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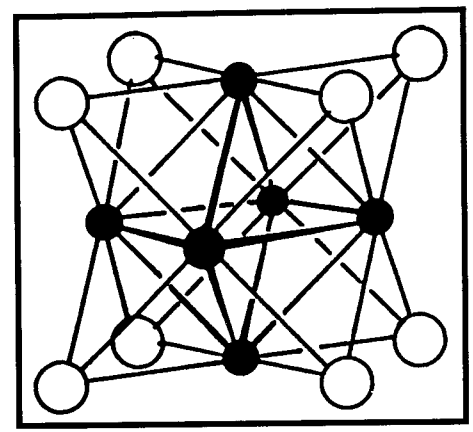
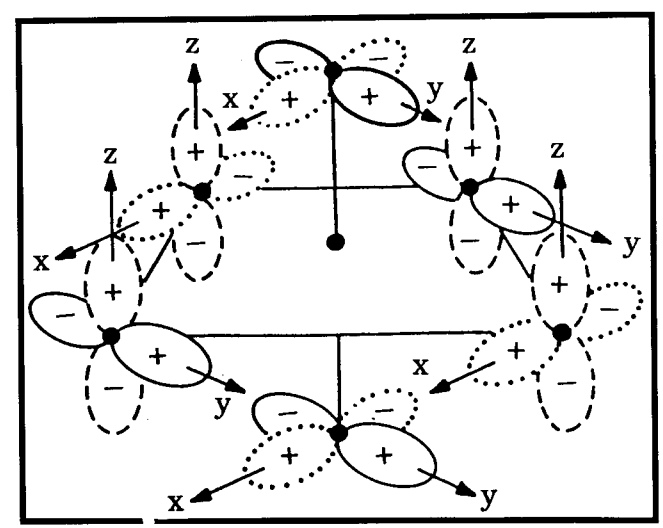


THE THEORY OF TRANSITION METAL COMPLEXES



CHEMISTRY CASSETTE
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THE THEORY OF TRANSITION METAL COMPLEXES

by
Sidney Kettle

Sidney Kettle graduated from the University of Leeds and obtained his doctorate at Cambridge, working on the chemistry of the tin hydrides. A post-doctoral period in the Department of Theoretical Chemistry at Cambridge kindled an interest in the theoretical aspects of Inorganic Chemistry along with the practical. A series of appointments over a ten year period at the University of Sheffield was followed by appointment to a chair in the University of East Anglia. Some thirteen years later he took early retirement but his work in chemistry, if anything, increased as a result. He currently carries out research in cooperation with a number of research groups, from Japan to Italy. He has published about two hundred research papers and is the author or co-author of five books, a number which continues to grow. He is Editor of *Spectrochimica Acta A*, is a Professorial Fellow of the University of East Anglia and Adjunct Professor at the Royal Military College, Kingston, Ontario. He has a particular interest in the application of symmetry to chemical problems, especially problems concerning the Solid State.

Professor Kettle is the author of two other cassette programmes in the series, *Symmetry in Chemistry* and *Coordination Chemistry*.

CHEMISTRY CASSETTE
Educational Techniques Group Trust
Royal Society of Chemistry

Chemistry Cassettes

General Editor: Peter Groves

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Please read before you start

This Chemistry Cassette programme has two components – the audio-cassette and this workbook. They are designed to be used together so make sure that you have them both with you before you start.

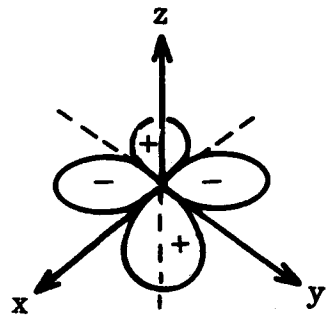
So that you can easily find material in the workbook it has been divided into numbered sections called 'frames'. These contain diagrams, tables and other relevant material and Professor Kettle will refer you to these as he proceeds through the programme.

The programme is 'self-pacing' – this means that you can work through it at your own pace, stopping the tape player whenever you want to pause for thought or to study material in the frames. You can also use the rewind control to repeat material that you may not have fully understood on a first hearing. You should also make appropriate notes to supplement the material in the workbook.

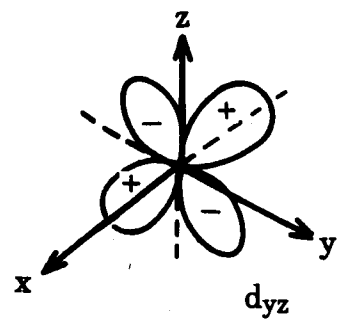
Introduction

In recent years the subject matter of this Chemistry Cassette programme has received less and less attention in most inorganic texts, to the point at which it has become almost inaccessible to students. This is in contrast to the situation some twenty years ago, when it was given an undue prominence. Unfortunately, at that time, the presentation generally left much to be desired and there can be little doubt that it was this, perhaps with the perceived inherent difficulty of parts of the subject, that led to the reduced time devoted to it. Unfortunately, along with the content have disappeared the insights. Further, the fascinating advances that have been made in recent years have shed new lights on parts of the subject but it is doubtful that this has been fully recognised. All this points to a need to attempt to present the subject matter of this programme in an accurate, understandable and non-mathematical way. This, of course, is what I have attempted to achieve. The method that I have adopted is to make use of the fact that many coordination compounds have highly symmetrical basic structures and I have therefore exploited symmetry to the full. While I have tried to introduce the symmetry concepts as fully as possible, I have not been able to explore the basics of the subject. However, this has been covered in another Chemistry Cassette programme *Symmetry in Chemistry* that should provide an adequate introduction and some time spent on this would be time well spent.

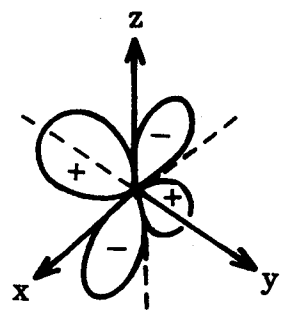
Sidney Kettle



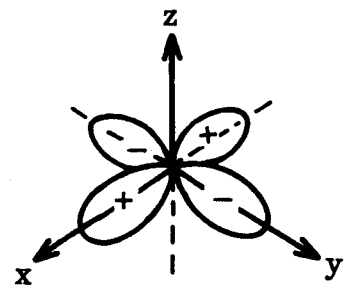
d_{xy}



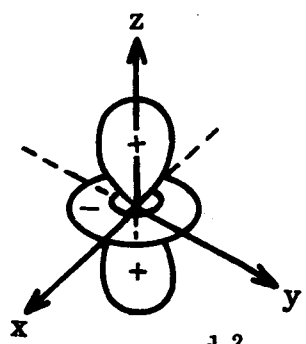
d_{yz}



d_{zx}

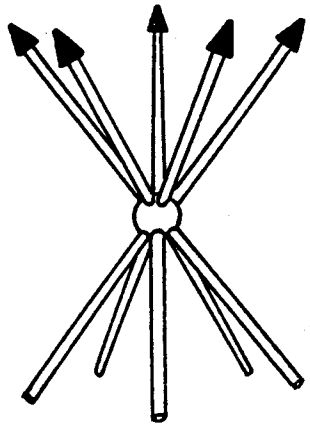


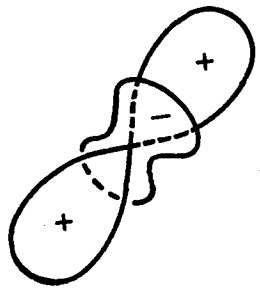
$d_{x^2-y^2}$



d_{z^2}

2



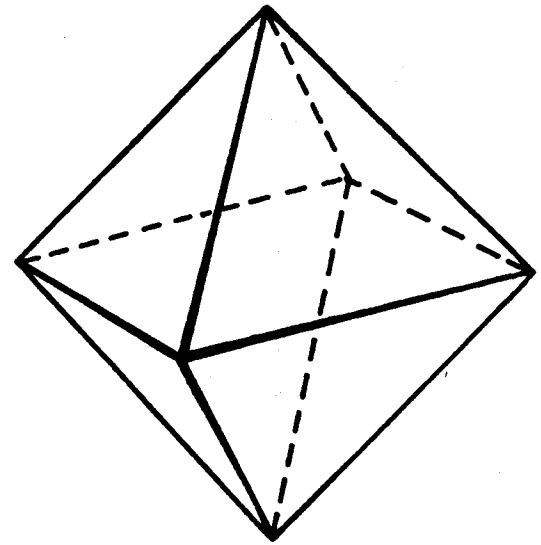


Top: axes of orientation of five d-orbitals of the same shape.

Bottom: one of the same-shape d-orbitals (that 'along' the right-hand axis in the upper half of the top diagram).

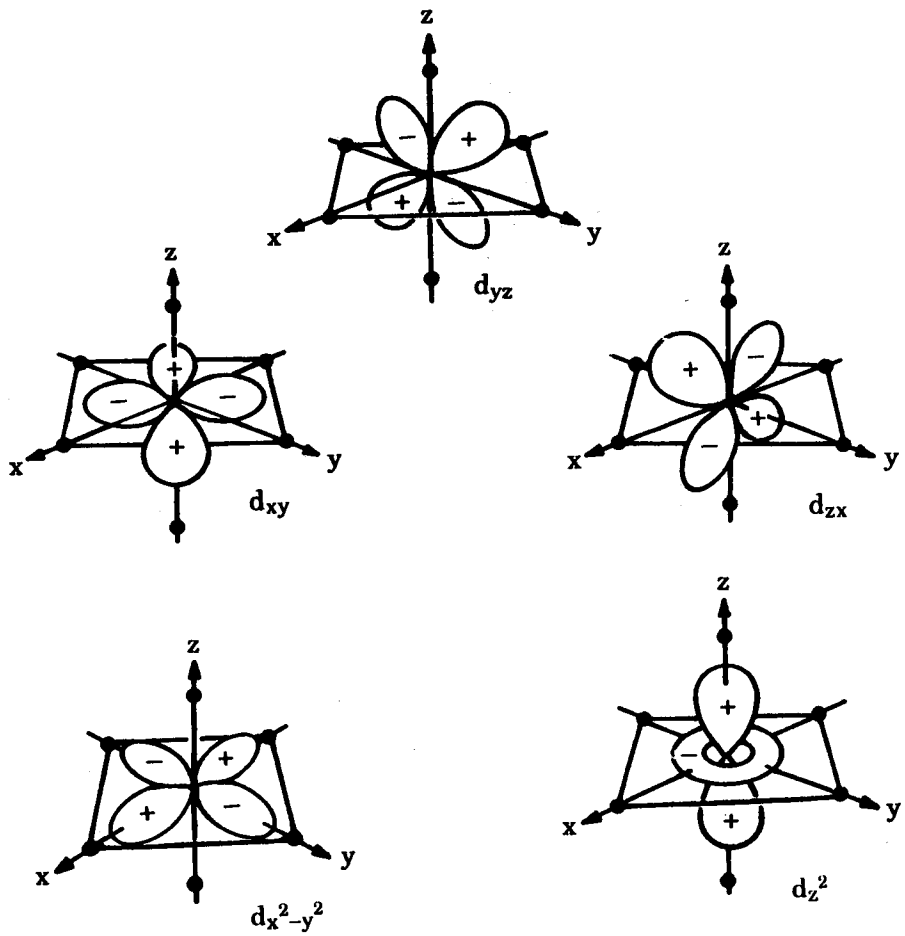
Note: there is also a second set of same-shape d-orbitals. For these the five axes are pitched lower, and the central orbital lobes larger, than those pictured above.

