

Short Communication  
Chromatographic studies of metal complexes  
VII. Thin-layer chromatography of cobalt(III) complexes

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(First received June 3rd, 1993; revised manuscript received April 26th, 1994)

**Abstract**

Thin-layer chromatography of a variety of inert cobalt(III) complexes of different charges (+3, +2, +1, 0, -1, -3) shows that silica gel is charged negatively in contact with water. Cationic complexes do not move on an anionic silica gel bed; strong adsorption is observed between the complex cation and the negatively charged silanol group of the silica gel. Such strong binding can be reduced considerably by using electrolytes such as KI, KCl, K<sub>2</sub>SO<sub>4</sub>, etc. In the case of neutral and anionic complexes no such binding is observed. A close connection between  $R_F$  values and charges of complexes was observed.

**1. Introduction**

The movement of cationic complexes on stationary phases may be correlated with the (1) overall charge of the complex species [1–4], (2) stereochemistry of the complex species [1,5], (3) concentration and composition of the mobile phase [1,6], (4) nature of the stationary phase (paper, silica gel, cellulose powder, alumina, etc.) [1,6,7], (5) surface tension of the developer (mobile phase) [8], (6) viscosity of the developer (pure solvent or mixed solvents) [8], (7) dielectric constant of the developer [8–10], (8) ion-pair formation between the complex cation and anion present in the developer solvent or between the complex cation and the anionic stationary phase [2,11], (9) equivalent conductance of the elec-

trolyte [11] and (10) joint effect of the surface tension of the developer and the anionic conductance of the electrolyte present in different developers [11].

The present paper describes the separation by TLC of a number of cationic, neutral and anionic cobalt(III) complexes with aqueous salt solutions as eluents. These separations are based on outer-sphere association between the complex cation and the anion present in the developer.

**2. Experimental**

**2.1. Materials**

The complexes were synthesized according to published procedures [12,13]. Their purity was established by elemental analysis and spectral

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measurements. Both the homo- and the heteroligand cobalt(III) biguanide complexes are very stable in the solid state as well as in solution [12,13].

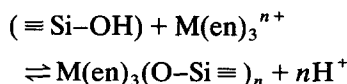
## 2.2. Procedure

Merck silica gel H was used as the adsorbent. Other experimental techniques have been described elsewhere [14].

## 3. Results and discussion

The surface of silica gel consists of silanol ( $\equiv\text{Si}-\text{OH}$ ) sites whose hydrogen atoms can be exchanged for cations [6,15]. From enthalpy, entropy and free energy change values for the exchange reaction between the metal ions and hydrogen atoms of the gel Dugger *et al.* [15] found that the bond energy of the gel varies directly with the charge density of the unhydrated ion. The fact that such adsorbed metal ions cannot be eluted by simple washing with water is evidence of the coordination of the silanol oxygen via exchange of the hydrogen atoms by the metal ion [16,17].

The degree of adsorption of complex cations on silica gel was found to be dependent upon the charge and charge distribution of the complex ion. Furthermore, the amount of acid liberated by sorption of the metal complex cation corresponds to the charge of the complex ion [11,18,19]:



When cobalt(III) complexes of different charges ( $-3$  to  $+3$ ) were developed with water, i.e. anionic and neutral complexes moved easily on the silica gel and exhibited high (*ca.* 0.9)  $R_F$  values, but the cationic complexes trailed from the point of application. Such strong adsorption of cationic complexes could be reduced by using other different electrolyte solutions or acidic solvents [1–4,20].

