

CHAPTER IV :

PAPER CHROMATOGRAPHY OF SQUARE PLANAR BIS(BIGUANIDE)
COMPLEXES OF COPPER(II), NICKEL(II) AND PALLADIUM(II).

Most studies on paper chromatography of inorganic cations have been directed with a view to their identification via characteristic R_f values in a chosen developer²⁹⁴⁻²⁹⁶. Paper chromatographic studies on metal complexes have mainly veered around inert cobalt(III)^{60,116,117,143,146}. Little work on paper chromatography of complexes of other transition metals has appeared in the literature^{138,144}. A series of square planar bis(biguanide) complexes of copper(II), nickel(II) and palladium(II) have been chosen for a paper chromatographic study. While cobalt(III) is substitution inert and provides a single coordination number six and a fixed octahedral geometry, copper(II), nickel(II) and palladium(II) are substitution labile and also are capable of assuming more than one coordination number and geometry. The purpose of this study of bis(biguanide) metal(II) complexes has been multi-fold :

- (i) to determine a suitable developer such that the complexes are chromatographed as genuine bis(biguanide) complexes;
- (ii) to study the effect, if any, of substitution in the biguanide moiety on the R_f values of the complexes and
- (iii) to determine the influence of the transition metals on R_f .

Methods and materials :

The complexes have been obtained by following published procedures. Their purity has been checked by analysis and spectral data (Chapter III). The general chromatographic techniques have also been described in Chapter III.

For the purpose of putting spots most of the complexes were dissolved in water at room temperature or in warm water. In a few cases (e.g. those of copper(II) dimethyl, diethyl and phenyl biguanide) complexes were dissolved in ethanol because of greater solubility in this solvent. The following developers were selected after a number of trials :

- Developer I : 100 ml 0.5M aqueous KCl + 5 ml pyridine
" II : 100 ml 1M aqueous KCl + 5 ml pyridine
" III : 70 ml 0.5M aqueous KCl + 30 ml 1:1 pyridine.

Bis(biguanide) copper(II) complex on spraying with rubeanic acid gave an oval shaped spot, the lower portion of the spot having a dominant brown colour while the upper part had the usual dirty green colour of copper(II) rubeanate. But most of the other substituted biguanide copper(II) complexes gave only a dirty green coloured spot on spraying with rubeanic acid. Nickel(II) complexes showed blue to blue violet colour of nickel(II) rubeanate and palladium(II) complexes a yellow colour of palladium(II) rubeanate. The brown shade in the spot of bis(biguanide) copper(II) chloride was not subjected to any further investigation.

Results and Discussion :

Developer I was quite satisfactory for identification and separation of copper(II) and palladium(II) bis(biguanide) complexes from one another as well as nickel(II) and palladium(II) complexes from each other. The same developer was also quite suitable for separation and identification of bis(biguanide) copper(II) from

bis(substituted biguanide) copper(II). In this developer both copper(II) and palladium(II) complexes provide well defined spots, those of copper(II) being 2-2.5 cm in length and those of palladium(II) ~ 1 cm. Bis(phenyl biguanide) palladium(II) chloride alone gives large tailing (~5 cm). Unfortunately this developer provided a big sized spots (~10 cm) for bis(biguanide) nickel(II) complexes and was therefore not considered a suitable choice for those nickel(II) complexes. Suitable sized spots (2.5 to 3.0 cm) of bis(biguanide) nickel(II) and bis(substituted biguanide) nickel(II) complexes were obtained using developer II which also allowed distinction between nickel(II) complexes themselves. But neither developer I nor developer II was found suitable for distinguishing bis(biguanide) palladium(II) and bis(substituted biguanide) palladium(II) complexes from one another. To achieve this distinction developer III was found suitable.

Yoneda¹¹⁶ from a study of cobalt(III) complexes concluded that the cationic complexes are held strongly on the negatively charged cellulose anion of the filter paper. Thus in pure water as developer positively charged complexes either did not travel at all or if they travelled they diffused considerably along the filter paper. With distilled water alone most of our complexes either did not travel at all or diffused to a long distance (Fig. 4.1). Remembering that metal biguanide complexes are stable to dissociation²²¹ only at pH ~ 7, we tried several electrolytes as developers so that the cations of the electrolytes may quench the undesirable effect of the cellulose anion. Satisfactory spots were obtained with two sets of developers :

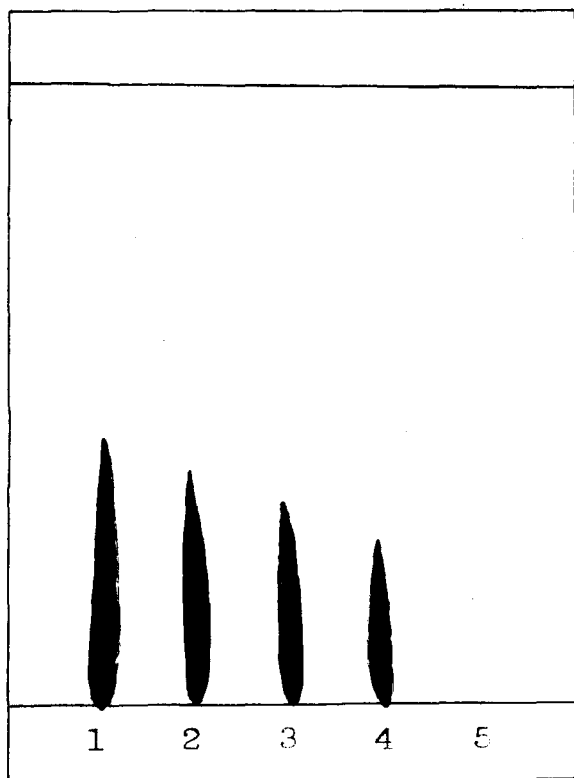


Fig.4.1. Chromatograms in 100ml distilled water as developer.

