'CHAPTER VII :

PAPER CHROMATOGRAPHIC STUDIES ON COPPER(II)
MIXED CHELATES.

'Mixed ligand complexes are of considerable current interest[244],[246-253]. Dutta and his students have been active in this area for several years now. During these pursuits they have successfully synthesised a good number of copper(II) mixed chelates. These mixed chelates have so far received synthetic, magnetic and spectral investigations. In this section the results of our studies on paper chromatographic behaviour of a number of these and some other copper(II) mixed chelates are presented.

Methods and materials :

The mixed chelates were obtained by following published procedures as given in Chapter III. Their purity was checked by elemental analysis and spectral measurements (Fig. 7.1). The following developers were tried :

Developer	I	:	Distilled water (100 ml)
"	II	:	100 ml 1(M) KCl
"	III	:	100 ml 0.5(M) KCl + 5 ml pyridine
"	IV	:	100 ml 1(M) KCl + 5 ml pyridine
"	V	:	70 ml 0.5(M) KCl + 30 ml (1:1)pyridine.

R_f values were reproducible to within $\pm$ 0.02 R_f units.

Results and Discussion :

We have reported earlier (Chapter IV) that with higher concentration of pyridine and low concentration of KCl (as in developer V), the homochelate $\underline{/}Cu(BigH)_2\underline{/}Cl_2$ provided two spots,
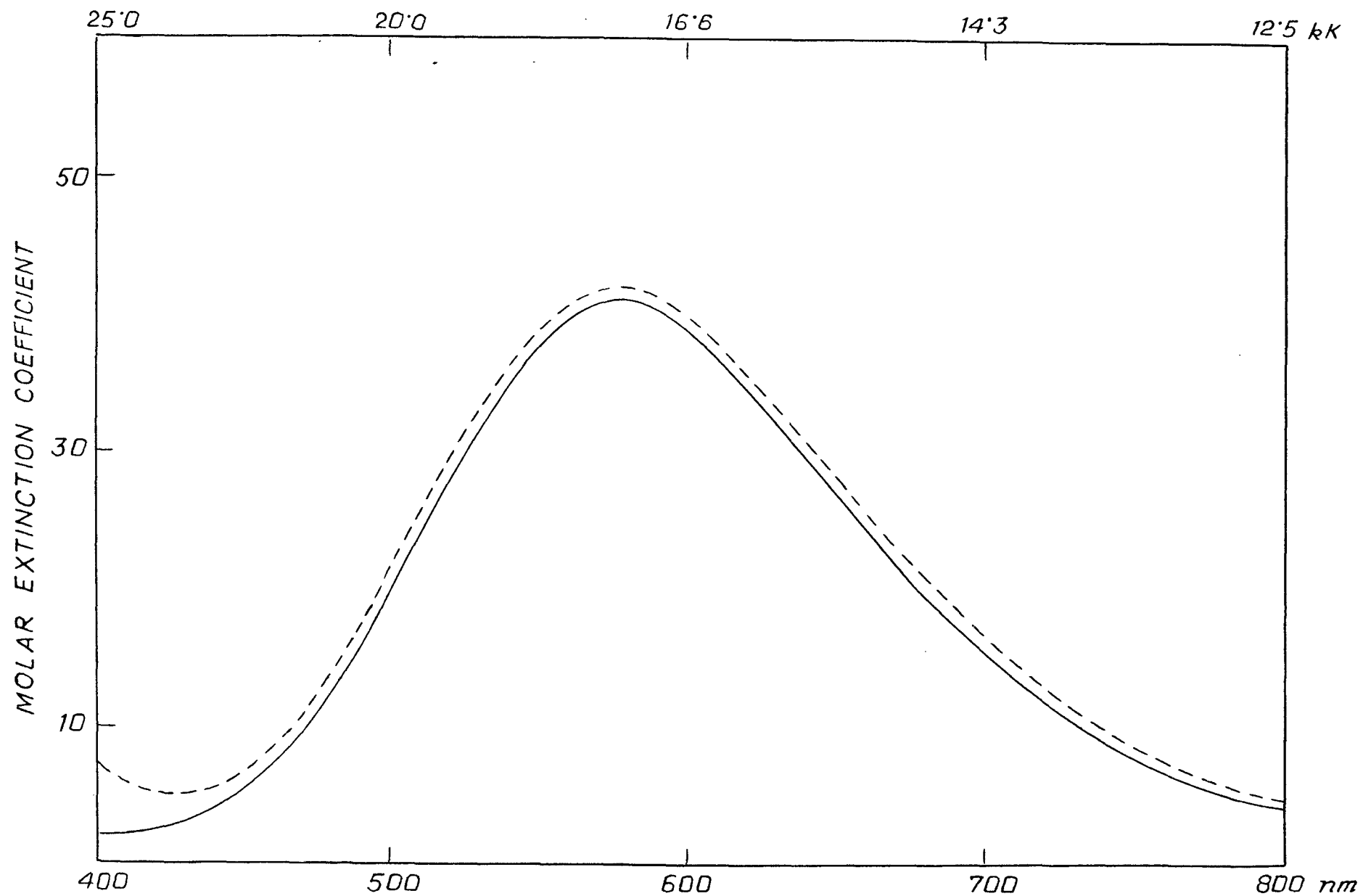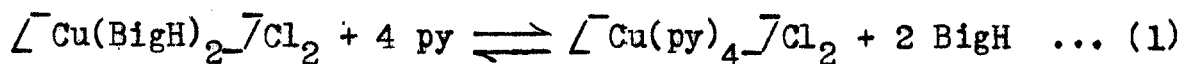
FIG. 7.1.   ELECTRONIC SPECTRA OF :

