

CHAPTER II :

PLAN OF THE PRESENT WORK.

A perusal of the foregoing review shows that major effort has been expended on the chromatographic behaviour of cobalt(III) complexes alone. Much less has been done on metal(II) ions. Coordination chemists' choice of cobalt(III) is quite understandable since it religiously shows a single coordination number six and an octahedral stereochemistry. Furthermore cobalt(III) is substitution inert which fact is destined to lead to minimum of complicated substitution reactions with developer solvents. Chromium(III) has been little investigated on paper and by TLC - presumably because its complexes cannot be synthesised as easily as these of cobalt(III) and also because there is not yet a good spot detection agent. As to the other bivalent metal ions such as copper(II), nickel(II), palladium(II), platinum(II) the literature is still quite poor so far as their chromatographic behaviours are concerned. Copper(II) and nickel(II) have mostly been investigated from the stand point of analytical detection. Studies of the chromatographic behaviour of these two metal ions might be quite disturbing and yet quite rewarding because of the fact that they are both substitution labile and they are capable of generating several stereochemistries. We find that there is hardly any report dealing with the chromatography of genuine square planar complexes of these two metal ions.

Chromatographic behaviour of any series of charged complexes will be dominated by several factors. Among these factors may be

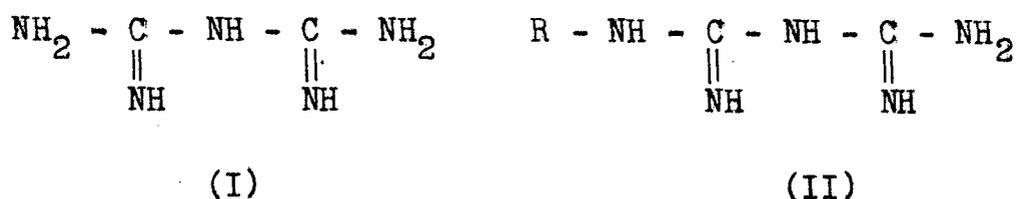
reckoned charge, size, solubility and outer sphere association of the complexes. Extremely limited number of reports are available on one or two of the above factors. Almost all the reports in this regard may be credited to Yoneda^{116,120-122,125,126}.

The best possible way to enrich this area is to undertake a study of a long series of complexes with the same geometry and with substitution in the ligand without changing the stereochemistry of the complex. It is our conviction that these studies have not so far appeared in the literature because of the paucity of such comparable complexes.

Presently a very active area in the field of coordination complexes is that of mixed chelate complexes. In view of the tendency of a mixed chelate to disproportionate into the homochelates, synthesis of such mixed chelates is often quite an assignment. Besides mixed chelates are likely to provide interesting informations on the magnetism, electronic spectra and flexible behaviour of the coordinating ligands. It is also our belief that chromatography of mixed chelate complexes is also likely to be rewarding, particularly when the metal ion involved is one of the substitution-labile type.

Our laboratory is exceptionally rich in square planar complexes of copper(II), nickel(II) and palladium(II). Besides we could lay our hands on a very large group of mixed chelate complexes of copper(II) and cobalt(III) as well.

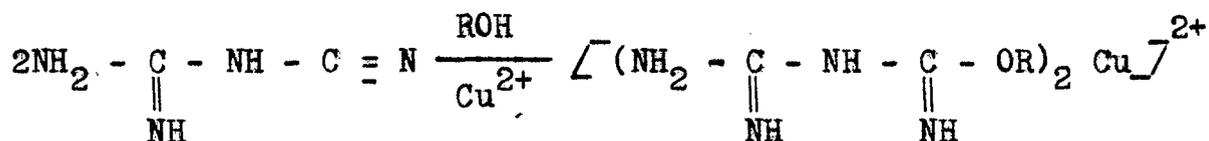
Biguanides(I) and N¹-substituted biguanides(II) are among the most formidable coordinating ligands. They function as very strong field NN bidentate donors and thus a series of square planar copper(II), nickel(II) and palladium(II)



complexes are well known for many years. Ray and his students²²¹ have been investigating these coordinating ligands since 1937. The square planar geometry of the copper(II) complexes is verified by their rose red colour²²¹⁻²²⁵ with a typical square planar $[\text{Cu N}_4]^{2+}$ absorption band at 19 kK²²⁶⁻²³⁰. The x-ray crystal structure of ethylenedibiguanide copper(II) also confirms a square planar geometry²³¹. The nickel(II) complexes are orange yellow or yellow and diamagnetic which amply proves the square planar geometry^{221,232,233}. The palladium(II) complexes^{221,234} are cream coloured and are square planar, since the only geometry known with palladium(II) is square planar when the coordination number is four. The formidable character of biguanides as coordinating ligands is most spectacularly revealed in stabilisation of silver(III)^{221,235}, manganese(IV) and manganese(III)^{221,236,237} etc. The inner sphere formation constant of tris(biguanide) cobalt(III) is extremely high-higher than even that of tris(ethylenediamine) cobalt(III)^{221,238}. Besides, it was from an appreciation of the racemisation kinetics of levo tris(biguanide)

cobalt(III) that Rây and Dutt^{221,239} suggested for the first time an intramolecular twist mechanism of racemisation. Furthermore, the complex also shows interesting kinetics and mechanistic behaviour during acid hydrolysis²⁴⁰. Recently one of our senior colleagues in this Department has worked out the outer sphere association constants of tris (biguanide) cobalt(III) with chloride, bromide, iodide and sulphate ions^{241,242}.

During the last fifteen years through the initiative of Dutta and his students^{223,243,244} a novel alcohol addition to dicyandiamide has been discovered. This reaction is prompted by transition metal ions and leads to another set of formidable coordinating ligands called 1-amidino-O-alkylureas.



These ligands are parallel to biguanides^{221,244} and give similarly coloured square planar bis(ligand) complexes with copper(II), nickel(II) and palladium(II)^{223,227,243-244}. They also offer a strong ligand field on the metal ion. Their chemistry is still being worked out in our laboratory.

It is gratifying to record that all metal complexes of biguanides and 1-amidino-O-alkylureas can be easily obtained in a very high state of purity and in highly crystalline nature. Their electronic spectra have also been extensively studied²⁴⁴ over many years - which can now serve as an index of purity of the samples.

All these considerations have led us to undertake an extensive chromatographic investigation of the square planar bis(biguanide) metal(II) and bis(1-amidino-O-alkylurea) metal(II) complexes. A large number of cobalt(III) biguanide chelates^{221,245} and cobalt(III) mixed chelates^{244,246-249} containing biguanides have also been investigated to throw light on their chromatographic behaviour. Finally a series of copper(II) mixed chelates^{221,250-253} have also been subjected to investigation. In the following sections we describe the results of such studies.