1. $\text{[Ni(BigH)}_2\text{]Cl}_2$
2. $\text{[Cu(BigH)}_2\text{]Cl}_2$
3. $\text{[Ni Et(BigH)}_2\text{]Cl}_2$
4. $\text{[Cu Et(BigH)}_2\text{]Cl}_2$
5. $\text{[Pd(BigH)}_2\text{]Cl}_2$

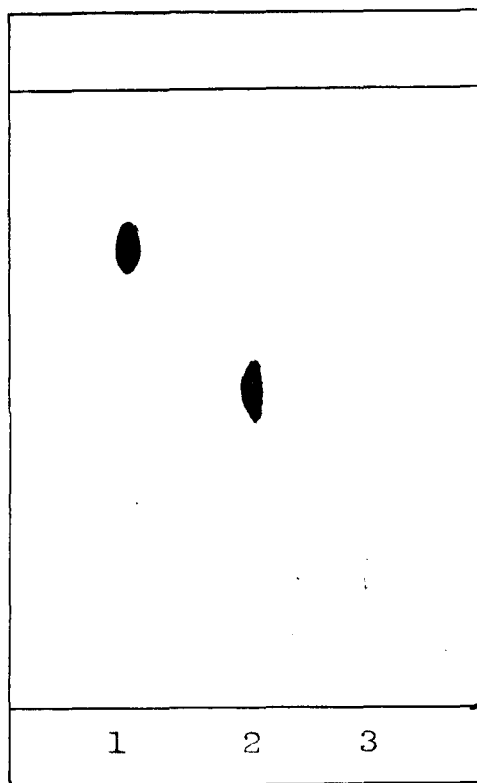


Fig.4.6. Chromatograms in 100ml 1M aqueous KCl + 5ml pyridine as developer.

1. $\text{[Ni(BigH)}_2\text{]Cl}_2$
2. $\text{[Cu(BigH)}_2\text{]Cl}_2$
3. $\text{[Pd(BigH)}_2\text{]Cl}_2$

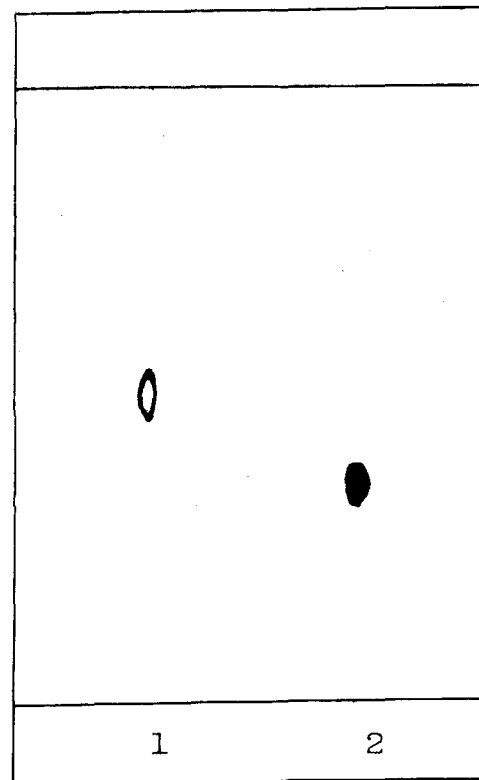


Fig.4.7. Chromatograms in 100ml 1M aqueous KCl + 5ml pyridine as developer.

1. $\text{[Cu Et(BigH)}_2\text{]Cl}_2$
2. $\text{[Ni Et(BigH)}_2\text{]Cl}_2$

- A. 0.5M (or 1M) aqueous ammonium acetate.
- B. 0.5M (or 1M) aqueous KCl containing pyridine.

The first of these developers (A), although gave a pH 6.5-6.8 where the metal biguanides do not dissociate appreciably were abandoned since spectrophotometric studies revealed that the electronic spectra of copper(II), nickel(II) and palladium(II) complexes had undergone substantial modification. These developers therefore do not give R_f values of the genuine complexes. The developers of category (B) provided the same electronic spectra of the complexes as is obtained in aqueous solution alone (Table 4.1 and Figs. 4.2, 4.3, 4.4 and 4.5). Thus in 100 ml 0.5M (or 1M) KCl containing 5 ml pyridine. We have the genuine chromatograms of our complexes (Figs. 4.6, 4.7 and Tables 4.2 and 4.3).