3



An octahedron. An octahedron has eight equivalent, equilateral triangular, faces, six equivalent vertices and twelve equivalent edges.

4

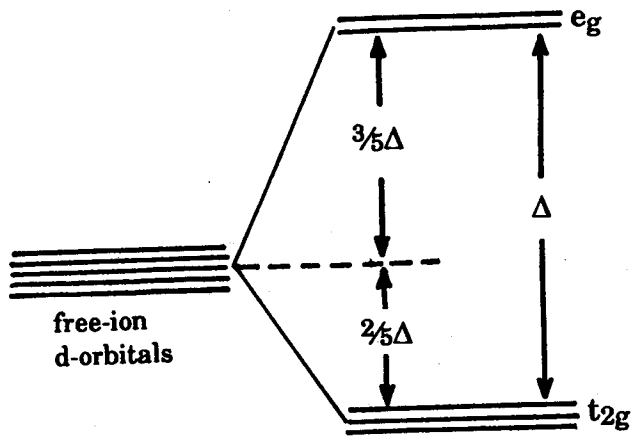


5

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$r^2 = x^2+y^2+z^2$
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	
E_g	2	–1	2	0	0	2	–1	2	0	0	(z^2, x^2-y^2)
T_{1g}	3	0	–1	1	–1	3	0	–1	1	–1	
T_{2g}	3	0	–1	–1	1	3	0	–1	–1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1	
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	
E_u	2	–1	2	0	0	–2	1	–2	0	0	
T_{1u}	3	0	–1	1	–1	–3	0	1	–1	1	(x, y, z)
T_{2u}	3	0	–1	–1	1	–3	0	1	1	–1	

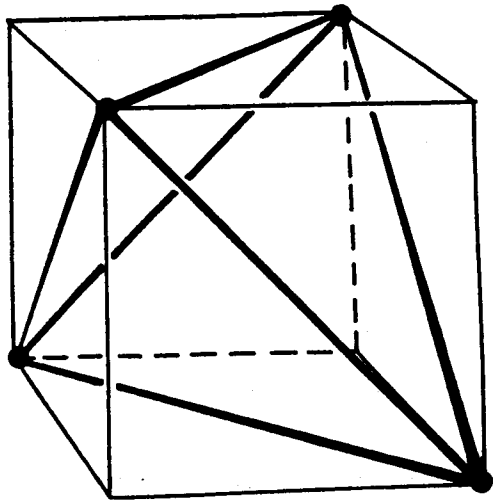
The O_h character table

6



Splitting of d-orbitals in an ML_6 octahedral complex

7



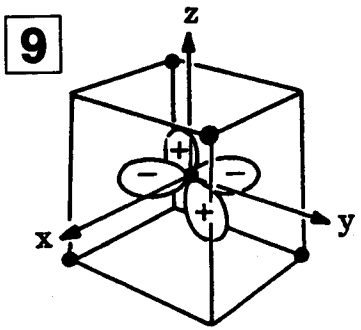
The relationship between a cube and a tetrahedron (the apices of the cube not involved in the tetrahedron shown actually define a second tetrahedron).

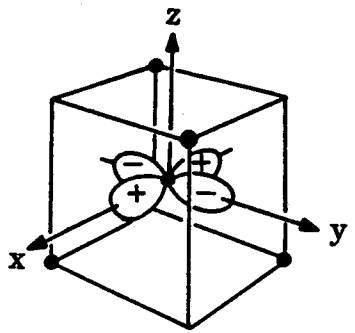
8

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$r^2 = x^2+y^2+z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	(z^2, x^2-y^2)
T_1	3	0	−1	1	−1	
T_2	3	0	−1	−1	1	(x, y, z) (xy, yz, zx)

The T_d character table

9





d_{xy} (d_{yz} and d_{zx} are similar) $d_{x^2-y^2}$ (d_{z^2} is degenerate with this)

d orbitals in a tetrahedral ligand field

10

Symmetries of the orbitals of the central metal atom in a ML_6 complex of octahedral (O_h) symmetry

Orbital	Symmetry
s	a_{1g}
(p_x, p_y, p_z)	t_{1u}
(d_{z^2}, $d_{x^2-y^2}$)	e_g
(d_{xy}, d_{yz}, d_{zx})	t_{2g}

11

	E	$8C_3$	$3C_2$	$6C_4$	$3C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
6 ligand σ	6	0	2	2	0	0	0	4	0	2
Number of operations in the class	1	8	3	6	3	1	8	3	6	6
Multiply:	6	0	6	12	0	0	0	12	0	12

(This line will be used for all the following calculations)

a) Test for A_{1g}

A_{1g}:	1	1	1	1	1	1	1	1	1	1
Multiply	6	0	6	12	0	0	0	12	0	12

Add = 48 (= 1 × order of the group [48]) : 1 A_{1g}

b) Test for A_{2g}

A_{2g}:	1	1	1	–1	–1	1	1	1	–1	–1
multiply	6	0	6	–12	0	0	0	12	0	–12

add = 0

c) Test for E_g

E_g:	2	–1	2	0	0	2	–1	2	0	0
multiply	12	0	12	0	0	0	0	24	0	0

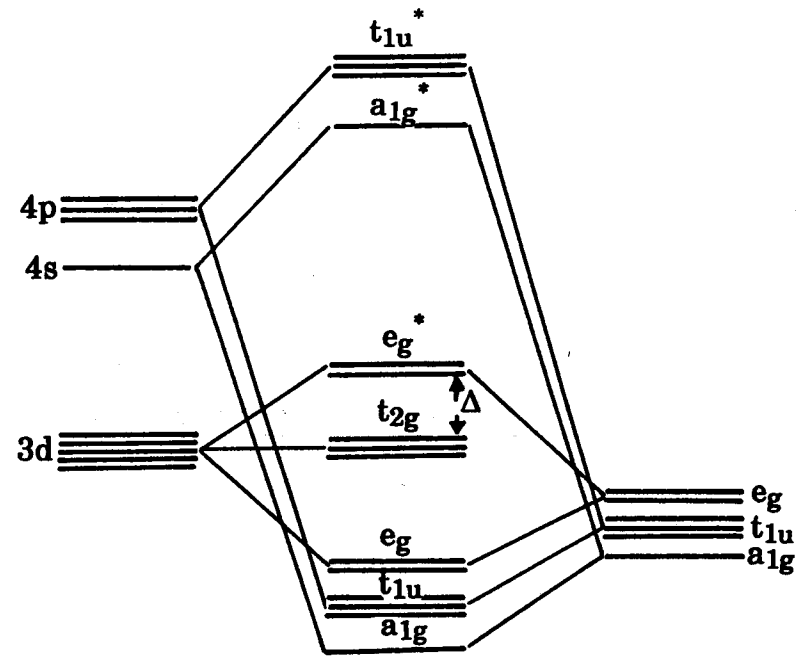
add = 48 ➡ $1E_g$

d) Test for T_{1u}

T_{1u}:	3	0	–1	1	–1	–3	0	1	–1	1
multiply	18	0	–6	12	0	0	0	12	0	12

add = 48 ➡ $1T_{1u}$

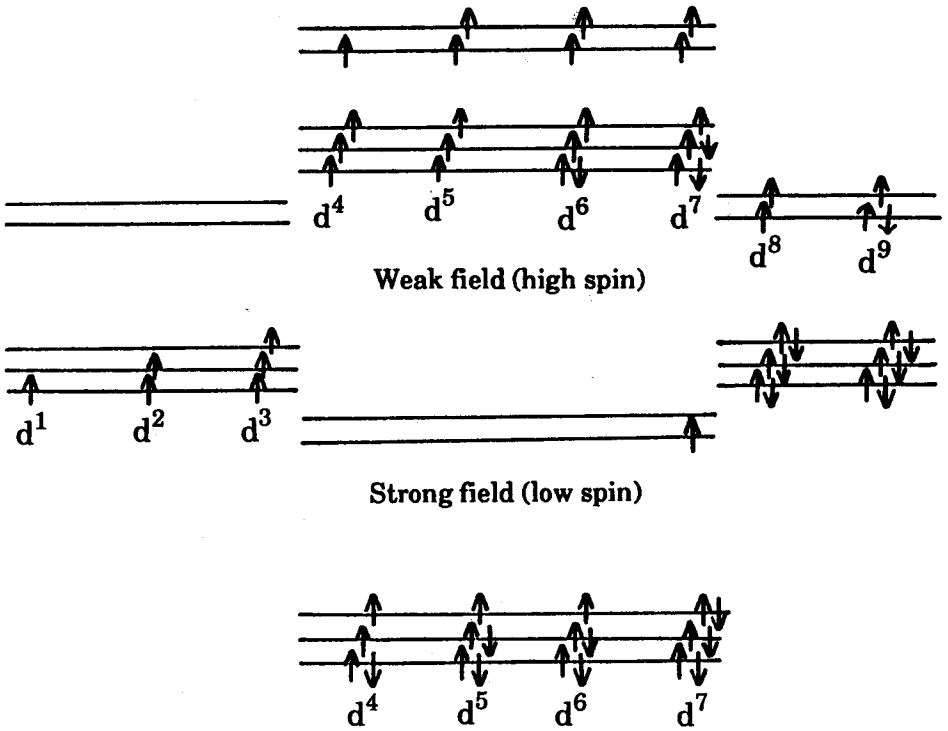
12



metal orbitals molecular orbitals ligand orbitals

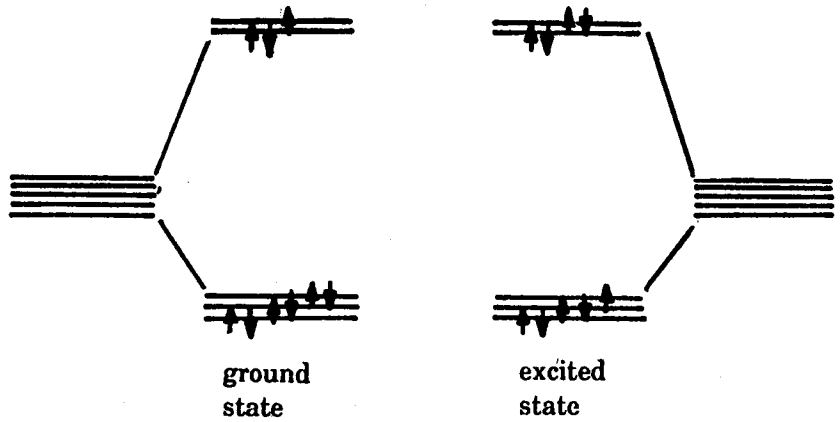
A schematic σ-orbital energy-level scheme for octahedral complexes

13



Weak and strong field arrangements of d electrons in an octahedral ligand field.

