6, are unknown. Thus, if we compare $Mo(NH_3)_6$ with the stable $Mo(CO)_6$ it is seen that since the CO ligand is a poor σ-donor and the effective π-acceptor while NH_3 is a strong σ-donor with essentially no π-acceptor ability, the electron density associated with the molybdenum centre will be much the greater in $Mo(NH_3)_6$, and it may be presumed that the negative charge on the molybdenum would exceed −1.

Fig. 7 presents a very qualitative description of the relationship between the Electroneutrality Principle (the build up of charge on the atom **M**) as a function of various ligand environments. Thus, the partial charge on the molybdenum centre of $Mo(CO)_6$ will be positive, and for $Mo(\eta\text{-}C_6H_6)_2$ it will be negative, so the molybdenum centre in the compound $Mo(\eta\text{-}C_6H_6)(CO)_3$ will be near neutrality.

3.3. The relationship between the MLX plot and properties of ligands: the identification of ligand domains

Before we discuss and interpret the MLX plot for molybdenum its relationships to reactivity, reaction mechanisms and the functional group properties of the various ligands listed in Table 1 will be described.

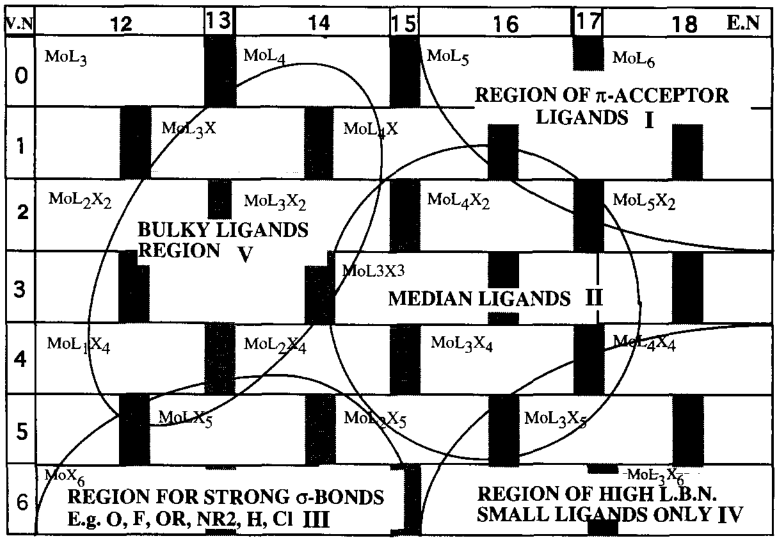

Fig. 8. The distribution of major ligand domains.

As stated earlier, the **MLX** plot for molybdenum is derived from compounds which represent essentially all the known ligand environments. The **MLX** plots for all the other d-block transition metals also contain compounds with many of the same or similar ligand environments. Close examination of the **MLX** plots of all the d-block metals shows that particular ligand environments are grouped in clearly identifiable regions of the **MLX** plot and they are substantially independent of the particular metal. The regions for individual ligand environments are designated as 'ligand domains'. For example, the ligand domains of the ligands CO, η-benzene and olefins are very similar. Likewise, the oxo and fluorine ligands have similar domains. Five principal ligand domains. I–V, can be identified (Fig. 8). They reflect both steric and electronic properties of the ligands. For example, inspection of the individual compounds (see the data for $\mathbf{ML_6}$ in Table 2) which are found in domain I at the top right hand corner of the MLX plot shows that ligands such as CO. η-benzene, PF_3, N_2, olefins, PR_3, RNC and combinations thereof, are dominant. The occurrence of these apparently very disparate molecules in the same ligand domain is associated with the presence on all these ligands of empty orbitals which can withdraw electron density from the metal centre by (secondary) bonding. These acceptor orbitals are normally of π- or δ-symmetry.

The classes of the compounds located in domain IV (Fig. 8) have high ligand bonds numbers, i.e. L.B.N. = 8 and 9. Therefore, an essential requirement for the ligand environments of these compounds is that the majority of the ligands are small or compact. This accounts for the observation that ligands commonly found in this domain are H, F, CN, =O, and η-C_5H_5. Examples of compounds in this domain are given in Table 2. The L_2X η-C_5H_5 ligand is not small, but given that it donates five electrons to the metal centre it is described as being compact compared, for example, with the three seperate ligands forming an L_2X group, e.g. $(PR_3)_2Cl$.

At present very few, if any, compounds have been isolated which are known to lie in domain V. This is because with ligands of normal size the compounds would be sterically unsaturated and would have empty valency orbitals, i.e. with E.N. < 16. However, it may be envisaged that with suitably designed ligands are very bulky and probably polydentate (and in the absence of agostic bonds), it will be possible to prepare and isolate compounds in this domain. Such compounds will need to be isolated in their own ligand matrix.

The identification of ligand domains in the **MLX** plot also relates to aspects of reactivity. A compound will react to give a product whose class lies towards the centre of the ligand domain of the product. When the ligand domain of a compound lies on the periphery of the domain of that ligand system then it will undergo redox reactions and the class of the product will lie in the centre of the ligand domain. For example, $[Mo(\eta\text{-}C_6H_6)_2]^+$ is readily reduced to $[Mo(\eta\text{-}C_6H_6)_2]$. This reactivity trend arises from the Electroneutrality Principle.

3.4. *Classification of reactions and the use of MLX plots for discussing reaction pathways*

All possible reactions of any molybdenum compound MoL_lX_x can be classified in terms of the changes in the values of l and or x in the product. For example

$$Mo(CO)_4(PR_3)_2 + I_2 \rightarrow Mo(CO)_3(PR_3)_2I_2 + CO$$

may be represented in terms of the MLX class of the compounds, e.g.

$$MoL_6 + X_2 \rightarrow MoL_5X_2 + L$$

therefore, the overall change for the reactant in general terms is the loss of one ligand L-function and the gain of two ligand X-functions. Thus, the reaction may be written as

$$ML_l \xrightarrow{-L,+X2} M_{l-1}X_2$$

This reaction may be called a replacement-addition, i.e. replacement of L by X_2. It should be noted that it is actually an "oxidation" reaction since x becomes larger (by 2), but the phrase oxidative-replacement-addition is cumbersome.

Another example is the reaction.

$$\underset{\text{Class } Mol_5X_2}{(\eta\text{-}C_5Me_5)(CO)_3Mo\text{-}Mo(CO)_3(\eta\text{-}C_5Me_5)}$$

$$\rightarrow \underset{\text{Class } MoL_4X_4}{(\eta\text{-}C_5Me_5)(CO)_2Mo{\equiv}Mo(CO)_2(\eta\text{-}C_5Me_5)} + 2CO$$

This is also a replacement-addition reaction $(-L, + X_2)$, i.e. loss of CO followed by the addition of two X-bonds to each metal centre, where the X-bonds are metal–metal bonds.

