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## Note

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# Thin-layer chromatography of trivalent cobalt(III) complexes on aluminium oxide and silica gel

M. LEDERER and M. BATTILOTTI
*Laboratorio di Cromatografia del C.N.R., Via Romagnosi 18/A, Rome (Italy)*

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In a study of the behaviour of inorganic anions on aluminium oxide layers, Lederer and Polcaro[1] concluded that strong adsorption of numerous anions occurs. However, this adsorption is in no way similar to ion-exchange adsorption (no desorption with higher concentrations of electrolyte or similarity of sequences) but rather follows the ion-pair formation sequence encountered, for example, in paper electrophoresis with aluminium nitrate as the electrolyte.

The purpose of this investigation was to re-examine the behaviour of cations on aluminium oxide layers. The usual hydrated metal ions, such as $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$, are not suitable for such a study as their hydrolytic adsorption has been established on numerous occasions. We therefore decided to study a series of cobalt(III) complexes ($NH_3$, ethylenediamine, dipyridyl and *o*-phenanthroline and mixed complexes with these ligands*), which are all trivalent but vary in size and number of amino groups. These complexes have already been examined by paper electrophoresis in various electrolytes[2] and their differences in the formation of outer-sphere complexes are well known.

Cobalt(III) complexes have been examined on alumina and silica gel layers by various workers[3–5], but so far no series of the type examined in this work has been studied.

## EXPERIMENTAL

The following ready-to-use thin layers were used with ascending development in square museum jars: MN Polygram Alox N (alumina thin layers made by Macherey, Nagel & Co., Düren, G.F.R.), and MN Polygram Sil G (silica gel thin layers made by Macherey, Nagel & Co.). Towards the end of the work we had to replace these by silica gel thin layers (without a fluorescent indicator) on glass obtained from Woelm (Eschwege, G.F.R.) as we had used up our supply of the former. However, both types of silica gel gave the same results. We also used cellulose sulphonate MN ion-exchange paper (Macherey, Nagel & Co.) with strongly acidic groups ($-SO_3H$).

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* Throughout this paper, the following abbreviations are used: en = ethylene diamine, dip = dipyridyl and ophen = *o*-phenanthroline.

## RESULTS AND DISCUSSION

Table I shows the $R_F$ values of the complexes studied on alumina layers with various aqueous salts as developing solvents. It is clear that whatever the solvent used, there is the same sequence:

$Co(NH_3)_6^{3+} > Co(en)_3^{3+} > Co(dip)_3^{3+} \approx Co(ophen)_3^{3+}$
Strongest adsorption Least adsorption

As regards the anion of the solvent (in comparison with chloride), there is a decrease in the $R_F$ values of $Co(dip)_3^{3+}$ and $Co(ophen)_3^{3+}$ in phosphate, sulphate, fluoride and also in acetate–ammonia buffer. This may be due to the effect of these solvents on the alumina surface increasing the number of aluminate ions or forming an adsorbed and "outer-sphere complexing" layer of anions on the alumina. Trichloracetate, which forms very strong outer-sphere complexes with both $Co(dip)_3^{3+}$ and $Co(ophen)_3^{3+}$, does not desorb or adsorb these ions in a manner which is in any way different from chloride, which is a poor "outer-sphere complexer".

Table II shows the $R_F$ values of the complexes in various concentrations of lithium chloride solution. It is evident that increasing the lithium chloride concentration desorbs the more strongly held complexes and there therefore exists an important difference from the behaviour of anions such as chromate or iodate, which have constant $R_F$ values in this range of concentrations. If $R_M$ values of the $R_F$ values in Table II are plotted against the logarithm of the lithium chloride concentration, approximately straight lines are obtained (Fig. 1). With the complexes that contain few amino