Effect of KCl/pyridine :

Variation of KCl concentration in aqueous pyridine reveals that R_f values of all complexes increase with increasing KCl concentration (Table 4.2). It is to be noted that neither KCl nor pyridine alone can give good spots (Figs. 4.8 and 4.9) but a suitable combination can (Fig. 4.6). Pyridine substantially increases the solubilities of the complexes.

Interestingly on raising the pyridine concentration and lowering the KCl concentration (developer III) bis(biguanide) copper(II) complex betrayed two distinct spots (Fig. 4.10), the one with higher R_f was less intense than the other with lower R_f .

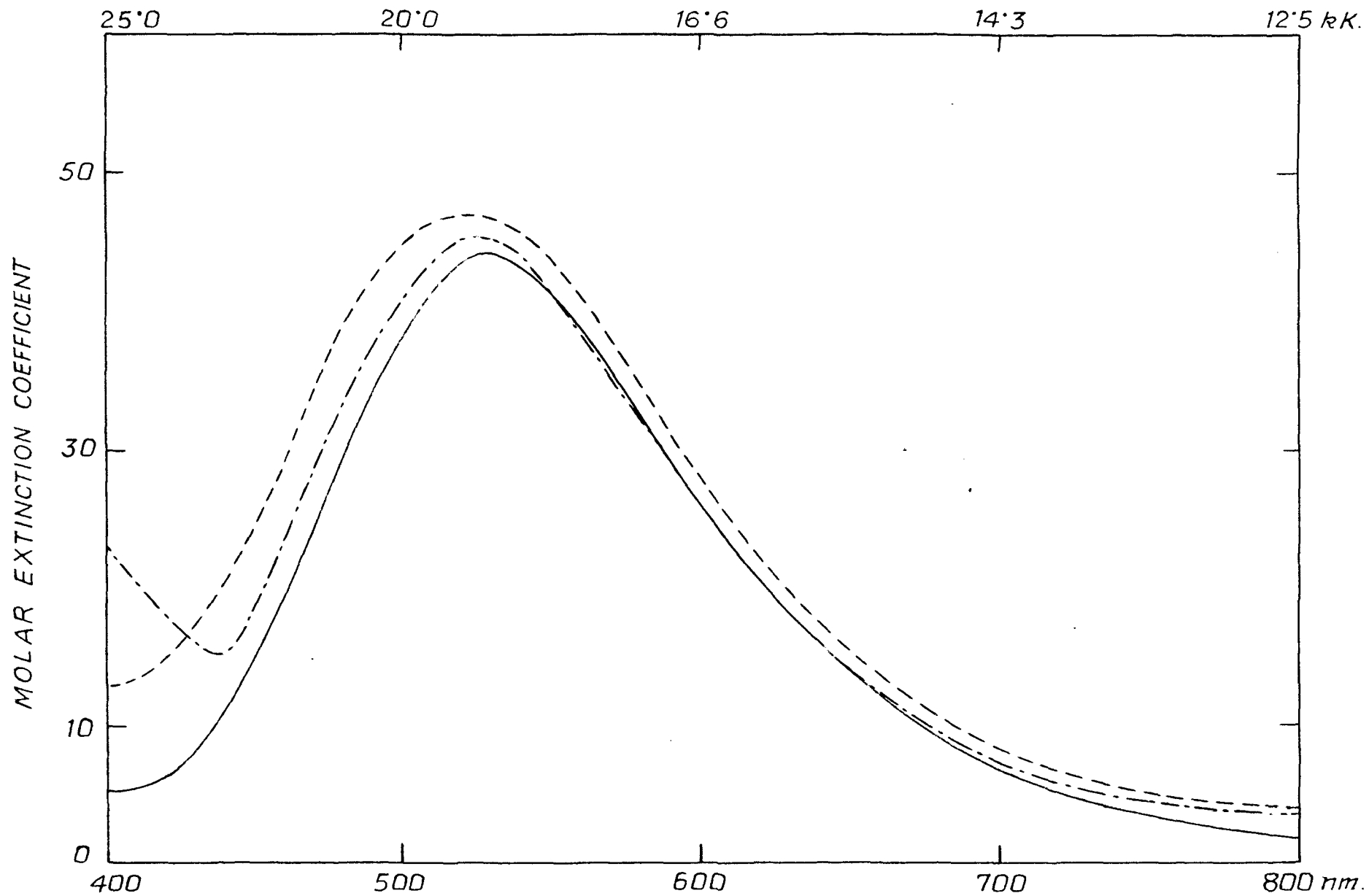


FIG.4'2. ELECTRONIC SPECTRA OF

$[Cu(BigH)_2]Cl_2$ in aqueous solution (—)

$[Cu(BigH)_2]Cl_2$ in developer I (---)

$[Cu(BigH)_2]Cl_2$ in developer III (-.-.-)