The addition of a proton to a metal centre, which does not increase the E.N., is a also replacement-addition reaction. This is quite common for 18e transition metal compounds with $n \geqslant 2$, provided that the d^n electrons have low ionisation energies. Such compounds are often described as having "electron-rich" or "high energy" metal centres. When the metal centre is exceptionally electron-rich the molecule can undergo a rare consecutive diprotonation reaction, e.g.

$$\underset{\text{Class } MoL_6}{Mo(dmpe)_3} + H^+ \rightarrow \underset{MoL_5X_2}{[Mo(dmpe)_3H]^+} + H^+ \rightarrow \underset{MoL_4X_4}{[Mo(dmpe)_3H_2]^{2+}}$$

The reactions given below show the sequential addition of three electrons to MoF_6. Each forward step is a one-electron reduction and this causes the class to change by $-X$, $+L$ at each step. The $-X$, $+L$ reaction is designated as a reductive-replacement (also

Table 4
Classification of reactions by the reaction products

Change in L and/or X_x	Change in		Name of reaction
	E.N.	V.N.	
$-L_l$ then $+L'_l$	0	0	L_l-substitution
$-X_x$ then $+X'_x$	0	0	X_x-substitution
$+L_l$	$+2l$	0	L_l-addition
$-L_l$	$-2l$	0	L_l-elimination
$+X_x$	$+x$	$+x$	X_x-oxidative-addition
$-X_x$	$-x$	$-x$	X_x-reductive-elimination
$+L$ then $-X$ [a]	$+1$	-1	reductive-replacement [a]
$-L$ then $+X$ [b]	-1	-1	oxidative-replacement [b]
$-L_n$ then $+X_{2n}$ $(n=1)$	0	$+2$	replacement-addition [c]
$+L_n$ then $-X_{2n}$ $(n=1)$	0	-2	replacement-elimination [d]
L goes to new L′	0	0	L-substitution
X goes to new X′	0	0	X-substitution

[a] When the ligands are unchanged the reaction is a one-electron reduction.

[b] When the ligands are unchanged the reaction is a 3-electron oxidation.

[c] Assuming $n = 1$. Generally called an n-replacement-addition.

[d] Assuming $n = 1$. Generally called an n-replacement-elimination.

commonly called a one-electron reduction),

$$\begin{array}{lllllll} MoF_6 & \rightarrow & [MoF_6]^- & \rightarrow & [MoF_6]^{2-} & \rightarrow & [MoF_6]^{3-} \\ \text{Class } MoX_6 & & MoLX_5 & & MoL_2F_4 & & MoL_3X_3 \end{array}$$

When the class of the product is the same as that of the reactant, i.e. $MoL_lX_x \rightarrow MoL_lX_x$, this is a substitution reaction and may be either L-substitution (i.e. the products is $MoL_{l-l}L'X_x$) or X-substitution (i.e. the product is $MoL_lX_{x-1}X'$).

All the possible reactions of a molybdenum compound MoL_lX_x which give products which lie in the nearby (and adjacent) neighbouring MoL_lX_x classes are shown in Fig. 9 and the reactions and their proposed names are listed in Table 4.

3.5. Mechanistic implications of MLX plots

These definitions provide an unambiguous classification of a reaction in terms of product, but the classification does not imply, and is independent of, any particular mechanism. However, the distribution pattern of compounds in the MLX plot of an element may provide clear indications of the likely mechanism of a particular reaction. The guiding principle leading to mechanistic insight based on the MLX plot is: "reaction intermediates resemble known compounds". This principle can be demonstrated for the chemistry of molybdenum by consideration of several regions of the MLX plot in (Fig. 1) as follows:

(i) Consider the classes $MoLX_6$,MoL_2X_6 and MoL_3X_6 which lie adjacent on the V.N. = 6 row. These are all populated to varying degrees. Therefore it is likely that $MoLX_6$ and MoL_2X_6 will undergo +L-addition reactions and that compounds MoL_3X_6 will undergo −L-elimination reactions. Furthermore, L-substitution or X-substitution for MoL_3X_6 will certainly proceed in a dissociative manner while, since the compounds MX_6 are rare, an associative pathway is indicated for $MoLX_6$.

(ii) Consider the classes MoX_6, $MoLX_5$, MoL_2X_4 and MoL_3X_3 which lie consecutively on the diagonal for which L.B.N. = 6. All are populated to varying degrees. Therefore reactions which convert a compound in one of these classes to one of the others are expected. The simplest reaction leading to interchange between these adjacent classes is either electron addition, i.e.

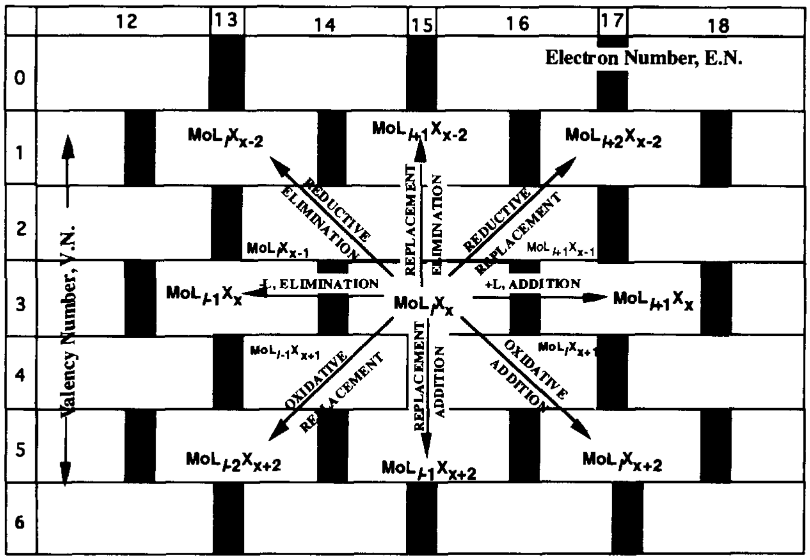

Fig. 9. Classification of reactions by MLX class.

$-X$, $+L$, or electron removal, $-L$, $+X$. In other words, the presence of such a consecutive diagonal relationship indicates the likelihood of the occurrence of redox reactions, as indeed is borne out by the chemistry of these classes of molybdenum compounds.

(iii) Compounds for which there are no adjacent populated compounds in a row (i.e. with a constant value of x) are expected to be inert to substitution. Examples are MoL_6 and MoL_4X_4. Further examples of relationships between reactivity and mechanism are given elsewhere [3].

4. Further interpretations of the population density patterns in the MLX plot for molybdenum

(i) The two factors most common to highly populated MLX classes are (a) E.N. = 18 and (b) location on the diagonal MoL_lX_x where $l+x=6$. The preponderance towards the 18-electron compounds reflects the favourable energies of the nine valency orbitals of molybdenum. The preference for six ligand functions (L.B.N. = 6) is a consequence of the relative steric requirements of most ligands coupled with the size of molybdenum, as discussed in Section 3.2.2., which leads to kinetic stability towards further reactions, both inter- and intra-molecular, which may in turn lead to decomposition.

(ii) Compounds of molybdenum are found for all the seven possible values of x (0–6). The compounds where $x=1$ or 2, which occur in the top right hand corner of the **MLX** plot, are associated with ligands which are capable of back-donation using π- or δ-symmetry acceptor orbitals, for example, CO, PR_3, η-benzene and N_2. Compounds with $x=5$ and 6 are found mostly at the bottom of the **MLX** plot and towards the left hand corner and are thus associated with strongly σ-bonding ligands such as =O, –OR, =NR, F and Me, i.e. X_x ligands where the ligating atom X is a first row element. The compounds with $x=3$ and 4 are associated substantially with the less electronegative ligand systems such as Cl, Br, I and CN or strongly donor L ligands, e.g. NR_3. However, for median values of x a variety of combinations of ligands can be brought together to satisfy the steric and electronic requirements of the molybdenum.

(iii) Except for those which lie along the $l+x=6$ diagonal, there are few compounds with $x=1$, 3 or 5. In other words, molybdenum compounds with an odd E.N. are most common when there is steric saturation. This arises because steric saturation of the molybdenum (metal) centre will provide a degree of kinetic stability, for example, it restricts ligand substitution reactions by associative processes.

The continuous population of compounds along the diagonal for which $l+x=6$ (i.e. for L.B.N. = 6) is reflected in the characteristic occurrence of redox reactions for the molybdenum compounds which lie along this diagonal. This follows since addition of an electron to MoL_lX_x gives $[MoL_lX_x]^-$, which corresponds to the neutral class $MoL_{l+1}X_{x-1}$.

