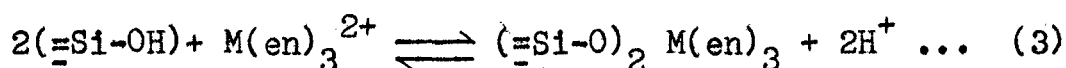
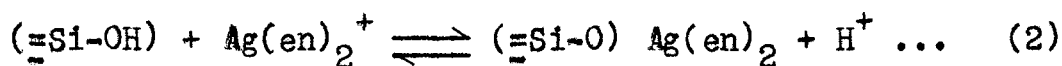
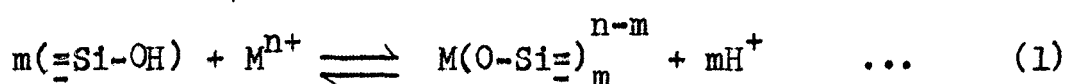


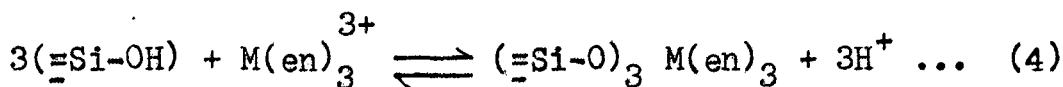
CHAPTER IX :

THIN LAYER CHROMATOGRAPHIC STUDIES ON METAL
COMPLEXES.

The silanol group ($\equiv \text{Si-OH}$) of the hydrated silica gel surface is weakly acidic and has cation exchange properties³¹⁵⁻³¹⁷. This exchange phenomenon has been studied by many workers^{64,318-324} and it has generally been accepted that the surface reaction proceeds via following steps :

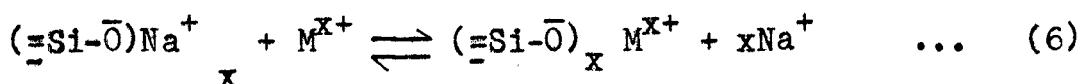
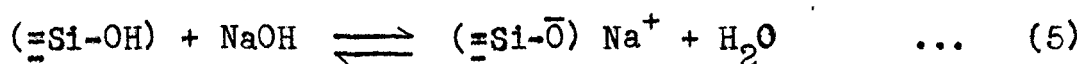


(M = Cu, Co, Zn)



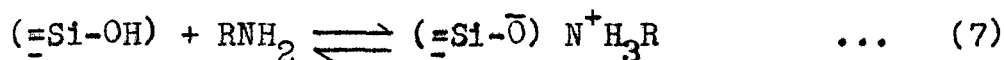
(M = Co, Fe, Al, Cr).

The forward reactions in the above equations are favoured by a highly charged cation and by a high pH³²⁵. At still higher pH, the following exchange reactions occur :



The adsorbed metal ions cannot be removed by washing with water alone^{64,325,326} but can be removed by acids^{64,317,325}.

Exchange on the surface of silica gel can also occur with amine ligands³²⁵ and is probably best represented by equation (7) :



Various workers have studied the different complexes on silica gel from different points of interests. The sorption of metal cationic complexes on silica gel has been extensively studied by Vydra et al³¹⁹⁻³²² and they observed that over a wide range of pH, the amount of acid released corresponds to the charge of the complex.

Burwell, Pearson, Haller, Tjok and Chock⁶⁴ had noticed that when $\left[\text{Co(en)}_2 \text{Cl}_2 \right]^+$ (both cis and trans isomers) cation was adsorbed on silica gel, substitution reaction occurred i.e. silanol group of the silica gel pushed out chloride ion from the coordination sphere. The extent of adsorption of the complexes on the silica gel bed depends upon the charge and overall charge distribution of the complex ions. So the greater retention of the cis-isomer than the corresponding trans isomer supports the greater charge polarisation of the cis complex than the trans.

Using silica gel TLC with aqueous phenol as the developer Jursik⁶⁶ had separated some nickel(II) amino acid complexes from one another. The R_f values of the nickel(II) complexes were found to gradually increase with increasing number of carbon atoms present in the chelate molecules.

With acidic methanol DMSO developer, Druding et al¹²³ had separated some cobalt(III) complexes which differed from one another in charge. They also successfully separated few cis-trans cobalt(III) complexes from each other. However, separation of the bi and tri positively charged ions was very poor. With a

formamide-methanol glacial acetic acid mixture as the mobile phase better separation of bi and tri positive cobalt(III) complexes was achieved⁶⁵.

Silica gel TLC of inert cobalt(III) complexes with water as the mobile phase had revealed that cationic complexes are held strongly on the base line while neutral and anionic complexes move close to the solvent front. With 0.1M KCl as the developer the R_f values of the complexes showed a regular increase with decrease of ionic charge. However, this order soon gets reversed when the concentration of the electrolyte in the developer solvent is increased¹²².

Hathaway and Lewis^{325,327,328} studied the electronic properties of transition metal complex ions $\overline{\text{Ni(II)}}$, $\overline{\text{Co(III)}}$, $\overline{\text{Co(II)}}$ and $\overline{\text{Cu(II)}}$ adsorbed on silica gel. For nickel(II) complexes, the spectral behaviour of adsorbed ion is similar to those of aqueous solution. A change of electronic spectra is revealed when the physically adsorbed water is driven out. When the ligand: nickel(II) concentration is high a cis-octahedral chromophore is suggested, otherwise five coordinated chromophore. A reverse process can be formed after the entrance of water. The hexaquo cobalt(II), $\overline{\text{Co(H}_2\text{O)}_6}^{2+}$, reacts with the hydrated surface of silica gel first forming a blue tetrahedral species (CoO_3 "O" chromophore) and then giving a pink colour due to the transformation to octahedral species. With en and dien ligands partial reaction occurs on the hydrated gel depending upon the ratio of ligand to cobalt(II) ion. Varying the experimental conditions

various species (e.g. four, five and six coordinated) are formed which are detected by electronic spectra. For copper(II) complexes of multidentate nitrogen ligands the most likely species on the hydrated gel are CuN_2O_4 (tetragonal-octahedral) or CuN_2O_3 (square pyramidal) chromophore. From the electronic spectra tetrahedral or trigonal bipyramidal structure was ruled out.

