Journal of Chromatography, 95 (1974) 81–89
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 7473

SELECTIVITY SEQUENCES OF A SERIES OF TRIPOSITIVE COBALT(III) COMPLEXES ON INORGANIC AND ORGANIC EXCHANGERS

M. BATTILOTTI and M. LEDERER
Laboratorio di Cromatografia del C.N.R., Via Romagnosi 18/A, 00196 Rome (Italy)

(Received April 3rd, 1974)

SUMMARY

The elution sequences of four cobalt(III) complexes on a wide range of papers loaded with inorganic exchangers, modified celluloses and resin papers were examined and the results are discussed in relation to the paper electrophoretic behaviour of these complexes and their tendency to form outer-sphere complexes.

INTRODUCTION

Two recent studies in this laboratory concerned the adsorption of inorganic anions from aqueous solutions on alumina[1] and the adsorption of the series of cobalt(III) complexes on alumina and silica gel[2]. The results of both investigations suggested that there is a similarity between adsorption sequences and electrophoretic sequences obtained in paper electrophoresis with certain electrolytes. The latter were interpreted previously as being due to outer-sphere complexing of the ions studied[3]. We therefore feel that there is an analogy between outer-sphere complexing and adsorption on hydrous oxides from aqueous solutions.

The present investigation deals with a survey of a range of inorganic exchangers, with emphasis on the group usually referred to as hydrous oxides. As we had found opposite adsorption sequences on alumina and silica gel[2], we thought that such a survey might be of use in the classification of inorganic exchangers.

The main difficulty in such work involves devising a means for comparing various materials that may vary in surface area and ion-exchange capacity, as is well known already. We decided to investigate only the actual sequences, *i.e.*, the selectivity of some cobalt(III) complexes, and for this purpose papers impregnated with the hydrous oxides are adequate.

EXPERIMENTAL

Preparation of the impregnated papers

Whatman No. 1 paper strips were dipped into 1 *M* solutions of aluminium, iron(III) and thorium(IV) nitrates, the excess of solution was removed between two pieces of adsorbent paper and the strips were hung in an atmosphere of concentrated ammonia solution for 30 min and then washed three times with distilled water, leaving the papers immersed for 30 min in each wash, and dried between blotting paper at room temperature.

For zirconium(IV) papers, the same procedure was used except that 1.5 *N* ammonia solution was employed.

As precipitation with gaseous ammonia gave some irregular results with some of the oxides, the papers that contained bismuth(III), antimony(V), tin(IV), lanthanum(III), magnesium(II) and titanium(IV) were first impregnated with a soluble salt (1 *M* throughout) and then immersed in 3 *N* ammonia solution for 30 min and washed as above three times with distilled water.

Manganese dioxide papers were prepared by dipping Whatman No. 1 filter paper into 0.1 *M* potassium permanganate solution, drying off the excess of liquid, leaving the papers in the air until the purple colour had changed to dark brown (several minutes) and then washing them thoroughly with distilled water.

The hydrous oxides were thus all precipitated from cold solution and were aged by drying them overnight at room temperature. Zirconium phosphate papers (Whatman development product: zirconium phosphate-impregnated papers) and resin papers were converted into the Li^+ form by equilibrating with 1 *N* lithium chloride solution and subsequently washing three times with distilled water.

Cellulose exchangers were used as received, *i.e.*, in the carboxylic or phosphoric acid form.

Ammonium molybdophosphate paper was prepared as described by Alberti and Grassini[5].

Chromatography

All of the paper strips were developed by ascending development in wide-mouthed jars closed with a rubber stopper. The cobalt(III) complexes could be detected with ammonium sulphide, except on the bismuth hydroxide paper, where Dragendorff reagent was used.

RESULTS

Adsorption of cobalt complexes on inorganic exchangers

We limited our investigation to four cobalt(III) complexes, all of which have a charge of 3+, *viz.*, $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(dip)_3^{3+}$ and $Co(phen)_3^{3+}$, where en = ethylenediamine, dip = dipyridyl and phen = *o*-phenanthroline.

The results are best illustrated as in Figs. 1 and 2, as R_F values would give only limited information and would not explain tailing, etc.

