

CHAPTER VIII :

PAPER CHROMATOGRAPHIC STUDIES ON INERT COBALT(III)  
COMPLEXES.

We describe in this chapter our results of paper chromatographic investigations on twenty two inert cobalt(III) complexes covering both homochelates and mixed chelates of different overall charge. This study has revealed a strong influence of ion-pair formation between the complex cobalt(III) cation and the anion of the developer electrolytes.

#### Methods and materials :

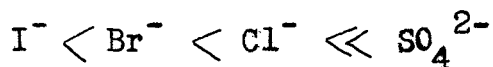
For the purpose of putting spots all the complexes were dissolved in water. The following developers were examined :

Developer	I	:	100 ml 0.2M aqueous KCl
"	II	:	100 ml 0.2M aqueous KI
"	III	:	100 ml 0.2M aqueous $K_2SO_4$
"	IV	:	100 ml 0.2M aqueous $Na_2S_2O_3$
"	V	:	100 ml 0.2M aqueous K-Na- tartrate.

#### Results and Discussion :

Recently ion electrophoresis and thin layer chromatography have provided evidence for outer sphere association between an inert complex cation and the developer electrolyte<sup>125,126,311,312</sup>. While describing filter paper chromatographic results Yoneda<sup>116</sup> had made a passing reference that the  $R_f$  ( $\sim 0.9$ ) value of  $[Co(NH_3)_6]Cl_3$  remained unchanged in 1N electrolytes such as HCl, NaCl, KBr,  $NaNO_3$ ,  $NaClO_4$  and  $K_2SO_4$ . We have collected  $R_f$

data of  $\left[ \text{Co}(\text{NH}_3)_6 \right] \text{Cl}_3$  and twenty one other cobalt(III) complexes in several electrolytes of different charge types and of 0.2M concentration. These data show that  $R_f$  values do vary in a way to indicate outer sphere association between these complex cations and the developer electrolytes. For example, there is a distinct change in the  $R_f$  values of  $\left[ \text{Co}(\text{NH}_3)_6 \right] \text{Cl}_3$  and other cobalt(III) complexes on switching from a uni-univalent electrolyte (e.g. KCl/KI) to a bi-univalent electrolyte (e.g.  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  or K-Na-tartrate). The lowest  $R_f$  is recorded for all the complexes in aqueous KI developer. In aqueous KCl developer the  $R_f$  is distinctly higher by 0.1 unit and in aqueous  $\text{K}_2\text{SO}_4/\text{Na}_2\text{S}_2\text{O}_3/\text{K-Na-tartrate}$  this again increases by another 0.1 - 0.20 (Table 8.1). We ascribe these effects to ion pair formation between the complex cobalt(III) cation and the anion of the developer electrolytes. It is an established fact that ion-association constants increase with increasing charge on the ions and decrease with increasing size of the ions<sup>313,314</sup>. Investigations on the outer sphere association constants of  $\left[ \text{Co}(\text{NH}_3)_6 \right]^{3+}$ ,  $\left[ \text{Co}(\text{en})_3 \right]^{3+}$ ,  $\left[ \text{Co}(\text{BigH})_3 \right]^{3+}$ ,  $\left[ \text{Co}(\text{dipy})(\text{BigH})_2 \right]^{3+}$ ,  $\left[ \text{Co}(\text{o-phen})(\text{BigH})_2 \right]^{3+}$  etc have shown that the association constants obey the following order<sup>241,242,314</sup> :



For example, in our laboratory De and Dutta<sup>241,242</sup> have determined the following outer sphere association constants for tris (biguanide) cobalt(III) salts :

Salt	Outer sphere association constant at	
	25°C	35°C
$\{ \text{[Co(BigH)}_3\text{]I} \}^{2+}$	22	24
$\{ \text{[Co(BigH)}_3\text{]Br} \}^{2+}$	34	37
$\{ \text{[Co(BigH)}_3\text{]Cl} \}^{2+}$	55	62
$\{ \text{[Co(BigH)}_3\text{]SO}_4 \}^+$	$12.6 \times 10^2$	$13.2 \times 10^2$