Recently Yoneda and Baba⁶⁷ made a comparative study of the behaviour of square planar and octahedral complexes on silica gel. Each complex showed different R_f values after being developed with aqueous salt solutions. This was believed to be due to the different degrees of anionic association of the complex cations. In the square planar complexes association occurs through direct coordination of anion to the metal ion while in octahedral complexes association takes place at the outer sphere.

Complementary to our studies of paper chromatography we now describe the results of silica gel thin layer chromatographic investigations on the following complexes :

- A. Square planar bis(biguanide) metal(II) and bis(1-amidino-O-alkylurea) metal(II) complexes.
- B. Copper(II) mixed chelate systems and
- C. Cobalt(III) inert complexes.

Experimental :

The complexes were the same as described earlier(Chapter III). For the purpose of putting spots, the complexes were dissolved either in water or in rectified spirit. The following developers were used for different complexes :

Developers for nickel(II) complexes :

Developer I : 400ml 0.2M KCl .
" II : 400ml 0.2M K_2SO_4
" III : 400ml 0.2M $Na_2S_2O_3$
" IV : 400ml 0.2M K-Na-tartrate.

Developers for copper(II) complexes :

Developer V : 400ml 0.5M KCl
" VI : 400ml 0.5M K_2SO_4
" VII : 400ml 0.5M $Na_2S_2O_3$
" VIII : 400ml 0.5M K-Na-tartrate.

Developer for palladium(II) and copper(II) mixed chelates :

Developer V was used.

Developers for cobalt(III) complexes : Besides developers I,II, III and IV, the following developers were also used.

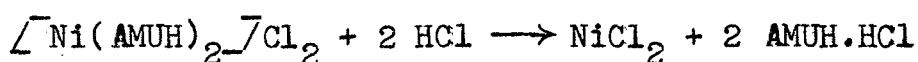
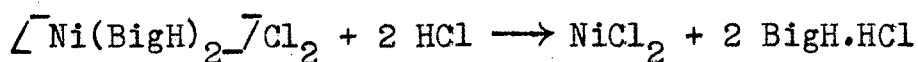
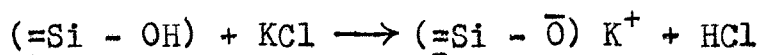
Developer IX : 400ml 0.1M KCl
" X : 400ml 0.2M KI
" XI : 400ml 0.2M KCl + pyridine (100:5)

Results and Discussion :

A.(1) Nickel(II) complexes :

When nickel(II) complexes are developed with distilled water as solvent, they remain at the point of application like what was observed during their paper chromatography (Chapter IV

and V). When silica gel comes in contact with water it becomes negatively charged and can easily attract complex cations either by electrostatic force^{67,122} or through ion exchange mechanism³¹⁹⁻³²². Such strong retention was also observed in paper chromatography and could be palliated for copper(II), nickel(II) and palladium(II) complexes by using aqueous KCl developer incorporated with pyridine^{299,300} and for cobalt(III) complexes aqueous KCl alone was satisfactory¹¹⁶ (Chapter VIII). In the present case we used developers containing various salt solutions (KCl, K₂SO₄, Na₂S₂O₃, K-Na-tartrate) and in every case we have the same R_f value for all the complexes. Surprisingly the aquo nickel(II) cation, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, also exhibit the same R_f. So on the basis of R_f values we have failed to distinguish between aquo nickel(II) cation and the nickel(II) complexes under study (Table 9.1) which we could in paper chromatography (Chapter IV and V). This anomalous behaviour indicated that during the development process the complexes were changed into the aquo nickel(II) cation by acid liberation from silica gel via ion exchange phenomenon :



This liberated acid is sufficient to decompose the spot of nickel(II) complexes to the corresponding aquo nickel(II) cation. In this connection we wish to emphasise that at pH 5,

Table 9.1. R_f values of nickel(II) complexes with different developers(TLC on silica gel).

Complex	0.2M KCl	0.2M K_2SO_4	0.2M $Na_2S_2O_3$	0.2M K-Na-tartrate
$\angle Ni(BigH)_2 \cdot 7Cl_2$	0.90	0.90	0.90	0.92
$\angle Ni(Me-BigH)_2 \cdot 7Cl_2$	0.90	0.91	0.93	0.94
$\angle Ni(Et-BigH)_2 \cdot 7Cl_2$	0.89	0.92	0.92	0.92
$\angle Ni(Pr^i-BigH)_2 \cdot 7Cl_2$	0.90	0.94	0.94	0.94
$\angle Ni(Me_2-BigH)_2 \cdot 7Cl_2$	0.90	0.92	0.90	0.92
$\angle Ni(Et_2-BigH)_2 \cdot 7Cl_2$	0.88	0.91	0.89	0.90
$\angle Ni(Ph-BigH)_2 \cdot 7Cl_2$	0.89	0.92	0.89	0.91
$\angle Ni Et(BigH)_2 \cdot 7Cl_2$	0.52	*	0.74	*
$\angle Ni(AMUH)_2 \cdot 7Cl_2$	0.89	0.90	0.91	0.92
$\angle Ni(AEUH)_2 \cdot 7Cl_2$	0.89	0.90	0.93	0.94
$\angle Ni(AP^nUH)_2 \cdot 7Cl_2$	0.89	0.89	0.94	0.94
$\angle Ni(AP^iUH)_2 \cdot 7Cl_2$	0.90	0.90	0.92	0.92
$\angle Ni(AB^nUH)_2 \cdot 7Cl_2$	0.89	0.89	0.91	0.93
$\angle Ni(AB^iUH)_2 \cdot 7Cl_2$	0.90	0.90	0.93	0.94
$\angle Ni(AA^nUH)_2 \cdot 7Cl_2$	0.90	0.90	0.90	0.92
$\angle Ni(AA^iUH)_2 \cdot 7Cl_2$	0.89	0.89	0.90	0.93
$\angle Ni(en)_3 \cdot 7Cl_2$	0.84(0.23)	0.89(0.62)	0.90(0.53)	0.90
$\angle Ni(H_2O)_6 \cdot 7Cl_2$	0.90	0.92	0.93	0.93