14

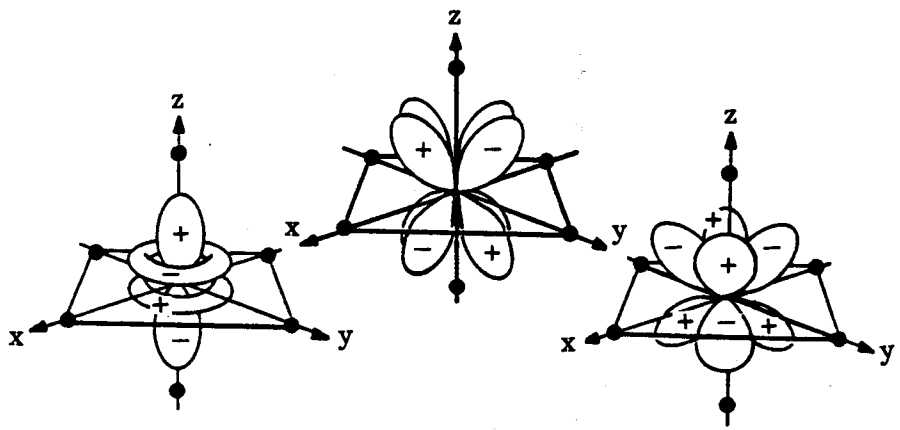


configuration:	$t_{2g}^{6}e_g^{3}$	$t_{2g}^{5}e_g^{4}$
term:	^2E_g	$^2T_{2g}$

Ground and electronic excited state configurations and terms for octahedral Cu(II), d^9

15

The three sets of f-orbitals in an octahedral crystal field



f_{z^3}	$f_{z(x^2-y^2)}$	f_{xyz}
(f_{x^3} and f_{y^3} are similar)	($f_{z(y^2-z^2)}$ and $f_{y(z^2-x^2)}$ are similar)	
t_{1u}	t_{2u}	a_{2u}

16

Orbitals and d-electron free-atom terms in an octahedral crystal field

orbital type	splitting in O_h	d-electron free atom term	splitting in O_h
s	a_{1g}	S	A_{1g}
p	t_{1u}	P	T_{1g}
d	e_g+t_{2g}	D	E_g+T_{2g}
f	$a_{2u}+t_{1u}+t_{2u}$	F	$A_{2g}+T_{1g}+T_{2g}$
g	$a_{1g}+e_g+t_{1g}+t_{2g}$	G	$A_{1g}+E_g+T_{1g}+T_{2g}$
h	$e_u+2t_{1u}+t_{2u}$	H	$E_g+2T_{1g}+T_{2g}$
i	$a_{1g}+a_{2g}+e_g+t_{1g}+2t_{2g}$	I	$A_{1g}+A_{2g}+E_g+T_{1g}+2T_{2g}$

[G, H and I terms occur but never with the highest spin multiplicity in d^n systems]

17

The direct product $T_{2g} \times E_g$

	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1
E_g	2	−1	2	0	0	2	−1	2	0	0
multiply	6	0	−2	0	0	6	0	−2	0	0

This is a sum of $T_{1g} + T_{2g}$

T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1
add	6	0	−2	0	0	6	0	−2	0	0

Alternatively, the more formal method detailed in frame 11 can be used to reduce the representation. So, the $t_{2g}^1 e_g^1$ configuration gives rise to the terms

$^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$

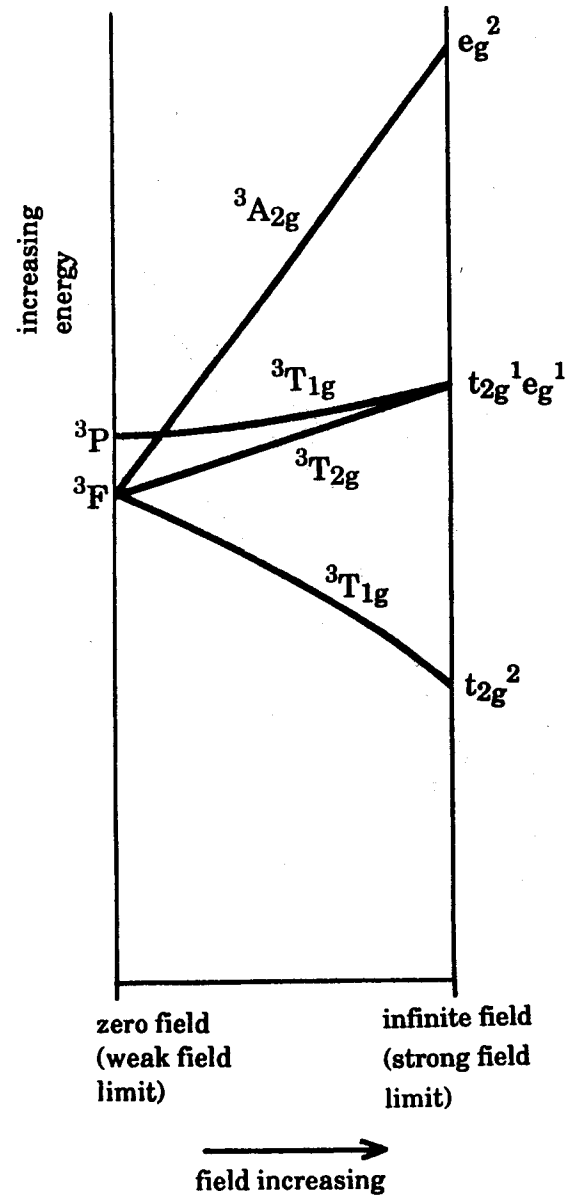
(since both spin triplets and singlets are equally admissible).

18

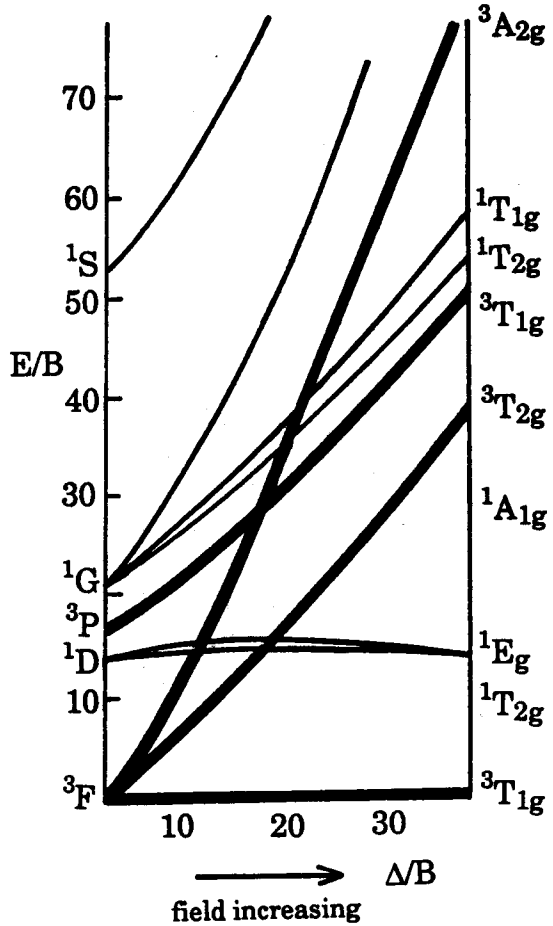
Direct products applicable to octahedral transition metal complexes.

	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{1g}	A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}
A_{2g}	A_{2g}	A_{1g}	E_g	T_{2g}	T_{1g}
E_g	E_g	E_g	$A_{1g}+A_{2g}+E_g$	$T_{1g}+T_{2g}$	$T_{1g}+T_{2g}$
T_{1g}	T_{1g}	T_{2g}	$T_{1g}+T_{2g}$	$A_{1g}+E_g+T_{1g}+T_{2g}$	$A_{2g}+E_g+T_{1g}+T_{2g}$
T_{2g}	T_{2g}	T_{1g}	$T_{1g}+T_{2g}$	$A_{2g}+E_g+T_{1g}+T_{2g}$	$A_{1g}+E_g+T_{1g}+T_{2g}$

19

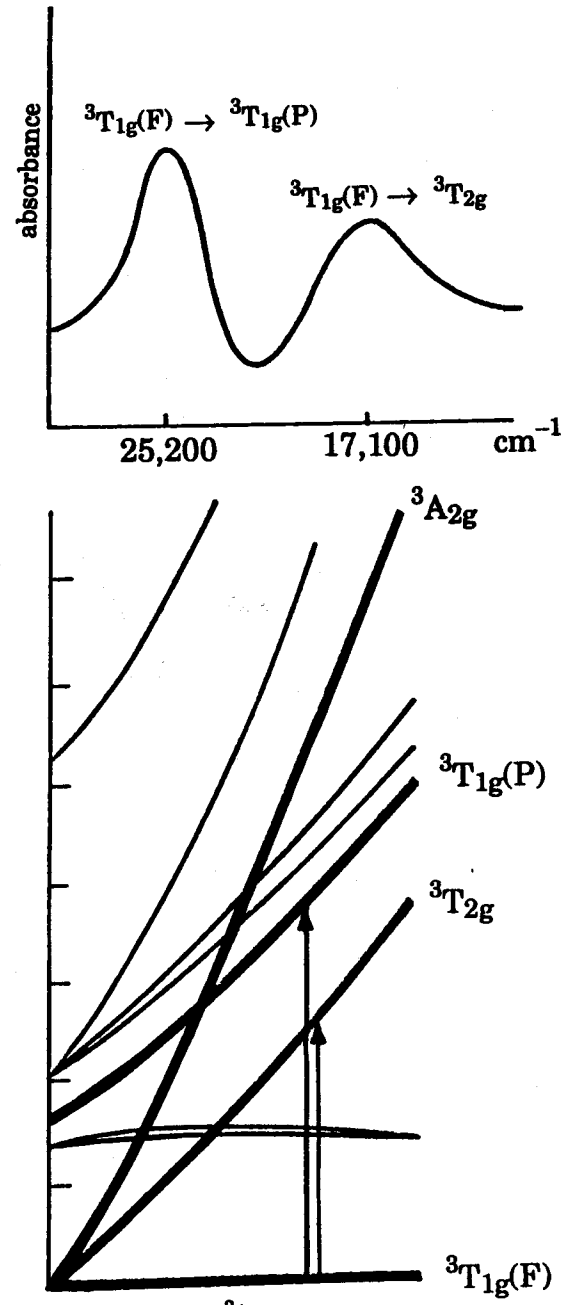


20



A Tanabe-Sugano diagram for the d^2 configuration. The lines corresponding to those in frame 19 are shown bold. Energies are plotted as the dimensionless quantities E/B and Δ/B (B is an electron repulsion energy which comes into the detailed theory).

21



Top: the d–d spectrum of $[V(H_2O)_6]^{3+}$ and (bottom) its interpretation using the Tanabe Sugano diagram of frame 20

frame 21 continues ➡

➡ frame 21 continued

As discussed on the cassette, despite its curvature in the above diagram, the energy of the $^3T_{2g}$ term is a linear function of Δ. However, the energies of both $^3T_{1g}$ terms depend on both Δ and the electron repulsion energy B.