The reported  $R_f$  values of the cobalt(III) complexes also obey this order (Table 8.1). In essence the anion of the developer electrolyte reduces the over all charge in the complex cation and thus allows a comfortable movement of the complex cation along the anionic filter paper. On raising the concentration of the same electrolyte developer, the  $R_f$  values of the complexes also increase but very slowly. For example,  $\text{[Co(NH}_3\text{)}_6\text{]Cl}_3$  has  $R_f$  values 0.65, 0.68, 0.70, 0.73 and 0.75 in 0.1M, 0.2M, 0.3M, 0.5M and 1M aqueous KCl.

Table 8.1.  $R_f$  values of cobalt(III) complexes with different developers.

Complex	0.2M KI	0.2M KCl	0.2M $K_2SO_4$	0.2M $Na_2S_2O_3$	0.2M K-Na-tartrate
$[Co(BigH)_3]^- Cl_3$	0.58	0.68	0.85	0.82	0.82
$[Co(BigH)_3]^- 2(SO_4)_3$	0.58	0.68	0.86	0.83	0.81
$[Co(NH_3)_6]^- Cl_3$	0.78	0.90	0.96	0.96	0.96
$[Co(en)_3]^- Br_3$	0.77	0.90	0.97	0.97	0.96
$[Co(dipy)(BigH)_2]^- Cl_3$	0.62	0.69	0.88	0.84	0.84
$[Co(o-phen)(BigH)_2]^- Cl_3$	0.60	0.67	0.82	0.80	0.80
$[Co(\alpha\text{-alan})(BigH)_2]^- Cl_2$	0.68	0.80	0.88	0.85	0.85
$[Co(\beta\text{-alan})(BigH)_2]^- I_2$	0.66	0.80	0.90	0.87	0.85
$[Co(leuc)(BigH)_2]^- Cl_2$	0.72	0.80	0.90	0.87	0.86
$[Co(val)(BigH)_2]^- Cl_2$	0.71	0.81	0.91	0.87	0.86
$[Co(hist)(BigH)_2]^- I_2$	0.67	0.77	0.90	0.83	0.84
$[Co(meth)(BigH)_2]^- I_2$	0.69	0.79	0.87	0.83	0.85
$[Co(pic)(BigH)_2]^- I_2$	0.66	0.76	0.88	0.86	0.84
$[Co(lut)(BigH)_2]^- Cl$	0.68	0.80	0.88	0.85	0.84

Table 8.1.(Contd.)

Complex	0.2M KI	0.2M KCl	0.2M K <sub>2</sub> SO <sub>4</sub>	0.2M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.2M K-Na-tartrate
$\text{[Co(IDA)(BigH)}_2\text{]Br}$	0.70	0.82	0.90	0.88	0.89
$\text{[Co(en)}_2\text{(CO}_3\text{)]Cl}$	0.78	0.89	0.94	0.89	0.91
$\text{[Co(en)}_2\text{(CO}_3\text{)]NO}_3$	0.79	0.90	0.94	0.90	0.90
$\text{[Co(NH}_3\text{)}_2\text{(NO}_2\text{)}_3\text{]}$	*	0.88	0.88	0.88	0.88
$\text{K [Co(gly)}_2\text{(NO}_2\text{)}_2\text{]}$	*	0.87	0.90	0.90	0.90
$\text{NH}_4 \text{[Co(NH}_3\text{)}_2\text{(NO}_2\text{)}_4\text{]}$	*	0.86	0.92	0.90	0.91
$\text{Na}_3 \text{[Co(NO}_2\text{)}_6\text{]}$	*	1.00	1.00	1.00	1.00
$\text{K}_3 \text{[Co(ox)}_3\text{]}$	*	1.00	1.00	1.00	1.00

\* = Not tried, as of no special interest.