PREFACE

Despite the fact that a considerable amount of interest has been paid in the past two decades on sulphur-containing ligands and their metal complexes, but the available data on the metal-sulphur bond are yet not sufficient to provide a fairly coherent picture of the donor-acceptor relationship between sulphur and the metal ions. The position of sulphur ligands in spectrochemical and nephelauxetic series also varies; thus it will be interesting to study the physico-chemical properties of complexes of sulphur-containing ligands in order to seek possible correlations between such diverse properties.

As a part of the investigation involving this thesis, an attempt has been made to seek a correlation between the metal-sulphur frequencies and the nature of metal ions. Variations of the metal-sulphur frequencies with the oxidation states of the central metal ion have also been studied.

The ligand employed for complexation is "allyl-isothiocyanate" or AITc. The metal ions used as central cations are: Co(II), Cu(II), Hg(II), Pd(II), Au(III), Fe(III), Rh(III), Ru(III), Ru(II), and Pt(IV). Whereas Cu(II), Co(II), and Ru(II) gave, on reaction with AITc, the complexes having the valence state of the central metal ion unchanged, the findings in the case of other metal ions were quite unusual and staggering. Thus, Pd(II) and Rh(III) gave Pd(I) and Rh(I) complex respectively; Ru(III) and Au(III) gave Ru(II) and Au(II) complex respectively; Pt(IV)
gave an entirely unusual Pt(III) complex; and Fe(III) formed an Fe(0) complex. Of all the result of the Hg(II)'s reaction with AITc was most amazing; instead of forming an usual or unusual metal complex, an organometallic (organomercuric) compound was formed instead. In this way, the reaction of the ligand with most metal ions proved to be highly interesting and unusual.

The complexes of the above mentioned cations with the ligand (AITc) have been characterized by analyses, spectro-photometric studies, magnetic data, and conductometric measurements. The spatial configurations of the complexes have been proposed on the basis of the above studies. It is proposed that Ru(II), Pt(III), and Fe(0) complexes are octahedral; Rh(I) and Cu(II) complexes are trigonal-bipyramidal; Au(II) and Pd(I) complexes are square-planar; Co(II) and Co(II)/pyridine complexes are tetrahedral.

The electronic (reflectance) spectra of the complexes (which are mostly insoluble or very sparingly soluble) were recorded in the solid state. Bands due to d-d transitions have been located and plausible assignments to these bands have been made. On the basis of the position and intensity of these bands, the proposed spatial configurations for these complexes have further been corroborated.

The infrared data of the complexes provide an unambiguous evidence of the involvement of not only the nitrogen and sulphur
of the -NCS group, but also the olefinic bond of the ligand (CH₂=CH-CH₂NCS).

Besides exhibiting complex-forming tendency, AITc has also been found to react in an entirely unusual and novel manner with a number of other metal ions to form the respective inorganic metal sulphides. Thus, while attempting to prepare complexes of Ag(I), Pb(II), Cd(II), Ce(IV), and Hg(II)/I⁻, with AITc employing the usual procedure, only sulphides of these metals were eventually isolated instead of the expected metal-ligand complexes. Yet many other metal ions did not react at all with 'this' ligand to yield any perceptible reaction product.

Because of these peculiar features, as described above, the ligand allyl-isothiocyanate has proven to be an highly unusual ligand. The work done on allyl-isothiocyanate, as incorporated in this thesis, is only a minor contribution by the author. And, keeping in view of the extremely unusual properties, there is need for further extensive research work on this ligand. Unforeseen results in the field of coordination chemistry are expected to emerge from further studies.

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