

Studies in Metal-Metal bonding in Metal cluster halides

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Abstract : The halides of low valent early metals often are clusters with extensive M-M bonding. These clusters are shown by metal having high energy of atomisation (high M.P. and B.P.) Most refractory metals like (Zn, Nb, Mo, Re, Ru, Rh, Os, In, Pt) have greater tendency to form cluster Metal halide derivatives in which the transition metal has a relatively low oxidation state. Metal cluster compounds are a molecular ion or neutral compound composed of three or more metals are featuring significant metal-metal interaction. For the earliest metals Zr and Hf, interstitial carbide ligands are also common. One example is $2r_6CCl_{12}$. Another common structure has six terminal halides and 8 bridging halides, eg. $Mo_6Cl_{14}^{2-}$. IN terms of history, Linus pauling showed that Mo_6Cl_2 consisted of Mo_6 octahedra. F. Albert cotton established that $ReCl_3$ in fact feature submits the cluster Re_3Cl_9 . X-ray crystallography and to a lesser extent mass spectrometry are also indispensable for the unambiguous identification of new metal cluster system.

Keywords : Metal-Metal bonding, Metal cluster halides, Refractory metal, X-ray crystallography.

I. INTRODUCTION

Metal-Metal bond is a bond between two metal centres particularly between two transition metal atoms which ranges from single to quadruple bond. The existence of metal-metal bond is mainly because of the presence of (N+1)s, (N+1)p and nd orbital as valence electronic configuration the transition metals can form three general types of bonds such as covalent bonds, dative bonds and weak metal-metal symmetry interactions, where covalent bond being the strongest and symmetry interactions are the weakest. The compounds containing a large number of metal-metal bonds forming triangular and large structures are called cluster. The metal clusters can also be defined as entity that contain a metal-metal bond. The Journey started with the identification of the Hg-Hg in Hg_2^{2+} ion in (Hg_2Cl_2) which was the first d-block metal-metal bonded species. Most of these cluster compounds are homo-metallic, however there are few exceptions with heterometallic cluster complexes.

II. TYPES OF BONDING IN METAL CLUSTERS

(i) Covalent Bonding

One electron from each metal atom constitutes a single M-M bond between the two metal atoms. This is the most common type of metal-metal bond ranging from a single to a quadruple metal-metal bond. Molecular orbital theory can be used to explain the overlap of various orbital to form three types of bonds namely the σ -bond, π -bond and recently introduced S-bond or the quadruple bond.

(ii) Oative Bond -

This type of bond is formed which one metal having filled d-orbitals co-ordinate to a metal atom containing empty d-orbitals by the donation of a lone pair of electron.

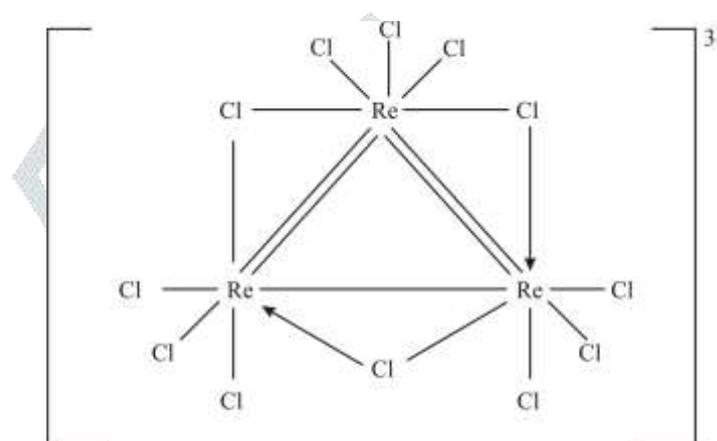
(iii) Weak-Metal symmetry interaction -

The weak metal-metal symmetry interactions are a result of symmetrical overlap of molecular orbital. The overlap is generally between filled and empty metal-metal bonding and / or antibonding orbitals.

III. EXPERIMENTAL AND STRUCTURE ELUCIDATION

Rhenium trichloride was prepared by thermal decomposition of rhenium pentachloride.

Reaction of rhenium trichloride with cesium chloride in hydrochloric acid produced a dark red salt of stoichiometry $Cs_3.ReCl_4$. For many years this salt was assumed to be a derivative of tetrahedral rhenium (III). However, in 1963 two independent research groups learnt via X-ray crystallography that this cesium salt was the trimetric derivative $Cs_3.Re_3Cl_{12}$. The $Re_3Cl_{12}^{3-}$ anion has structure with three two way bridging chlorine atoms and nine terminal chlorine atoms.