[Cu(gly)(BigH)]Cl   in aqueous solution (——)

[Cu(gly)(BigH)]Cl   in developer IV   (———)

which was traced to be due to an equilibrium of the type :

$$\sqrt{ }Cu(BigH)_2\underline{ }7Cl_2 + 4 \text{ py} \rightleftharpoons \sqrt{ }Cu(py)_4\underline{ }7Cl_2 + 2 \text{ BigH} \quad \dots \text{ (1)}$$

In view of the above results it appeared likely that copper(II) mixed chelates will provide interesting solvent dependent chromatographic behaviour. A fairly good number of copper(II) mixed chelates were selected for this study. The mixed chelates were repeatedly crystallised. They all provided good analytical values and looked homogeneous single species under the microscope. Their spectra also conformed to published absorption maxima and molar extinction coefficients (page 70).

Developer I was not a suitable one. The mixed complexes, whether charged or uncharged, either did not move at all from their point of application or if they moved they diffused to a long distance along the filter paper. This is not surprising for cationic complexes as they are known to be strongly held on the negatively charged cellulose anion of the filter paper[116,299]. With developer II, although the complexes move from their point of application, the spots are too large. With this developver $\sqrt{ }$Cu(gly)(BigH)$\underline{ }7$Cl, $\sqrt{ }$Cu(gly)(Me-BigH)$\underline{ }7$Cl, $\sqrt{ }$Cu(gly)(Et-BigH)$\underline{ }7$Cl, $\sqrt{ }$Cu(α-alan)(BigH)$\underline{ }7$Cl, $\sqrt{ }$Cu(α-alan)(Me-BigH)$\underline{ }7$, $\sqrt{ }$Cu(α-alan)(Et-BigH)$\underline{ }7$Cl, $\sqrt{ }$Cu(gly)(o-phen)$\underline{ }7$Cl, $\sqrt{ }$Cu(dipy)(BigH)$\underline{ }7$Cl$_2$, $\sqrt{ }$Cu(dipy)(Me-BigH)$\underline{ }7$Cl$_2$, $\sqrt{ }$Cu(dipy)(Et-BigH)$\underline{ }7$Cl$_2$, always give two spots instead of one. $\sqrt{ }$Cu(gly)(dipy)$\underline{ }7$Cl alone provides single spot in this developer II. Best results are obtained with developer IV, the R_f values being given in Table 7.1.