The R_f values of $\angle Ni(gly)_2(H_2O)_2 \cdot 7$ is 0.84 in 0.1M KCl; 0.80(0.82) in 0.1M KI; 0.90(0.85) in 0.1M K_2SO_4 . Values reported in the parenthesis were reported by Yoneda⁶⁷.

* indicates the spot remained at the point of application.

biguanide and 1-amidino-0-alkylurea nickel(II) complexes totally decompose into the corresponding aquo nickel(II) cation^{221,244}. Developers K_2SO_4 , $Na_2S_2O_3$ and K-Na-tartrate also behave similarly and thus provide the same R_f values for the nickel(II) complexes studied as also for aquo nickel(II) cation. It is noteworthy that $\overline{Ni(BigH)_2}Cl_2$ is likely to generate the very insoluble $\overline{Ni(BigH)_2}SO_4$ in aqueous K_2SO_4 developer. By virtue of its extreme insolubility^{221,329,330} we would expect it to stay at the base line as had happened in paper chromatography. But in reality this too does travel and gives the same R_f value as does $\overline{Ni(H_2O)_6}Cl_2$. Thus the very insoluble $\overline{Ni(BigH)_2}SO_4$ is also destroyed by liberated acid via ion exchange process and exhibit its R_f not as genuine complex but as aquo complex. The only exception is complex $\overline{Ni\{Et(BigH)_2\}}Cl_2$ which shows an $R_f = 0.52$ in KCl developer (developer I). It remained stationary at the base line in K_2SO_4 developer (developer II) which indicates that the complex is not decomposed but is converted into the insoluble sulphate salt. Being a complex of a quadridentate ligand its stability towards acid is likely to be higher than bis(biguanide) nickel(II), as has been the case with bis(biguanide) copper(II) and ethylenedibiguanide copper(II)^{221,331}.

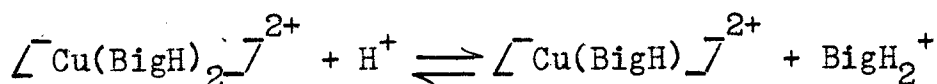
Incidentally we had occasion to look into the R_f values of $\overline{Ni(en)_3}Cl_2$ in the above developers (developers I - IV). This particular compound was earlier investigated by Yoneda⁶⁷. Unfortunately our R_f values are widely different from those reported by Yoneda⁶⁷ although the chromatographic conditions are

the same. We believe $\overline{\text{Ni(en)}_3\text{Cl}_2}$ is also destroyed to $\overline{\text{Ni(H}_2\text{O)}_6\text{Cl}_2}$ through an ion exchange mechanism between the developer cations and silanol group (Si - OH) of the silica gel.

These results with a large group of nickel(II) complexes indicate that one should not lose sight of the possibility of a nickel(II) complex being decomposed to hexa aquo nickel(II), $\overline{\text{Ni(H}_2\text{O)}_6}^{2+}$, by silica gel in aqueous electrolyte developer as a result of sufficient acid liberation via ion exchange mechanism.

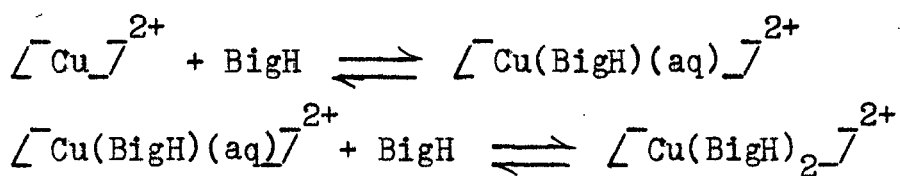
(2). Copper(II) complexes :

The behaviour of copper(II) complexes on silica gel is quite different from that of nickel(II) complexes. These complexes revealed R_f values which differed from complex to complex as also from that of aquo copper(II) chloride, $\overline{\text{Cu(H}_2\text{O)}_6\text{Cl}_2}$. This means that bis(biguanide/substituted biguanides) copper(II) complexes persist either as genuine bis(biguanide) complexes, $\overline{\text{Cu(BigH)}_2\text{Cl}_2}$ etc. or as mono(biguanide) complexes due to acid liberation on silica gel. It is well known²²¹ that around a pH 5, bis(biguanide) copper(II), $\overline{\text{Cu(BigH)}_2}^{2+}$, transforms into the mono(biguanide) copper(II), $\overline{\text{Cu(BigH)}}^{2+}$:



As the chain length of the alkyl substituent in biguanide and 1-amidino-O-alkylurea increases, the R_f values of the corresponding copper(II) complexes decrease in aqueous KCl developer

due to enhanced insolubility (Table 9.2). With aqueous K_2SO_4 as developer, all biguanide copper(II) complexes remained at the point of application due to extreme insolubility of the bis(biguanide/substituted biguanide) copper(II) sulphate^{221,330,332}. It is well established that the bis(biguanide) copper(II) complexes are formed from aque copper(II) in two steps²²¹ :



while the corresponding bis(biguanide) nickel(II) is formed in a single step^{221,331}. The copper(II) complex is more resistant to acid than the nickel(II) complex. But the corresponding 1-amidino-0-alkylurea (AAUH) copper(II) complexes travel in K_2SO_4 developer (developer VI). This again is due to the 1-amidino-0-alkylurea complexes being more susceptible to acid^{221,244}. In $Na_2S_2O_3$ (developer VII), all copper(II) complexes moved to the solvent front and exhibited $R_f = 1.00$ possibly due to the reduction of copper(II) to copper(I) species being followed by the formation of anionic thiosulphato copper(I) complexes. In K-Na-tartrate, all copper(II) complexes have the same R_f values indicating that they are not being chromatographed as genuine complexes but as some tartrato copper(II) species.

(3). Palladium(II) complexes :

The movement of palladium(II) complexes on silica gel is very slow. Although with high concentration of KCl (developer V) the complexes travel but their sizes are too large,

Table 9.2. R_f values of copper(II) complexes in different developers.
(TLC on silica gel).

Complex	0.5M KCl	0.5M K_2SO_4	0.5M $Na_2S_2O_3$	0.5M K-Na- tartrate *
$\text{Cu}(\text{BigH})_2\text{Cl}_2$	0.66	-	1.00	0.96
$\text{Cu}(\text{Me-BigH})_2\text{Cl}_2$	0.58	-	1.00	0.97
$\text{Cu}(\text{Et-BigH})_2\text{Cl}_2$	0.46	-	1.00	0.96
$\text{Cu}(\text{Pr}^i\text{-BigH})_2\text{Cl}_2$	0.35	-	1.00	0.98
$\text{Cu}(\text{Me}_2\text{-BigH})_2\text{Cl}_2$	0.48	-	1.00	0.97
$\text{Cu}(\text{Et}_2\text{-BigH})_2\text{Cl}_2$	0.52	-	1.00	0.96
$\text{Cu}(\text{Ph-BigH})_2\text{Cl}_2$	0.32	-	1.00	0.90
$\text{Cu Et}(\text{BigH})_2\text{Cl}_2$	0.49	-	1.00	-
$\text{Cu}(\text{AMUH})_2\text{Cl}_2$	0.46	0.56	1.00	0.96
$\text{Cu}(\text{AEUH})_2\text{Cl}_2$	0.37	0.40	1.00	0.95
$\text{Cu}(\text{AP}^n\text{UH})_2\text{Cl}_2$	0.26	0.30	1.00	0.97
$\text{Cu}(\text{AP}^i\text{UH})_2\text{Cl}_2$	0.30	0.35	1.00	0.93
$\text{Cu}(\text{AB}^n\text{UH})_2\text{Cl}_2$	0.20	0.21	1.00	0.92
$\text{Cu}(\text{AB}^i\text{UH})_2\text{Cl}_2$	0.22	0.25	1.00	0.91
$\text{Cu}(\text{AA}^n\text{UH})_2\text{Cl}_2$	0.14	0.23	1.00	0.93
$\text{Cu}(\text{AA}^i\text{UH})_2\text{Cl}_2$	0.16	0.24	1.00	0.92
$\text{Cu}(\text{en})_2(\text{NO}_3)_2$	0.60(0.14)	0.75(0.33)	1.00(1.00)	0.80
$\text{Cu}(\text{gly})_2$	0.70(0.13)		**	0.98
$\text{Cu}(\text{H}_2\text{O})_6\text{Cl}_2$	0.75	0.82	1.00	1.00

- = This spot either did not travel at all or diffused from the point of application.

* = The complexes are decomposed.

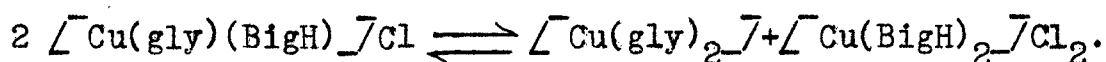
** = The complex was reduced by thiosulphate.

Values given in the parenthesis were reported by Yoneda⁶⁷.

(e.g. $\overline{\text{Pd}}(\text{BigH})_2\overline{\text{Cl}}_2$ 3.5 cm and other bis(substituted biguanide) palladium(II) chlorides 2.5 cm to 2 cm). With other developers e.g. K_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and K-Na-tartrate etc. either the complexes remained at the base line or diffused to a long distance.

B. Copper(II) mixed chelates :

A paper chromatographic study of fifteen copper(II) mixed chelates in aqueous KCl-pyridine developer has been made (Chapter VIII). There we have seen that $\overline{\text{Cu}}(\text{gly})(\text{BigH})\overline{\text{Cl}}$, $\overline{\text{Cu}}(\alpha\text{-alan})(\text{BigH})\overline{\text{Cl}}$ etc always give two spots in all the developers studied. An equilibrium of the following type was suggested :



$\overline{\text{Cu}}(\text{gly})(\text{o-phen})\overline{\text{Cl}}$ also shows similar behaviour. Such disproportionation reaction was less favoured in $\overline{\text{Cu}}(\text{gly})(\text{dipy})\overline{\text{Cl}}$. $\overline{\text{Cu}}(\text{dipy})(\text{BigH})\overline{\text{Cl}}_2$ and $\overline{\text{Cu}}(\text{o-phen})(\text{BigH})\overline{\text{Cl}}_2$ provided single spot on proper choice of the developer (Chapter VIII).

We now examine the behaviour of the copper(II) mixed chelates when the stationary phase is changed from paper (cellulose) to silica gel (silanol group).