Acidic solvents, however, were found to be unsuitable, particularly for cobalt(III) biguanidine complexes, since spectrophotometric studies showed substantial modification of electronic spectra. Thus acidic developers do not give  $R_F$  values of genuine complexes. It should be noted that for the  $[\text{Co}(\text{bigH})_3]^{3+}$  ion  $\lambda_{\text{max}} = 480$  nm, with  $\epsilon = 203$  in water and in different electrolyte solutions, but in acidic solvents it becomes 490 nm, with  $\epsilon = 125$ , corresponding to the  $[\text{Co}(\text{H}_2\text{O})_2(\text{bigH})_2]^{3+}$  ion [21]. The formation of the  $[\text{Co}(\text{H}_2\text{O})_2(\text{bigH})_2]^{3+}$  ion is also evident from the immediate shift in the absorption maxima of  $[\text{Co}(\text{OH})(\text{H}_2\text{O})(\text{bigH})_2]^{2+}$  from 480 nm to 490–495 nm by the addition of acid [22].  $[\text{Co}(\text{H}_2\text{O})(\text{bigH})_2]^{3+}$  may dissociate further to  $[\text{Co}(\text{H}_2\text{O})_4(\text{bigH})]^{3+}$  and finally to  $\text{Co}^{2+}$  with simultaneous release of biguanide if the concentration of acid present in the developer solvent is much greater [22]. Because  $[\text{Co}(\text{bigH})_3]^{3+}$  and  $[\text{Co}(\text{H}_2\text{O})_2(\text{bigH})_2]^{3+}$  have the same charge, their mobility on silica gel is almost identical ( $R_F$  values of 0.72 and 0.68, respectively). Biguanide is more basic ( $\text{p}K_1 = 13.0$ ) than ethylenediamine ( $\text{p}K_1 = 9.93$ ) because of an exceptionally high enthalpy of protonation [23,24]. Therefore protonation takes place at the free basic imino group ( $=\text{NH}$ ) of the biguanide molecule to the cobalt atom. This causes a strain in the chelate ring, resulting in its rupture from the central metal atoms [21,22,25,26].

Protonation of the complex  $[\text{Co}(\text{bigH})_3]^{3+}$  ion will naturally facilitate bond breaking by exerting a pull on the electrons of the outer shells of the adjacent atoms of the molecule; thus the metal–nitrogen bond becomes weaker and finally breaks (Fig. 1).

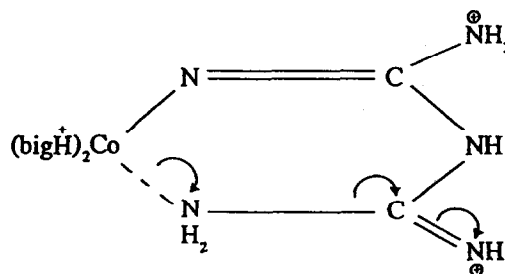
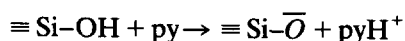


Fig. 1. Protonation of  $[\text{Co}(\text{bigH})_3]^{3+}$ .

The addition of pyridine (py) in aqueous KCl developer lowers the  $R_F$  values of cationic complexes (Table 1). Because pyridine is a base, it easily removes a proton from the silica gel ( $\equiv \text{Si-OH}$ ), making the adsorbent more negative:



Therefore cationic complexes exhibit much lower  $R_F$  values.

In this study we observed a peculiar but definite fact: when cationic complexes were developed with 0.1 M KCl or 0.1 M KI, the  $R_F$  values showed a regular increase with the decrease in the cationic charges (Fig. 2, line ABCD), but a reverse order of  $R_F$  values resulted when the same cationic complexes were

developed with 0.2 M  $\text{K}_2\text{SO}_4$  solutions (Fig. 2, line EFGH). A similar variation of  $R_F$  values was also noted when sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) and potassium sodium tartrate ( $\text{KNaC}_4\text{H}_4\text{O}_6$ ) solutions were used as mobile phases (Table 1). The change of  $R_F$  values with higher concentration of electrolyte is also shown (Fig. 2, line IJKL). Some of our results corroborate those of Baba *et al.* [20] on another group of cobalt(III) complexes.

In water silica gel becomes negative so that it can hold all the complex cations on its surface, resulting in low  $R_F$  values. Adding electrolytes (KI, KCl) to the developer can reduce such strong binding, and the migration of the complex cations on the silica gel bed becomes easy. As expected, the order  $R_F + 1 > R_F + 2 > R_F + 3$  is

Table 1  
 $R_F$  values of cobalt(III) complexes with developers of different concentrations