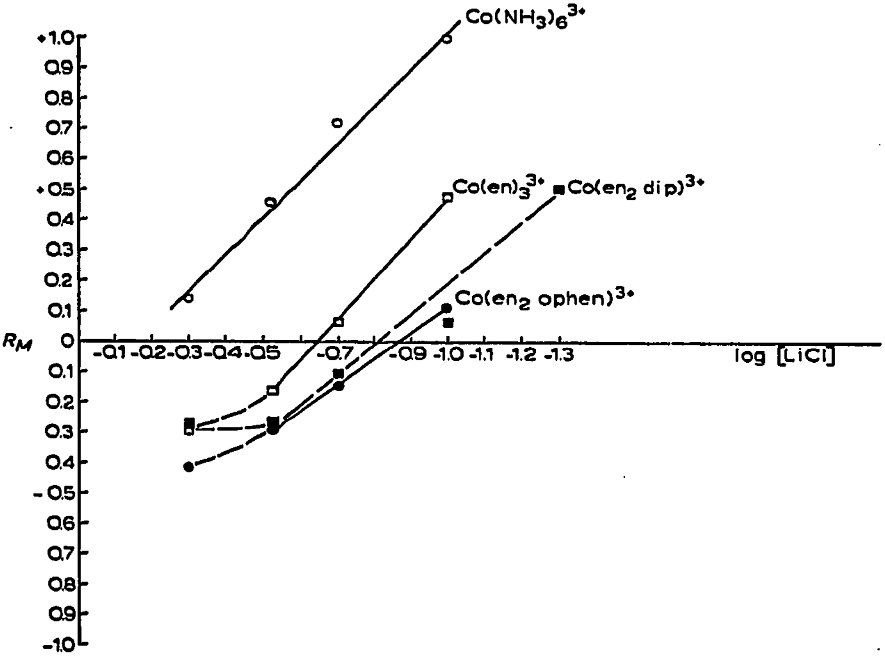

Fig. 1. Plots of $R_M$ *versus* log [LiCl] on MN Polygram Alox N thin layers developed with various concentrations of lithium chloride solution.

TABLE I

$R_F$ VALUES OF COBALT(III) COMPLEXES ON MN POLYGRAM ALOX N THIN LAYERS

| *Solvent* | $Co(NH_3)_6^{3+}$ | $Co(en)_3^{3+}$ | $Co(en_2\,dip)^{3+}$ | $Co(en_2\,ophen)^{3+}$ | $Co(en\,ophen_2)^{3+}$ | $Co(dip)_3^{3+}$ | $Co(dip_2\,ophen)^{3+}$ | $Co(ophen)_3^{3+}$ |
|---|---|---|---|---|---|---|---|---|
| 0.05 *N* LiCl | 0.03 | 0.14 | 0.24 | 0.17 | 0.41 | 0.48 | 0.55 | 0.45 |
| 0.1 *N* LiCl | 0.10 | 0.29 | 0.55 | 0.45 | 0.66 | 0.68 | 0.71 | 0.67 |
| 0.1 *N* $K_2SO_4$ | 0.04 | 0.16 | | | | 0.36 | | 0.31 |
| 0.1 *N* $Na_3PO_4$ | 0.02 | 0.03 | | | | 0.08 | | 0.07 |
| 0.1 *N* NaF | 0.01 | 0 | | | | 0.16 | | 0.16 |
| 0.1 *N* Na acetate | 0.08 | 0.32 | | | | 0.58 | | 0.58 |
| 0.1 *N* Na acetate + 0.1 *N* acetic acid | 0.07 | 0.24 | | | | 0.52 | | 0.47 |
| 0.1 *N* Na acetate + 0.1 *N* $NH_4OH$ | 0.04 | 0.13 | | | | 0.38 | | 0.35 |
| 0.1 *N* $NaClO_4$ | 0.05 | 0.32 | | | | 0.72 | | 0.66 |
| 0.1 *N* NaBr | 0.11 | 0.39 | | | | 0.66 | | 0.64 |
| 0.1 *N* KI | 0.19 | 0.40 | | | | 0.69 | | 0.68 |
| 0.1 *N* Na trichloroacetate | 0.08 | 0.30 | | | | 0.67 | | 0.66 |

TABLE II

$R_F$ VALUES OF COBALT(III) COMPLEXES ON MN POLYGRAM ALOX N THIN LAYERS WITH VARIOUS CONCENTRATIONS OF LITHIUM CHLORIDE SOLUTION AS ELUENT

| *Concn. of LiCl (N)* | $Co(NH_3)_6^{3+}$ | $Co(en)_3^{3+}$ | $Co(en_2\,dip)^{3+}$ | $Co(en_2\,ophen)^{3+}$ | $Co(en\,ophen_2)^{3+}$ | $Co(dip)_3^{3+}$ | $Co(dip_2\,ophen)^{3+}$ | $Co(ophen)_3^{3+}$ |
|---|---|---|---|---|---|---|---|---|
| 0.05 | 0.03 | 0.15 | 0.24 | 0.17 | 0.41 | 0.51 | 0.55 | 0.45 |
| 0.1 | 0.09 | 0.25 | 0.46 | 0.43 | 0.66 | 0.71 | 0.72 | 0.64 |
| 0.2 | 0.16 | 0.46 | 0.56 | 0.58 | 0.69 | | | 0.70 |
| 0.3 | 0.26 | 0.59 | 0.65 | 0.66 | 0.78 | | | 0.80 |
| 0.5 | 0.42 | 0.66 | 0.65 | 0.72 | 0.76 | | | 0.76 |

