

## Note

### Chromatographic studies of metal complexes

#### I. Paper chromatography of cobalt(III) complexes

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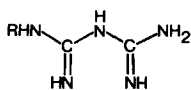
Biguanide and substituted biguanides (I) form numerous compounds with di-positive and tripositive transition metal ions<sup>1,2</sup> (II and III). Of these complexes, the tris(biguanide)cobalt(III) ion is remarkable in several respects. It has a very high inner sphere formation constant ( $\log K = 54$ )<sup>1</sup>, much greater than that of  $[\text{Co}(\text{en})_3]^{3+}$  ( $\log K = 48.69$ )<sup>3</sup>, it follows the racemization kinetics of *levo*-tris(biguanide)cobalt(III), the first case of a proposed intramolecular twist mechanism (rhombic) of racemization<sup>1</sup>, it exhibits interesting kinetics and mechanistic behaviour during acid hydrolysis<sup>1,4</sup> and it also exhibits a high outer sphere association constant<sup>5</sup>.

In this paper we report on a further interesting aspect of this complex and related cobalt(III) complexes, both homochelates and mixed chelates and cationic, neutral and anionic compounds, *viz.*, their chromatographic behaviour. Our studies revealed a strong influence of ion-pair formation between the complex cobalt(III) cation and the anion of the developer electrolyte.

#### EXPERIMENTAL

##### Materials

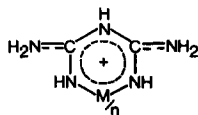
The complex compounds were synthesized according to published procedures<sup>1,2,6-10</sup>. Their purity was established by elemental analysis and spectral measurements.



I

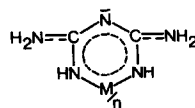
Biguanide (R = H)  
Substituted biguanide

(R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>5</sub>, etc.)



II

Charged metal biguanide  
complex



III

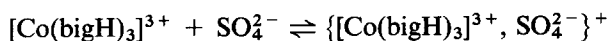
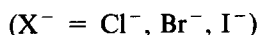
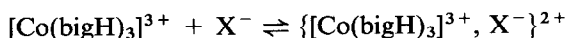
Neutral metal biguanide  
complex

### Procedure

The complex compounds were dissolved in water and subjected to ascending chromatography using Whatman No. 1 paper strips (3 cm × 52 cm). The solutions were applied with a capillary tube at a point 8 cm from the end of the strip, and the developer was allowed to travel 28–30 cm from the point of application; 0.1 *M* aqueous solutions of various salts were used as developers (Table I). The chromatograms were developed for about 3 h at 25°C. The cobalt(III) complexes were detected by spraying with an aqueous solution of sodium sulphide, which colours the spots black.

### RESULTS AND DISCUSSION

Ion electrophoretic and thin-layer chromatographic studies have provided evidence for outer-sphere association between an inert complex cation and the developer electrolyte<sup>11–13</sup>. While describing filter-paper chromatographic results, Yoneda<sup>14</sup> made a passing reference to the fact that the  $R_F$  value of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (0.9) remained unchanged in 1 *N* electrolytes such as hydrochloric acid, sodium chloride, potassium bromide, sodium nitrate, sodium perchlorate and potassium sulphate solutions. Our  $R_F$  values for  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and seventeen other cobalt(III) complexes in 0.1 *M* solutions of several electrolytes of different charge types vary so as to indicate outer-sphere association between these complex cations and the developer electrolytes. For example, there is a distinct difference between the  $R_F$  values of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and other cobalt(III) complexes in a uni-univalent electrolyte (*e.g.*, potassium iodide or chloride) and in a bi-univalent electrolyte (*e.g.*, potassium sulphate, sodium thiosulphate or potassium sodium tartrate). The lowest  $R_F$  values for all the complexes were obtained in aqueous potassium iodide developer. In aqueous potassium chloride developer the  $R_F$  values are higher by 0.1 unit, and in aqueous potassium sulphate, sodium thiosulphate or potassium sodium tartrate they likewise increase by a further 0.1–0.20 unit (Table I). We ascribe this effect to ion-pair formation between the complex cobalt(III) cation and the anion of the developer electrolyte, because it is an established fact that ion-association constants increase with increasing charge on the ion and decrease with increasing size of the ion<sup>15,16</sup>. Studies of the outer-sphere association constants of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{bigH})_3]^{3+}$ ,  $[\text{Co}(\text{dipy})(\text{bigH})_2]^{3+}$ ,  $[\text{Co}(\text{o-phen})(\text{bigH})_2]^{3+}$ , etc., have shown that these constants follow the order<sup>5,16</sup>  $\text{I}^- < \text{Br}^- < \text{Cl}^- \ll \text{SO}_4^{2-}$ . Interestingly, the  $R_F$  values of cobalt(III) complexes follow this order (Table II). 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 filter-paper, *e.g.*,