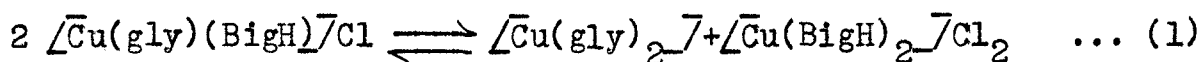
Mixed chelates containing iminodiacetic group (IDA) :

Here only the $\overline{\text{Cu}}(\text{IDA})(\text{BigH})\overline{\text{Cl}}$ travelled while $\overline{\text{Cu}}(\text{IDA})(\text{dipy})\overline{\text{Cl}}$ and $\overline{\text{Cu}}(\text{IDA})(\text{o-phen})\overline{\text{Cl}}$ remained at the point of application even when developed with developer V. Both $\overline{\text{Cu}}(\text{IDA})(\text{dipy})\overline{\text{Cl}}$ and $\overline{\text{Cu}}(\text{IDA})(\text{o-phen})\overline{\text{Cl}}$ have zero charge, still they remained at

the base line (Fig. 9.1). These low R_f values are possibly connected with the presence of at least one aromatic ring in the complexes. It will be premature to advance any explanation for this peculiar yet definite observation.

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

In paper chromatography [Cu(gly)(BigH)]Cl always gave two spots in all the developers studied (Chapter VII) and the following equilibrium was suggested :



In view of the above result it appeared likely that the same complex would also provide two spots with the developer V. We have, however, obtained a single spot which was somewhat bigger in size (~ 2 cm) than shown by $\text{[Cu(BigH)}_2\text{]Cl}_2$ and $\text{[Cu(gly)}_2\text{]}$ (~ 1.5 cm). In view of the fact that $\text{[Cu(BigH)}_2\text{]Cl}_2$ and $\text{[Cu(gly)}_2\text{]}$ exhibit spots with about the same R_f values (0.68 and 0.70 respectively) in developer V, it is not unlikely that the two expected spots have got fused together. Equilibrium of type (1), therefore, has neither been definitely established nor dispelled in the case of [Cu(gly)(BigH)]Cl on silica gel. Similarly we got single spots for the other copper(II) mixed chelates (Table 9.3). However the R_f values of some mixed chelates and the respective homo chelates e.g. $\text{[Cu}(\alpha\text{-alan)(BigH)]Cl}$,

Table 9.3. R_f values of copper(II) mixed chelate with developer V.

Complex	R_f
[Cu(dipy)(IDA)]^-	-
$\text{[Cu(o-phen)(IDA)]}^-$	-
[Cu(BigH)(IDA)]^-	-
$\text{[Cu(gly)(BigH)]}^- \text{Cl}$	0.68
$\text{[Cu(gly)(Me-BigH)]}^- \text{Cl}$	0.57
$\text{[Cu(gly)(Et-BigH)]}^- \text{Cl}$	0.48
$\text{[Cu}(\alpha\text{-alan)(BigH)]}^- \text{Cl}$	0.62
$\text{[Cu}(\alpha\text{-alan)(Me-BigH)]}^- \text{Cl}$	0.54
$\text{[Cu}(\alpha\text{-alan)(Et-BigH)]}^- \text{Cl}$	0.47
$\text{[Cu(gly)(o-phen)]}^- \text{Cl}$	-
$\text{[Cu(gly)(dipy)]}^- \text{Cl}$	-
$\text{[Cu(pic)(BigH)]}^- \text{Cl}$	-
$\text{[Cu(dipy)(BigH)]}^- \text{Cl}_2$	-
$\text{[Cu(dipy)(Me-BigH)]}^- \text{Cl}_2$	-
$\text{[Cu(dipy)(Et-BigH)]}^- \text{Cl}_2$	-
$\text{[Cu(o-phen)(BigH)]}^- \text{Cl}_2$	-

Under similar condition R_f values of the homochelates are :

$$\begin{aligned} & \text{[Cu(gly)}_2\text{]}^- = 0.70; \text{[Cu}(\alpha\text{-alan)}_2\text{]}^- = 0.60; \text{[Cu(BigH)}_2\text{]}^- \text{Cl}_2 \\ & = 0.68; \text{[Cu(Me-BigH)}_2\text{]}^- \text{Cl}_2 = 0.60; \text{[Cu(Et-BigH)}_2\text{]}^- \text{Cl}_2 = 0.48; \\ & \text{[Cu(dipy)}_2\text{]}^- \text{Cl}_2 = 0.00 \text{ and } \text{[Cu(o-phen)}_2\text{]}^- \text{Cl}_2 = 0.00 \end{aligned}$$

- = remained at the point of application.

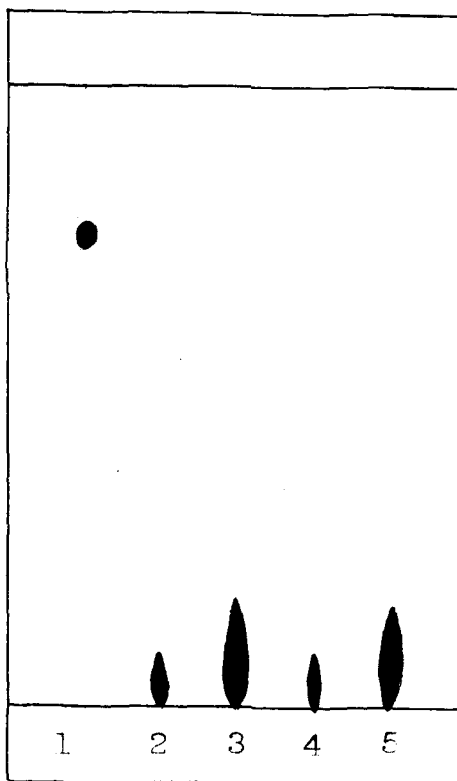


Fig.9.1. Chromatograms in 0.5M aqueous KCl as developer.