Explicitly, detailed calculations give:
energy of the lower energy band

$$= \tfrac{1}{2}[\Delta - 15B + \sqrt{(225B^2 + 18B\Delta + \Delta^2)}]$$

energy of the higher energy band

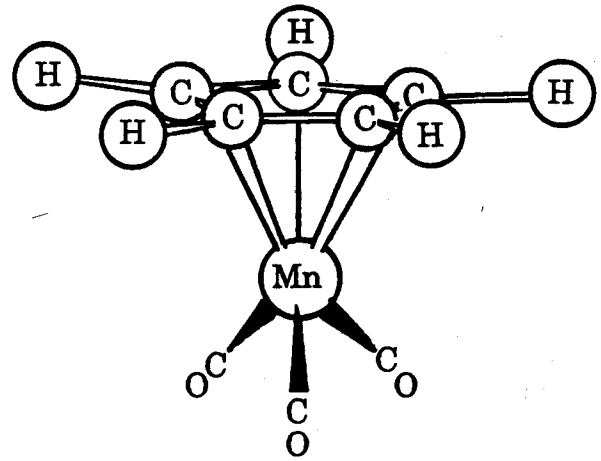
$$= \sqrt{(225B^2 + 18B\Delta + \Delta^2)}$$

These equations contain two unknowns, Δ and B. If B is given its free ion value (the crystal field model) then two values of Δ are obtained from the spectra (19,600 cm^{-1} and 15,500 cm^{-1}). If B is also determined from the spectra (the ligand field model), it is found to be 665 cm^{-1} (free ion value = 860 cm^{-1}) and Δ = 18,600 cm^{-1}. The reduced value of B, a smaller repulsion energy, in the complex is associated with a more diffuse, more delocalized, electron density distribution, indicating covalency.

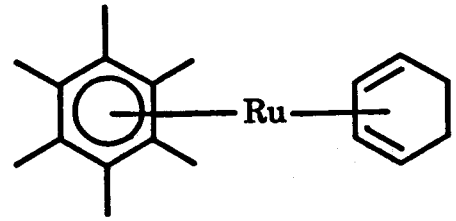
22

Some molecules containing ligands typical of transition metal organometallc complexes.

a) The molecule $C_5H_5Mn(CO)_3$, cyclopentadiene tricarbonylmanganese



b) The molecule 1,3 cyclohexadiene hexamethylbenzeneruthenium

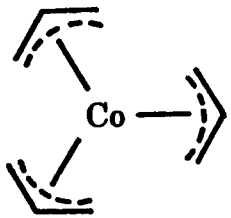


This molecule is represented in a way which is more common than that used in the first example.

frame 22 continues ➡

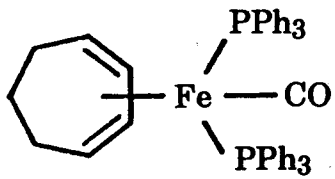
➡ frame 22 continued

c) The molecule tris-allyl cobalt



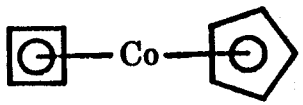
This structure shows an alternative way that delocalised π electrons are represented.

d) The molecule 1,3 cycloheptadiene bis (triphenylphosphine)carbonyl iron.



Ligands containing P, S, N and, sometimes, O donor atoms are quite common.

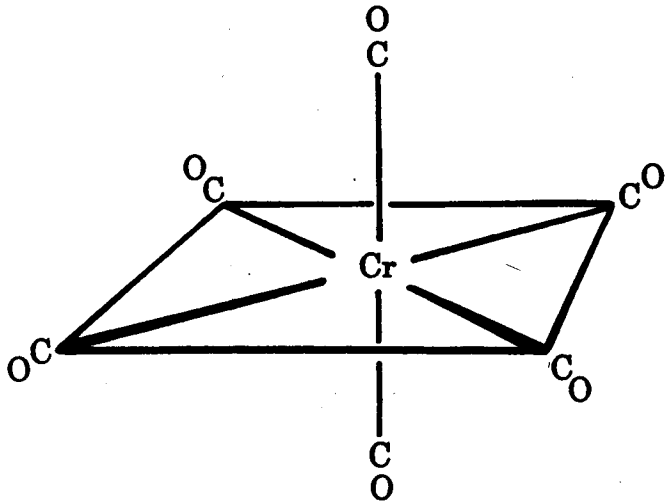
e) The molecule cyclobutadiene cyclopentadienyl cobalt.



This complex contains a ligand, C_4H_4, which is not stable as a free molecule.

Note: the names used for compounds in this frame are relaxed – of the sort chemists use when talking. Longer, more systematic, names also exist.

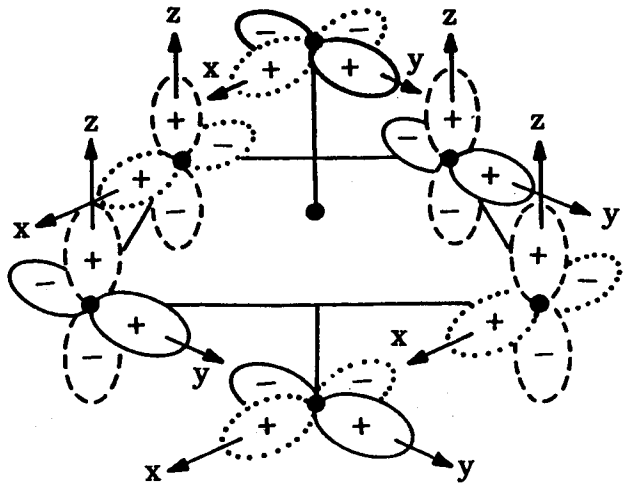
23

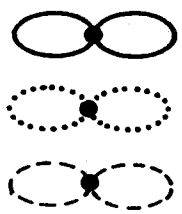


The octahedral molecule $Cr(CO)_6$. The chromium(0) has the free atom configuration .....$3d^5 4s^1$, but in the complex all these valence shell electrons would be accommodated within the d-orbitals and, therefore, in the complex the configuration is .....t_{2g}^6. The lines between CO groups are included as an aid to identification of this as an octahedral complex – they are not bonds.

24

In the diagram each π orbital is represented as a p-orbital on the carbon.





π_y orbitals are shown solid

π_x orbitals are shown dotted

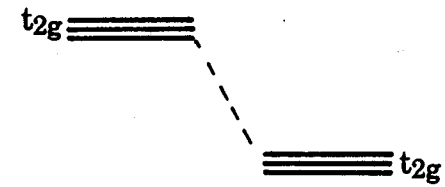
π_z orbitals are shown dashed

The transformation of these twelve π orbitals is given below.

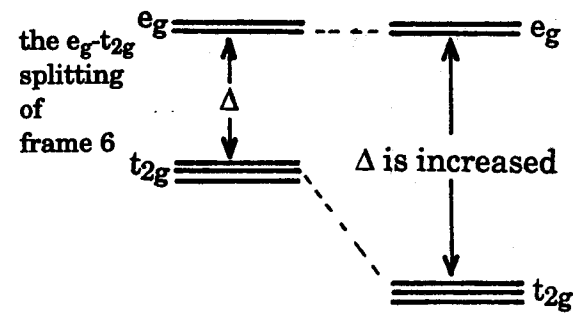
	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
12 ligand π	12	0	−4	0	0	0	0	0	0	0
This is a sum of:										
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1
	12	0	−4	0	0	0	0	0	0	0

as may also be shown by using the method of frame 11.

25



the carbon monoxide (empty) t_{2g} π^* orbitals of frame 24

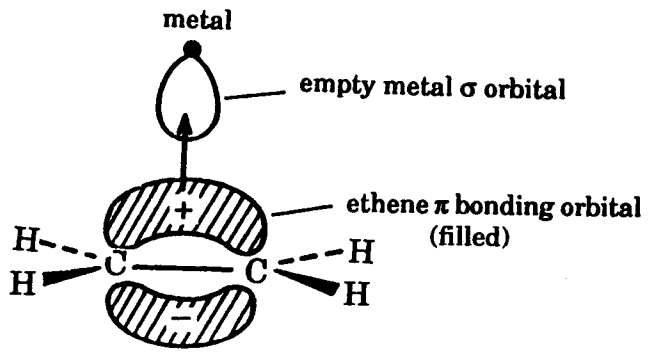


the e_g-t_{2g} splitting of frame 6

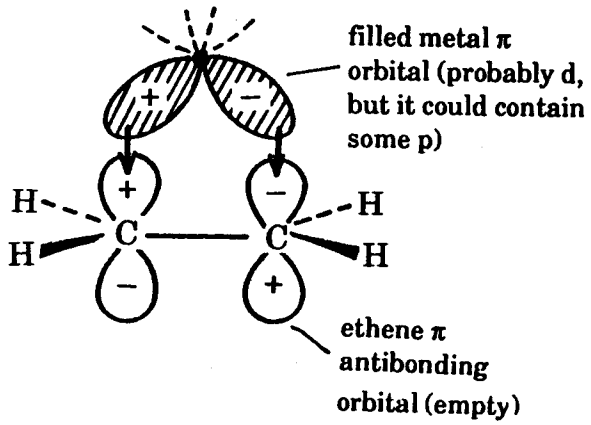
The interaction between the metal t_{2g} orbitals and the CO t_{2g} (π^*) leads to an increase in Δ compared to the hypothetical value with no CO π^* involvement.

26

σ donation
alkene → metal

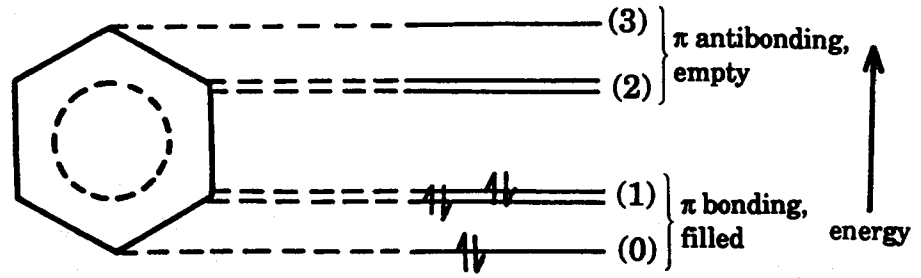


π back-donation
metal → alkene



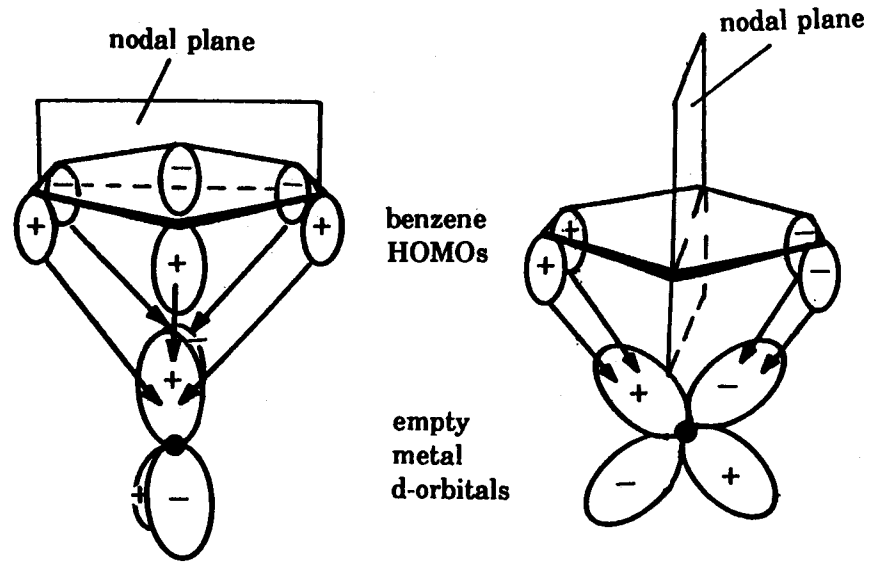
27

The π molecular orbitals of benzene:



The number of nodes associated with an orbital (or each member of a pair of orbitals) is given in brackets.