For a given developing electrolyte, the  $R_F$  values of all the cationic complexes increase, but very slowly, with increasing concentration of the developer. For ex-

ample,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  has  $R_F$  values of 0.60, 0.66, 0.70, 0.73, and 0.74 in 0.1, 0.2, 0.5 and 1  $M$  aqueous potassium chloride.

Other workers have used acidic or basic solvents<sup>17,18</sup> or acetic acid-sodium acetate buffer mixtures<sup>19</sup> for the paper chromatographic separation of cationic, neutral and anionic cobalt(III) complexes, but no definitive mechanisms were established for these separations. We were unable to use acidic solutions (e.g., hydrochloric or perchloric acid) as developers since the tris(biguanide)cobalt(III) ion readily aquates and first forms the diaquabis(biguanide)cobalt(III) ion<sup>4</sup>,  $[\text{Co}(\text{H}_2\text{O})_2(\text{bigH})_2]^{3+}$ , which further dissociates to form the tetraaqua(biguanide)cobalt(III) ion,  $[\text{Co}(\text{H}_2\text{O})_4(\text{bigH})]^{3+}$ , and finally decomposes to yield the cobalt(II) ion with the simultaneous release of biguanide<sup>20</sup>. We tried but failed to detect any intermediate species formed. We obtained a single spot whose  $R_F$  value (0.90) is identical with that of the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion ( $R_F$  0.90). As biguanide is more basic ( $\text{p}K_1 = 12.5$  at  $32^\circ\text{C}$ ) than ethylenediamine ( $\text{p}K_1 = 9.93$  at  $32^\circ\text{C}$ )<sup>20</sup>, protonation of biguanide takes place at the free basic =NH group of the biguanide molecule bonded to the cobalt atom. This causes a strain in the chelate ring, resulting in its rupture from the central metal atom<sup>21</sup>. The tris(ethylenediamine)cobalt(III) ion does not possess any basic site, and consequently it is not hydrolysed by acid. Hence the  $[\text{Co}(\text{en})_3]^{3+}$  ion is completely

TABLE I

$R_F$  VALUES OF COBALT(III) COMPLEXES WITH VARIOUS DEVELOPERS (0.1  $M$ )

When the liquid front travelled 30 cm, the salt fronts travelled 25 cm (KI), 26 cm (KCl), 29.5 cm ( $\text{K}_2\text{SO}_4$ ), 29.8 cm ( $\text{Na}_2\text{S}_2\text{O}_3$ ), and 29.8 cm ( $\text{KNaC}_4\text{H}_4\text{O}_6$ ).

Complex*	HCl	$\text{C}_2\text{H}_5\text{NH}_2$	KI	KCl	$\text{K}_2\text{SO}_4$	$\text{Na}_2\text{S}_2\text{O}_3$	$\text{KNaC}_4\text{H}_4\text{O}_6$
$[\text{Co}(\text{bigH})_3]\text{Cl}_3$	**	***	0.50	0.60	0.81	0.85	0.84
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	0.92	***	0.40	0.65	0.85	0.87	0.90
$[\text{Co}(\text{en})_3]\text{Cl}_3$	0.81	***	0.30	0.50	0.90	0.83	0.82
$[\text{Co}(\text{bipy})(\text{bigH})_2]\text{Cl}_3$	**	***	0.41	0.53	0.79	0.81	0.83
$[\text{Co}(o\text{-phen})(\text{bigH})_2]\text{Cl}_3$	**	***	0.43	0.54	0.80	0.80	0.82
$[\text{Co}(\text{gly})(\text{bigH})_2]\text{Cl}_2$	**	***	0.65	0.70	0.93	0.91	0.93
$[\text{Co}(\text{alan})(\text{bigH})_2]\text{I}_2$	**	***	0.62	0.72	0.91	0.92	0.94
$[\text{Co}(\text{leuc})(\text{bigH})_2]\text{Cl}_2$	**	***	0.63	0.70	0.92	0.93	0.94
$[\text{Co}(\text{hist})(\text{bigH})_2]\text{I}_2$	**	***	0.59	0.69	0.91	0.93	0.94
$[\text{Co}(\text{meth})(\text{bigH})_2]\text{I}_2$	**	***	0.60	0.69	0.93	0.92	0.93
$[\text{Co}(\text{lut})(\text{bigH})_2]\text{Cl}$	**	***	0.74	0.83	0.95	0.96	0.97
$[\text{Co}(\text{IDA})(\text{bigH})_2]\text{Br}$	**	***	0.77	0.82	0.95	0.93	0.94
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	1.00	0.94	0.95	0.96	1.00	1.00	1.00
$[\text{Co}(\text{gly})_3]$	1.00	0.95	0.96	0.96	1.00	1.00	1.00
$\text{K}[\text{Co}(\text{gly})_2(\text{NO}_2)_2]$	§	1.00	1.00	1.00	1.00	1.00	1.00
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	§	1.00	1.00	1.00	1.00	1.00	1.00
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	§	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