Complex	$R_F$								
	KI		KCl		$\text{K}_2\text{SO}_4$ , 0.2 M	$\text{K}_2\text{SO}_4$ , 0.2 M +	$\text{Na}_2\text{S}_2\text{O}_3$ , 0.2 M	$\text{KNaC}_4\text{H}_4\text{O}_6$ , 0.2 M	KCl + pyridine (100:5, v/v, 0.2 M)
	0.1 M	0.2 M	0.1 M	0.2 M		KCl, 0.2 M			
$[\text{Co}(\text{bigH})_3]\text{Cl}_3$	0.28	0.72	0.40	0.72	0.90	0.95	0.90	0.91	0.62
$[\text{Co}(\text{MebigH})_3]\text{Cl}_3$	0.28	0.71	0.38	0.69	0.89	0.96	0.89	0.89	0.60
$[\text{Co}(\text{PhbigH})_3]\text{Cl}_3$	0.30	0.72	0.40	0.74	0.90	0.95	0.90	0.92	0.64
$[\text{Co}(\text{nPr-bigH})_3]\text{Cl}_3$	0.29	0.70	0.40	0.71	0.89	0.97	0.89	0.91	0.59
$[\text{Co}(\alpha\text{-alanO})(\text{bigH})_2]\text{Cl}_2$	0.41	0.52	0.51	0.62	0.73	0.75	0.72	0.73	0.66
$[\text{Co}(\beta\text{-alanO})(\text{bigH})_2]\text{Cl}_2$	0.43	0.53	0.52	0.63	0.75	0.76	0.73	0.74	0.64
$[\text{Co}(\text{leucO})(\text{bigH})_2]\text{Cl}_2$	0.40	0.50	0.49	0.61	0.74	–	0.73	0.75	0.56
$[\text{Co}(\text{methO})(\text{bigH})_2]\text{Cl}_2$	0.40	0.51	0.50	0.61	0.72	0.74	0.71	0.74	0.58
$[\text{Co}(\text{valO})(\text{bigH})_2]\text{Cl}_2$	0.41	0.50	0.51	0.60	0.73	0.74	0.71	0.72	0.60
$[\text{Co}(\text{IDA})(\text{bigH})_2]\text{Br}$	0.52	0.68	0.62	0.72	0.83	0.75	0.86	0.84	0.62
$[\text{CoCO}_3(\text{en})_2]\text{Cl}$	0.53	0.69	0.61	0.71	0.84	0.95	0.83	0.82	0.61
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	0.82	0.91	0.87	0.92	0.92	0.94	0.93	0.94	0.92
$[\text{Co}(\text{glyO})_3]$	0.83	0.93	0.89	0.93	0.95	0.96	0.94	0.95	0.93
$\text{K}[\text{Co}(\text{NO}_2)_2(\text{glyO})_2]$	0.95	0.96	0.97	0.98	0.96	–	0.97	0.98	0.97
$\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$	0.94	0.95	0.96	0.98	0.96	–	0.96	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	1.00
$\text{K}_3[\text{Co}(\text{Ox})_3]$	1.00	1.00	1.00	1.00	1.00	–	1.00	1.00	1.00

$\alpha$ -alanOH =  $\alpha$ -Alanine;  $\beta$ -alanOH =  $\beta$ -alanine; bigH = biguanide; en = ethylenediamine; glyOH = glycine; IDAH<sub>2</sub> = iminodiacetic acid;  $\text{KNaC}_4\text{H}_4\text{O}_6$  = potassium sodium tartrate; leucOH = leucine; MebigH = methylbiguanide; methOH = methionine; OxH<sub>2</sub> = oxalic acid; PhbigH = phenylbiguanide; nPr-bigH = *n*-propylbiguanide; valOH = valine; – = not tried.

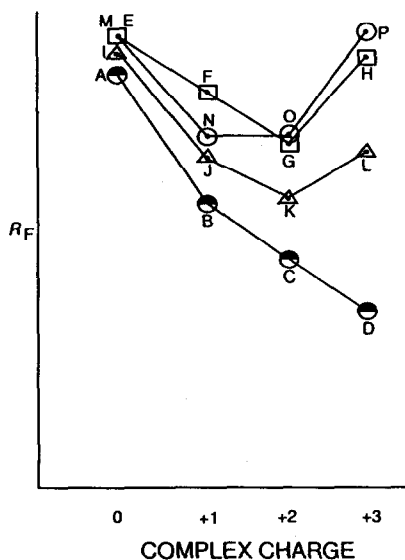
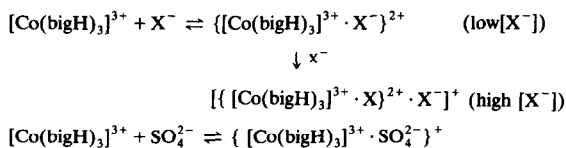


