Chapter 6

Metal Atom Clusters (Non-Carbonyl clusters)

Note: for Metal Atom Carbonyl clusters please see the other graduate course Organometallic Chemistry 23523 (Chapter 6 Metal Carbonyls).

METAL-TO-METAL BONDS & METAL-ATOM-CLUSTERS

① F.A. Cotton & G. Wilkinson, 4th ed, p. 1080

② Hikmat S. Hilal

Introduction

Wernerian Compounds are well known - with only one metal atom surrounded by some ligands. chemical & physical properties are determined by:

i) nature of M
ii) nature of L
iii) nature of M–L bond
iv) geometry.

Wernerian concept doesn't deal with M–M bonding, although he recognized the existence of polynuclear complexes, but explained only by M(L)M being connected by ligands, without M–M bonding.

In 1907–13 / $TaCl_5 \cdot 2H_2O$ was found as $Ta_6Cl_{14} \cdot 7H_2O$ other compounds were discovered in 1920's, (polynuclear halide without Wernerian nature, but structures unknown.

X-Ray ~~the~~ crystallography revealed many things, that non-Wernerian one or more M–M direct bonds were recognized, such as $\{W_2Cl_9\}^{-3}$

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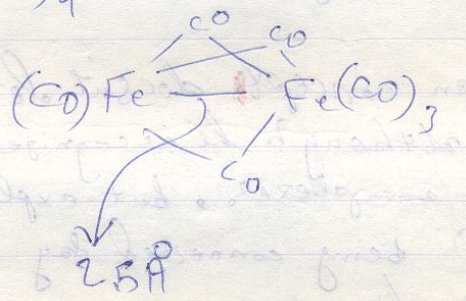
metal atom-cluster: is a group of two or more metal atoms in which there are substantial direct bonds between the metal atoms.

So, metal-atom cluster is not just an ordinary polynuclear complex. In metal-atom-cluster, there must be significant M–M bonding.

Some borderline cases appear, in which no definite answer whether there is true M–M bonding is chemically significant.

But; if the M–M bonding is truly chemically important, then called Metal-atom-cluster.

In 1938, $Fe_2(CO)_9$ was determined as



Furthermore, $Mn_2(CO)_{10}$ $(CO)_5Mn—Mn(CO)_5$ with direct M–M bonding actually occurs.

Such clusters occur in $M_n(CO)_x$, carbonylate anions, M(CO)-hydrides, isocyanides, ...

(Co.5 – Co.4).

M–M BONDS IN NONCARBONYL COMPDS

here, we are concerned with chemical bonding in these clusters, and are limiting ourselves to:

M_6X_8 clusters $(Mo_6Cl_8)^{+4}$, $(W_6Cl_8)^{+4}$

M_6X_{12} clusters $(Nb_6Cl_{12})^{+2}$, $(Ta_6Br_{12})^{+4}$

Re_3X_9 (X = Cl)

$X_3M \equiv MX_3$ triple bond $Mo_2(NMe)_6$, $W_2(CH_2SiMe_3)_6$

$X_4M \equiv MX_4$ quadruple bond $[Re_2X_8]^{-2}$, $[Mo_2(SO_4)_4]^{-4}$, $Cr_2(AcO)_4$

with M always having +2 to +3 formal charge.

(in $M(CO)_x$ formal charge was ≥0 or −ve).

this difference has an important consequence.

= for neutral T.M. atom, (n+1)s, (n+1)p & (n)d energy levels are comparable.

= when ionized, the energy barrier increases, thus for $M^{+2,+3}$ nd ⟶ (n+1)s, (n+1)p energy

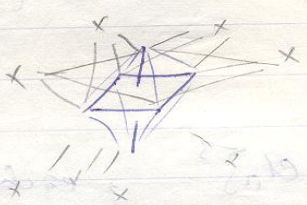
thus, ~~only~~ (n)d are actually valence shell but (n+1)s & (n+1)p play only very minor role in bonding.

∴ bonding is analysed almost entirely using nd orbital contributions only.