\* alanH = alanine; bigH = biguanide; bipy =  $\alpha,\alpha'$ -bipyridyl; en = ethylenediamine; glyH = glycine; histH = histidine; IDAH<sub>2</sub> = iminodiacetic acid; leucH = leucine; lutH<sub>2</sub> = lutidinic acid; methH = methionine; *o*-phen = *o*-phenanthroline; OxH<sub>2</sub> = oxalic acid.

\*\* The complex decomposed into aqua ion.

\*\*\* Diffused to a long distance from the point of application.

§ Not run, because not of interest.

TABLE II

ASSOCIATION CONSTANTS ( $K_A$ ) AND CORRESPONDING  $R_F$  VALUES AT 25°C FOR OUTER-SPHERE COBALT(III) COMPLEXES

Complex	Developer	Ion pair*	$K_A$	$R_F$
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	KI	{[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , I <sup>-</sup> } <sup>2+</sup>	17	0.40
	KBr	{[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , Br <sup>-</sup> } <sup>2+</sup>	46	0.55
	KCl	{[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , Cl <sup>-</sup> } <sup>2+</sup>	74	0.65
	K <sub>2</sub> SO <sub>4</sub>	{[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , SO <sub>4</sub> <sup>2-</sup> } <sup>+</sup>	2.2 · 10 <sup>3</sup>	0.85
[Co(en) <sub>3</sub> ] <sup>3+</sup>	KI	{[Co(en) <sub>3</sub> ] <sup>3+</sup> , I <sup>-</sup> } <sup>2+</sup>	9	0.30
	KBr	{[Co(en) <sub>3</sub> ] <sup>3+</sup> , Br <sup>-</sup> } <sup>2+</sup>	21	0.48
	KCl	{[Co(en) <sub>3</sub> ] <sup>3+</sup> , Cl <sup>-</sup> } <sup>2+</sup>	52	0.57
	K <sub>2</sub> SO <sub>4</sub>	{[Co(en) <sub>3</sub> ] <sup>3+</sup> , SO <sub>4</sub> <sup>2-</sup> } <sup>+</sup>	2.8 · 10 <sup>3</sup>	0.90
[Co(bigH) <sub>3</sub> ] <sup>3+</sup>	KI	{[Co(bigH) <sub>3</sub> ] <sup>3+</sup> , I <sup>-</sup> } <sup>2+</sup>	22	0.50
	KBr	{[Co(bigH) <sub>3</sub> ] <sup>3+</sup> , Br <sup>-</sup> } <sup>2+</sup>	33	0.54
	KCl	{[Co(bigH) <sub>3</sub> ] <sup>3+</sup> , Cl <sup>-</sup> } <sup>2+</sup>	55	0.60
	K <sub>2</sub> SO <sub>4</sub>	{[Co(bigH) <sub>3</sub> ] <sup>3+</sup> , SO <sub>4</sub> <sup>2-</sup> } <sup>+</sup>	1.26 · 10 <sup>3</sup>	0.82

\* bigH = biguanide; en = ethylenediamine.

stable at 80°C in the presence of 1 M perchloric acid<sup>4,20</sup>. As basic solvents such as ethylamine or pyridine react with cellulose, making the paper higher negatively charged, these solvents could not be used as developers. The migration of cationic complexes over the anionic cellulose body would thus be prevented.

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