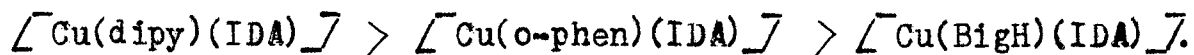Table 7.1. R_f values of copper(II) mixed chelates with developer IV.

Charge	Complex	R_f
0	$[Cu(dipy)(IDA)]$	0.87
	$[Cu(o-phen)(IDA)]$	0.80
	$[Cu(BigH)(IDA)]$	0.70
+1	$[Cu(gly)(BigH)]Cl$	0.53, 0.93
	$[Cu(gly)(Me-BigH)]Cl$	0.60, 0.93
	$[Cu(gly)(Et-BigH)]Cl$	0.66, 0.93
	$[Cu(\alpha-alan)(BigH)]Cl$	0.53, 0.94
	$[Cu(\alpha-alan)(Me-BigH)]Cl$	0.60, 0.94
	$[Cu(\alpha-alan)(Et-BigH)]Cl$	0.66, 0.94
	$[Cu(gly)(o-phen)]Cl$	0.80, 0.91
	$[Cu(gly)(dipy)]Cl$	0.80
	$[Cu(pic)(BigH)]Cl$	0.83
+2	$[Cu(dipy)(BigH)]Cl_2$	0.74
	$[Cu(dipy)(Me-BigH)]Cl_2$	0.77
	$[Cu(dipy)(Et-BigH)]Cl_2$	0.81
	$[Cu(o-phen)(BigH)]Cl_2$	0.71

Under similar condition R_f values of the homochelates are:
$[Cu(gly)_2] = 0.93$; $[Cu(\alpha-alan)_2] = 0.94$; $[Cu(pic)_2] = 0.87$;
$[Cu(BigH)_2]Cl_2 = 0.53$; $[Cu(Me-BigH)_2]Cl_2 = 0.60$;
$[Cu(Et-BigH)_2]Cl_2 = 0.66$; $[Cu(dipy)_2]Cl_2 = 0.91$;
$[Cu(o-phen)_2]Cl_2 = 0.80$; $[Cu(py)_4]Cl_2 = 0.86$.
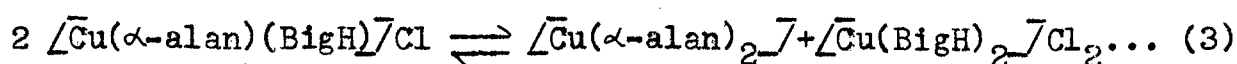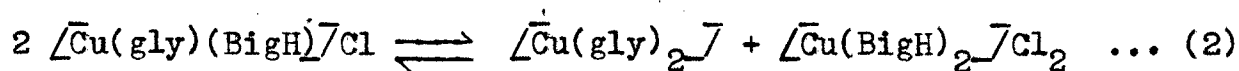
Mixed chelates containing iminodiacetate group (IDA) :

All the three complexes are neutral and provide single spots in developer IV (Fig. 7.2). Their R_f values have the order:

$$\underline{/}\,Cu(dipy)(IDA)\,\underline{/} \;>\; \underline{/}\,Cu(o\text{-}phen)(IDA)\,\underline{/} \;>\; \underline{/}\,Cu(BigH)(IDA)\,\underline{/}.$$

This order is also the order of increasing solubility of the complexes in aqueous KCl - pyridine developer. The mixed chelates seem to possess nonelectrolytic nature rather than the electrolytic structure $\underline{/}\,Cu(dipy)_2\,\underline{/}\,\underline{/}\,Cu(IDA)_2\,\underline{/}$ etc. The electrolytic structure would admit of two spots.