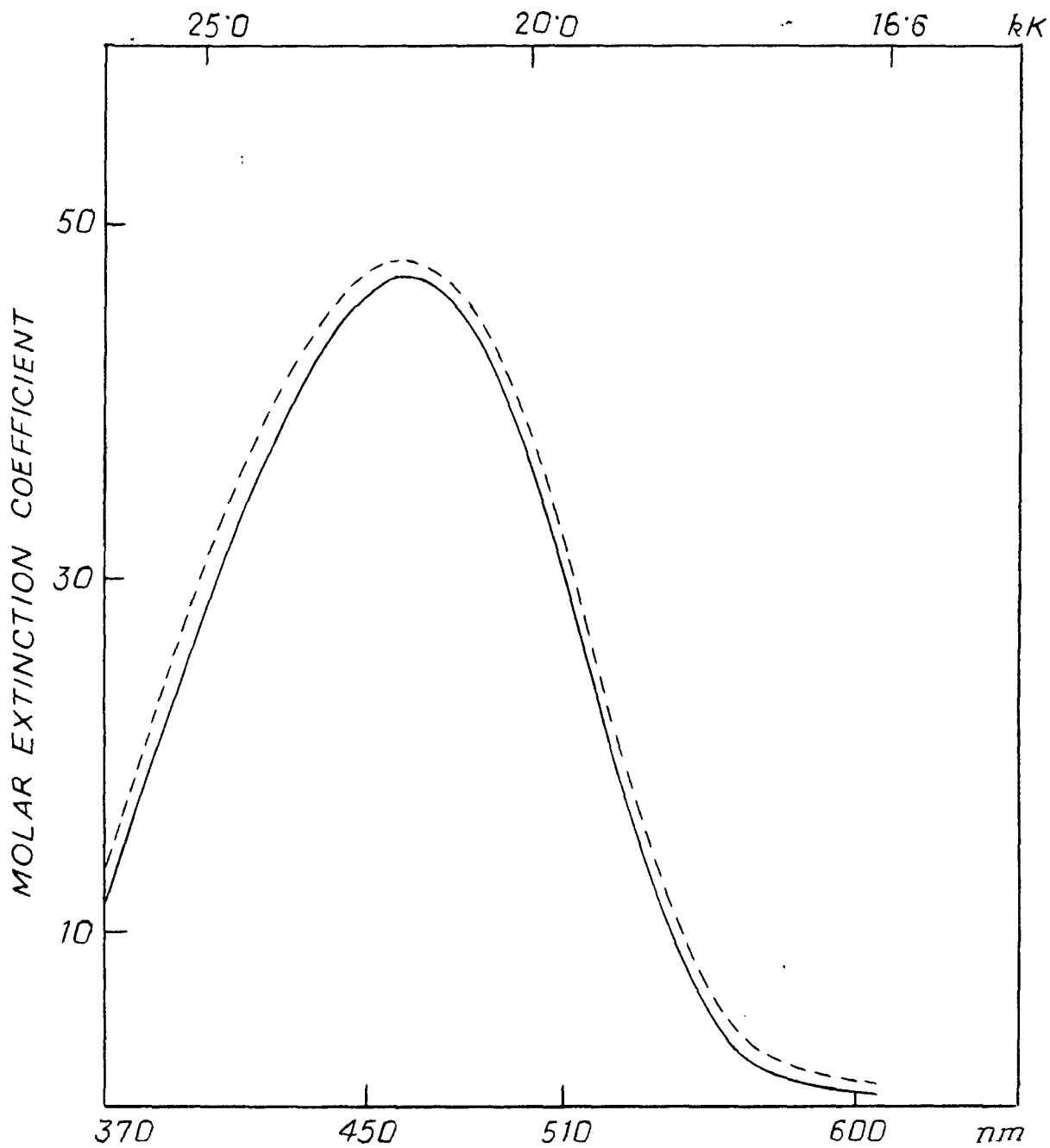


FIG. 4'3. ELECTRONIC SPECTRA OF :

$[Ni(BigH)_2]Cl_2$ in aqueous solution (—)

$[Ni(BigH)_2]Cl_2$ in developer II (----)