**Fig. 1**

The idea of rhenium-rhenium double bonding in $Re_3Cl_{12}^{3-}$ is supported further by the subsequent discovery and characterization by X-ray crystallography of binuclear rhenium (III) derivative $Re_2Cl_8^{2-}$ (formulated with fig.2 containing a rhenium - rhenium quadruple bond).

**Fig. 2**

The rhenium-rhenium distances in compounds with rhenium-rhenium bonds are consistent with these bond-orders. The Re(III) ions have d^4 -configuration. If Re ions are bonded with Re-Re single bond only, the complex would have been a paramagnetic complex. However the complex is diamagnetic which implies that Re ions are doubly bonded.

In $\text{Re}_2(\text{CO})_{10}$ cited in fig. (3) which clearly contain a rhenium-rhenium single bond. The rhenium-rhenium distance is 3.02 Å. This distance contracts to 2.47 Å in $\text{Re}_2\text{Cl}_{12}^{3-}$ with rhenium-rhenium double bonds and even further to 2.24 Å in $\text{Re}_2\text{Cl}_8^{2-}$ in Fig. 2 with a rhenium-rhenium quadruple bond.

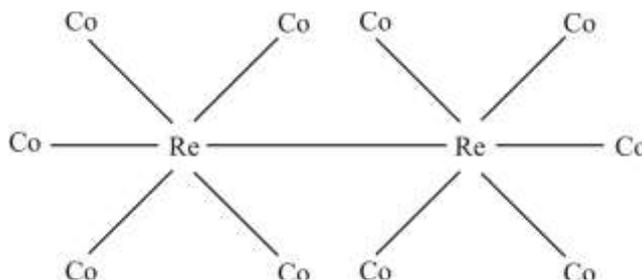


Fig. (3)

Rhenium (III) bromide reacts with silver bromide. Addition of dimethyl sulfoxide to the resulting solution gives a red aiorphous solid of stroichiometry $[(\text{CH}_3)_2\text{SO}]_2\text{Re}_3\text{Br}_3(\text{OsO}_4)_2$ indicated by its electronic spectrum still to contain the rhenium (III) triangle. A novel structure in Fig.(4) has been postulated for this complex on the basis of IR data. Similar compounds can be obtained from rhenium (III) bromide and silver phosphate (Ag_3PO_4) or silver arsenite (Ag_3AsO_3).

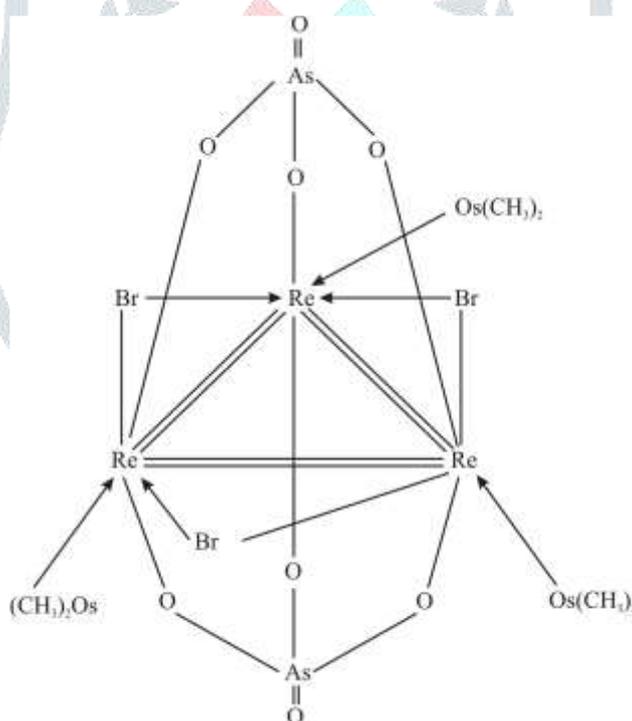


Fig. 4

IV. CONCLUSION

Multi metallic metal complexes possessing metal-metal bonds are called cluster compound. They are of variety of geometries such as linear M-M bond, triangular and larger. There can be homometallic as well as hetero-metallic M-M bond. A subclass of unsupported metal-metal bonded arrays are linear chain compounds. In such cases the M-M bonds is weak as signaled by longer M-M bonds and the tendency of such compounds to dissociate in solution.

The metal-metal bond is a chromophoric group, the extensive networks of such bonds often cause transition metal cluster compounds to have colours more intensive than those of comparable transition metal derivatives without any metal-metal bonding. The colour of the analogous cluster derivatives decreases intensity upon going from 3rd through 4d or 5d transition metal (i.e. upon descending a column of the periodic table).

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