Similarly, a one-electron oxidation of MoL_lX_x gives the corresponding neutral class $MoL_{l-1}X_{x+1}$. This ability for molybdenum to take part in redox reactions over a wide range of ligand environments is a key characteristic of this element and no doubt accounts in part for the widespread catalytic properties of molybdenum.

(iv) The oxidative addition reaction ($+X_2$), e.g. the addition of H_2 or MeI to a metal centre, converts a compound in the class MoL_lX_x to MoL_lX_{x+2} and thus increases the value of V.N. by 2. Inspection of the more populated classes in the **MLX** plot in Fig. 1 shows that **MLX** classes which differ by $+X_2$ occur for the combination of the rare, 16-electron compounds MoL_4X_2 and the common 18-electron MoL_4X_4. The **MLX** plot reflects the rarity of oxidative-addition reactions in molybdenum chemistry but accounts for the strong tendency for the very rare compounds MoL_4X_2 to undergo such reactions. For example, molybdenocene, which only exists as a reactive intermediate undergoes intermolecular dimerisation by insertion of molybdenum into a C–H bond of another molecule, eventually leading to the red dimer $[(Mo\text{-}\eta^5\text{-}C_5H_5)_2(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_5)_2]$. This situation is in marked contrast to that for an element such as palladium or platinum for which the classes ML_2X_2 and ML_2X_4 are well populated (see the **MLX** plots for Pd and Pt in the Section A.8, Fig. 14).

(v) Addition of a ligand L to a molybdenum compound MoL_lX_x causes an increase of E.N. by 2. Therefore, this reaction will not occur readily for 18-electron compounds and this accounts for the fact that such compounds of molybdenum are inert to substitution by associative processes. However, where there are populated classes which are related by $+L$ and $-L$ reactions, e.g. for $[MoL_lX_6]$, where $l=1$ or 2, then substitution reactions by L ligands occur quite readily.

(vi) Finally, we note that stable compounds with L.B.N. <6 are virtually unknown. This reflects the fact that such compounds have empty valency orbitals (i.e. E.N. <18) and are also normally sterically unsaturated. Further, except for the 18e compounds MoL_5X_2, there are relatively few examples of compounds which have L.B.N. = 7 (or C.N. = 7). This arises because there is the loss of favourable bonding associated with the more symmetrical L.B.N. = 6 (octahedral or trigonal prismatic coordination) and also because there is generally a greater relative increase in steric repulsion energy on changing from L.B.N. = 6 to L.B.N. = 7 than from L.B.N. = 7 to L.B.N. = 8. In other words, most of the overall increase of steric repulsion arising from a change of L.B.N. from 6 to 8 is accounted for by the formation of the intermediate with L.B.N. = 7. (Similarly, the increase of steric repulsion from 4- to 6-coordination is mostly accounted for by the change from 4- to 5-coordination.) A more detailed discussion of individual MLX classes of molybdenum compounds has been published elsewhere [3].

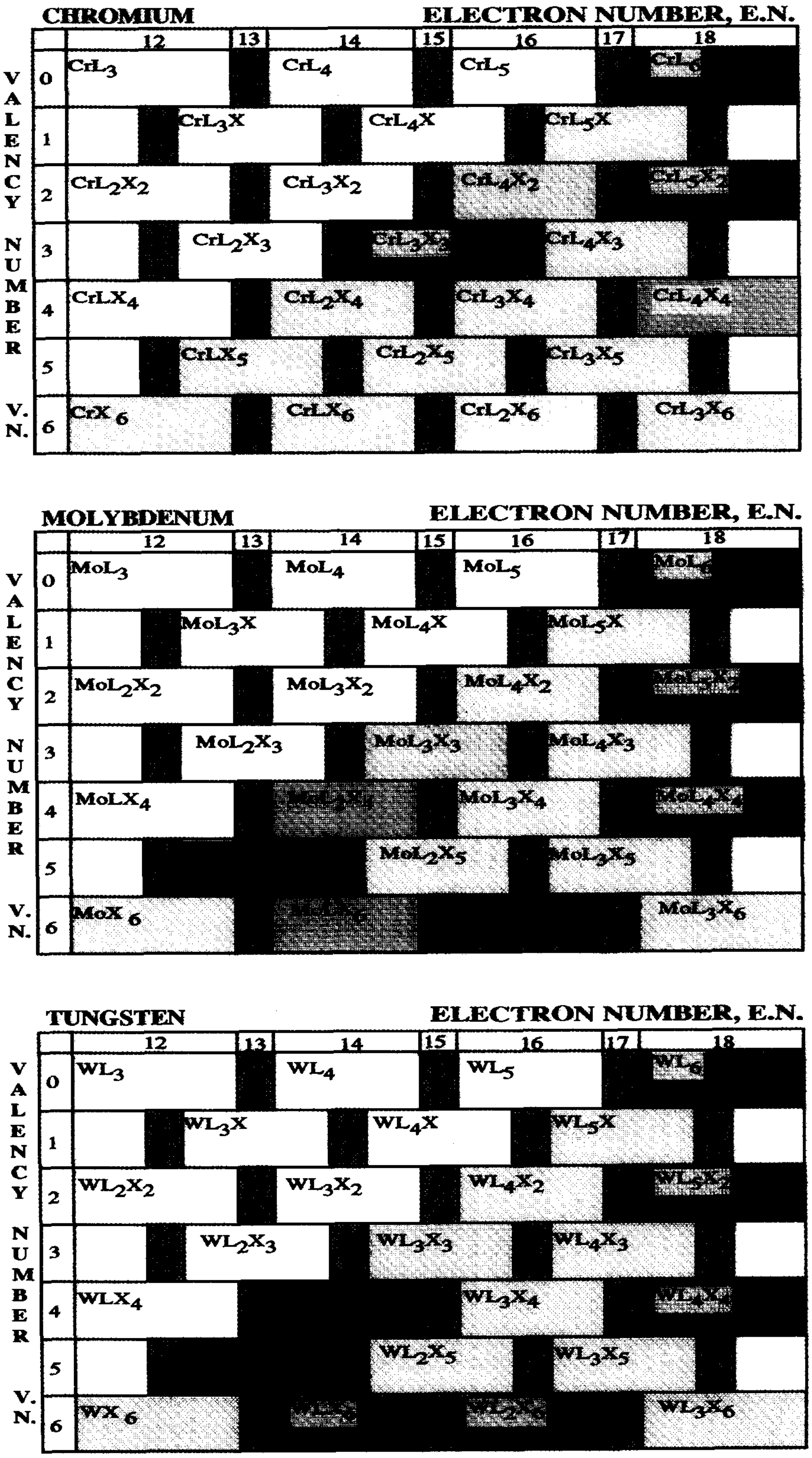

Fig. 10. The MLX plots for chromium, molybdenum and tungsten.

5. Comparison of general trends in the chemistries of chromium, molybdenum and tungsten

The MLX plots for chromium, molybdenum and tungsten are given in Fig. 10. Inspection of these enables the important similarities and differences in the chemistries of the three elements as a function of the range of ligands to be identified, as follows:

(i) The 18-electron rule is well obeyed by all three elements.

(ii) Compounds with L.B.N. < 6 are almost unknown (a possible exception is CrR_4. where R = alkyl. L.B.N. = 4 in the absence of agostic bonds).

(iii) Compounds with L.B.N. = 6 are well represented and a similar pattern for this diagonal relationship is found for all three elements, but is less extensive for chromium.