Most important in donation to the metal will be the benzene HOMO (the highest occupied molecular orbital):

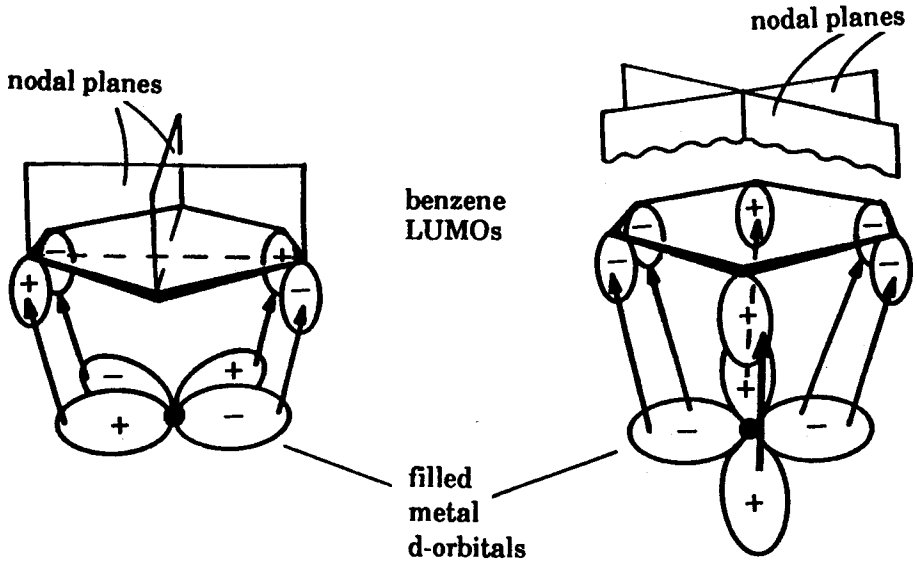


For simplicity, only the bottom half of the p_π orbitals on the benzene are shown.

frame 27 continues ➡

➡ frame 27 continued

Most important in accepting electrons from the metal will be the LUMO (lowest unoccupied molecular orbital):



Notice that although the principle follows that shown in frame 26 (hydrocarbon HOMO donating, LUMO accepting) the actual nodal planes differ. Notice, too, that the HUMO π^* (highest unoccupied π^* antibonding molecular orbital) has too many nodal planes to interact with any metal orbital.

Note, too, that in 18-electron rule counts (frame 29) the two electrons in the lowest π bonding molecular orbital are counted in. These electrons can be donated into an empty metal orbital similar to that shown for ethene in frame 26.

28

Zerovalent tin has the electron configuration $\ldots 5s^2 5p^2$ but the promotion energy required to give $5s^1 5p^3$ is more than compensated by the ability to form two more bonds.

According to one's taste one could say that the tin is sp^3 hybridised and so forms 'conventional' σ bonds with $CH_3\bullet$ groups to give the tetrahedral molecule $SnMe_4$. Alternatively, one could say that in tetrahedral $SnMe_4$ the tin 5s orbital interacts with a combination of methyl σ orbitals of A_1 symmetry and the tin 5p orbitals interact with three combinations of methyl σ orbitals which, together, have T_2 symmetry (see frame 8).

29

We take as examples of the 18-electron rule those molecules given in frame 22.

a) $C_5H_5Mn(CO)_3$

$C_5H_5^-$ contributes	6 valence electrons
Mn^+ contributes	6 valence electrons
each CO contributes 2, a total of	6 valence electrons
	18

b) $C_6H_8RuC_6Me_6$

the C_6H_8 contributes	4 valence electrons
the Ru(0) contributes	8 valence electrons
the C_6Me_6 contributes	6 valence electrons
	18

frame 29 continues ➡

➡ frame 29 continued

c) $(C_3H_5)_3Co$

each C_3H_5 contributes 3, a total of	9 valence electrons
the Co(0) contributes	9 valence electrons
	18

d) $C_7H_{10}Fe(CO)(PPh_3)_2$

the C_7H_{10} contributes	4 valence electrons
the Fe(0) contributes	8 valence electrons
the CO contributes	2 valence electrons
each PPh_3 contributes 2, a total of	4 valence electrons
	18

e) $C_4H_4CoC_5H_5$

the C_4H_4 contributes	4 valence electrons
the Co^+ contributes	8 valence electrons
the $C_5H_5^-$ contributes	6 valence electrons
	18

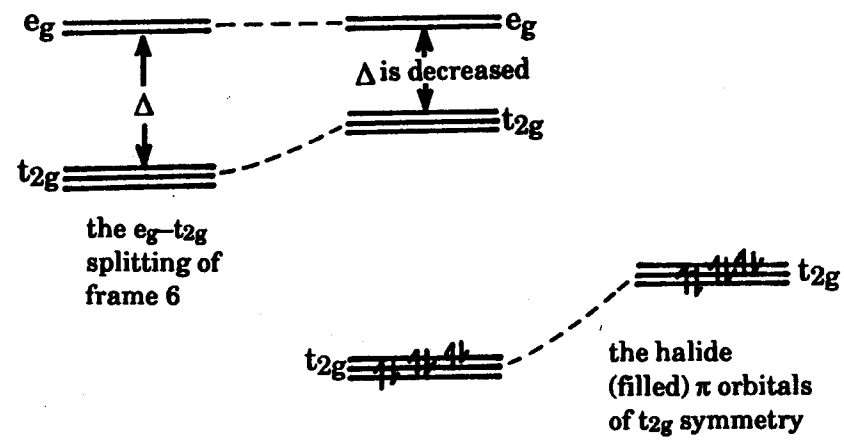
Note 1: In examples a) and e) we could have used C_5H_5 — five valence electrons — and zerovalent metal without changing the final electron count.

Note 2: The basis of the 18-electron rule seems to be that there are nine valence orbitals on a transition metal ($1\times$ s, $3\times$ p, $5\times$ d) and each is associated with a bonding molecular orbital.

Note 3: Species which fail to 'obey' the 18-electron rule are usually 16-electron species and have an obvious 'hole' – they are square planar complexes, for instance.

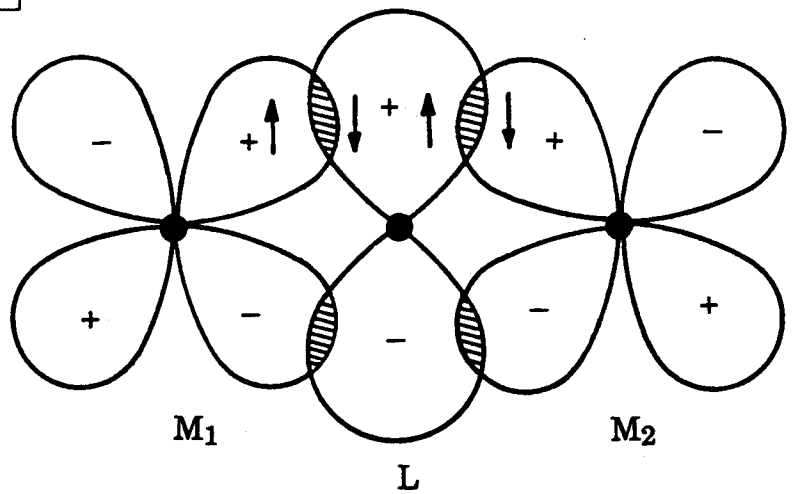
Note 4: In example e the C_4H_4 could be regarded as $C_4H_4^{2-}$ and a six electron donor, in which case the cobalt would have to be regarded as Co^{3+}. The electron sum would be unchanged.

30



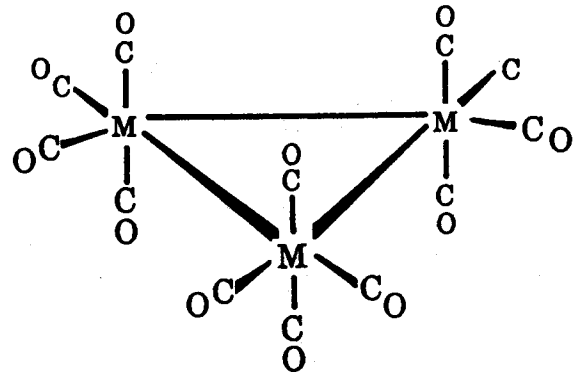
The interaction between the metal t_{2g} orbitals and halide filled π orbitals of t_{2g} symmetry leads to a decrease in Δ compared to the hypothetical value of Δ with no halide π involvement.

31

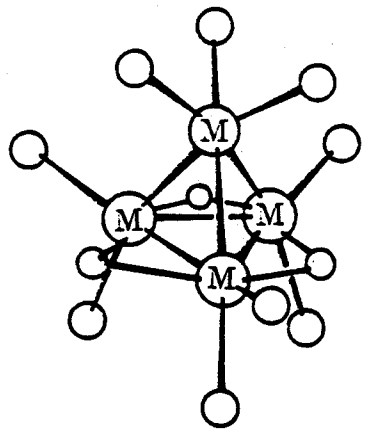


In the simple example of super-exchange shown above, two metal atoms, M_1 and M_2, interact via a ligand, L. The d orbitals of M_1 and M_2, each containing an unpaired electron, overlap with a p orbital of L which contains an electron pair. Weak pairing in the overlap region between unpaired d-electron and the (paired) p-electron of opposite spin leads to a polarization of the two opposite spins in a p-orbital. As a consequence the two d-electrons will tend to have opposite spins — just as would have happened had the two d-orbitals overlapped with each other.

32



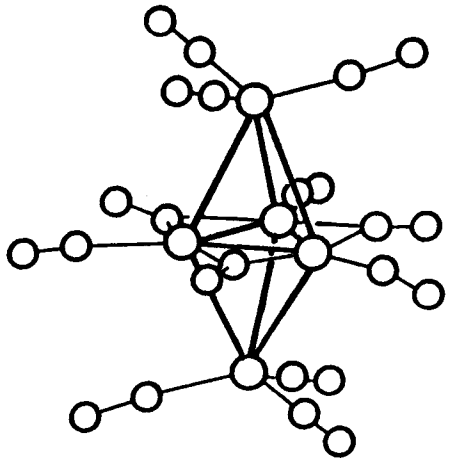
The species $M_3(CO)_{12}$, M = Os, Ru. All four compounds — Os_3, Os_2Ru, $OsRu_2$ and Ru_3 are known. Note that $Fe_3(CO)_{12}$ has a different structure.



