

## CHAPTER V

## SUMMARY AND CONCLUSIONS

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The study of co-ordination chemistry is important due to its many applications in pure as well as in applied sciences. The development of research in co-ordination chemistry is due to the phenomenal progress in experimental techniques such as infrared spectroscopy, visible and ultraviolet spectroscopy, electron diffraction, electron paramagnetic resonance, nuclear magnetic resonance, X-ray spectroscopy etc.

X-ray spectroscopic studies on cobalt in the form of pure metal, alloys, inter-metallic compounds, complexes etc., have been carried out widely. In complexes cobalt exhibits valency two or three. The complexes in which cobalt has valency three are more stable than those of valency two. Almost all cobalt(III) complexes are octahedral in symmetry. With two kinds of ligands for a complex having general formula  $[\text{Co}(\text{AA})_2(\text{B})_2]$ , two geometric isomers cis-trans are possible. The gradual replacement of ligand will cause the effective atomic charge on the central cobalt atom to change. These factors are bound to influence the X-ray absorption process and hence the X-ray absorption spectrum.

In the work presented investigations were carried out on octahedral Co(III) complexes using X-ray absorption technique. The octahedral cis and trans Co(III) complexes with general formula  $[\text{Co}(\text{AA})_2(\text{B})_2]^{+1}$  where AA indicates the bidentate ligands

en, tn, pn and B indicates the monodentate ligands  $\text{NO}_2^-$ ,  $\text{Cl}^-$  were prepared using A.R. grade starting chemicals, according to the procedures given in the standard text-books in inorganic synthesis. The fine powder of a complex, obtained by grinding the complex in agate mortar, was used to prepare the absorption screen. The absorption screens were prepared by spreading uniformly the fine powder of a complex on a cellophane tape. The X-ray K-absorption spectra of the complex<sup>es</sup> were recorded on Kodak Dental X-ray films using a 400 mm Cauchois type bent mica crystal spectrograph designed and fabricated in the departmental work-shop. Microphotometer records of the films were obtained on Carl Zeiss Jena rapid microphotometer GII coupled with potentiometric recorder GIBI. The microphotometer records were obtained with magnification 25x and 50x, the corresponding chart speed being 300 mm/min and 120 mm/min.

Co-K edges in complexes studied in the present investigation do not show any structure or splitting. This confirms octahedral co-ordination as reported by Van Nordstrand (1,2).

The shift of K-absorption edge of cobalt in a complex is measured in comparison with the K-absorption edge of cobalt in pure metallic state. For all the complexes the shift is found towards the high energy side. The effective atomic charge 'q' on the central cobalt ion is estimated using experimental chemical shifts of the complexes investigated and the plot between the theoretical shifts in binding energy of the K-electron and the oxidation number of cobalt atom (3).

For the complexes with general formula  $\text{trans}[\text{Co}(\text{AA})_2(\text{NO}_2)_2]$   $\text{NO}_3$  (AA = en, tn, pn), the gradual replacement of the bidentate ligand causes change in the chemical shift. This variation of chemical shift is correlated with the size of the chelate ring (4). Further, the stability of these complexes is discussed on the basis of effective atomic charge 'q' on the central cobalt ion.

In the complex ions  $\text{trans}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{+1}$  and  $\text{trans}[\text{Co}(\text{tn})_2(\text{NO}_2)_2]^{+1}$ , the gradual replacement of monodentate ligand  $\text{NO}_2^-$  by  $\text{Cl}^-$  causes suppression of chemical shift which is correlated with spectrochemical series (5,5a) and electronegativity series of ligands.

For the cis-trans isomers of complexes having general formula  $[\text{Co}(\text{AA})_2(\text{NO}_2)_2]^{+1}$  (AA = en, tn, pn), the chemical shift is found to be less for a cis-form complex as compared to the corresponding trans-form. This suppression of chemical shift in the cis-form of a complex is attributed to the percentage increase in covalency of the metal-ligand bond due to the asymmetric distribution of electro-static field in the cis-form.

The extended X-ray absorption fine structure on the high energy side of Co-K-edge in Co(III) complexes gives interesting results. The absence of the low energy absorption feature is explained as due to the absence of unfilled 4p orbitals (6). Further on the basis of Pauling's hybridization theory, the main peak 'A' is assigned to  $1s \rightarrow 5p$  transition as is done by Bhat *et al.* (7).

The extended absorption fine structure is explained on the basis MOT. The MO energy level diagram for low spin octahedral Co(III) complexes is used to assign  $1s \rightarrow tlu^*$  transition to the main absorption peak 'A'.

The nature of 'A' peak is helpful in distinguishing between cis and trans isomers of a complex. The main absorption peak 'A' appears a relatively broad structure in case of cis-isomers. This broadening of the 'A' peak in the cis-form is attributed to the lowering in symmetry in the cis-form complex as is done by Obashi (8). In the case of cis-complexes, the absorption maxima and minima are not well defined and are flattened. This is attributed to the complicated distortion in a cis-complex.

The average metal-ligand distances for the Co(III) complexes are determined using Levy's and Lytle's method. The metal-ligand distances calculated from the Levy's method are found to be in good agreement with those obtained from the Lytle's method.

It is found that the Lytle plots for complexes do not pass through the origin. It has been reported (9) that only in the case of metals and compounds with metallic character the Lytle plots pass through the origin while in case of insulators, they do not. The intercept  $V_c$  on the E axis of a Lytle plot is a measure of effective nuclear charge. The variation of  $V_c$  is found to be consistent with the chemical shifts.

For the complexes having general formula  $\text{trans}[\text{Co}(\text{AA})_2(\text{NO}_2)_2]\text{NO}_3$  where AA = en, tn, pn, the metal-ligand distance varies with gradual replacement of bidentate ligand. This variation in bond distance is explained as due to the out-stretching of the metal-ligand bond because of the substitution of a bulky bidentate ligand.

In the case of complexes  $\text{trans}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{1+}$  and  $\text{trans}[\text{Co}(\text{tn})_2(\text{NO}_2)_2]^{1+}$  the gradual replacement of monodentate, ligand  $\text{NO}_2^-$  by  $\text{Cl}^-$  causes an increase in the metal-ligand distance. This is attributed to the magnitude of the crystal field offered by the monodentate ligands  $\text{NO}_2^-$  and  $\text{Cl}^-$ .

LSS theory is applied to the complexes with a general formula  $\text{trans}[\text{Co}(\text{AA})_2(\text{NO}_2)_2]\text{NO}_3$  where AA = en, tn, pn. The chemical bonding parameter in each complex is determined from the slope of n versus K plot and the average metal-ligand distance  $R_1$  calculated from Levy's theory. The variation in  $\alpha_1$  with ligand substitution is correlated with the changing iono-covalent metal-ligand bonding as is done by Lokhande et al. (10). Further using this theory the bond lengths for these complexes are determined.

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