1. $\left[\text{Cu}(\text{IDA})(\text{BigH}) \right]^- \text{Cl}_2$
2. $\left[\text{Cu}(\text{dipy})_2 \right]^- \text{Cl}_2$
3. $\left[\text{Cu}(\text{IDA})(\text{dipy}) \right]^-$
4. $\left[\text{Cu}(\text{o-phen})_2 \right]^- \text{Cl}_2$
5. $\left[\text{Cu}(\text{IDA})(\text{o-phen}) \right]^-$

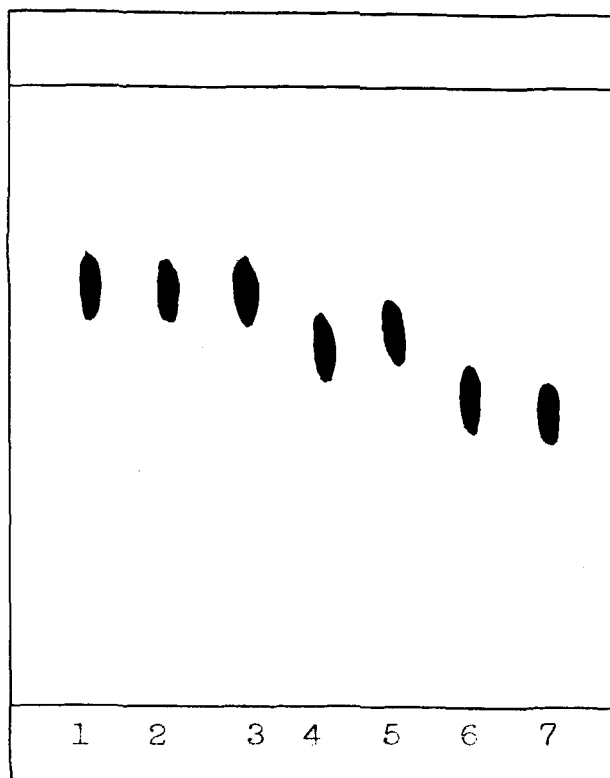


Fig.9.2. Chromatograms in 0.5M aqueous KCl as developer.

1. $\left[\text{Cu}(\text{BigH})_2 \right]^- \text{Cl}_2$
2. $\left[\text{Cu}(\text{gly})(\text{BigH}) \right]^- \text{Cl}$
3. $\left[\text{Cu}(\text{gly})_2 \right]^-$
4. $\left[\text{Cu}(\text{gly})(\text{Me-BigH}) \right]^- \text{Cl}$
5. $\left[\text{Cu}(\text{Me-BigH})_2 \right]^- \text{Cl}_2$
6. $\left[\text{Cu}(\text{gly})(\text{Et-BigH}) \right]^- \text{Cl}$
7. $\left[\text{Cu}(\text{Et-BigH})_2 \right]^- \text{Cl}_2$

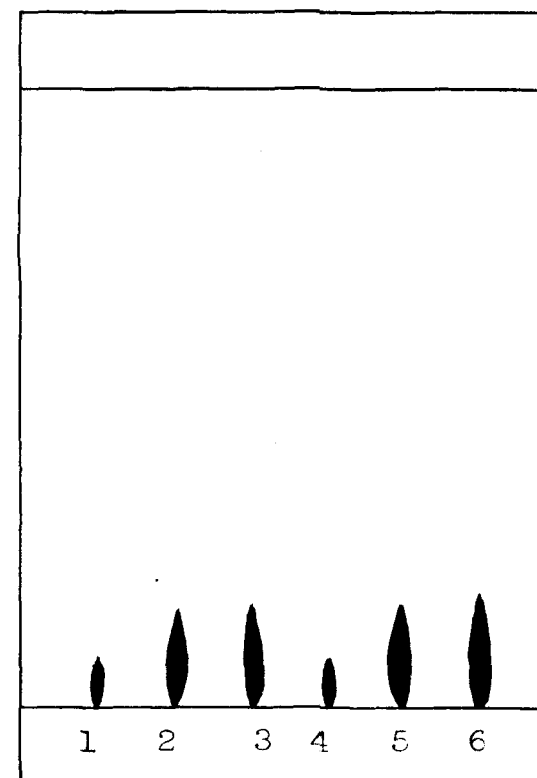


Fig.9.3. Chromatograms in 0.5M aqueous KCl as developer.

1. $\left[\text{Cu}(\text{o-phen})_2 \right]^- \text{Cl}_2$
2. $\left[\text{Cu}(\text{gly})(\text{o-phen}) \right]^- \text{Cl}$
3. $\left[\text{Cu}(\text{gly})(\text{dipy}) \right]^- \text{Cl}$
4. $\left[\text{Cu}(\text{dipy})_2 \right]^- \text{Cl}_2$
5. $\left[\text{Cu}(\text{dipy})(\text{BigH}) \right]^- \text{Cl}_2$
6. $\left[\text{Cu}(\text{o-phen})(\text{BigH}) \right]^- \text{Cl}_2$

$[\text{Cu}(\alpha\text{-alan})_2]^-$ and $[\text{Cu}(\text{Et-BigH})_2]^- \text{Cl}_2$ being not as close as that for say $[\text{Cu}(\text{gly})(\text{BigH})]^- \text{Cl}$ etc., one may claim that there is a scope for obtaining double spots. However one has to appreciate that R_f is a ratio wherein we take into account the midpoint of the spot disregarding the size of the spot. A careful scrutiny of the sizes of the spots of the two relevant homochelates alongwith that of the mixed chelate shows that one cannot discount the possibility of the two spots still getting fused together.

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

All these complexes remained at the point of application in all the developers (e.g. water, aqueous KCl, aqueous KCl-pyridine) probably due to the presence of a dipyridyl/o-phenanthroline complexes (Fig. 9.3).