Glycinato mono(biguanide) copper(II) and/ α-alaninato mono-(biguanide) copper(II) and related complexes :

Ray and Das Sarma[250] noted that on several crystallisations of these compounds the chemical analysis remained unaffected. We also observed no change in the crystalline behaviour (under the microscope) or in the analysis on several fractional crystallisations. Yet their chromatograms in developer IV provide two spots with very different R_f values. Interestingly the oval shaped spot with lower R_f corresponds to the spot of bis(biguanide) copper(II) and the upper spot with higher R_f is identical with that of bis(aminoacidato) copper(II) under similar conditions (Fig. 7.3). These observations point to the following disproportionation reactions :
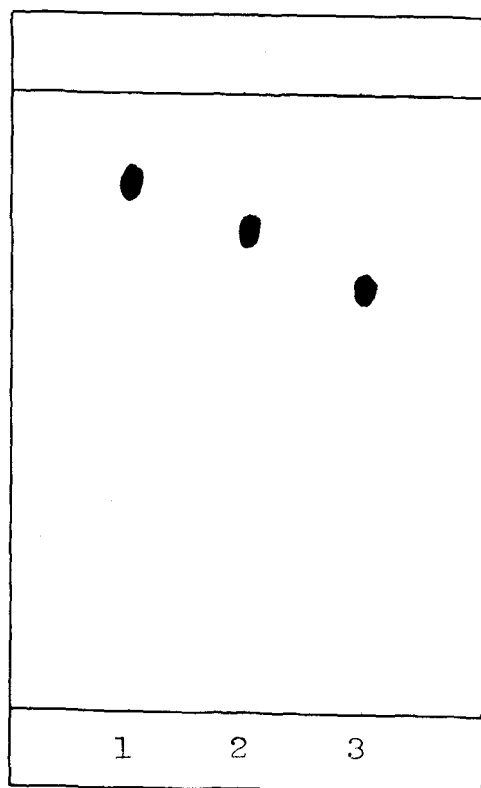
$$2\,\underline{/}\,Cu(gly)(BigH)\,\underline{/}\,Cl \;\rightleftharpoons\; \underline{/}\,Cu(gly)_2\,\underline{/} + \underline{/}\,Cu(BigH)_2\,\underline{/}\,Cl_2 \quad \cdots \text{(2)}$$

$$2\,\underline{/}\,Cu(\alpha\text{-alan})(BigH)\,\underline{/}\,Cl \;\rightleftharpoons\; \underline{/}\,Cu(\alpha\text{-alan})_2\,\underline{/} + \underline{/}\,Cu(BigH)_2\,\underline{/}\,Cl_2 \cdots \text{(3)}$$

Fig.7.2. Chromatograms in 100ml 1M KCl + 5ml pyridine as developer(Developer IV).

1. $\angle$ Cu(dipy)(IDA) $\angle$
2. $\angle$ Cu(o-phen)(IDA) $\angle$
3. $\angle$ Cu(BigH)(IDA) $\angle$
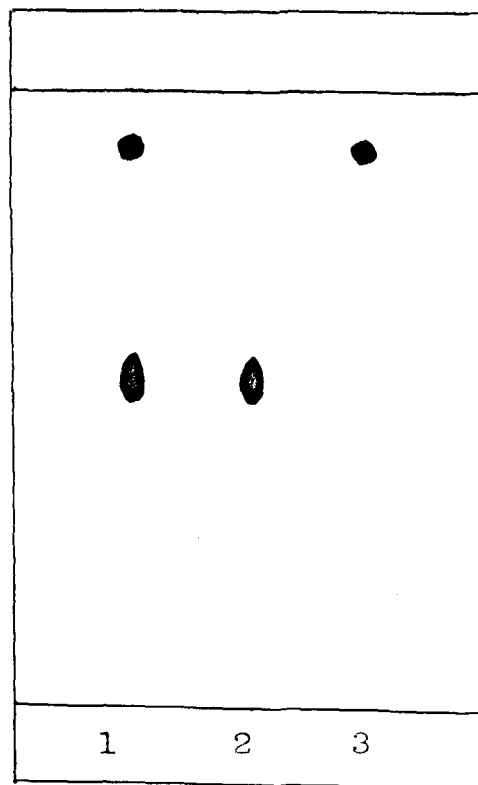
Fig.7.3. Chromatograms in 100ml 1M KCl + 5ml pyridine as developer (Developer IV).