(iv) The bottom left-hand side regions of the MLX plots are clearly similar for molybdenum and tungsten but substantially less populated for chromium. In this region of high V.N. (domain III) the ligating atoms of the X ligands are highly electronegative and form strong σ-bonds to the metals. Therefore, these ligand environments develop an induced partial positive charge at the metal centre. Since the sensitivity of 3d-orbitals to such induced partial charges is much greater than for the more shielded 4d- and 5d-orbitals it is correspondingly more difficult for chromium in a given ligand environment to achieve higher valencies than it is for molybdenum or tungsten. The MLX plots show that high valency numbers occur more readily for the 2nd and 3rd row elements.

(v) In contrast to the differences between chromium compared with molybdenum and tungsten observed at high V.N., the regions where the values for V.N. are 0–2 are very similar for all three elements. This arises because the donor–acceptor nature of the ligand environments in this region do not cause a substantial increase or decrease in the energies of the unused d^n electron on the metal centre. Therefore, the different sensitivities to partial charge of the 3d, 4d and 5d orbitals (as detailed above) are not relevant.

(vi) The historically important and classically inert octahedral d^3 chromium compounds in the class CrL_3X_3 have substantially fewer counterparts in the chemistries of molybdenum and tungsten. The inertness of CrL_3X_3 compounds to substitution is reflected by the virtual absence of compounds in the adjacent classes CrL_2X_3

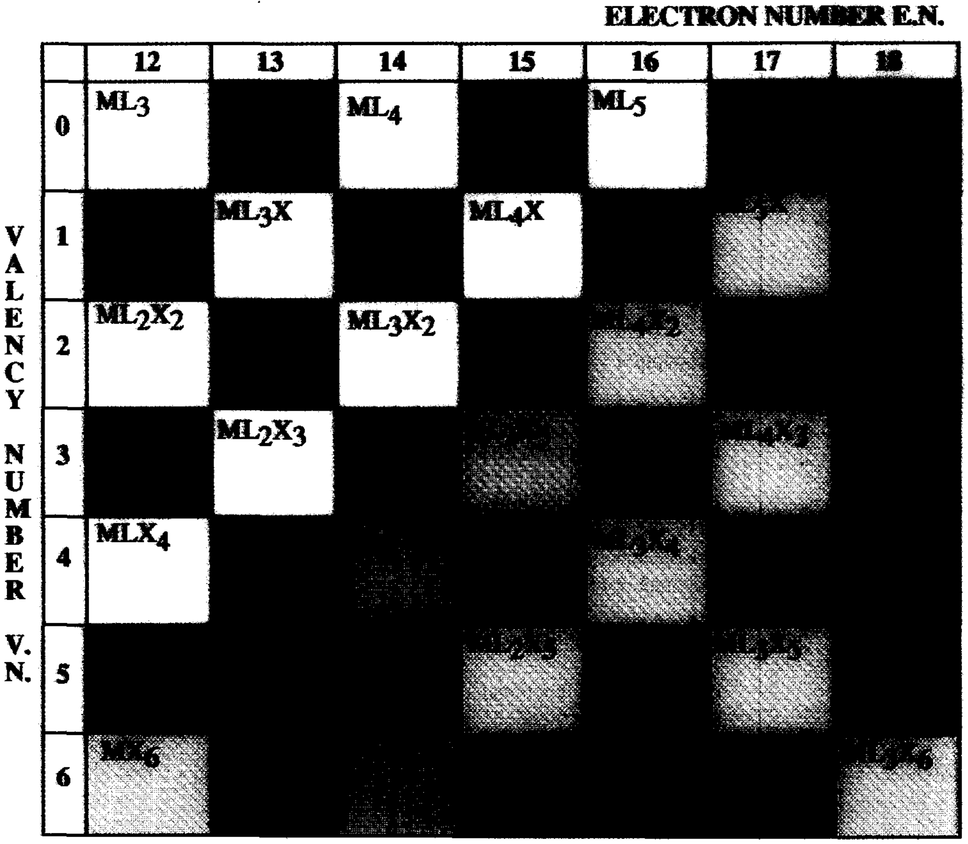

Fig. 11. An alternative representation of an MLX plot for which the element M has six valency electrons. The dark grey boxes which have no ML_lX_x class shown are those for which compounds cannot by definition, exist (no-go areas).

and CrL_4X_3. The absence of the former class may be due to the undesirable L.B.N. = 5, associated with steric unsaturation and with the partially filled valency shell (13-electrons). The paucity of the class CrL_4X_3 may be associated with the steric disadvantages of seven-coordination and the relatively smaller size of Cr (compared with Mo and W) and also with the loss of both crystal field stabilisation energy (CFSE) and exchange energy compared with those for octahedral d^3 t_{2g} chromium compounds. The MLX plot for chromium shows that the class CrL_4X_2, which is diagonally related to CrL_3X_3, has a modest population density. Therefore, redox reactions are expected to occur between these two classes, as is indeed observed.

6. Conclusions

A new approach to the classification of the covalent compounds of the elements has been introduced and illustrated by specific reference to the chemistry of molybdenum. The classification allows the construction of MLX plots which provide a broad overview of the population abundance of different classes of compounds which the element forms. The MLX plots enable the major characteristic trends of the compounds formed by an element to be readily identified and provides a direct and detailed basis for illustrating the comparative chemistry of the elements. Closer examination of an MLX plot provides insight into characteristic reactivity trends of the element and, further, allows mechanistic insight. A study of MLX plots for a range of related elements allows identification of ligand domains which reflect common electronic and steric features of ligands, i.e. their functional group properties.

Appendix A

Further comments on the classification of covalent compounds by valency number, electron Number and ligand bond number, are given below.

A.1. An alternative form for MLX plots

Fig. 11 shows an alternative form of MLX plot which differs from that shown in Fig. 1 in that the boxes which have no possible compound class are the same size as those which do.

A.2. Definitions of ligand functionality and denticity

When a ligand bonds to the central atom using one-ligating atom and one orbital then the ligating atom is called a monodentate, monofunctional ligating atom. The orbital may contain two, one or zero electrons.

When a ligand bonds to the central atom using one-ligating atom and two orbitals then the ligating atom is called a monodentate, bifunctional ligand. Each orbital may contain two, one or zero electrons.

When a ligand bonds to the central atom using one-ligating atom and three orbitals then the ligating atom is called a monodentate, trifunctional ligand. Each orbital may contain two, one or zero electrons. Examples of the above and other ligand systems are shown in Table 5.

A.3. Definition of d^n

In the Crystal Field theory or the Ligand Field theory of transition metal compounds the term d^n is used. It indicates the number of electrons n remaining in essen-

Table 5
Examples of ligand functionality and denticity

Number of ligating atoms	Number of orbitals [a] used in bond formation	Description	Typical examples of ligands
1	1	monodentane, monofunctional	H, Me, NR_2 (bent), NH_3, CO, H_2
1	2	monodentate, bifunctional	NR_2 (planer), $=CR_2$, =O
1	3	monodentate, trifunctional	N, CR (carbyne)
1	4	monodentate, tetrafunctional	quadruple bonds
2	1 and 1	bidentate, each monofunctional	oxolate, acetate, ethylenediamine
2	2 and 1	bidentate, one bifunctional the other monofunctional	$R_2N(CH_2)_2NR$ with planer CNR
2	1(M.O.)	bidentate,-monofunctional	η-ethene [b]
2	1 + 1(A.O.s)	bidentate, bifunctional	C_2H_4 in a metallacyclopropane [b]
3	2(MOs)	tridentate, bifunctional	η-allyl
5	3(M.O.s)	pentadentate, trifunctional	η-cyclopentadienyl
6	3 (M.O.s)	hexadentate, trifunctional	η-benzene

[a] Essentially atomic orbitals (A.O.) unless otherwise indicated. M.O. indicates a molecular orbital.
[b] These are alternative descriptions, for the bonding of ethene.