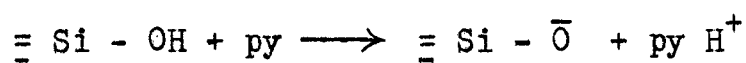
C. Thin layer chromatography of cobalt(III) complexes :

When cobalt(III) complexes of different charges (-3 to +3) were developed with water only anionic and neutral complexes easily moved from the point of application and exhibited high R_f values (~ 0.9). But the cationic complexes stayed at the baseline (Fig. 9.4). Such strong adsorption of the complex cations could be removed by the use of different aqueous salts solutions¹²².

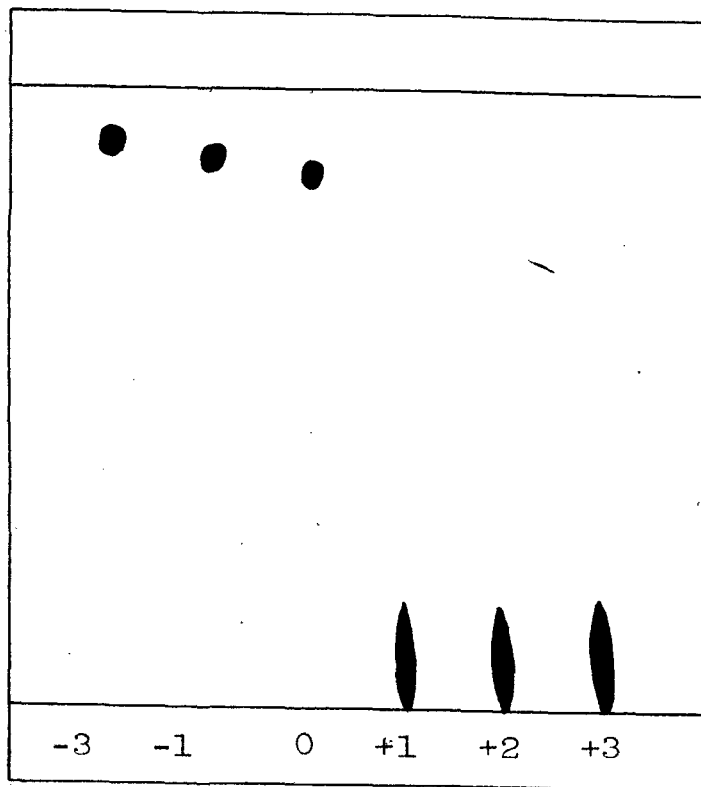
Effect of electrolyte concentration on R_f values :

Previously (Chapter IV) we have shown that as the concentration of KCl increases the corresponding R_f values of the complexes also increase. In the present case, a peculiar but definite observation was noticed. When the cationic complexes are developed with developer IX (0.1M KCl aq.), the R_f values of the complex cations showed a regular increase with the decrease of the ionic charges (Fig. 9.5). But a reverse order of R_f values was noted when developed with developer I (i.e. with 0.2M aq.KCl see Fig. 9.6). Similar variation of R_f values was also noticed when KI, K_2SO_4 , $Na_2S_2O_3$ and K-Na-tartrate solutions were used as the mobile phases.

It has been observed that the addition of pyridine in aqueous KCl developer lowers the R_f value of the cationic complexes (Table 9.4) because pyridine, being a base, easily extracts the proton from the silica gel ($=Si-\bar{O}H^+$) and makes the silica gel more negative charge :

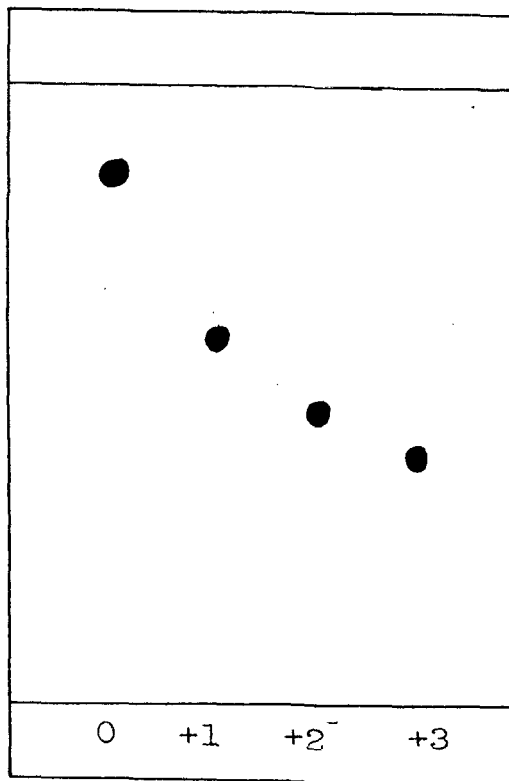


As a result movement of the cationic complexes along the negatively silica gel bed becomes disturbed to some extent due to electrostatic force. But the corresponding R_f values of neutral and anionic complexes remains the same (unity) and did not show the dependence on the nature and concentration of the developer electrolytes. Some of our above results corroborate those of Yoneda et al on another set of cobalt(III) complexes.



