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## Scope of the Work

### 2.1 Introduction

The geometry and electron distribution of a molecule has great significance in the physical and chemical properties of the molecule. The stereochemistry of the molecule which emphasise the importance of the repulsion between electron clouds in molecule is found to be successful in providing a frame work to rationalise<sup>1,2</sup> a large body of structural data, in discovering a number of hitherto unrecognised structural relationships and in predicting new stereochemistries pointing the way to new research fields.

Metals of first transition series frequently possesses coordination number four or six and less frequently five. Four-coordination may be either tetrahedral or square planar and in six coordination the structure will be octahedral. Those metal ions or metal-ligand combinations, that form square-planar complexes may also form five-coordinate complexes having stereochemistries that are markedly different than those predicted from repulsion calculation based on the assumption of five equivalent metal-ligand bonds as the sole repelling entities. This "anomalous" behaviour is centred around metal ions such as rhodium (I), iridium (I), palladium (II), platinum (II) and gold (III) and around ligands that are conventionally regarded as being capable of utilising  $\pi$  orbitals in the metal ligand bond, but the range of intermediate behaviour between these complexes and completely 'normal' molecule is not a simple matter to determine precisely.

There may be a relationship between those metal ions exhibiting anomalous stereochemistry and those that have been classified as class (b) metals or “soft acids” these classifications being based on complex stability rather than on stereochemistry. But in this work complexes of certain elements of first transition series are modified with the use of polymer-support. Metal complexes with usual coordination of four can be changed to five-coordinate species with this strategy. A major feature of five-coordination is that there must be considerable differences among the different-ligand sites and the preference for certain sites by some ligands is determined by these repulsion values. The calculation are made on the basis of the minimisation of the total repulsion energy, obtained by summing the repulsion over every pair of metal-ligand bonds. It can be considered that this repulsion originates from the donor atoms themselves, from the metal-ligand bonds, or from some mixture of the two, which might not necessarily be the same for all compounds. But this kind of theoretical calculation are not made in this work. But complexes with unusual geometries and electronic arrangements are generated using crosslinked polymer-supports.

## **2.2 Brief survey of the present work**

In the present study, variety of Schiff-base (SB) complexes of certain metals of first transition series are considered and attempts made to modify them both geometrically and electronically by using polymer supports bearing appropriate functional groups.<sup>3,4</sup> The supports employed are DVB-crosslinked chloromethyl polystyrene (A-Cl), DVB-crosslinked aminomethyl polystyrene (BH<sub>2</sub>) or (C) and DVB-crosslinked poly(4-vinyl pyridine) (D). Attempts are also made to generate novel variety of complexes making use of these supports. The study broadly covers the following aspects.

- (i) Synthesis and characterisation of mono-SB complexes of Cu(II) complexes which also contain an anion function. The preparation of these complexes are not possible by normal solution procedure. A systematic change in the nature of complexes is also brought about by altering the substituents on the SB functions.
- (ii) Copper(II) complexes bearing two dissimilar SB functions are also prepared by employing polymer support that contain covalently linked SB moieties and reacting them with bis-SB complexes of Cu(II) taken in solutions. A variety of such asymmetric bis-SB complexes are synthesised and their structural characterisation made.
- (iii) Novel penta-coordinate bis-SB complexes of Cu(II) are generated on polymer supports by employing the support **C** and **D** and using solid-solution phase reaction technique. A wide variety of such species have been generated with change in substituents and their structural characterisation made by appropriate techniques.
- (iv) The penta-coordinated species generated as above are made to react with Lewis bases by solid-solution phase and solid-gas phase reactions. Six-coordinated species so generated are characterised by detailed spectral studies.
- (v) The  $d^1$  system of VO(IV) complexes with single SB function and having an anionic function and overall pentacoordinate structure are generated on appropriate polymer support. The Schiff-base functions are chosen with variety of substituents.
- (vi) Several asymmetric bis-Schiff-base complexes of VO(IV) were also generated as in the case of Cu(II) species and their structural and electronic characterisation made.

- (vii) Six-coordinated complexes of bis-SB VO(IV) were synthesised by reacting penta-coordinated SB complexes with polymer supports and several of such complexes with varying SB functions were generated and their systematic characterisation carried out.
- (viii) Several Co(II) complexes bearing four-coordination are synthesised which contain bidentate SB, tetradentate SB and mercaptoazo ligands. These complexes are supported on **C** and **D** and interesting modification brought about within them. Their relative uptake by the supports was also studied spectroscopically.
- (ix) The penta-coordinated cobalt species show strong affinity to molecules like water, dioxygen, H<sub>2</sub>S in the normal preparative conditions. The reversible binding of these ligand molecules are studied as a function of temperature. The reversible uptake of H<sub>2</sub>S and mercaptans by bis-mercapto azolato cobalt (II) complexes on polymer support is quite interesting from the point of view of pollution control.
- (x) Several asymmetric bis-SB complexes of Co(II) were also generated as in the case of the other two metal ions and their structural and electronic characterisation made. All the Co(II) complexes supported on the polymer support are characterised by detailed spectral studies.
- (xi) Since Co(III) complexes are catalytically important,<sup>5</sup> several of its Co(III) SB complexes are prepared and supported on polymer support bearing covalently linked SB functions. A closer look at the reaction shows that one of the SB functions of Co(SB)<sub>3</sub> is replaced by the supported SB. The electronic modification brought about by the polymer support is also studied in these classes.

- (xii) The effect of the polymer support on ligation characteristics of perfect tetradentate ligands like salen is also studied. For this salen derivatives employing 2,4-dihydroxy benzaldehyde and ethylene diamine (en) and O-phenylene diamine (phen) were synthesised and supported covalently on polymer A-Cl. Interestingly, they behave as bidentate ligand, rather as tetradentate ligands. This is accounted for.

### References

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