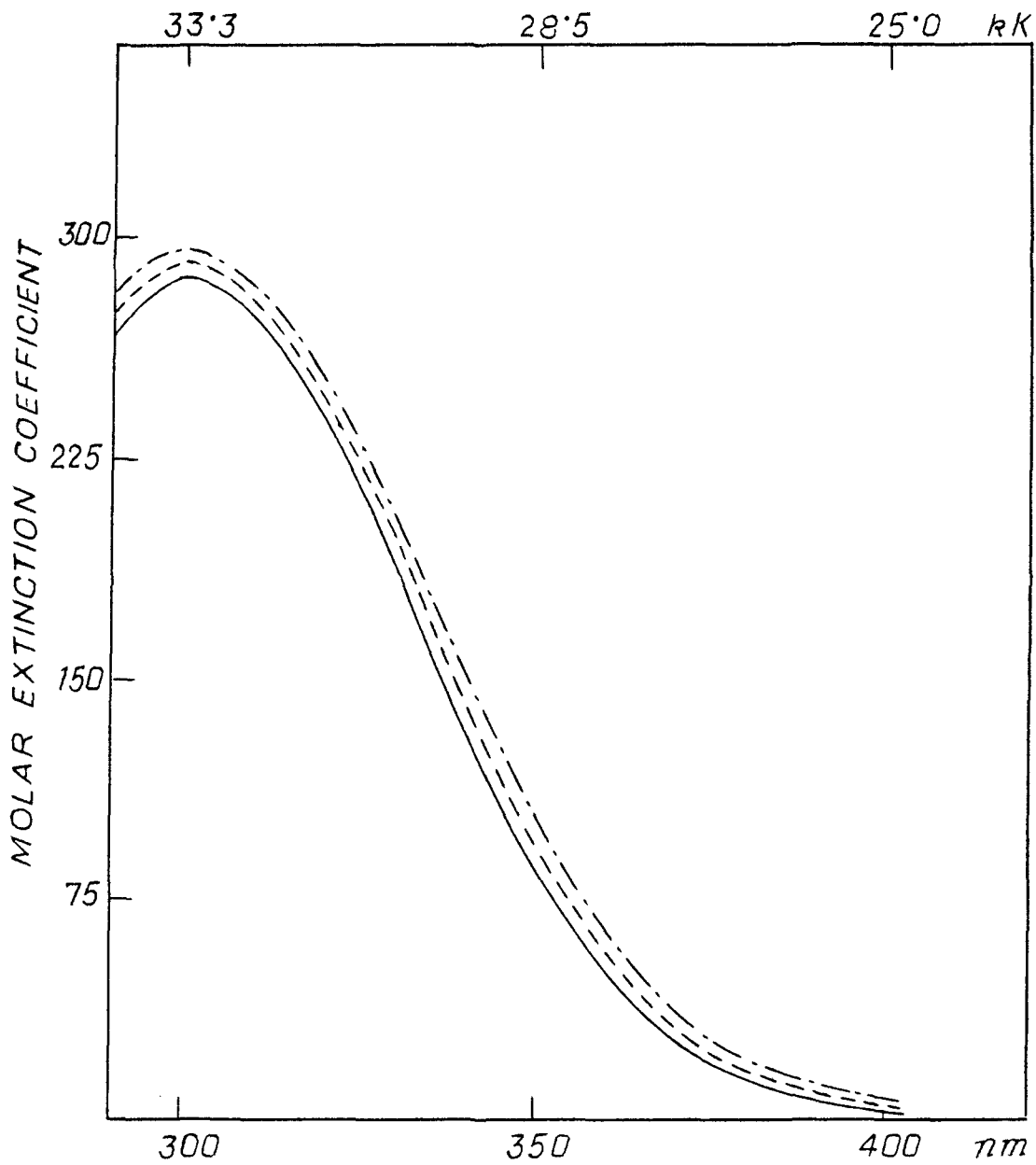


FIG.4'4. ELECTRONIC SPECTRA OF :

- $[Pd(BigH)_2]Cl_2$ in aqueous solution (—)
- $[Pd(BigH)_2]Cl_2$ in the developer II (---)
- $[Pd(BigH)_2]Cl_2$ in the developer III (-.-)