TABLE III

$R_F$ VALUES OF COBALT(III) COMPLEXES ON MN POLYGRAM SIL G THIN LAYERS

| *Solvent* | $Co(NH_3)_6^{3+}$ | $Co(en)_3^{3+}$ | $Co(en_2\,dip)^{3+}$ | $Co(en_2\,ophen)^{3+}$ | $Co(en\,ophen_2)^{3+}$ | $Co(dip)_3^{3+}$ | $Co(dip_2\,ophen)^{3+}$ | $Co(ophen)_3^{3+}$ |
|---|---|---|---|---|---|---|---|---|
| 0.1 *N* LiCl | 0.65 | 0.35 | 0.12 | 0.06 | 0.02 | 0 | 0.02 | 0 |
| 1 *N* LiCl | 0.89 | 0.83 | 0.26 | 0.15 | 0.02 | 0 | 0.02 | 0 |
| 2 *N* LiCl | | | 0.12 | 0.06 | 0.02 | | 0.02 | |
| 0.1 *N* $Na_3PO_4$ | Comet | Comet | | | | 0 | | 0 |
| 1 *N* $Na_3PO_4$ | 0.73 | 0.62 | | | | 0 | | 0 |
| 0.1 *N* $CCl_3COONa$ | Comet | Comet | | | | 0 | | 0 |
| 1 *N* $CCl_3COONa$ | 0.72 | 0.55 | | | | 0 | | 0 |
| 0.1 *N* $K_2SO_4$ | 0.80 | 0.67 | | | | 0 | | 0 |
| 1 *N* $K_2SO_4$ | 0.89 | 0.77 | | | | 0 | | 0 |
| 0.1 *N* $HClO_4$ | 0.80 | 0.79 | | | | 0.05 | | 0.02 |
| 1 *N* $HClO_4$ | 0.95 | 0.95 | | | | 0.18 | | 0.09 |

TABLE IV

$R_F$ VALUES OF COBALT(III) COMPLEXES ON SILICA GEL LAYERS (WITHOUT FLUORESCENT INDICATOR) FROM WOELM IN VARIOUS CONCENTRATIONS OF LITHIUM CHLORIDE SOLUTION

| *Concn. of LiCl (N)* | $Co(NH_3)_6^{3+}$ | $Co(en)_3^{3+}$ | $Co(en_2\,dip)^{3+}$ | $Co(en_2\,ophen)^{3+}$ | $Co(en\,ophen_2)^{3+}$ | $Co(dip)_3^{3+}$ | $Co(dip_2\,ophen)^{3+}$ | $Co(ophen)_3^{3+}$ |
|---|---|---|---|---|---|---|---|---|
| 0.01 | 0.05 | 0.02 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.02 | 0.09 | 0.03 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.05 | 0.43 | 0.12 | 0.02 | 0 | 0 | 0 | 0 | 0 |
| 0.1 | 0.69 | 0.37 | 0.02 | 0 | 0 | 0 | 0 | 0 |
| 0.2 | 0.82 | 0.61 | | 0.10 | 0 | 0 | 0 | 0 |
| 0.3 | 0.88 | 0.69 | 0.16 | 0.11 | 0 | 0 | 0 | 0 |
| 0.4 | 0.90 | 0.72 | 0.20 | 0.13 | 0 | 0 | 0 | 0 |