1. $\angle$ Cu(gly)(BigH) $\angle$Cl
2. $\angle$ Cu(BigH)$_2$ $\angle$Cl$_2$
3. $\angle$ Cu(gly)$_2$ $\angle$.
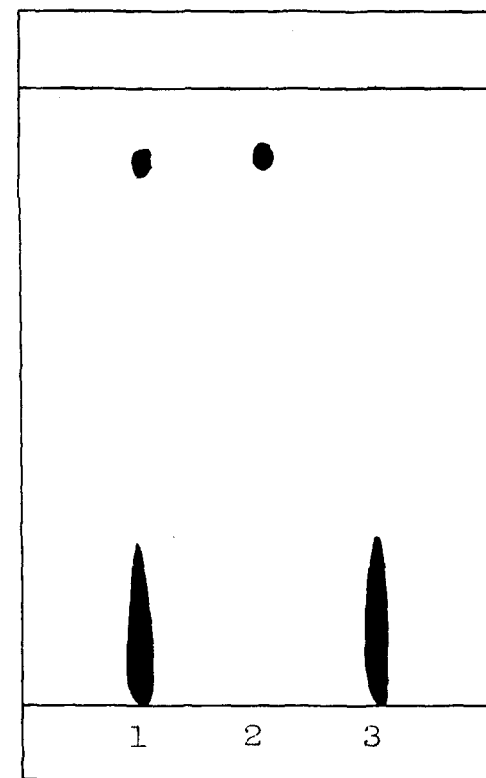
Fig.7.4. Chromatograms in 100ml distilled water as developer (Developer I).

1. $\angle$ Cu(gly)(BigH) $\angle$Cl
2. $\angle$ Cu(gly)$_2$ $\angle$
3. $\angle$ Cu(BigH)$_2$ $\angle$Cl$_2$.

Whichever developer is chosen, these mixed chelates give consistently two spots. That the presence of pyridine in the developer is not responsible for the appearence of two spots was verified by the fact that even distilled water (as in developer I) and aqueous KCl (as in developer II) could separate the mixed chelates into two component homochelates (Fig. 7.4 and Fig. 7.5).

In our earlier studies (Chapter IV) of $\angle$Cu(BigH)$_2\angle$Cl$_2$ in developer V we had reported chromatographic evidence in favour of equilibrium (I). One would therefore expect three spots out of $\angle$Cu(gly)(BigH)$\angle$Cl in developer V, resulting from a secondary equilibrium of $\angle$Cu(BigH)$_2\angle$Cl$_2$ with large excess of pyridine present in developer V giving another species $\angle$Cu(py)$_4\angle$Cl$_2$ according to the following equilibrium :

$$2 \angle Cu(gly)(BigH)\angle Cl \rightleftharpoons \angle Cu(gly)_2\angle + \angle Cu(BigH)_2\angle Cl_2$$

$$\Big\updownarrow py$$

$$\angle Cu(py)_4\angle Cl_2 + 2 \text{ BigH}$$
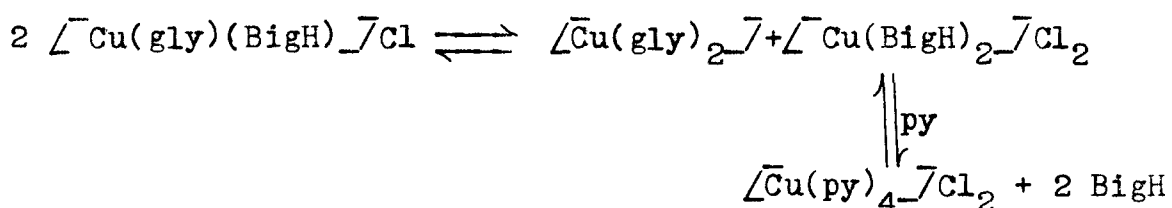
But we have obtained no more than two spots in developer V. This is readily explained when we consider that $\angle$Cu(gly)$_2\angle$ and $\angle$Cu(py)$_4\angle$Cl$_2$ show almost the same R_f in this developer ($\angle$Cu(gly)$_2\angle$ = 0.85; $\angle$Cu(py)$_4\angle$Cl$_2$ = 0.86).