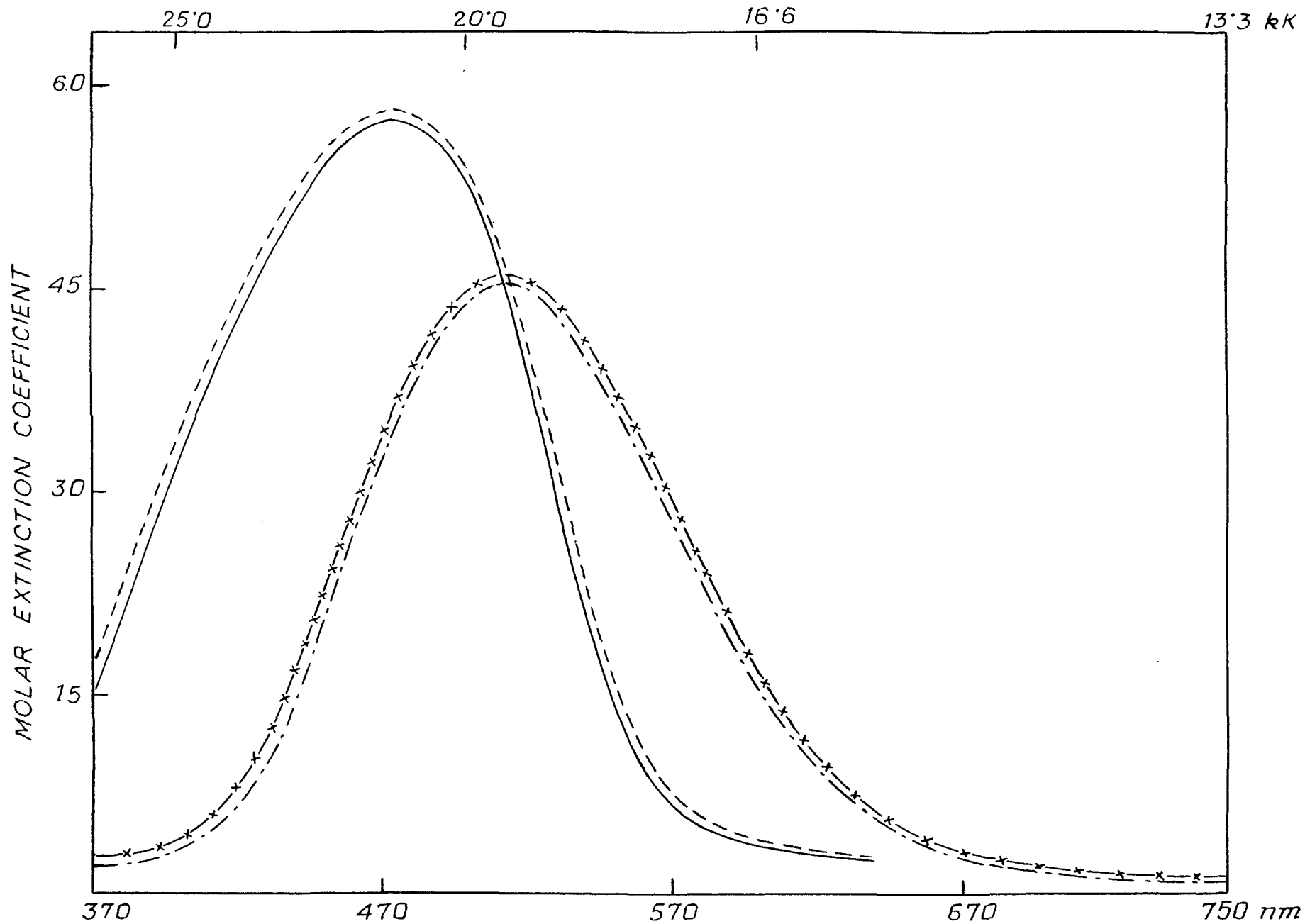


FIG. 4'5. ELECTRONIC SPECTRA OF :

$[\text{NiEt}(\text{BigH})_2]\text{Cl}_2$ (— in aqueous solution; --- in developer I)

$[\text{CuEt}(\text{BigH})_2]\text{Cl}_2$ (-·-· in aqueous solution; -x- in developer I)

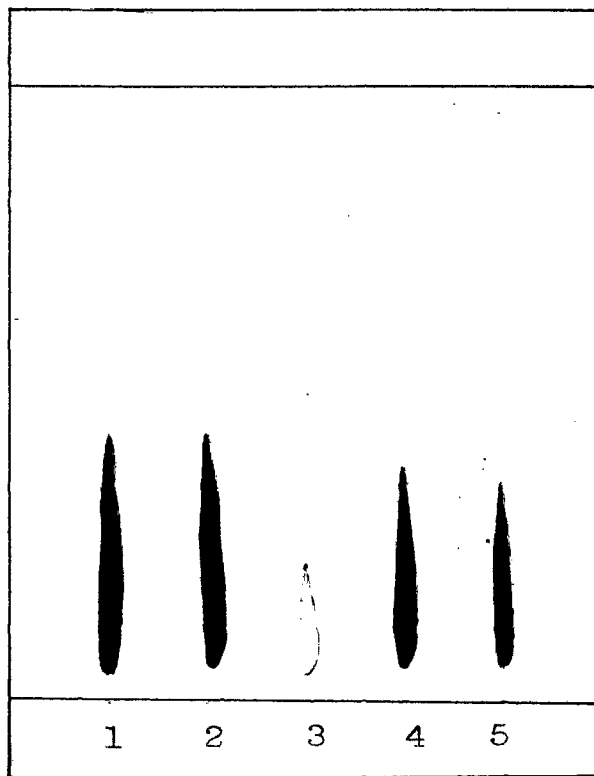


Fig.4.8. Chromatograms in 100ml 1M aqueous KCl as developer.

1. $\angle \text{Ni}(\text{BigH})_2 \text{Cl}_2$
2. $\angle \text{Cu}(\text{BigH})_2 \text{Cl}_2$
3. $\angle \text{Pd}(\text{BigH})_2 \text{Cl}_2$
4. $\angle \text{Ni Et}(\text{BigH})_2 \text{Cl}_2$
5. $\angle \text{Cu Et}(\text{BigH})_2 \text{Cl}_2$

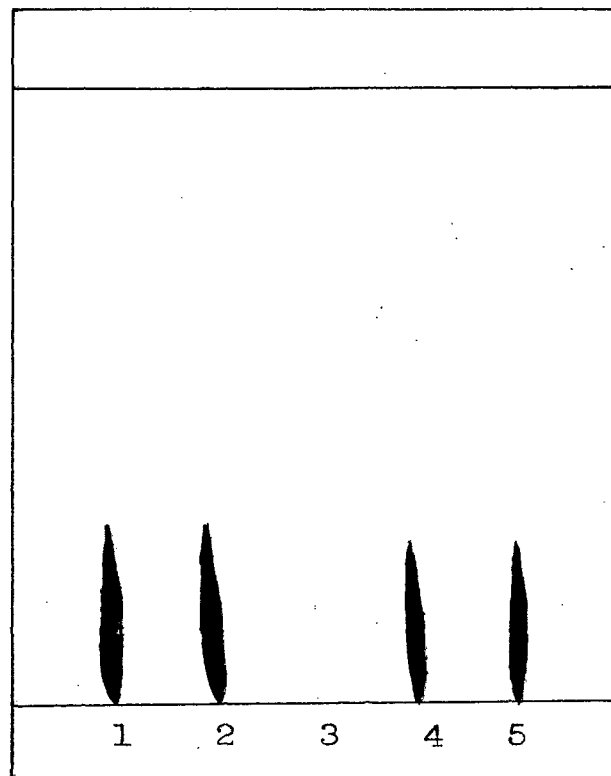


Fig.4.9. Chromatograms in 5% pyridine in water as developer.