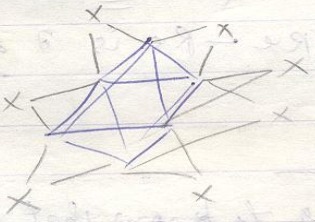
O_h and Re_3 clusters

look at fig. 26-8 (page 1096)

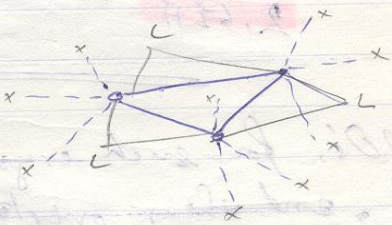
M_6X_8



M_6X_{12}



$Re_3X_9L_3$



one question is: are all M–M bonds localized??

In $[Mo_6Cl_8]^{+4}$, twelve pairs of M–M, each Mo^{II} provides 4 e⁻s

thus, 24 e⁻s are involved,

thus, 24 e / 12 M–M bonds i.e. 1 e pair for each Mo–Mo pair

In $[Nb_6Cl_{12}]^{+2}$ has 12 M–M pairs, but only 8 e pairs since the 6 Nb atoms give $(5\times6 = 30\ e^-s - 6\times2-2 = 14e) = \frac{16e}{2} = 8$ pairs

So, we assign only fractional ($\frac{2}{3}$) bond orders to each Nb–Nb pair.

In Re_3Cl_9 or $[Re_3Cl_9]^3$, each Re^{III} has 4 e⁻ to give

$\therefore 3\times4 = \frac{12}{2} = 6\ e^-$ pairs for the 3 (Re–Re) bonds

Thus, each Re–Re is a double bond

It is interesting to know that bond distances M–M agree with bond orders 1 for $(Mo_6Cl_8)^{+4}$, $\frac{2}{3}$ for $(Nb_6Cl_{12})^{+2}$ & 2 for (Re_3Cl_9)

2.61 Å 2.82 Å 2.47 Å

⇒

To devise M.O's, for such ~~crystals~~ clusters, we consider only d orbitals, and their overlaps.

One d orbital of each metal → goes to M–Cl bond

remain 4 d orbitals on each metal → for M–M bond formn.

energies of M.O's, ~~are~~ depend on overlap integrals.

Using extended Hückel theory, the M.O's. are constructed, fig. 26.9 (p. 1097)

See Page 1097 4th ed. and p. 1080 5th ed.

In M_6X_8 = { four antibonding
1 nonbonding
five bonding { A_{1g} (singly deg.), T_{1u}, E_g, T_{1g}, T_{2u} }

~~6 × 5 = 8 = 2 orbitals~~ ~~5(8)~~

occupy 12 $\bar{e}$ pairs, so it fits with $[Mo_6Cl_8]^{+4}$ & $[W_6Cl_8]^{+4}$ clusters & derivatives.

In M_6X_{12} = four bonding orbitals { A_{1g}, A_{2u}, $T_{1u}^{(1)}$ & $T_{2g}^{(1)}$ }

holding the 16 $\bar{e}$'s in $[Nb_6Cl_{12}]^{+2}$ and $[Ta_6Cl_{12}]^{+2}$ clusters

In M_3X_9 = four bonding orbitals to hold 12 $\bar{e}$'s, Re_3Cl_9 or $[Re_3Cl_{12}]^{-3}$

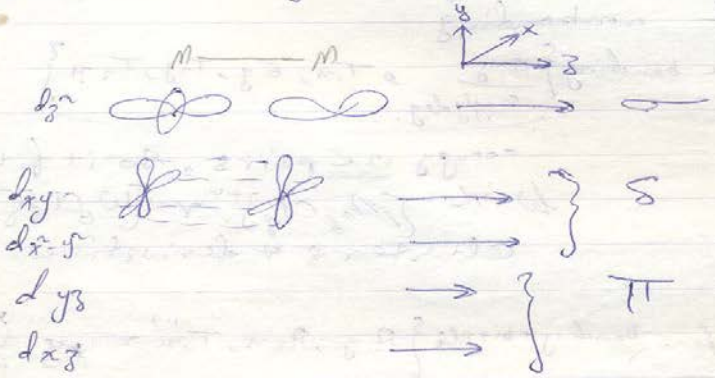
the (primes) → for $\overline{=}$ bonds
the (double primes) → for $\overline{\overline{=}}$ bonds

3 σ-sets and 3 π-sets in Re–Re bonds.