Glycinato mono(dipyridyl) copper(II) and glycinato mono-(o-phenanthroline) copper(II) :

$\angle$Cu(gly)(dipy)$\angle$Cl provides, in developer IV, a single spot with R_f = 0.80 while $\angle$Cu(gly)(o-phen)$\angle$Cl gives two spots
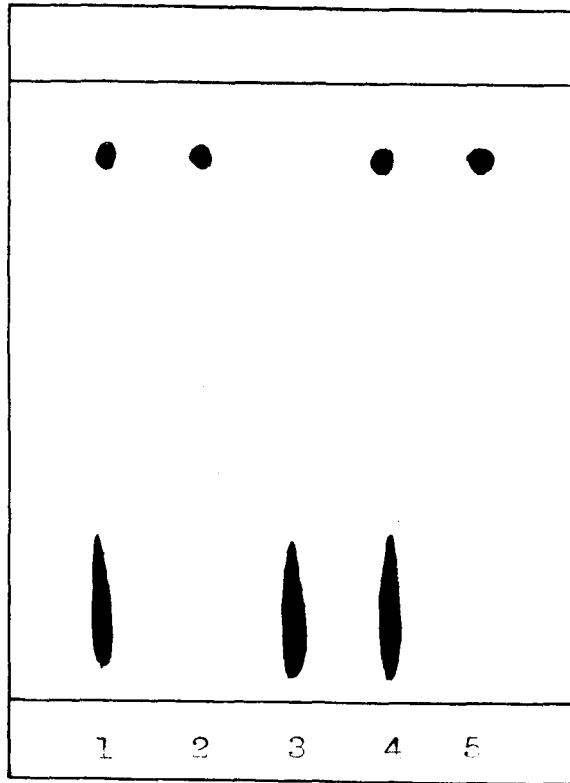
Fig.7.5. Chromatogram in 100ml
1M aqueous KCl as developer
(Developer II).

1. $\angle$ Cu(gly)(BigH)$\angle$Cl

2. $\angle$ Cu(gly)$_2\angle$

3. $\angle$ Cu(BigH)$_2\angle$Cl$_2$

4. $\angle$ Cu(-alan)(BigH)$\angle$Cl

5. $\angle$ Cu(-alan)$_2\angle$
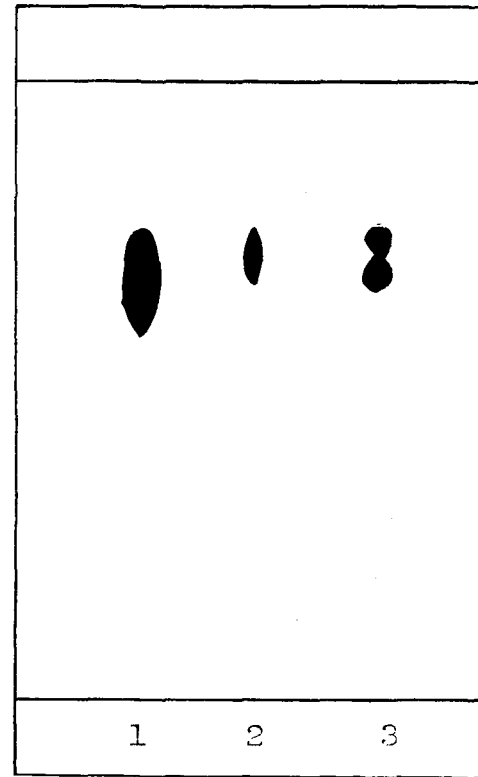
Fig.7.6. Chromatograms of
$\angle$Cu(o-phen)(BigH)$\angle$Cl$_2$
in different developers.