1. $\angle \text{Ni}(\text{BigH})_2 \text{Cl}_2$
2. $\angle \text{Cu}(\text{BigH})_2 \text{Cl}_2$
3. $\angle \text{Pd}(\text{BigH})_2 \text{Cl}_2$
4. $\angle \text{Ni Et}(\text{BigH})_2 \text{Cl}_2$
5. $\angle \text{Cu Et}(\text{BigH})_2 \text{Cl}_2$

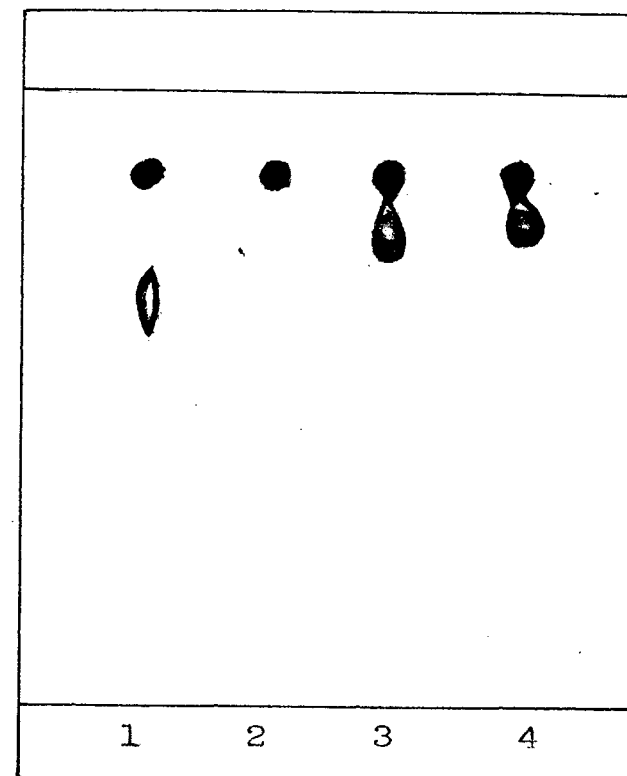


Fig.4.10. Chromatograms in 70ml 0.5M KCl + 30ml 1:1 pyridine as developer.

1. $\angle \text{Cu}(\text{BigH})_2 \text{Cl}_2$
2. CuCl_2
3. $\angle \text{Cu}(\text{Me-BigH})_2 \text{Cl}_2$
4. $\angle \text{Cu}(\text{Et-BigH})_2 \text{Cl}_2$

Table 4.1. Absorption spectral data of metal biguanide complexes.

Complex	State	Colour	Absorption spectral band in nm	ϵ_{\max}	Ref.
$\angle \bar{\text{Cu}}(\text{BigH})_2 \bar{\text{Cl}}_2$	Aqueous solution	Rose red	520 - 530	38	226
	" "	"	530	41	251
	" "	"	530	44	This study
	Developer I	"	530	45	
	Developer III	"	520 - 530	46	
$\angle \bar{\text{Ni}}(\text{BigH})_2 \bar{\text{Cl}}_2$	Aqueous solution	Golden yellow	460	-	297
	" "	"	460	46	This study
	Developer II	"	460	47	
$\angle \bar{\text{Ni}} \text{Et}(\text{BigH})_2 \bar{\text{Cl}}_2$	Aqueous solution	"	475	55	254
	" "	"	475	57	This study
	Developer I	"	475	58	
$\angle \bar{\text{Cu}} \text{Et}(\text{BigH})_2 \bar{\text{Cl}}_2$	Aqueous solution	Rose red	520	50	226
	" "	"	510 - 515	45	This study
	Developer I	"	510 - 515	46	
$\angle \bar{\text{Pd}}(\text{BigH})_2 \bar{\text{Cl}}_2$	Aqueous solution	Colour less	300	300	298
	" "	"	300	285	This study
	Developer II	"	300	292	
	Developer III	"	300	298	

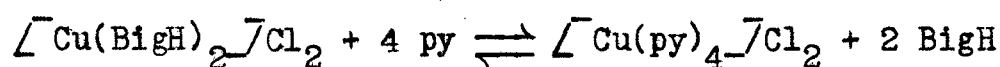
Table 4.2. R_f values of $\overline{\text{M}}(\text{BigH})_2\overline{\text{Cl}}_2$ ($\overline{\text{M}} = \text{Cu(II)}, \text{Ni(II)}, \text{Pd(II)}$) and $\overline{\text{M}}\text{Et}(\text{BigH})_2\overline{\text{Cl}}_2$ ($\text{M} = \text{Cu(II)}$ and Ni(II)) with different developers.