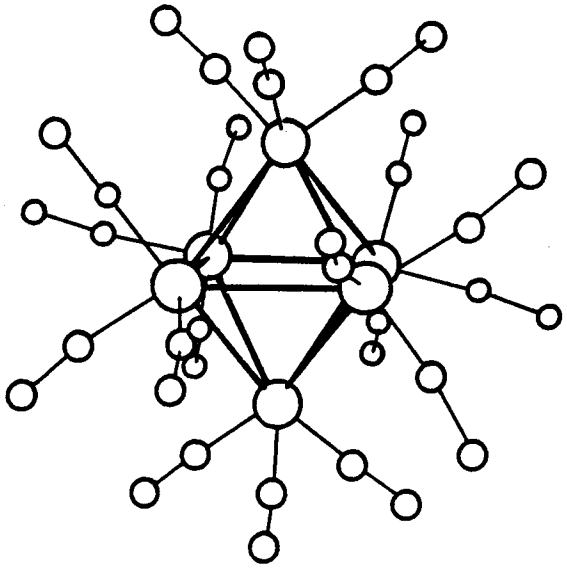
The species $M_4(CO)_{12}$. This structure is found for M = Rh, Co and also for a number of isoelectronic species such as $[FeIr_3(CO)_{12}]^-$ and $[Fe_2Ir_2(CO)_{12}]^{2-}$. In the latter two species an iridium atom is always unique. For simplicity only the carbon atoms of CO groups (three of which are bridging) are shown.

frame 32 continues ➡

➡ frame 32 continued

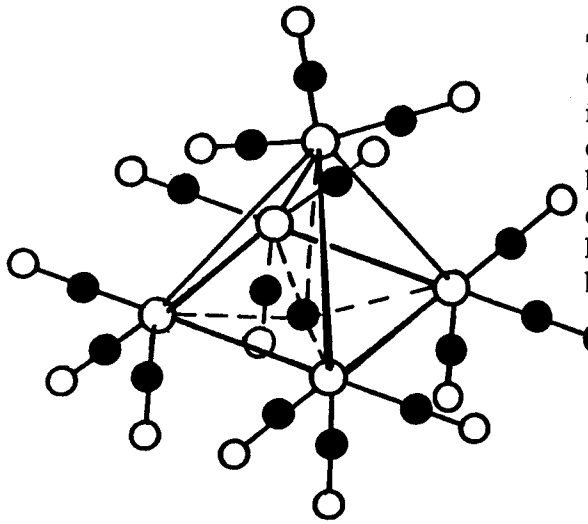


An M_5 species, $[Ni_5(CO)_{12}]^{2-}$



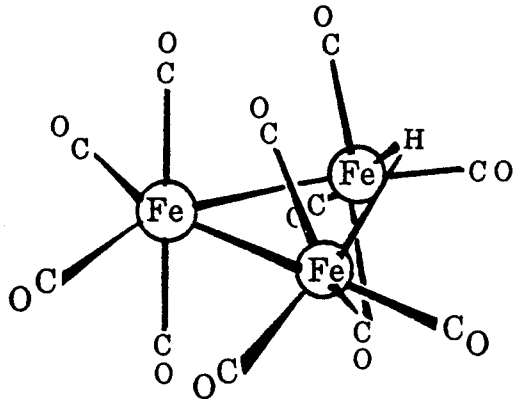
An M_6 species, $[Os_6(CO)_{18}]^{2-}$. By making the 'CO's small and the 'O's big the octahedral arrangement of these atoms is revealed. In practice, the central metal core in metal carbonyl clusters is usually totally encapsulated within a sheath of CO groups.

In all of the above examples CO is the only ligand. Although if there are any CO ligands in a cluster there tend to be a lot of them, plenty of other ligands also exist. The two following simple examples are indicative of quite large areas of carbonyl cluster chemistry. Examples of clusters with no CO ligands are given in frames 39 and 40.



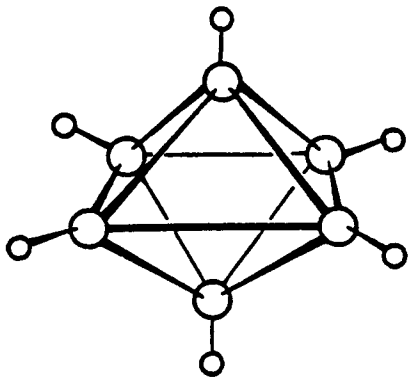
The molecule $Fe_5C(CO)_{15}$. Carbon atoms are black, iron atoms white and oxygens also white but a bit smaller. Note the carbon atom slightly below the plane of the four basal iron atoms.

$[Fe_3(CO)_{11}H]^-$. The presence of a bridging hydrogen — in other species it is terminal — indicates that not *every* ligand has to be involved in π-bonding to the metal. It is difficult to believe that H could be.



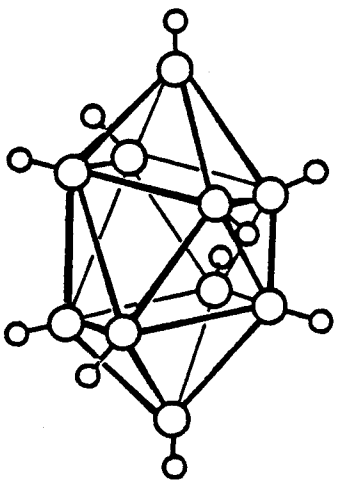
33

closo boranes



There are seven electron pairs involved in the cage bonding
= n+1, where n = 6

$B_6H_6^{2-}$

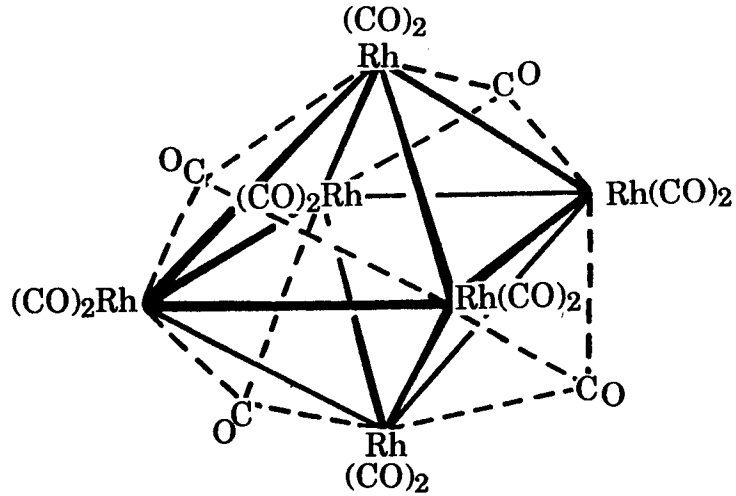


There are eleven electron pairs involved in the cage bonding
= n+1, where n = 10

$[B_{10}H_{10}]^{2-}$

34

The structure of $Rh_6(CO)_{16}$ (a closo cluster)



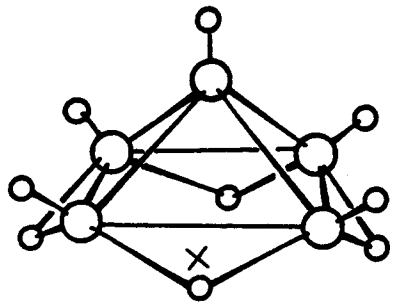
The four bridging carbonyls span alternate faces of the Rh_6 octahedron and so lie at the apices of a regular tetrahedron.

Zerovalent rhodium is $...4d^9 5s^0 5p^0$, nine valence shell orbitals and nine valence shell electrons. In the above configuration, therefore, there will be
a) four empty valence-shell orbitals (available for acceptance of CO σ electron density; that from the bridging COs will contribute to the cage stability)
b) four filled valence-shell orbitals (which may be non-bonding or involved in donation of electron density into CO π^* orbitals)
c) we are left with one electron per rhodium, a total of six. To these have to be added the $4\times2 = 8$ electrons from the bridging COs giving a total of fourteen electrons involved in cage bonding, seven electron pairs, just the number that the (n+1) rule requires for a metal octahedron (n = 6).

frame 34 continues ➡

➡ frame 34 continued

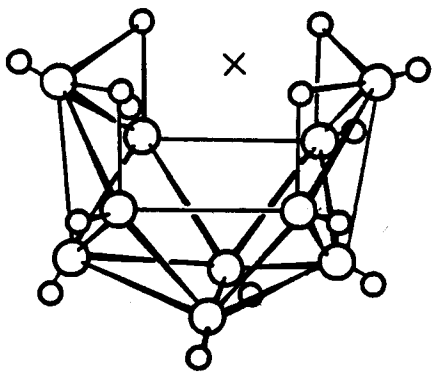
nido boranes



B_5H_9

There are seven electron pairs involved in the cage bonding, most easily seen if B_5H_9 is written $(BH)_5H_4$ = 5+2 = 7 electron pairs.

An approximate position for the 'missing' BH unit is indicated by a cross.

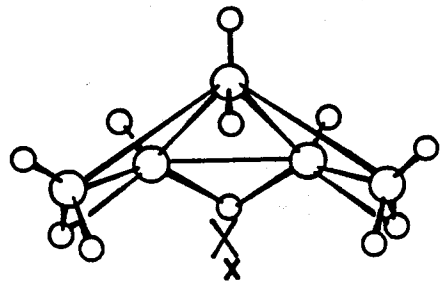


$B_{10}H_{14}$

There are twelve electron pairs involved in the cage bonding — $B_{10}H_{14}$ is $(BH)_{10}H_4$ = 10+2 = 12 electron pairs. An approximate position for the 'missing' BH unit is indicated by a cross.

Note that in both the above examples the H atoms 'sew up' the hole left by the 'missing' BH group.

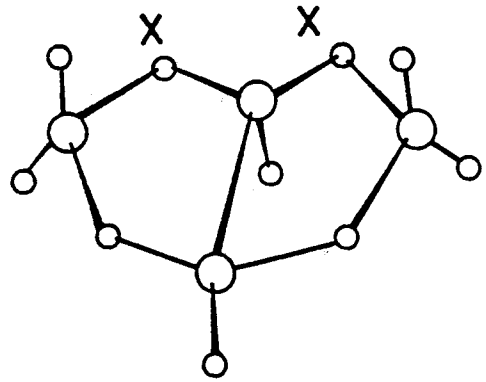
arachno boranes



B_5H_{11}

There are eight electron pairs involved in the cage bonding $(BH)_5H_6$ = 5+3 = 8

Approximate positions for the two 'missing' BH units are indicated by crosses (in perspective).



B_4H_{10}

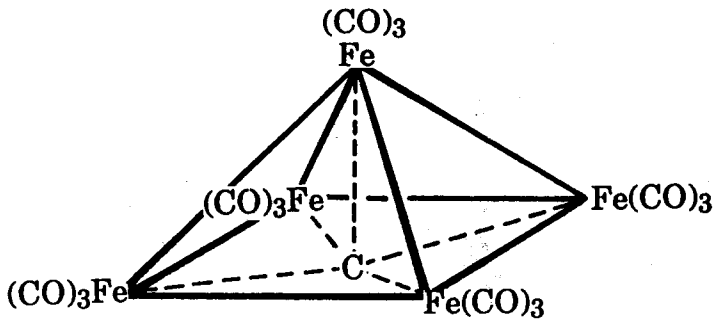
There are seven electron pairs involved in the cage bonding $(BH)_4H_6$ = 4+3 =7

Approximate positions for the two 'missing' BH units are indicated by crosses.

