

F O R E W O R D

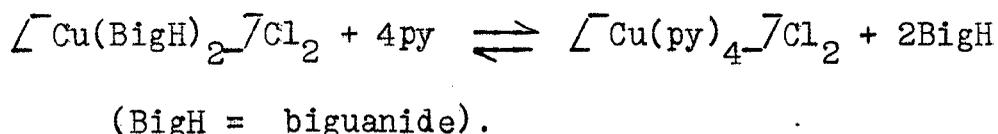
The thesis opens with a review of chromatographic studies on coordination complexes. This review begins with the development of the art of chromatography and goes on to unfold the beauty and power of chromatography as a tool with particular reference to metal complexes. The task of writing the review has been made particularly difficult because of the availability of an excellent article by Druding and Kauffman (Coord.Chem.Revs., 1968, 3,409). However efforts have been made to keep our review as distinct and to-date as possible.

The review is followed by a chapter describing the plan of the present work (Chapter II).

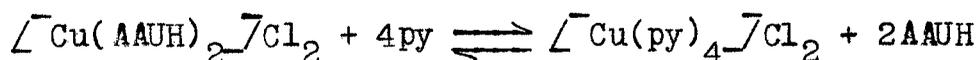
Chapter III : This chapter gives the characterisation data of a large number of homochelates of copper(II), nickel(II), palladium(II) and cobalt(III) and mixed chelates of copper(II) and cobalt(III) alongwith relevant references to the original literature describing their synthesis. This section describes the synthesis and characterisation of the new square planar picolinato mono(biguanide) copper(II). This chapter also includes the chromatographic techniques used in this study.

Chapter IV : In this chapter the results of paper chromatographic studies of square planar bis(biguanide) and bis(substituted biguanide) complexes of copper(II), nickel(II) and palladium(II)

in aqueous KCl-pyridine developer are described. R_f values follow the order : Ni(II) > Cu(II) > Pd(II). Among the complexes of a particular metal ion R_f values increase with increasing alkyl substitution in the biguanide moiety. Phenyl substitution lowers the R_f . Substantial amount of pyridine in the developer results in two spots with bis(biguanide) copper(II). The following equilibrium is suggested :



Chapter V : In this chapter the salient points of paper chromatographic studies of square planar bis(1-amidino-O-alkylurea) copper(II) and nickel(II) complexes in aqueous KCl-pyridine developers are included. R_f values follow the order : Ni(II) > Cu(II). Solubilities of the complexes in different developer solvents are believed to play a more significant role than the inductive effects of the substituent groups and hydrogen bond forming abilities of the ligand. An equilibrium of the following type

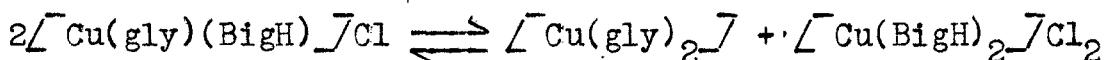


has neither been proved nor dispelled (AAUH = 1-amidino-O-alkylurea).

Chapter VI : This chapter describes filter paper chromatography of $\left[\text{Pd}(\text{AMUH})_2 \right] \text{Cl}_2$ (AMUH = 1-amidino-O-methylurea) in aqueous KCl-pyridine developer. This study has helped in the synthesis

and identification of hitherto unknown $\text{[Pd(AMUH)Cl}_2\text{]}^-$. The synthesis of $\text{[Pd(AMUH)Cl}_2\text{]}^-$ has been accomplished via two routes : (1) palladium(II) promoted addition of methanol to dicyandiamide and (2) treating $\text{Li}_2\text{[PdCl}_4\text{]}^-$ with AMUH.HCl in 1:1 ratio with dilute HCl at pH 3.0. A number of other dichloro mono(1-amidino-O-alkylurea) palladium(II) compounds have also been synthesised. These compounds readily aquate in dilute aqueous solution giving bi-univalent electrolyte conductance values. The isomeric $\text{[Pd(AMUH)}_2\text{]}^- \text{[PdCl}_4\text{]}^-$ has also been prepared and shown to be different from $\text{[Pd(AMUH)Cl}_2\text{]}^-$.

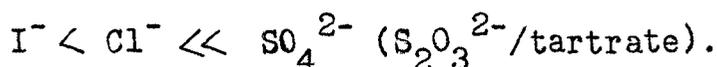
Chapter VII : In this chapter paper chromatographic studies of sixteen copper(II) mixed chelates in aqueous KCl-pyridine developer has been made. [Cu(gly)(BigH)]Cl , $\text{[Cu(}\alpha\text{-alan)(BigH)]Cl}$ etc. (glyH = glycine; α -alanH = α -alanine) give two spots in all the developers studied. An equilibrium of the following type is suggested :



$\text{[Cu(gly)(o-phen)]Cl}$ (o-phen = o-phenanthroline) shows similar behaviour. Such disproportionation reaction is less favoured in [Cu(gly)(dipy)]Cl (dipy = dipyridyl). $\text{[Cu(o-phen)(BigH)]Cl}_2$ and $\text{[Cu(dipy)(BigH)]Cl}_2$ provide single spot on proper choice of the developer solvent.

Chapter VIII : Twenty two inert cobalt(III) complexes of different overall charges have been subjected to paper chromatography in

aqueous developers containing varying concentrations of such electrolytes as KCl, KI, K_2SO_4 , $Na_2S_2O_3$ and K-Na-tartrate. In general, R_f values of complexes belonging to a particular charge type (+3, +2, and +1) are lowest in KI and then increase as the electrolyte changes to KCl and then to bi-univalent K_2SO_4 , $Na_2S_2O_3$ and K-Na-tartrate. This variation in R_f is in conformity with the established order of outer sphere association constants of the complex cations with anions :



Chapter IX : In this chapter silica gel chromatographic studies of square planar bis(biguanide) and bis(1-amidino-O-alkylurea) complexes of copper(II), nickel(II) and palladium(II) in aqueous developer containing different salts have been made. These studies reveal that all the nickel(II) complexes are totally decomposed to the corresponding aquo complexes due to liberation of free acid from silica gel. Many of the copper(II) complexes studied were found to be resistant to decomposition by silica gel. Cobalt(III) complexes are strongly held on the negatively charged surface of the silica gel when water alone is used as the developer. With electrolyte developer the movement of the complexes on the silica gel bed is comfortable. A distinction in R_f values of complexes of varying over all charge was observed (+1 > +2 > +3) to a certain point. Outer sphere association between the complex cation and the electrolyte anion takes place and this effect is large, the larger the charge on the complex is.

The thesis ends in an Appendix which includes some of our published papers.