Table 6
Rules for classification of covalent molecules and molecular ions

Initial class		Rule for reduction to E.N.C.	V.N. given by	L.B.N. given by	Limits
$\mathbf{MX}_x$	neutral	—	x	x	$x \leqslant \mathbf{Me}$
$[\mathbf{MX}_x]^{m-}$	anions	$X^- \rightarrow L$	$x-m$	x	$m \leqslant x$
$[\mathbf{MX}_x]^{m+}$	cations	$X^+ \rightarrow Z$	$x-m$	x	$m \leqslant x$
$\mathbf{ML}_l$	neutral	—	$x=0$	l	availability of **M** orbitals, 18e rule
$[\mathbf{ML}_l]^{m-}$	anions	$L^- \rightarrow LX$	m	$l+m$	availability of ligand orbitals
$[\mathbf{ML}_l]^{m+}$	cations	$L^+ \rightarrow X$	m	l	$m \leqslant n$
$\mathbf{ML}_l X_x$	neutral	—	x	$l+x$	$x \leqslant \mathbf{Me}$, availability of M orbitals
$[\mathbf{M}_{l1}\mathrm{X}_x]^{m-}$	anions	$X^- \rightarrow L$, then	$x-m\ (m \leqslant x)$	$l+x$	as for $[\mathbf{ML}]^{m-}$ and $[\mathbf{MX}]^{m-}$ anions
		$L^- \rightarrow LX$	$m-x\ (l+x>m>x)$	$l+m+x$	
$[\mathbf{ML}_l\mathrm{X}_x]^{m+}$	cations	$L^+ \rightarrow X$, then	$x+m\ (m<l)$	$l+x$	as for $[\mathbf{ML}]^{m+}$ and $[\mathbf{MX}]^{m+}$ cations
		$X^+ \rightarrow Z$	$2l+x-m\ (m>l)$	$l+x$	

tially d-orbitals on the metal. d^n is defined similarly using the MLXZ formalism by d^n, $n = \mathbf{Me} - x - 2z$.

For elements where the unused valency electrons are not in d-orbitals then the general symbol v^n can be used to indicate there are n unused valency electrons remaining in the valency orbitals of the element **M** of $\mathbf{ML}_l\mathrm{X}_x\mathrm{Z}_z$. Examples are,

$[Mo(\eta\text{-}C_5H_5)_2H_2] = L_4MX_4$ $n = 6-4 = 2;\ d^2$
$[Mo(\eta\text{-}C_5H_5)_2H_2(AlMe_3)] = L_4MX_4Z$ $n = 6-4-2 = 0;\ d^0$
$NH_3 = \mathbf{M}X_3,$ $n = 5-3;\ v^2$
$NH_4^+ = \mathbf{M}X_3Z,$ $n = 5-3-2;\ v^0$

A.4. The classification of covalent anions

The central atom and all ligands are treated in the first place as neutral. Thus, chlorine as a ligand is regarded as Cl not as Cl^-; similarly the nitrosyl ligand is regarded as NO and not as NO^+. One advantage of this approach is that it is not necessary to make any decision about the partial charge on the ligand. A molecular ion is therefore first classified as though there was no charge and the total charge is placed outside the bracket.

Thus the general representation of a molecular cation or anion is $[ML_lX_xZ_z]^{n+ \text{ or } n-}$. In order to determine the E.N., V.N. or L.B.N. and for convenience in classifying molecular ions in V.N./E.N. plots, (i.e. **MLX** plots), the general representation for a molecular ion has to be transposed to the Equivalent Neutral Class (E.N.C). The general rules for this procedure are given in Table 6. Although, at first sight, these may seem to be complicated, the procedure is extremely simple and is demonstrated in Table 7.

Table 7
Examples of conversion of the classes of ions to the equivalent neutral class (E.N.C.) [a]

Compound	Molecular ion	Rearrange	Rule applied	E.N.C.
$[Co(NH_3)_6]^{3+}$	$[ML_6]^{3+}$	$[ML_3(L^+)_3]$	$L^+ = X$	ML_3X_3
$[CoF_6]^{3-}$	$[MX_6]^{3-}$	$[MX_3(X^-)_3]$	$X^- = L$	ML_3X_3
$[Co(NH_3)_4Cl_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[Mn(CO)_5]^-$	$[ML_5]^-$	$[ML_4(L^-)]$	$L^- = LX$	ML_5X
$[Mn(CO)_6]^+$	$[ML_6]^+$	$[ML_5(L^+)]$	$L^+ = X$	ML_5X
$[Co(\eta\text{-}C_5H_5)_2]^+$	$[ML_4X_2]^+$	$[ML_3(L^+)X_2]$	$L^+ = X$	ML_3X_3
$[NiCl_4]^{2-}$	$[MX_4]^{2-}$	$[MX_2(X^-)_2]$	$X^- = L$	ML_2X_2
$[Pt(NH_3)Cl_3]^-$	$[MLX_3]^-$	$[MLX_2(X^-)]$	$X^- = L$	ML_2X_2
$[Cr(CO)_5]^{2-}$	$[ML_5]^{2-}$	$[ML_3(L^-)_2]$	$L^- = LX^+$	ML_5X_2
$[Ir(PR_3)_2H_6]^+$	$[ML_2X_6]^+$	$[ML(L^+)X_5]$	$= X$	MLX_7
NH_4^+	$[ML_4]^+$	$[MX_3(X^+)]$	$X^+ = Z$	ML_3Z
PCl_4^+	$[ML_4]^+$	$[MX_3(X^+)]$	$X^+ = Z$	ML_3Z

[a] The rules used in this table are summarised thus: $L^+ = X$, 2e − 1e = 1e; $X^- = L$, 1e + 1e = 2e; X^+ (in the absence of available L) = Z, 1e − 1e = 0; L^- (in the absence of available X) = LX, 2e + 1e = 3e. Very occasionally, the question of the order of precedence of these rules arises, see Table 6.

Table 8
Examples of ligands with polyfunctional ligating atoms

Ligand	Class	Representation	Examples
O	$\bar{X}_2$	$M{=}O$	CO_2, $[Mo(\eta\text{-}C_5H_5)_2O]$, OsO_4, $MoCl_2O_2$
S	$\bar{X}_2$	$M{=}S$	$[MoS_4]^{2-}$, CS_2
NR	$\bar{X}_2$	$M{=}NR$	$RC{=}NR$
CR_2	$\bar{X}_2$	$M{=}CR_2$	$H_2C{=}CH_2$, $[Ta(\eta\text{-}C_5H_5)_2({=}CH_2)Me]$
CR	$\bar{X}_3$	$M{=}C$	$HC{=}CH$, $Mo({=}CR)Br(CO)_4$
N	$\bar{X}_3$	$M{=}N$	N_2, $(PR_3)_4Re({=}N)Cl_2$ [a]
NO	$\bar{X}L$ [b]	M–NO	NO in $Cr(NO)_4$, $Co(CO)_3NO$
Cl_4Re	$\bar{X}_4$	$M{=}M$	$[Cl_4Re{=}ReCl_4]^{2-}$

[a] Re–N = 1.79 Å.

[b] For reduction to E.N.C. is $[\bar{X}L]^- \rightarrow L_2$.

A.5. Classification of molecular anions which contain polyfunctional ligating atoms

It is necessary to distinguish between ligands with monofunctional ligating atoms and those with polyfunctional ligating atoms because the rules for reduction of a molecular anion to the E.N.C. differ for the two cases. Examples of the more common ligands with polyfunctional coordinating atoms are given in Table 8. By far the most commonly encountered polyfunctional ligand is the oxygen atom.