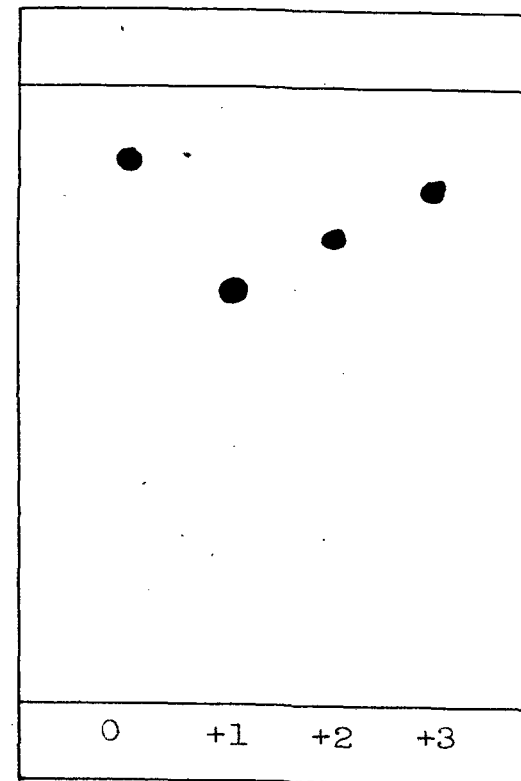
Charge of the complex

Fig.9.4. Chromatogram for distilled water system.



charge of the complex

Fig.9.5. Chromatogram for 0.1M KCl system.



Charge of the complex

Fig.9.6. Chromatogram for 0.2M KCl system.

Table 9.4. R_f values of cobalt(III) complexes with different developers(TLC on silica gel).

Complex	0.1M KCl	0.2M KCl	0.2M KI	0.2M KCl+py	0.2M K_2SO_4	0.2M $Na_2S_2O_3$	0.2M K-Na-tartrate
$\angle^- Co(NH_3)_6-\overline{Cl}_3$	0.40	0.85	0.85	0.75	0.90	0.92	0.89
$\angle^- Co(BigH)_3-\overline{Cl}_3$	0.38	0.72	0.74	0.60	0.80	0.80	0.81
$\angle^- Co(en)_3-\overline{Cl}_3$	0.40	0.72(0.24)	0.75(0.26)	0.59	0.80(0.57)	0.82(0.79)	0.79
$\angle^- Co(Ph-BigH)_3-\overline{Cl}_3$	0.25	0.30	0.30	0.26	0.24	0.26	0.22
$\angle^- Co(dipy)(BigH)_2-\overline{Cl}_3$	0.20	0.25	0.27	0.22	0.21	0.20	0.22
$\angle^- Co(o-phen)(BigH)_2-\overline{Cl}_3$	0.18	0.22	0.25	0.20	0.20	0.18	0.20
$\angle^- Co(\alpha\text{-alan})(BigH)_2-\overline{Cl}_2$	0.51	0.78	0.80	0.66	0.88	0.88	0.88
$\angle^- Co(\beta\text{-alan})(BigH)_2-\overline{Cl}_2$	0.52	0.76	0.79	0.65	0.86	0.89	0.87
$\angle^- Co(leuc)(BigH)_2-\overline{Cl}_2$	0.49	0.62	0.60	0.56	0.74	0.72	0.73
$\angle^- Co(meth)(BigH)_2-\overline{Cl}_2$	0.50	0.64	0.64	0.58	0.75	0.76	0.74
$\angle^- Co(val)(BigH)_2-\overline{Cl}_2$	0.52	0.65	0.66	0.60	0.74	0.75	0.74
$\angle^- Co(hist)(BigH)_2-\overline{I}_2$	0.53	0.67	0.66	0.61	0.68	0.75	0.68
$\angle^- Co(pic)(BigH)_2-\overline{I}_2$	0.47	0.52	0.52	0.49	0.55	0.56	0.50

Table 9.4.(Contd.)

Complex	0.1M KCl	0.2M KCl	0.2M KI	0.2M KCl+py	0.2M K ₂ SO ₄	0.2M Na ₂ S ₂ O ₃	0.2M K-Na-tartrate
$[\text{Co}(\text{IDA})(\text{BigH})_2]^- \text{Br}$	0.62	0.74	0.72	0.62	0.84	0.84	0.84
$[\text{Co}(\text{en})_2 \text{CO}_3]^- \text{Cl}$	0.62	0.73	0.73	0.61	0.75	0.80	0.76
$[\text{Co}(\text{Lut})(\text{BigH})_2]^- \text{Cl}$	0.48	0.54	0.54	0.50	0.60	0.62	0.60
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]^-$	0.87	0.92	0.91	0.92	0.96	0.98	0.95
$\text{K} [\text{Co}(\text{gly})_2(\text{NO}_2)_2]^-$	0.97	0.96	0.96	0.96	0.98	0.98	0.98
$\text{NH}_4 [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$	0.96	0.98	0.97	0.98	0.98	0.98	0.98
$\text{Na}_3 [\text{Co}(\text{NO}_2)_6]^-$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$\text{K}_3 [\text{Co}(\text{Ox})_3]^-$	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Values in the parenthesis were reported by Yoneda⁶⁷.

In water as developer silica gel becomes negative so that it can hold all the complex cations strongly on its surface resulting in low R_f values. On feeding electrolytes into the developer, the thirst of silica gel anions is largely quenched by the cations in the electrolyte, thereby allowing a more comfortable journey of the complex cation up the silica gel bed. A distinction in R_f : $+1 > +2 > +3$ is expectedly observed but to a certain point. If the concentration of the electrolyte in the developer is considerable, outer sphere association between the complex cation and the electrolyte anions takes place and this effect is large the larger the charge on the cation is. A reversal of R_f order is therefore not out of order.

Only three complexes e.g. $\left[\text{Co}(\text{Ph-BigH})_3 \right]^{3+}$, $\left[\text{Co}(\text{dipy})(\text{BigH})_2 \right]^{3+}$, $\left[\text{Co}(\text{o-phen})(\text{BigH})_2 \right]^{3+}$ show scant respect to the above explanation and always show very low R_f values (Table 9.4). These low values are possibly connected with the presence of aromatic ring in the complexes. As stated earlier, it will be premature to advance any explanation for this peculiar yet definite observation, particularly in the absence of solubility data.