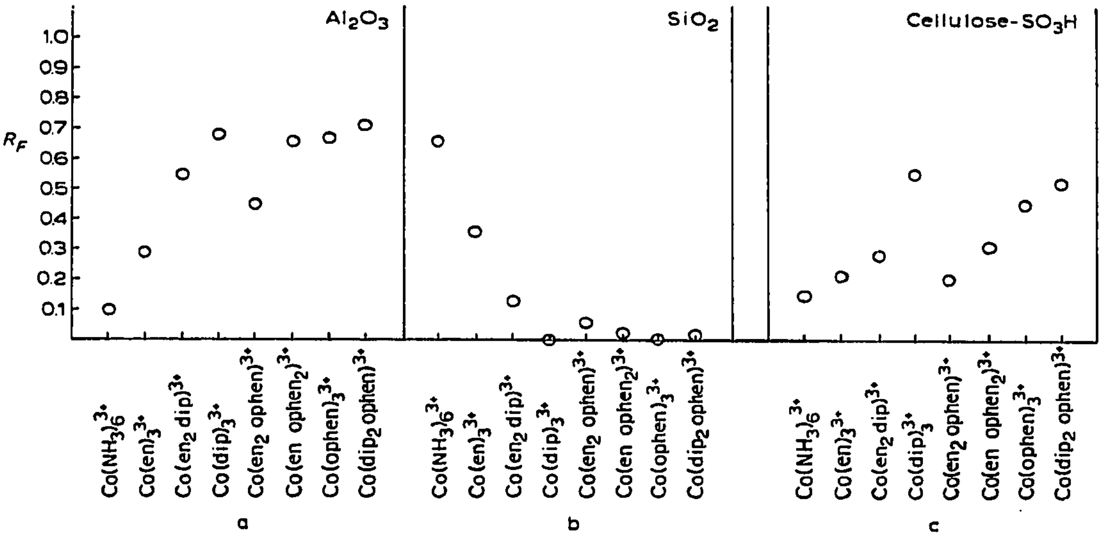

Fig. 2. Graphical representation of the $R_F$ values of cobalt(III) complexes: (a) on MN Polygram Alox N thin layers developed with 0.1 *N* lithium chloride solution; (b) on MN Polygram Sil G thin layers developed with 0.1 *N* lithium chloride solution; (c) on MN ion-exchange paper with strong acidic (sulphonic) groups developed with 0.5 *N* LiCl.

groups, the $R_F$ values are too high for meaningful plots to be made and in the range of chloride concentrations examined they seem to be roughly constant.

The most interesting results obtained are in the comparison of the $R_F$ values of the complexes on alumina with those on silica gel and on cellulose sulphonate, as shown in Fig. 2. The $R_F$ values on silica gel and cellulose sulphonate are given in Tables III and V. In Fig. 2, it is evident that the sequence on alumina is the same as that on cellulose sulphonate and the opposite of that on silica gel.

These sequences were then compared with those obtained in paper electrophoresis. To summarise the findings from paper electrophoretic evidence, there are three types of outer-sphere complexing: (a) with anions of the sulphate type, which form strong hydrogen bonds with amino groups (and hence with amino complexes and

TABLE V

$R_F$ VALUES OF COBALT(III) COMPLEXES ON MN ION-EXCHANGE PAPER WITH STRONGLY ACIDIC GROUPS ($-SO_3H$)

Solvent: 0.5 *N* lithium chloride solution.

| *Complex* | *$R_F$ value* |
|---|---|
| $Co(NH_3)_6^{3+}$ | 0.15 |
| $Co(en)_3^{3+}$ | 0.21 |
| $Co(en_2\ dip)^{3+}$ | 0.28 |
| $Co(en_2\ ophen)^{3+}$ | 0.20 |
| $Co(en\ ophen_2)^{3+}$ | 0.31 |
| $Co(dip)_3^{3+}$ | 0.55 |
| $Co(dip_2\ ophen)^{3+}$ | 0.52 |
| $Co(ophen)_3^{3+}$ | 0.45 |

ethylenediamine complexes, but not with dipyridyl and *o*-phenanthroline complexes); (b) with poorly hydrated anions, such as perchlorate and trichloroacetate, which interact strongly by hydrophobic interaction with large groups such as dipyridyl and *o*-phenanthroline; and (c) hydrated anions, such as chloride and acetate, which interact only weakly and increase in interaction with an increase in the size of the complex.

There is close agreement between the sequences found on alumina and on cellulose sulphonate with the interactions found in paper electrophoresis with sulphate ions (anions forming hydrogen bonds with $NH_3$ groups), while on silica gel the sequence is typical of that obtained with non-hydrated anions, such as perchlorate and trichloroacetate. In other words, there are different mechanisms operating in the adsorption of trivalent metal complexes in aqueous solution on alumina and on silica gel.

On silica gel, there is also a gradual increase in $R_F$ values for the lesser adsorbed ions (Table IV); however, this occurs in the concentration range 0.01–0.05 *N*, while on alumina it takes place in the range 0.1–0.5 *N*.

To conclude, alumina and silica gel adsorb trivalent cobalt(III) complexes with opposite sequences from aqueous lithium chloride solutions and there is a close analogy between the adsorption sequences and the two types of outer-sphere complexing as observed in paper electrophoresis.

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