The classification of neutral oxo compounds such as OsO_4, $[Mo(\eta\text{-}C_5H_5)_2O]$ and CrO_2Cl_2 proceeds in an identical manner as for other neutral compounds. The representations MX_8 and $M(X_2)_4$ for the neutral OsO_4 are equivalent. In both cases each oxygen requires two electrons from the metal and contributes a p_π lone pair, as discussed earlier. However, for a molecule anion such as carbonate $[CO_3]^{2-}$ if we define the class as $[M(X_2)_3]^{2-} = [MX_6]^{2-}$ and then use the normal rule $X^- = L$ for reduction to the E.N.C., this leads to the E.N.C. of $[CO_3]^{2-}$ as MX_4L_2. This assigns an E.N. of 12 to the carbon which is clearly absurd since carbon in its vast range of compounds never exceeds an E.N. of eight, i.e. the class MX_4. We can achieve this desired class for carbon in the carbonate anion in the following manner. The bifunctional oxo ligand atom O is represented not as X_2 but as $\bar{X}_2$; the bar above the ligand class serves to identify the ligating atom as being polyfunctional. The rule for reduction of anions with polyfunctional ligands to the E.N.C. is $\bar{X}_2^- \rightarrow X$.

Using this rule we may classify the carbonate ion as follows:

$$[CO_3]^{2-} = \left[M(\bar{X}_2)_3\right]^{2-} = \left[M(\bar{X}_2)(\bar{X}_2)_2^-\right]$$

$$= \left[M(\bar{X}_2)X_2\right] = MX_4$$

Table 9
Determination of MLXZ class and reduction to the neutral class of oxygen derivatives, where O is a $\bar{X}_2$ class ligand

Molecular or ion	Class	Rule	Equivalent Neutral Class
CO_2	$M(\bar{X}_2)_2$	—	MX_4
CO_3^{2-}	$M\bar{X}_2(\bar{X}_2^-)_2$	$\bar{X}_2^-{}'X$	MX_4
MoO_2Cl_2	$M(\bar{X}_2)_2X_2$	—	MX_6 [b]
SO_3	$M(\bar{X}_2)_3$	—	MX_6
SO_2Cl_2	$M(\bar{X}_2)_2X_2$	—	MX_6
Me_2CO	$[M(\bar{X}_2)X_2]$	—	MX_4
MoO_4^{2-}	$[M(\bar{X}_2)_2(\bar{X}^-)_2]$	$\bar{X}_2^- \rightarrow X$	MX_6 [b]
ReO_4^-	$[M(\bar{X}_2)_3(\bar{X}^-)_2]$	$\bar{X}_2^- \rightarrow X$	MX_7 [b]
NO_2^-	$[M(\bar{X}_2)(\bar{X}_2^-)]$	$\bar{X}_2^- \rightarrow X$	MX_3
PHO_3^{2-}	$[M(\bar{X}_2)(\bar{X}_2^-)_2X]$	$\bar{X}_2^- \rightarrow X$	MX_5
$[VO(H_2O)_4]^{2+}$	$[M(\bar{X}_2)L_2(L^+)_2]$	$L^+ \rightarrow X$	ML_2X_4 [b]
$VO(acac)_2$	$[M\bar{X}_2(LX)_2]$	—	ML_2X_4 [b]
$[VO(SCN)_4]^{2-}$ [a]	$[M(\bar{X}_2)^-X_3X^-]$	$\bar{X}_2^- \rightarrow LX$ $X^- \rightarrow L$	ML_2X_4 [b]

[a] The V=O distance = 1.62 Å so O is classified as $(\bar{X}_2)^-$.

[b] The metal centre has empty d-orbitals, if p_π-lone pair electrons on the oxygen donate to the metal the number of L-functions increases by one or more according to symmetry considerations.

Once all the charges on the anion have been dealt with there is no longer any need to distinguish between the classes $\overline{X}_2$ and X_2 so that the final step is $[\mathbf{M}(\overline{X}_2)X_2] = \mathbf{MX}_4$, as shown above.

The general rule for the reduction of ions containing $\overline{X}_x$ ligands to the E.N.C. is

$$(\overline{X}_x)^- \rightarrow \overline{X}_{x-1}.$$

When both poly- and mono-functional atoms are present then the electron is added first to the polyfunctional atoms. For example, the anion $[CrO_3Cl]^-$ is treated as follows:

$$[CrO_3Cl]^- = [\mathbf{M}(\overline{X}_2)_3X]^- = [\mathbf{M}(\overline{X}_2)_2(\overline{X}_2^-)X]$$
$$= [\mathbf{M}(\overline{X})_2X_2] = \mathbf{MX}_6$$

Further examples of the classification of covalent oxides and oxyanions are given in Table 9.

A simple aide-memoir for determining the E.N.C. of an anion containing polyfunctional ligands is to envisage protonation (or methylation) of the polyfunctional ligand. The class of the resulting neutral molecule will be the same as that of the anion. For example protonation of $[SO_4]^{2-}$ gives $SO_2(OH)_2$ (sulphuric acid) which clearly has the class $\mathbf{MX}_6$.

The reduction of the molybdate anion $[MoO_4]^{2-}$ to the E.N.C. also gives the class with V.N. = 6. However, in this case there are empty valency (d) orbitals on the molybdenum centre. Therefore, the class is MoL_lX_6 where l remains to be determined. In the tetrahedral symmetry of the molybdate anion the six X-function bonds are formed by the five molybdenum 4d-orbitals and the single 5s-orbital which are in combination with the e, $1t_2$ and a_1 combinations of orbitals formed by the four oxygen ligands. There remain six electrons arising from the four oxygen ligands which form the $2t_2$ set and these can be donated to the corresponding $2t_2$ molybdenum based orbitals. Therefore, if we deem that the $2t_2$ electrons on the oxygens take part in primary bonding to the molybdenum centre, then the class of the $[MoO_4]^{2-}$ anion is MoL_3X_6, in which case, the anion has an electron count of E.N. = 18. The six electrons in the t_1 set of oxygen-based orbitals cannot be donated to the molybdenum since there are no orbitals of appropriate symmetry on the molybdenum. The variety of ligand systems which can be formed by O, OH and H_2O is shown in Fig. 12.

A.6. Comments on Table 1

In this table NH_3 is classified as L whilst ethylenediamine $H_2NCH_2CH_2NH_2$ is classified as L_2. Clearly, such a distinction is trivial and in chemical terms can only have significance with respect to possible consequences of pre-organisation, such as the entropy-based chelate effect. In any event, this distinction is lost in the final statement of the class of a molybdenum compound, where the only information required is the total number of L- or X-functions without regard to the particular ligands from which they are derived. Therefore, it is reasonable to ask why such a distinction is made which seems at first sight to unnecessarily complicate the table. The reason is that for some polydentate ligand systems and polyfunctional ligands the class is less obvious, e.g. the η-unsaturated hydrocarbon ligands and the linear imido NR ligand (class X_2L). Therefore to help those who wish to identify the class of a compound which contains such ligands it is sensible to indicate their classes. In which case, for the sake of consistency, the trivial distinctions fall better into the organisation than to let them lie outside. Once it is understood that $Mo(CO)_6$ is class ML_6, that MoF_6 is MX_6 and $Mo(PR_3)_3Cl_3$ is MoL_3X_3 then most chemistry students can immediately classify most ligands without the need for the elaborate Table 1. It is the less obvious ligands which introduce the need for a more rigorous, albeit rather pedantic classification.