Complex	Developer I	Developer II
$\overline{\text{Ni}}(\text{BigH})_2\overline{\text{Cl}}_2$	0.64	0.78
$\overline{\text{Cu}}(\text{BigH})_2\overline{\text{Cl}}_2$	0.46	0.53
$\overline{\text{Pd}}(\text{BigH})_2\overline{\text{Cl}}_2$	0.10	0.23
$\overline{\text{Ni}}\{\text{Et}(\text{BigH})_2\}\overline{\text{Cl}}_2$	0.30	0.35
$\overline{\text{Cu}}\{\text{Et}(\text{BigH})_2\}\overline{\text{Cl}}_2$	0.46	0.52

Table 4.3. R_f values of $\overline{\text{M}}(\text{BigH})_2\overline{\text{Cl}}_2$ and $\overline{\text{M}}(\text{substituted-BigH})_2\overline{\text{Cl}}_2$ with different developers.

Complex	Developer II M = Ni(II)	Developer I M = Cu(II)	Developer III M = Pd(II)
$\overline{\text{M}}(\text{BigH})_2\overline{\text{Cl}}_2$	0.78	0.46	0.40
$\overline{\text{M}}(\text{Me-BigH})_2\overline{\text{Cl}}_2$	0.83	0.52	0.51
$\overline{\text{M}}(\text{Et-BigH})_2\overline{\text{Cl}}_2$	0.86	0.64	0.58
$\overline{\text{M}}(\text{Pr}^i\text{-BigH})_2\overline{\text{Cl}}_2$	0.88	0.66	-
$\overline{\text{M}}(\text{Me}_2\text{-BigH})_2\overline{\text{Cl}}_2$	0.90	0.72	-
$\overline{\text{M}}(\text{Et}_2\text{-BigH})_2\overline{\text{Cl}}_2$	0.92	0.78	-
$\overline{\text{M}}\{\text{Et}(\text{BigH})_2\}\overline{\text{Cl}}_2$	0.35	0.46	-
$\overline{\text{M}}(\text{Ph-BigH})_2\overline{\text{Cl}}_2$	0.76	0.44	0.33

Furthermore, the spots with higher R_f coincided with the spot of copper(II) chloride in the same developer and that with lower R_f had the characteristic shape of bis(biguanide) copper(II) as noticed from other developers (developers I and II). An explanation possibly lies in the assumption of the following equilibrium:



The low intensity of the tetrapyridino copper(II) spot would point to the fact that the equilibrium is still favoured towards bis(biguanide) copper(II). With bis(alkyl substituted biguanide) copper(II) distinct separation into two spots could not be achieved possibly because of the higher R_f values of the bis(alkyl substituted biguanide) copper(II) complexes compared to that of the bis(biguanide) copper(II). This would lead to a smaller gap between the spots of tetrapridine copper(II) and bis(alkyl substituted biguanide) copper(II) (Fig. 4.10). But with developer III, nickel(II) complexes did not betray two distinct spots, although the size of the spots was substantially large (~ 9 cm). Bis(biguanide) palladium(II), however, exhibited only one sharp spot which is an evidence towards preponderance of only one species.

Effect of size of the complexes on R_f values :

The increasing R_f values : Pd < Cu < Ni corresponds to the decreasing size and weight of the complexes Pd > Cu > Ni (Table 4.2). But a reverse order of R_f values e.g., $\left[\text{Cu}\{\text{Et}(\text{BigH})_2\} \right]^{2+}$ < $\left[\text{Ni}\{\text{Et}(\text{BigH})_2\} \right]^{2+}$ is observed (Table 4.2). This can not be

explained on the basis of size and weight of the complexes but can be explained on the basis of the difference in solubilities. In developer I, the solubility order is $\left[\text{Cu}\{\text{Et}(\text{BigH})_2\}^{2+} \right]$ (for copper(II) = 0.35 g/100 ml and nickel(II) = 0.24 g/100 ml). But for other bis(biguanide) metal(II) complexes (M = Cu, Ni) the solubility order : $\left[\text{Ni}(\text{BigH})_2 \right]^{2+} > \left[\text{Cu}(\text{BigH})_2 \right]^{2+}$ is observed. This aspect has been discussed in greater details in the next section.

Effect of substitution in biguanide moiety on R_f values :

On increasing alkyl substitution on N^1 -atom of biguanide the R_f values of the corresponding copper(II), nickel(II) and palladium(II) bis(biguanide) complexes also increase. But phenyl substitution lowers the R_f (Table 4.3). Since biguanide and alkyl biguanide have more or less similar basic character^{221,227} it is a reasonable guess that the attractive influence of the bipoisitive cations on the cellulose anion will be quite close. However, substitution of the hydrogen atom attached to the N^1 -atom of the ^{biguanide} \wedge considerably reduce the chances of forming hydrogen bonded species with cellulose anions. This is expected to lead to a higher R_f with increasing substitution. Had solubility alone been responsible for differences in R_f values we would have observed a reverse order with increasing alkyl substitution. Increase of R_f values from biguanide to methyl biguanide and then to other alkyl biguanide is also likely to be connected with inductive influence of the electron releasing alkyl groups whereby the overall charge on the

complex cation may be diminished to some extent. This lowering of charge will enhance the R_f values. On the contrary electron withdrawing phenyl substitution will lead to a lower R_f .