

M. Sc. Semester I

Inorganic chemistry I

Paper - CC-I

Unit - IV

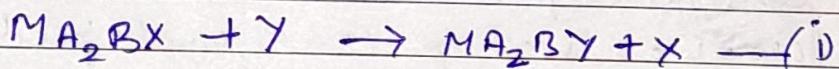
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Ligand Substitution Reaction In

Square Planar Complexes (II) (contd.)

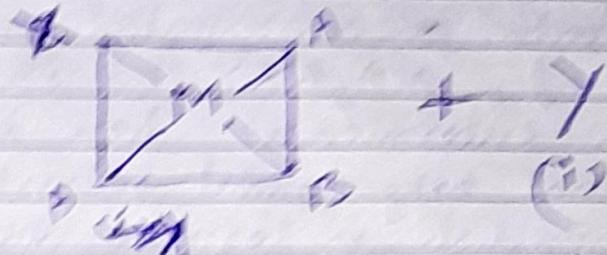
(2) π -Bonding Theory to explain trans effect:-

This theory can explain well the trans effect of those attached ligand in square planar complexes which are π -acids or π -acceptors. Take for example phosphine, CN^- , CO , C_2H_4 , PR_3 etc.

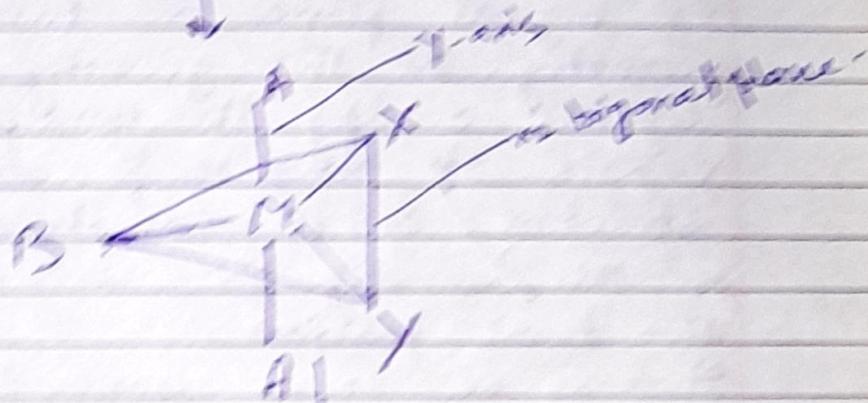


In this reaction X is replaced by γ . Obviously X is the leaving group and γ is the entering group. In MA_2BX , B is a π -bonding ligand. The ligand B is also called trans labelling ligand. In this complex B and X is trans to each other in square planar complex. According to π bonding theory, the ligand substitution reaction (i) given above takes place through

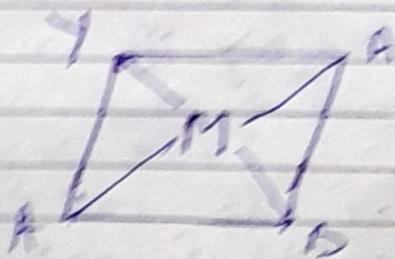
The shifts showing below -



(I) Sqaure planar complex (Mg₂B₂X₄)



II Tungsten hexagonal bismuthide
(Bismuth shale)
(Mg-BX₃)



(II) Sqaure planar complex Mg₂X₃

(a)

In step I the entering ligand (Y) attacks the square planar complex, MA_2BX (I) and an intermediate activated 5-coordinated complex (transition state), $MA_2BX Y$ (II) is obtained. This intermediate has trigonal bipyramidal geometry. This intermediate is formed due to the movement of X and Y ligands in the trigonal plane of trigonal bipyramidal geometry. In this geometry the two A ligands occupy the trans position along Y-axis. It may be seen from the structure of trigonal bipyramidal geometry that in this geometry the two A ligands occupy the trans position.

It may be seen from the structure of trigonal bipyramidal intermediate state (II) that the leaving group (X), entering group (Y) and π-bonding ligand (B) from the trigonal plane (x^2 plane) give the trigonal bipyramidal geometry.

(b)

In step (intermediate) transition state (II) loses X and square planar complex MA_2BY (III) is formed. In the formation of this square planar complex the bond angle BMY which is equal to 120° in trigonal bipyramidal structure (II) is expanded to 180° in square planar complex, MA_2BY (III).

The entering group (Y) ~~is~~ is placed trans to π acid ligand (π -bonding ligand) (B). The position of the entering group (Y) is placed in MA_2BY (III) in the same as that of leaving group (X) in MA_2BX (I)