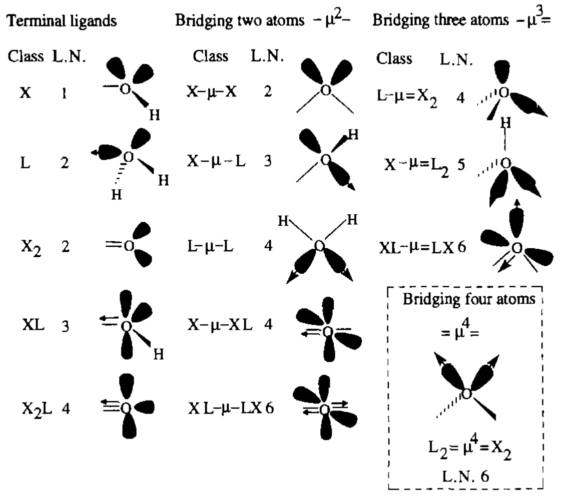

Fig. 12. Examples of ligands which are present in the aqueous environment. They are listed by their **MLX** class and by L.N., the total number of electrons donated to the metal centre by the ligand. Pure p-orbitals (filled) are indicated by + and − symmetry assignments. Orbitals (filled) which are sp^{1-3} hybrids (shaded lone pairs) have no sign given.

It may be noted that ligands which have very different bonding properties occur in the same class, for example, the molecules NH_3 and the π-acid CO. However, the differences in properties of these ligands are strikingly manifested by the very different ligand domains for the two ligands: the compounds $[Mo(NH_3)_6]$ and $[Mo(CO)_6]^{3+}$ are unknown.

A.7. Comments on the definition of coordination number and the relationship to ligand bond number

The C.N. of any chosen atom in a molecule may be defined as the number of ligands atoms which the evidence shows are bonding to the chosen atom. In transition metal compounds it is normally the central transition metal atom whose C.N. is of interest. The only ambiguity with this definition lies in the identification of whether the atoms nearest the central atom are bonding or not. The most important criteria are normally bond distances, vibrational frequencies, etc. However, the advent of unsaturated hydrocarbon ligands, in particular, has caused the term coordination number to be used in a different manner from the definition given above and, for example, some textbooks refer to compounds such as ferrocene and bis-η-benzenechromium

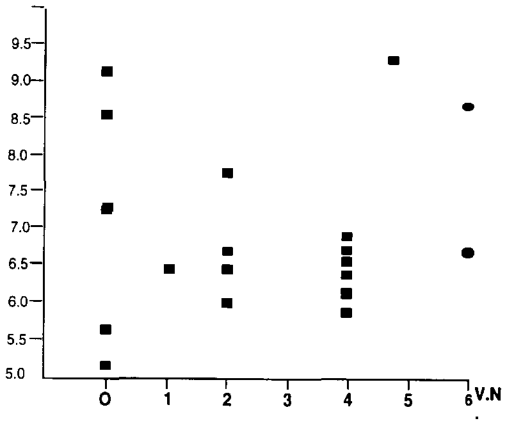

Fig. 13. Showing the distribution of first ionisation energies (eV) of some volatile molybdenum compounds as a function of their valency number (or indeed, their formal oxidation state). It is clear that there is no correlation. ■ ionisation of d^n electrons; ● ionisation of Mo=Mo bonds (d^0 compounds).

Table 10
Comparison of the classification of some manganese compounds by V.N., L.B.N. and E.N. [a] and by formal O.S. and C.N.

Compound	O.S.	C.N.	d^n from O.S. [b]	E.N.	Class	V.N. = x	L.B.N. = $l+x$	d^n from V.N. [b]
$Mn(CO)_5$	? + 1 [c]	6	d^6	18	MnL_5X	1	6	d^6
$Mn(CO)_5Me$	+1	6	d^6	18	MnL_5X	1	6	d^6
$Mn(CO)_5Cl$	+1	6	d^6	18	MnL_5X	1	6	d^6
$Mn(CO)_5(SiMe_3)$	? + 1 [d]	d^6?	18	MnL_5X	1	6	d^6	
$Mn(CO)_5(HgMe)$	? + 1 [d]	d^6?	18	MnL_5X	1	6	d^6	
$Mn(CO)_4NO$	−1	5	d^8	18	MnL_5X	1	6	d^6
$[Mn(CO)_6]^+$	+1	6	d^6	18	MnL_5X	1	6	d^6
$[Mn(CO)_5]^-$	−1	5	d^8	18	MnL_5X	1	6	d^6
$(CO)_5Mn$-$Mn(CO)_5$	0	6	d^7	18	MnL_5X	1	6	d^6
$(CO)_5Mn$-$Re(CO)_5$	?0 [d]	6	d^7?	18	MnL_5X	1	6	d^6
$Mn(\eta$-$C_5H_5)(CO)_3$	+1	8	d^6	18	MnL_5X	1	6	d^6
$Mn(\eta$-$C_5H_5)(CO)_2(\eta-C_2H_4)$	+1	9	d^6	18	MnL_5X	1	6	d^6
$[Mn(\eta$-$C_6H_6)_2]^+$	+1	12	d^6	18	MnL_5X	1	6	d^6

[a] The electron number E.N. must be the same for both methods of classification.

[b] The definition of n for d^n differs for the O.S. method and the CBC method. Thus, n = **Me** − O.S., or, n = **Me** − V.N.

[c] It might be argued (incorrectly) that this compound is acidic and the H should be taken to be H^+.

[d] It might be thought that in this compound the Mn–X bond is sufficiently similar to the Mn–Mn bond in $(CO)_5Mn$–$Mn(CO)_5$ to warrant the value O.S. = 0.

Table 11
First ionisation energies of some molybdenum compounds

Compound	V.N.	I.E. (eV)	Compound	V.N.	I.E. (eV)
$Mo(\eta$-$C_6H_3Me_3)_2$	0	5.13	$Mo_2(CMe_3COO)_4$	6	6.75
$Mo(\eta$-$C_6H_6)_2$	0	5.52	$Mo_2(NMe_2)_4$	6	6.76
$Mo(\eta$-$C_5H_5)(\eta$-$C_7H_7)$	4	5.87	$Mo(\eta$-$C_5H_5)_2Cl_2$	4	6.8
$Mo(\eta$-$C_5H_5)_2(\eta$-$C_2H_4)$	2	6.0	$Mo(\eta$-$C_5H_5)_2CO$	2	6.9
$Mo(\eta$-$C_5H_5)_2NPr^i$	4	6.09	$Mo(\eta$-$C_4H_6)_3$	0	7.23
$Mo(\eta$-$C_5H_5)_2Me_2$	4	6.1	$Mo(\eta$-$C_6H_3Me_3)(CO)_3$	0	7.24
$Mo(\eta$-$C_5H_5)_2H_2$	4	6.4	$Mo(\eta$-$C_5H_5)(CO)_3Me$	2	7.78
$Mo(\eta$-$C_6H_6)(\eta$-$C_3H_5)_2$	2	6.44	$Mo(CO)_6$	0	8.5
$Mo(\eta$-$C_5H_5)(\eta$-$C_6H_6)$	1	6.46	$Mo_2(CF_3COO)_4$	6	8.67
$Mo(\eta$-$C_5H_4Me)_2(O)$	4	6.55	$Mo(PF_3)_6$	0	9.2
$Mo_2(\eta$-$C_3H_5)_4$	4	6.72	$MoCl_5$	5	9.27