Note that in addition to bridging H atoms (three and four, respectively) the above molecules also have three and two, respectively, BH_2 groups.

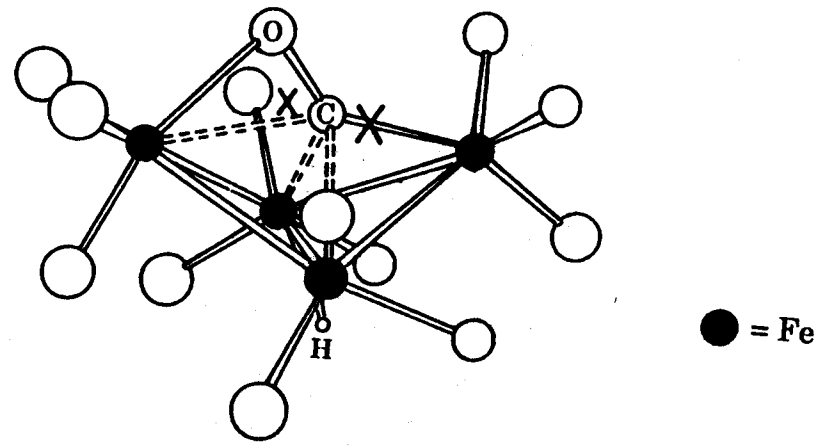
35

The structure of $Fe_5(CO)_{15}C$, a *nido* cluster:



Each iron(0) has eight valence shell electrons and each terminal CO contributes two, a total of fourteen. Subtracting twelve leaves two for cluster bonding. The basal C atom contributes four, giving a total of fourteen electrons for cluster bonding, as required by Wades's rules for a nido cluster of five atoms — (n + 2) electron pairs where n = 5. The twelve electrons subtracted are a pair each for the four Fe–C bonds and four for Fe–$(CO)_3$ p back bonding. It is often a useful trial first step to allocate twelve electrons to metal-ligand bonding – this makes an obvious sense when the metal is octahedrally surrounded with ligands.

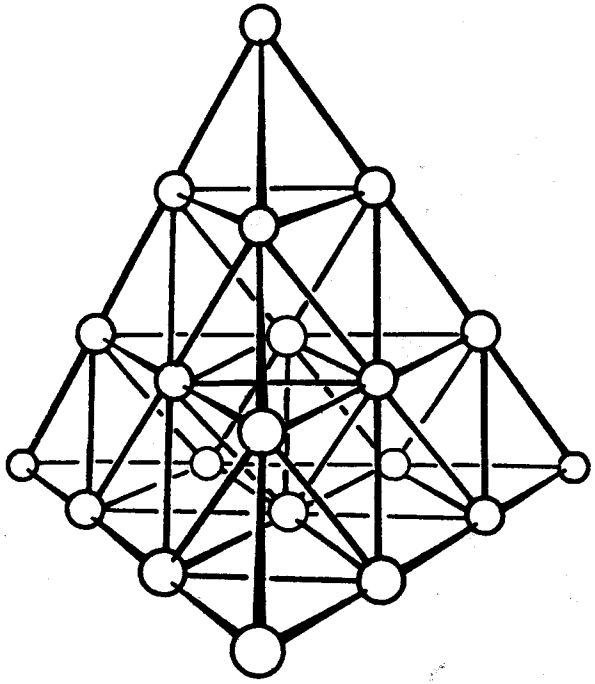
The structure of $[Fe_4(CO)_{13}H]^-$.



The iron atoms (black) are in a 'butterfly' arrangement (wings to the top, left and right). There is a basal H, and terminal COs are indicated by a single white circle. There is a bridging CO in which the C atom interacts strongly with one Fe and weakly with three; the O of the CO also bonds weakly to an Fe. To complete the (octahedral) cage one would need Fe atoms roughly as indicated by X's.

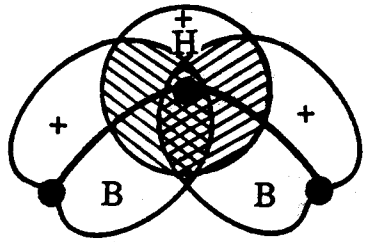
The electron count is: each $Fe(CO)_3$ contributes two electrons to the cage bonding (as above), the bridge CO four (because of the involvement of the O in the bonding), the H and negative charge one each, a total of fourteen — as required by Wade's rules for an arachno cluster — (n + 3) electron pairs, where n = 4.

36

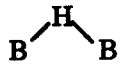


The anion $[Os_{20}(CO)_{40}]^{2-}$. For simplicity only the metal atoms are shown.

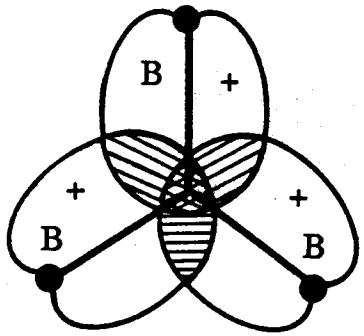
37



Schematic picture of the orbital interactions that give rise to a



bridge (edge) bond.

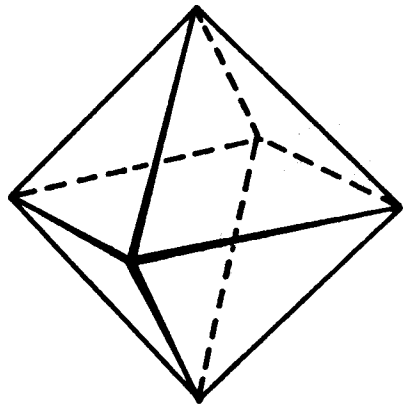


Schematic picture of the orbital interactions that give rise to a

face bond

38

The octahedron of $B_6H_6^{2-}$ (frame 33).



The transformation of the eight face bonds is (frame 5):

E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
8	2	0	0	0	0	0	0	0	4

As may be shown by the technique illustrated in frame 11, this is the sum $A_{1g} + T_{1u} + T_{2g} + A_{2u}$.
Check:

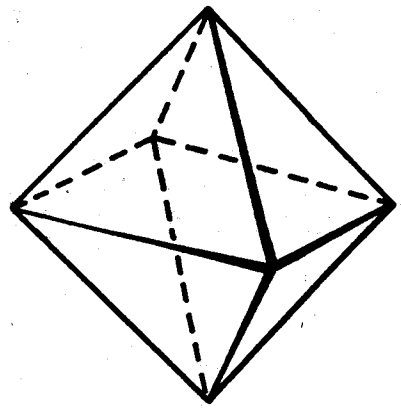
A_{1g}	1	1	1	1	1	1	1	1	1	1
T_{1u}	3	0	–1	1	–1	–3	0	1	–1	1
T_{2g}	3	0	–1	–1	1	3	0	–1	–1	1
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1
	8	2	0	0	0	0	0	0	0	4

The sequence given above is in order of increasing nodality and, so, energy.
$A_{1g}(0) < T_{1u}(1) < T_{2g}(2) < A_{2u}(3)$.

The (n+1) = 7 electron pairs available for cage bonding are, then, exactly accommodated in the $A_{1g} + T_{1u} + T_{2g}$ face orbital combinations. Remember that each face orbital is inherently bonding so that it takes a high nodality for a combination to become antibonding.

39

The octahedron of $B_6H_6^{2-}$ (frame 33)



The transformation of the twelve B—B edge bonds (those of frame 36 but with no hydrogen involvement) is (frame 5):

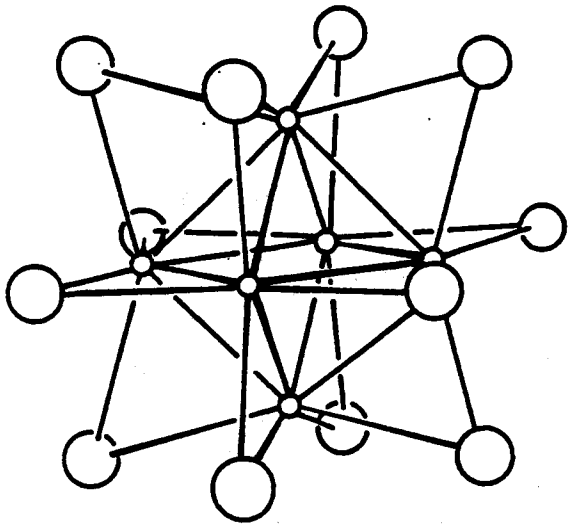
E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
12	0	0	0	2	0	0	4	0	2

As may be shown by the technique illustrated in frame 11, this is a sum $A_{1g} + T_{1u} + T_{2g} + A_{2u}$.
Check:

A_{1g}	1	1	1	1	1	1	1	1	1	1
T_{1u}	3	0	–1	1	–1	–3	0	1	–1	1
T_{2g}	3	0	–1	–1	1	3	0	–1	–1	1
E_g	2	–1	2	0	0	2	–1	2	0	0
T_{2u}	3	0	–1	–1	1	–3	0	1	1	–1
	12	0	0	0	2	0	0	4	0	2

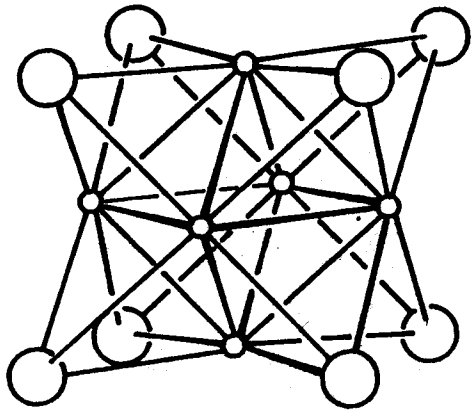
Again, the sequence is in order of increasing energy.
$A_{1g}(0) < T_{1u}(1) < T_{2g}(2) < E_g(2) < T_{2u}(3)$
so, as with frame 37, we conclude that the seven cage bonding electron pairs in $B_6H_6^{2-}$ occupy orbitals of $A_{1g} + T_{1u} + T_{2g}$ symmetries.

40



The structure of the $Ta_6Cl_{12}^{2+}$ cluster. Six Ta atoms define an octahedron; the twelve chlorines are one above each octahedron edge. Ta(II) is a d^3 system so there are $6 \times 3 - 2 = 16$ electrons available for cluster bonding. These can be allocated one pair to each 'face' orbital. Calculations indicate, indeed, that the occupied metal-metal bonding molecular orbitals have $A_{1g} + T_{1u} + T_{2g} + A_{2u}$ symmetries (c.f. frame 38). Because of the higher inherent nodality of d orbitals the A_{2u} molecular orbital is not destablised in the same way as for the boron octahedron in frame 38.