Multiple M–M bonds

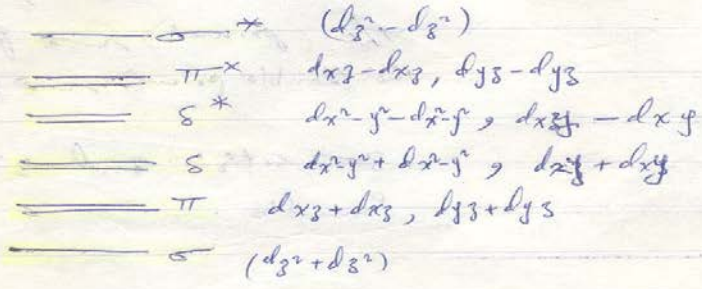
Re_3X_9 have double Re–Re bonds.

If we consider two isolated M atoms, then the d orbitals may interact in different ways to give M_2



For a system containing M–M bonds {σ, π & δ} the MO energy level is:

- σ – overlap very strong
- π – overlap intermediate
- δ – overlap is weak



M_2

this is for isolated M_2 molecule.

When ligands come, there will be alteration on M_2 M.O. energy levels:

(See Page 1099) 4th ed.

or Page 1088 (5th ed.)

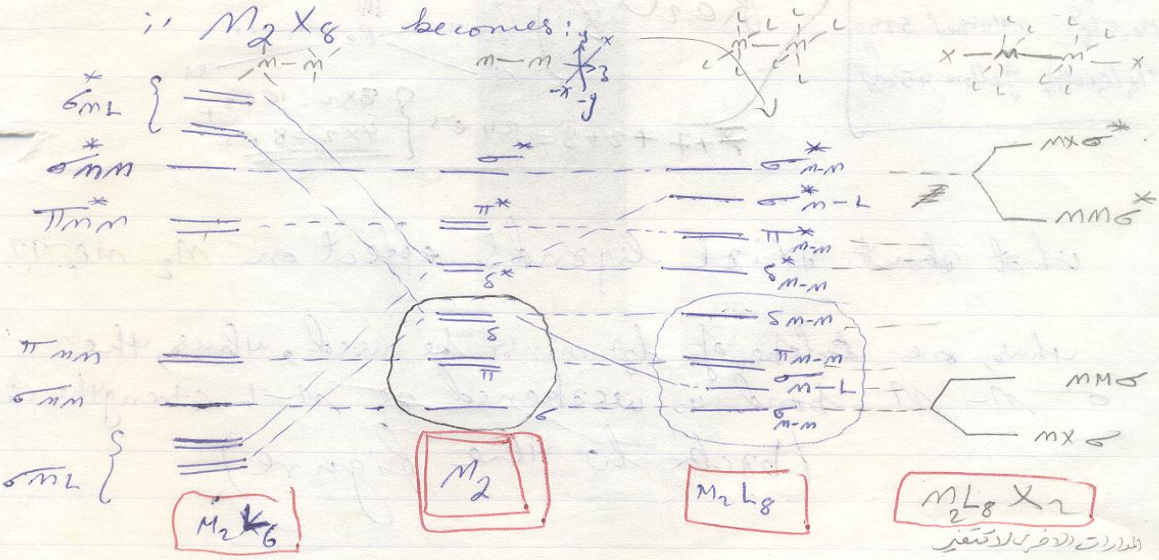
Quadruple Bonds

If 4 Ligands come to M via x, -x, y, -y directions,

∴ $d_{x^2-y^2}$ will be used for the four ligands (to give M–L σ-bonds)

thus, one δ bond goes away from M_2, and one δ*.

∴ M_2X_8 becomes:



So, M_2 is left with 1σ, 2π & 1δ bonds only, the bond is 4 ∴ called Metal–Metal quadruple bond.

with $\sigma^2\pi^4\delta^2$ in M_2L_8

Jul. 6th Eve

the quadruple bond is:

(1) very strong & very short

(2) its strength depends on M—M rotation, because $d_{xy}-d_{xy}$ will be affected

∴ strongest δ if eclipsed structure is achieved;

eclipsed

but, L—L repulsion increases in the eclipsed structure

∴ some twisting may occur actually, but only in few cases.