1. 100ml 0.5M KCl + 5ml pyridine (Developer III).

2. 100ml 1M KCl + 5ml pyridine (Developer IV).

3. 70ml 0.5M KCl + 30ml 1:1 pyridine (Developer V).

with R_f = 0.80 and 0.91. The upper spot with higher R_f is of low intensity and its R_f is comparable to that of $\angle Cu(gly)_2\angle$. The R_f value of $\angle Cu(o\text{-phen})_2\angle Cl_2$ is also around 0.80. So the following disproportionation reaction is suggested :

$$2\ \angle Cu(gly)(o\text{-phen})\_\angle Cl \rightleftharpoons \angle Cu(gly)_2\angle + \angle Cu(o\text{-phen})_2\angle Cl_2$$
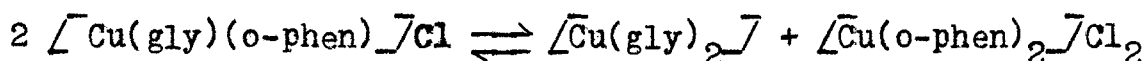
Similar disproportionation of $\angle Cu(gly)(dipy)\_\angle Cl$ into two homochelates is less favoured since we get one spot with R_f = 0.80 which is different from that of either $\angle Cu(dipy)_2\angle Cl_2$ or $\angle Cu(gly)_2\angle$.

Dipyridyl mono(biguanide) copper(II) and o-phenanthroline mono(biguanide) copper(II) etc. :

Development of these complexes with developer II provides two spots : R_f value of one of the spots coincides with that of $\angle Cu(dipy)_2\angle Cl_2$ or $\angle Cu(o\text{-phen})_2\angle Cl_2$ in the same developer while the second spot, which diffuses to a long distance, is reminiscent of $\angle Cu(BigH)_2\angle Cl_2$. A careful visual inspection of the spots of $\angle Cu(dipy)(BigH)\_\angle Cl_2$ and $\angle Cu(o\text{-phen})(BigH)\_\angle Cl_2$ obtained with developers III and V reveals that although the spots are continuous the chromatographed materials are concentrated towards the ends of the spots (Fig. 7.6). Developer IV is found to be the suitable one as it alone provides single spots (Fig. 7.6). So neither too much pyridine (as in developer V) nor too little KCl (as in developer III) can be tolerated.

Effect of substitution in biguanide moiety on R_f values :
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We have seen earlier (Chapter IV) that on increasing the
alkyl substitution on N^1-atom of biguanide the R_f values of the
corresponding copper(II), nickel(II) and palladium(II) bis(bigua-
nide) complexes also increase. Similar observation is also noted
in the mixed complex systems. R_f value increases from
$\angle^-Cu(dipy)(BigH)\angle 7Cl_2$ to $\angle^-Cu(dipy)(Me-BigH)\angle 7Cl_2$ and then to
$\angle^-Cu(dipy)(Et-BigH)\angle 7Cl_2$ although this increase is less vigorous
compared to the change in the R_f values of bis(biguanide)
copper(II) and bis(substituted biguanide) copper(II).

Concluding remarks :

A good single spot can be obtained with a mixed chelate
only when its tendency to disproportionation into the two compo-
nent homochelates is not too large, and furthermore when a right
choice has been made of a developer which can suppress the dis-
proportionation reaction. We wish to emphasize that obtaining
two spots out of a mixed chelate cannot be immediately interpre-
ted to mean that the mixed chelate is not a pure single species.
Two spots may mean that there is an equilibrium between the mixed
chelate and the component homochelates in developer solution and
that continued development merely helps in the separation of the
two homochelates.