

12.5: Stereochemistry of Octahedral Reactions

The stereochemical outcomes of a reaction can depend on numerous factors. For simplicity, the discussion in this section will be limited to octahedral complexes that react through dissociative mechanisms, with emphasis on those that occur through the limiting case of a dissociative (*D*) mechanism. In light of this focus, the reactions of Co(III) complexes, particularly those with ethylenediamine ligands, provide appropriate examples of well-characterized systems.

In the purely dissociative case, the octahedral metal complex completely loses one ligand to become a five-coordinate intermediate. Therefore, the structure of the product depends primarily on the structure of the intermediate and its interaction with the entering ligand. The outcome of a *D* reaction should not be influenced by the identity of the leaving group. However, the identity of the entering group and the reaction conditions are appropriate considerations. For example, under basic aqueous conditions, the conjugate base mechanism can alter the stereochemical outcome compared to the same reaction under more acidic conditions.

Structure of the intermediate

When an octahedral metal complex reacts through a *D* mechanism, a six-coordinate metal complex forms a five-coordinate intermediate, which goes on to react with the entering group. The structure of that 5-coordinate intermediate has a major influence on the stereochemistry of the product. Recall from a previous section (Section 9.4) that 5-coordinate metal complexes can adopt either a **square pyramidal** or **trigonal bipyramidal geometry**. * In general, if the intermediate adopts a square pyramidal structure, the incoming ligand will enter at the same site where the leaving group was lost, and stereochemistry is retained from reactant to product. On the other hand, if the intermediate structure is a trigonal pyramid, at least some of the product will not retain the original configuration.

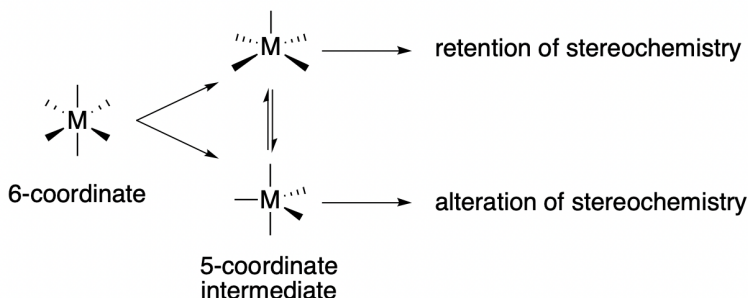


Figure 12.5.1: In the context of a substitution reaction, the loss of a ligand from an octahedral complex results in a five-coordinate intermediate. When the intermediate structure is a square pyramid, the new ligand enters so that the original stereochemistry is retained. The adoption of a trigonal bipyramid leads to changes in the stereochemistry of at least some of the product compared to the reactant. (CC-BY-SA; Kathryn Haas)

* Note: Recall from a previous section (Section 9.4) that square pyramid and trigonal bipyramid geometries typically have similar energies and readily interconvert through pseudorotation. However, during a *D* reaction, the intermediate exists for such a short moment in time, that interconversion is assumed not to occur unless there is an unusually long-lived intermediate.

Cis vs trans reactants

This section will present generalizations for the stereochemical consequences of substitution in *trans*-bisethylenediamine (*trans*-en) and *cis*-bisethylenediamine (*cis*-en) octahedral Co(III) complexes. *Cis*-en complexes tend to retain a square pyramidal intermediate structure and retain the *cis* stereochemistry of the product, except when the conjugate base mechanism promotes isomerization. On the other hand, *trans*-en complexes are more likely to undergo stereochemical rearrangements through a trigonal pyramidal intermediate. However, especially in the case of *trans*-en complexes, the product ratios are a result of mixtures of intermediates.

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