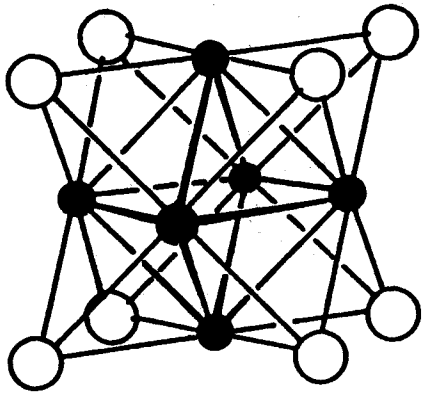
41



The structure of the $Mo_6Cl_8^{4+}$ cluster. Six Mo atoms define an octahedron; the eight chlorine atoms are one above each octahedron face. Mo(II) is a d^4 system so there are $6 \times 4 = 24$ electrons available for cluster bonding (the compound is '$MoCl_2$', $Mo_6Cl_8^{4+}.4Cl^-$; our concern is with 'Mo' electrons). These twenty-four can be allocated one pair to each 'edge' orbital. Calculations indicate, indeed, that the occupied metal-metal bonding molecular orbitals have $A_{1g} + T_{1u} + T_{2g} + E_g + T_{2u}$ symmetries (c.f. frame 39). As for frame 40, the inherent nodality of the metal d-orbitals means that all of the molecular orbitals are bonding.

42

Consider the cluster $[Mo_6Cl_8]^{4+}$

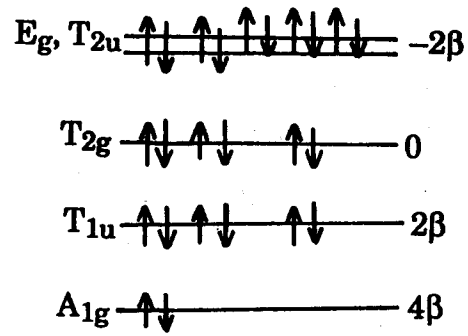


Wade's rules.

Although, as we shall see, it is possible to modify them and obtain a different conclusion, Wade's rules in the form that they have been presented in this programme indicate that no metal-metal bonding exists. Regard $[Mo_6Cl_8]^{4+}$ as $6Mo^{2+} + 8Cl^-$. Each Mo^{2+} has four valence shell electrons. If the four chloride ions which surround it, at the corners of a square plane, each donate two electrons then each molybdenum has a total of twelve, leaving none for metal-metal bonding. We therefore conclude that the molecule is held together not by metal-metal bonds but because each chloride bridges, and holds in place, three molybdenums.

Topological equivalent orbital.

This model simply says 'let us assume appropriate orbitals exist' and, of itself, says nothing about their importance — simply that, if they interact, then the sequence will be ... . In the case of $[Mo_6Cl_8]^{4+}$, the assumption that there is an interaction (of magnitude β) along the octahedron edges leads to the energy level sequence:



Note that we are selecting just some of the molybdenum orbitals in the above sequence. We are actually saying that each molybdenum is square-planar surrounded by chlorine and that the Mo-Cl bonding involves just the Cl^- electrons. All the molybdenum electrons (four per molybdenum) are therefore available for cluster bonding, a total of twenty-four. These have been fed into the orbital sequence above. Wade's rules lead to the same conclusion if one says that each molybdenum, being square planar, requires eight, not twelve electrons. However, the number of electron pairs that results, twelve, is not the seven — (n + 1), n= 6 — predicted by Wade's rules.

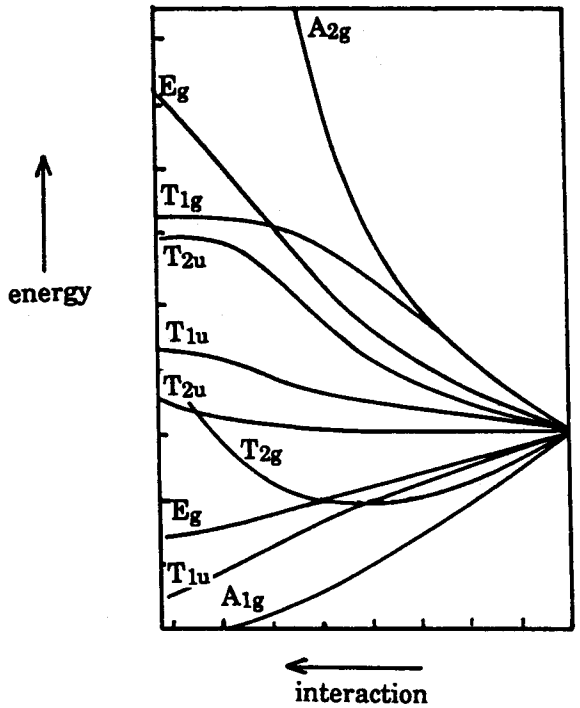
frame 42 continues ➡

➡ frame 42 continued

Extended Hückel Calculations

The diagram below shows the orbital sequence as the orbital interaction is varied.

Twenty-four electrons have to be fed in, just as for the TEO model.



43

H			
0.01			
Li			N
0.02			0.05
Na			P
0.08			0.11
K	Cr	Cu	As
0.14	0.18	0.21	0.24
Rb	Mo	Ag	Sb
0.27	0.31	0.34	0.37
Cs	W	Au	Bi
0.40	0.54	0.58	0.61
	U		
	0.67		

Approximate 1s electron velocities relative to the speed of light = 1. The relationship used for these data is

$$\frac{v}{c} \approx \frac{Z}{137}$$

where Z is the atomic number of the element.

The value of v/c increases the (relativistic) mass of the electron because

$$m_{relativistic} = m_{rest} \cdot \frac{1}{\sqrt{1-(v/c)^2}}$$

This, in turn, means that the 1s orbital contracts because the most probable distance of the electron from the nucleus is

$$r = \frac{h^2}{4\pi^2 me^2 Z}$$

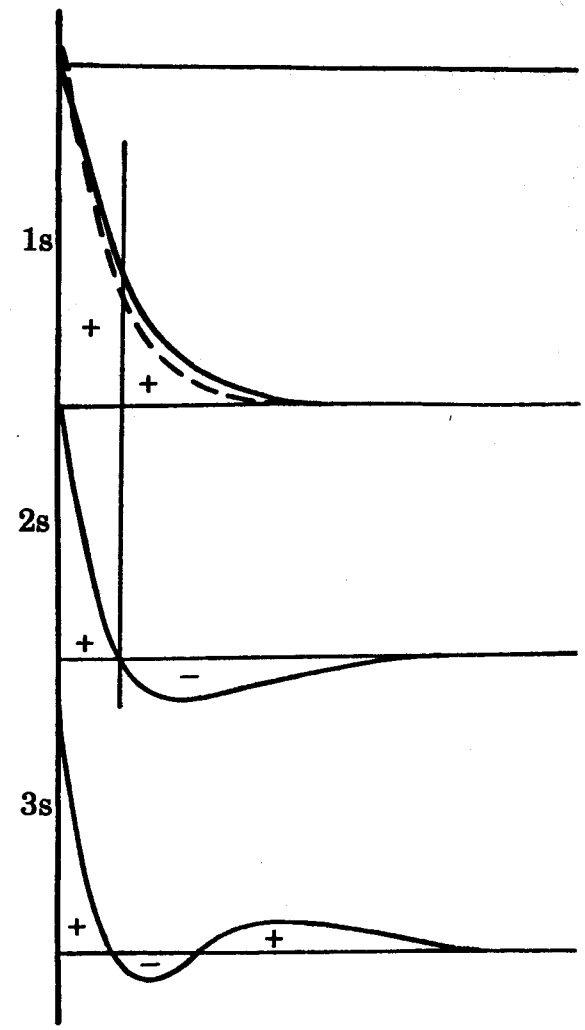
44

H			
1.000			
Li			N
1.000			1.001
Na			P
1.003			1.006
K	Cr	Cu	As
1.01	1.02	1.02	1.03
Rb	Mo	Ag	Sb
1.04	1.05	1.06	1.08
Cs	W	Au	Bi
1.09	1.19	1.23	1.26
	U		
	1.35		

The approximate relativistic mass of 1s electrons as a multiple of their rest mass. The above data are calculated from those of frame 43 using

$$m_{relativistic} = m_{rest} \frac{1}{\sqrt{(1 - v^2/c^2)}}$$

45



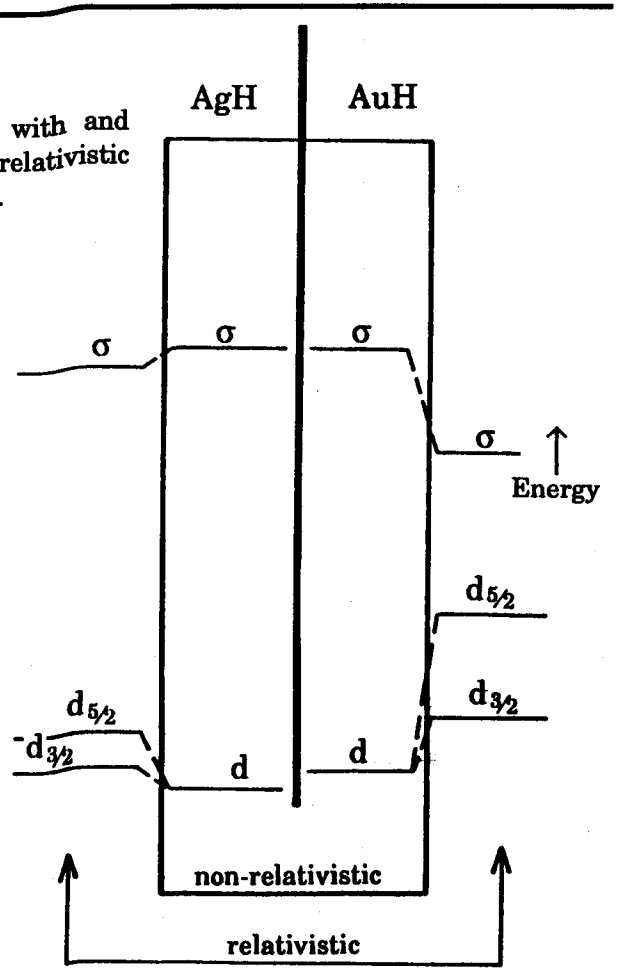
The 1s (solid line), 2s and 3s radial functions for hydrogen. The radial node in the 2s function is at such a position that the overlap with the 1s orbital is exactly zero. (Compare the overlaps on either side of the vertical line representing the position of the 2s radial node.)

If the 1s orbital contracts (to give the dashed line radial function) the overlap with 2s is no longer zero. The only way in which it can become so (i.e. for 2s to remain orthogonal to 1s) is for the 2s radial function to contract also. A similar pattern holds for 3s and higher s functions.

46

Calculated orbital energies (eV) and radii (Å) for uranium.

	Orbital	non-relativistic	relativistic	change
energies	7s	–4.54	–5.51	increase
	6d	–7.25	–5.69	decrease
	5f	–16.26	–9.01	decrease
radii	7s	2.67	2.30	decrease
	6d	1.52	1.71	increase
	5f	0.67	0.76	increase

47

Results of calculations, with and without inclusion of relativistic effects, on AgH and AuH.