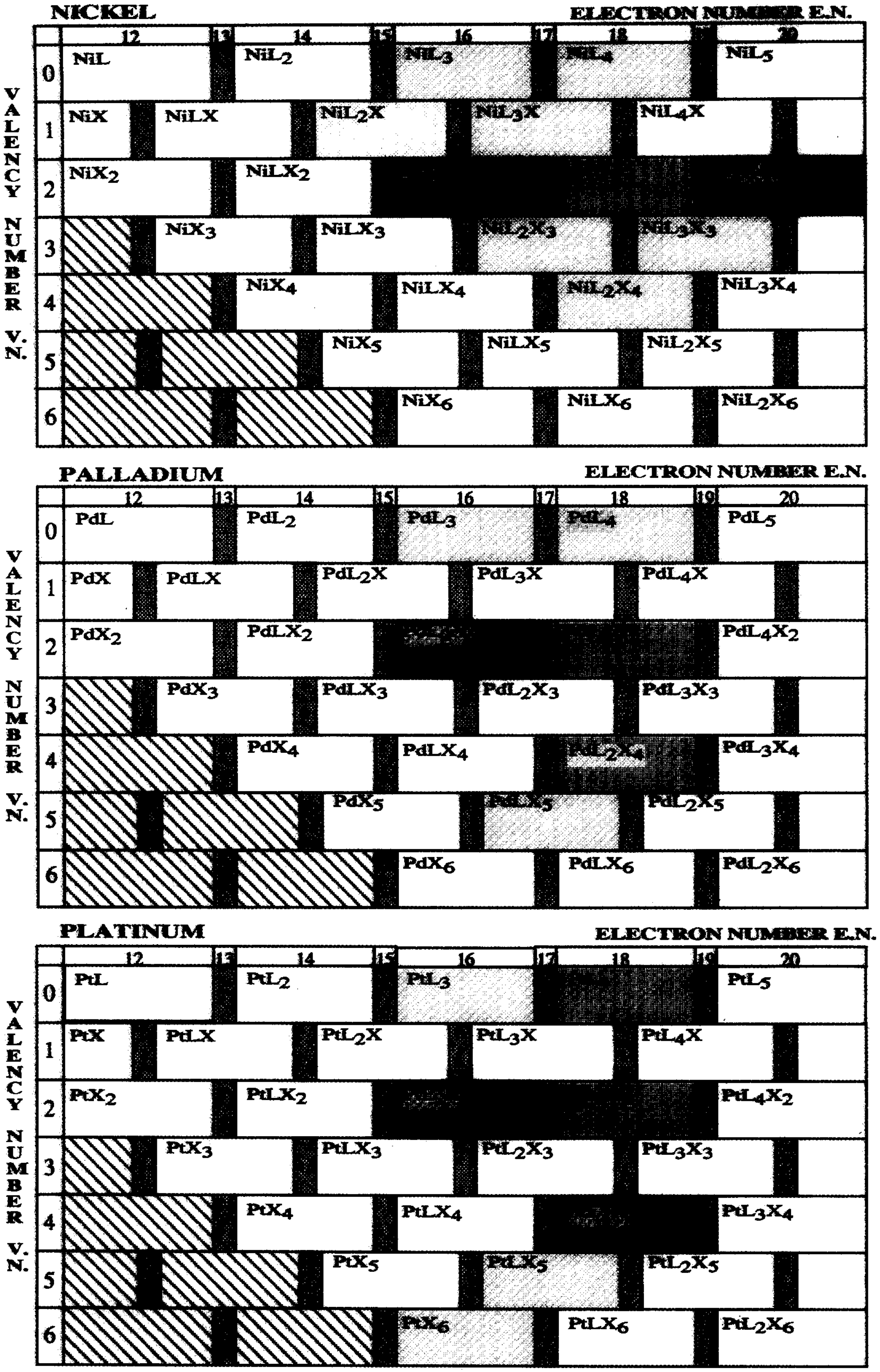

Fig. 14. The MLX plots for nickel, palladium and platinum.

as having a "pseudo-coordination number" of six rather than ten and twelve, respectively. This "pseudo" extension of the concept of coordination number is clearly not rigorous and is of little or no value for classification purposes. The ligand bond number, defined as L.B.N. = $l + x$, relates directly to the class of a compound in a chemically meaningful manner and provides a more useful method of classification than C.N. Meanwhile, the use of C.N. as "the number of coordinating atoms" remains a clearly defined and often useful concept. Table 10 compares the C.B.C. method and the traditional classification method by formal O.S. state and C.N. for a selection of manganse compounds. Clearly, the C.B.C. method provides a higher degree of organisation.

There is no simple correlation between the V.N. or O.S. of compounds and the electron "richness" or "poorness" of the metal centres. This point is demonstrated in Fig. 13 which shows the total lack of correlation between values of the first ionisation energies for a selection of molybdenum compounds. The data for the I.E. vs. V.N. plot in Fig. 13 are given in Table 11. The first ionisation energies arise from electrons located in essentially d-orbitals for d^n compounds where $n = 6$–1.

A.8. The future of molybdenum chemistry

It is interesting to consider how the the general appearance of the **MLX** plot for molybdenum has developed during the last fifty years or so and how it will change in the future. To provide an accurate answer to the first question would require many library hours. Most of the early compounds would have been stable to oxygen and water. The greatest change in the last 20–30 years has been the development of the low V.N. chemistry of molybdenum, for example the compounds in the classes MoL_6 and MoL_5X_2 which are now amongst the most abundant classes but which were virtually unknown before the 1950s.

As to the future, I predict that whilst many more molybdenum compounds will be prepared the general pattern will change little, but there may be some chemistry in the domain V, as discussed in Section 3.3. This prediction is based in the assumption that by now the extremes of electronic and steric properties for all possible ligand environments have been explored.

A.9. MLX plots for nickel, palladium and platinum

The title plots are shown in Fig. 14. These have been provided to demonstrate the use of **MLX** plots as a powerful aid for the identification of the similarities and differences between the chemistries of the Group 6 metals Cr, Mo and W and the Group 10 metals. Inspection of the **MLX** plots of clearly leads to the following observations:

(i) The favourable stability of square-planar, 16-electron, d^8 compounds of the Group 10 elements is self evident from their **MLX** plots. Nonetheless, 18-electron compounds are also quite common.

(ii) Odd-electron compounds, i.e. V.N. = 1 or 3, are very rare indeed for all of these elements, for which **Me** is even. The elements Ni, Pd and Pt show no consecutive diagonal sequences of compounds with a constant L.B.N. and, in marked contrast to Cr, Mo and W, they have very little redox chemistry.

(iii) The elements Pd and Pt show two well-populated classes related by $+/-X_2$ reactions; these are the classes Pd(or Pt)L_2X_2 and Pd(or Pt)L_2X_4. Therefore, oxidative-addition and reductive-elimination reactions are expected to be a dominant feature of the chemistry of these palladium and platinum compounds, as is observed. As noted earlier oxidative-addition reactions are rare for molybdenum.

(iv) Nickel, and to a lesser degree palladium, show a limited chemistry for V.N. > 2. This is a consequence of the higher ionisation potentials for Ni and Pd (compared with molybdenum). The greater population of V.N. = 4 for platinum is clear and reflects the general trends towards increasing occurence of higher V.N. in the sequence 6d > 5d > 3d.

(v) For Ni, Pd and Pt (**Me** = 10) the highest observed ligand bond numbers are 6 and these occur when the electron number is 18 (20 for Ni). Contrast Cr, Mo and W which have compounds with values of L.B.N. of 6–9. However, Ni, Pd and Pt compounds are found with L.B.N. = 3 (rare) and 4 (common) and these values are unknown for Cr, Mo or W (except CrR_4, where R = a bulky alkyl). Such low L.B.N. values mean that ligand addition reactions (and hence ligand substitution by associative processes) will have low steric barriers.

(vi) The occurrence of the sequence of populated classes for nickel NiL_lX_2, where $l = 2$, 3 and 4, shows considerable substitutional lability. NiL_2X_2 compounds should perform substitution reactions by associative processes and NiL_4X_2 compounds will react by dissociative mechanisms while for NiL_3X_2 both associative and dissociative processes will occur. In contrast, Pd(and Pt)L_3X_2 compounds will be expected to undergo substitution by dissociative mechanisms.

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