Study Notes on M-M Bonded Compounds

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Metal—Metal Bonded Compounds

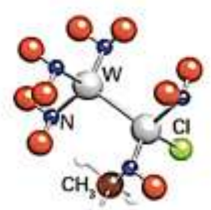
With the development of improved techniques for the determination of structure, it has been recognized that there are many d-metal compounds that contain metal-metal (M — M) bond distances comparable to or shorter than those in the elemental metal. A rigorous definition of metal clusters restricts them to molecular complexes with metal-metal bonds that can form triangular or larger structures. This definition, however, would exclude linear M – M compounds, and is normally relaxed.

(a). Metal-metal Bonds:

Metal-metal bonds with bond orders up to five are formed by many d metals in low oxidation states. The first d-block metal—metal bonded species to be identified was the Hg_2^{2+} ion of mercury (I) compounds, as occurs in Hg_2Cl_2, and examples of metal-metal bonded compounds and clusters are now known for most of the d metals. Some of their common structural motifs are an ethane-like structure **(1)** an edge-shared bioctahedron **(2)** and so on.

If we consider the possible overlap between d orbitals on adjacent metal atoms, then,

- a σ bond between two metal atoms can form from the overlap of d_{z^2} orbital from each atom.
- two π bonds can arise from the overlap of d_{zx} or d_{yz} orbitals.
- two δ bonds can be formed from the overlap of two face-to-face d_{xy} or $d_{x^2-y^2}$ orbitals



1 $[(Me_2N)_3WWCl(NMe_2)_2]$, Me = CH_3

2 $[(Cl)_2(py)_2W(\mu\text{-}Cl)_2W(Cl)_2(py)_2]$

Thus, a quintuple bond formation can take place if all the bonding orbitals are occupied to give the electron configuration $\sigma^2\pi^4\delta^4$.

Many other species with multiple metal-metal bonds, where the $d_{x^2-y^2}$ orbital is involved in bonding to ligand species, are known, A well-known example is the quadruple bonded compound molybdenum (II) acetate which is prepared by heating Mo (CO), with acetic acid:

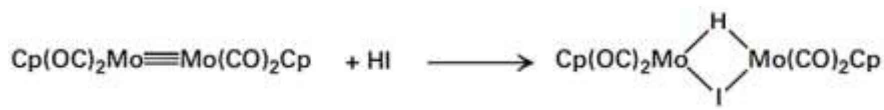
$2Mo(CO)_6 + 4CH_3COOH \rightarrow Mo_2(O_2CCH_3)_4 + 2H_2 + 12CO$

The dimolybdenum complex is an excellent starting material to prepare other Mo-Mo compounds. For example, the quadruple bonded chloride complex is obtained when the acetato complex is treated with concentrated hydrochloric acid at below room temperature:

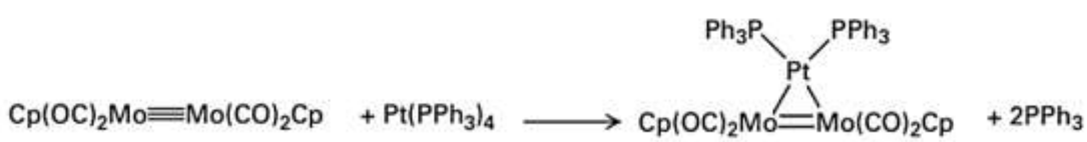
$Mo_2(O_2CCH_3)_4(aq) + 4H^+(aq) + 8\ Cl^-(aq) \rightarrow [Mo_2Cl_8]^{4-}(aq) + 4CH_3COOH\ (aq)$

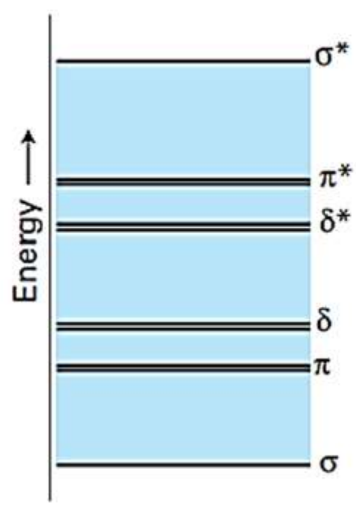
An incomplete occupation of the bonding orbitals can result in a reduction of the formal bond order to 3.5 or to the triply bonded M=M systems. These complexes are more numerous than the quadruple bonded complexes and, because δ bonds are weak, M = M bond lengths are often like those of quadruple bonded systems. A decrease of bond order can also stem from the occupation of both the δ* orbitals and, once these are fully occupied, successive occupation of the two higher lying π* orbitals lead to further decrease in the bond order from 2.5 to 1.

As with carbon-carbon multiple bonds, metal-metal multiple bonds are centers of reaction. However, the variety of structures resulting from the reactions of metal-metal multiple bonded compounds is more diverse than for organic compounds. For example:

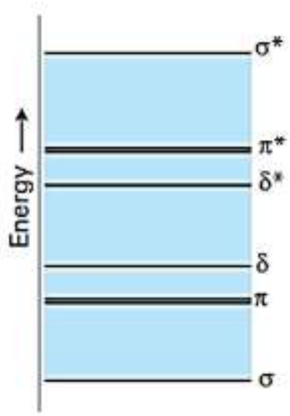


In this reaction, HI adds across a triple bond, but both the H and I bridge the metal atoms; the outcome is quite unlike the addition of HX to an alkyne, which results in the formation of a substituted alkene. The reaction product can be regarded as containing a 3c,2e MHM bridge and an iodide anion bonding by two conventional 2c,2e bonds, one to each Mo atom. Larger metal clusters can be synthesized by addition to a metal-metal multiple bonds. For example, Pt $(PPh_3)_4$, loses two triphenylphosphine ligands when it adds to the Mo ≡ Mo triple bond, resulting in a three-metal cluster:





The above diagram represents the approximate molecular orbital energy level scheme for M – M interactions.



This diagram represents the approximate molecular orbital energy level scheme for the M – M interactions in a quadruple bonded system, where only the $d_{x^2-y^2}$ will be utilized in bonding.