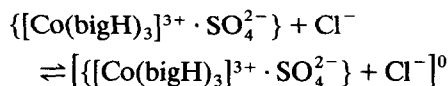
Fig. 2. Complex charge versus  $R_F$ . ● = 0.1 M KCl developer; △ = 0.2 M KCl developer; □ = 0.2 M  $K_2SO_4$  developer; ○ = 0.2 M KCl + 0.2 M  $K_2SO_4$ . (i) A, E, I and M are the spots of  $[Co(NO_2)_3(NH_3)_3]$  when developed with 0.1 M KCl, 0.2 M KCl, 0.2 M  $K_2SO_4$  and 0.2 M KCl + 0.2 M  $K_2SO_4$ , respectively. (ii) B, J, N and F are the spots of  $[Co(IDA)(bigH)_2]Br$  when developed with 0.1 M KCl, 0.2 M KCl, 0.2 M KCl + 0.2 M  $K_2SO_4$  and 0.2 M  $K_2SO_4$ , respectively. (iii) C, K, G and O are the spots of  $[Co(\alpha\text{-alan-O})(bigH)_2]Cl_2$  developed with 0.1 M KCl, 0.2 M KCl, 0.2 M KCl + 0.2 M  $K_2SO_4$  and 0.2 M  $K_2SO_4$ , respectively. (iv) D, L, H and P are the spots of  $[Co(bigH)_3]Cl_3$  developed with 0.1 M KCl, 0.2 M KCl, 0.2 M  $K_2SO_4$  and 0.2 M KCl + 0.2 M  $K_2SO_4$ , respectively.

observed (Table 1). If the concentration of the electrolyte in the developer is high (0.2 M KI or KCl), much greater  $R_F$  values for all the complex cations are observed (Table 1). We ascribe this effect to ion-pair formation between the complex cobalt(III) cation and the anion of the developer electrolyte because it is known that ion-association constants increase with increasing charge on the ion and decrease with increasing size of the ion [27,28]. Studies of the outer-sphere dissociation constants of  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$  and  $[Co(bigH)_3]^{3+}$  have shown these constants to follow the order [28,29]:  $I^- < Br^- < Cl^- \approx SO_4^{2-}$ . Interestingly, the  $R_F$  values for cobalt(III) complexes follow this order. In essence, the anion of the developing electrolyte reduces the

overall charge of the complex cation and thus allows easy passage of the complex ion along the anionic silica gel:



That such an assumption is not unusual is verified by running additional experiments using 0.2 M KCl + 0.2 M  $K_2SO_4$  mixed developer solvent (Table 1) where  $[Co(LH)_3]^{3+}$  (LH = bigH, etc.),  $[Co(glyO)_3]$  and  $[Co(NO_2)_3(NH_3)_3]$  show  $R_F$  values of almost 1 (Fig. 2, line MNOP). Therefore formation of the neutral species by  $[Co(bigH)_3]^{3+}$  in mixed developer solvent is not unlikely:



#### 4. Conclusions

The degree of adsorption of the cationic complexes on negative silica gel ( $\equiv Si-O^-$ ) was dependent on the charge and charge distribution of the complex ion. Such strong binding can easily be reduced by using ionic electrolytes. The variation in  $R_F$  values for a particular cationic complex in different electrolytes indicates different ion-pair formation between that complex cation and the anion present in the developer solvent, resulting in considerable reduction of the overall effective charge of the complex cation. The larger the association constant ( $K_A$ ) of the cationic complex, the larger is the  $R_F$  value. Such  $K_A$  values increase with increasing charge of the ion and decrease with increasing size of the ion [28]. Our results fully agree with the above-mentioned theory.

#### Acknowledgements

R.K.R. is grateful to Professors R.L. Dutta and D. Banerjea for laboratory facilities. The

authors are also indebted to the referees for valuable suggestions for improving this article.

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