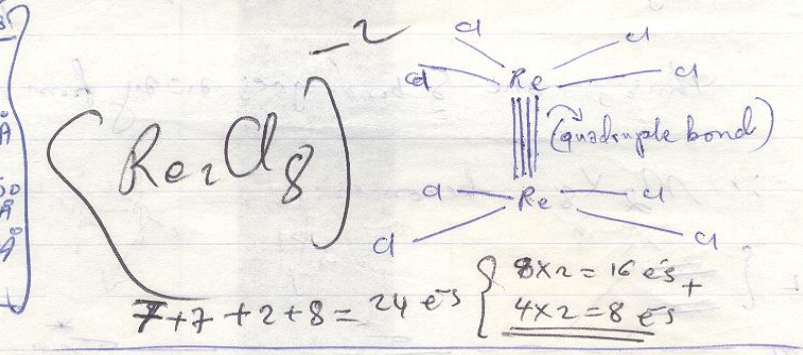
~~5+5 [illegible] = 10 e⁻s~~

δ → δ* transitions give colours:

$Re_2Cl_8^{2-}$ Royal blue 7000 Å

$Mo_2Cl_8^{4-}$ intense red 5250 Å

$Mo_2(O_2CCH_3)_4$ yellow 4520 Å°



~~7~~ +7 +2 +8 = 24 e⁻s { 8×2 = 16 e⁻s + 4×2 = 8 e⁻s

what about axial ligands effect on M_2 M.O.s ??

thus, one lobe of d_{z^2} must be used, thus, the σ—M bond is weakened as M—L strengthens.

(back to the figure)

δ-bond is weak,
i.e. gain or loss of e⁻'s on δ and/or δ* M.O.'s should have only slight effect on M–M bond strength.

but, however removal of δ or δ* e⁻ effects Effective atomic charge so must affect bond length only slightly

$\{Re_2Cl_4(PMe_2Ph)_4\}$ $\sigma^2\pi^4\delta^2\delta^{*2}$ $d = 2.241$ Å

$[Re_2Cl_4(PMe_2Ph)_4]^+$ $\sigma^2\pi^4\delta^2\delta^{*1}$ $d = 2.218$ Å

$[Re_2Cl_4(PMe_2Ph)_4]^{+2}$ $\sigma^2\pi^4\delta^2\delta^{*0}$ $d = 2.215$ Å

Note the distance is only slightly effected with formal bond order 3.0 → 3.5 → 4.0

with $\{Tc_2Cl_8\}^{3-}$ + $\{Tc_2Cl_8\}^{2-}$

loss of e⁻ gives a shortening of 0.03 Å (unexpectedly) with loss of one δ* e⁻.

however best way to study contribution of δ e⁻s is geometry

{{staggered vs. eclipsed}}

$\{Mo_2Cl_4(PPh_2-PPh_2)_2\}$ δ preferred in ~~staggered~~ eclipsed

when twisted, δ is lost.
(so we expect M–M bond lengthening)
this is experimentally true, with 0.1 Å lengthening.

Mo–Mo (single bond) ~ 2.60 Å

Mo—Mo (quadruple) ~ 2.10 Å } 20% of the di is due t δ compone

Triple Bonds

① either by removal of $2\bar{e}$ from quadruple bonds

② or by addition of e^-'s to δ^* such as $\{Tc_2Cl_8\}^{-3}$ $\quad \sigma^2\pi^4\delta^2\delta^{*1}$

$\{Re_2Cl_8\}^{-2} \longrightarrow \{Re_2Cl_4(PR_3)_4\}$ has Re–Re triple bond.

$\{Re_2Cl_4(PR_3)_4\}^{+} \leftarrow$ air

③ also exist in $X_3M \equiv MX_3$ $\{M = Mo, W\}$

⇐ See figure back ☞

the d_{xy} + $d_{x^2-y^2}$ will be used for ~~M–X~~

One dimensional solids ⟹ Page 1111.