It is evident that the inorganic exchangers can be divided into three groups:

Group (i): $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ are more strongly adsorbed than $Co(dip)_3^{3+}$ and $Co(phen)_3^{3+}$. Most of the hydrous oxides and zirconium phosphate belong to this group.

Group (ii): The complexes are not adsorbed strongly and move with high R_F values. These are mainly the strongly basic oxides such as those of magnesium, cadmium and lanthanum(III) and, unexpectedly, also that of antimony(V).

Group (iii): Inorganic exchangers on which $Co(dip)_3^{3+}$ and $Co(phen)_3^{3+}$ are

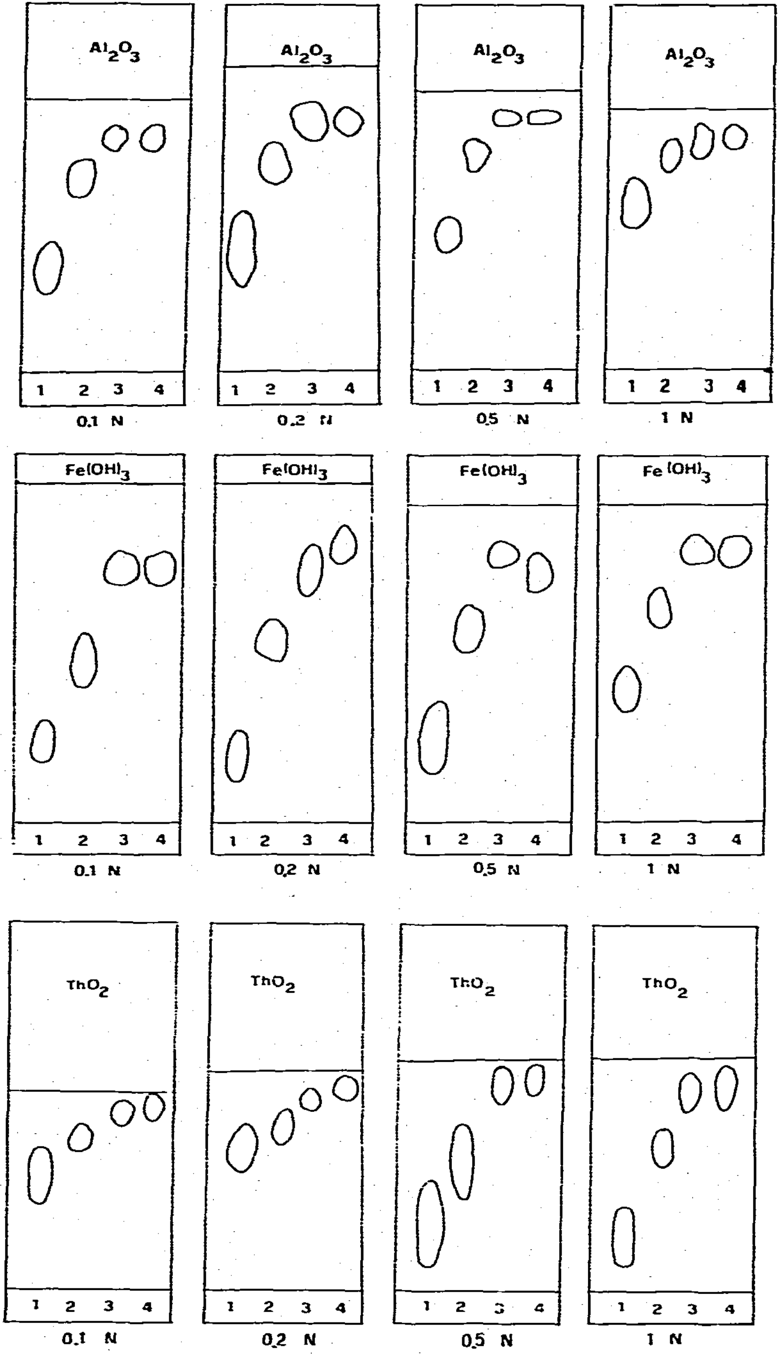

Fig. 1.

(Continued on p. 84)

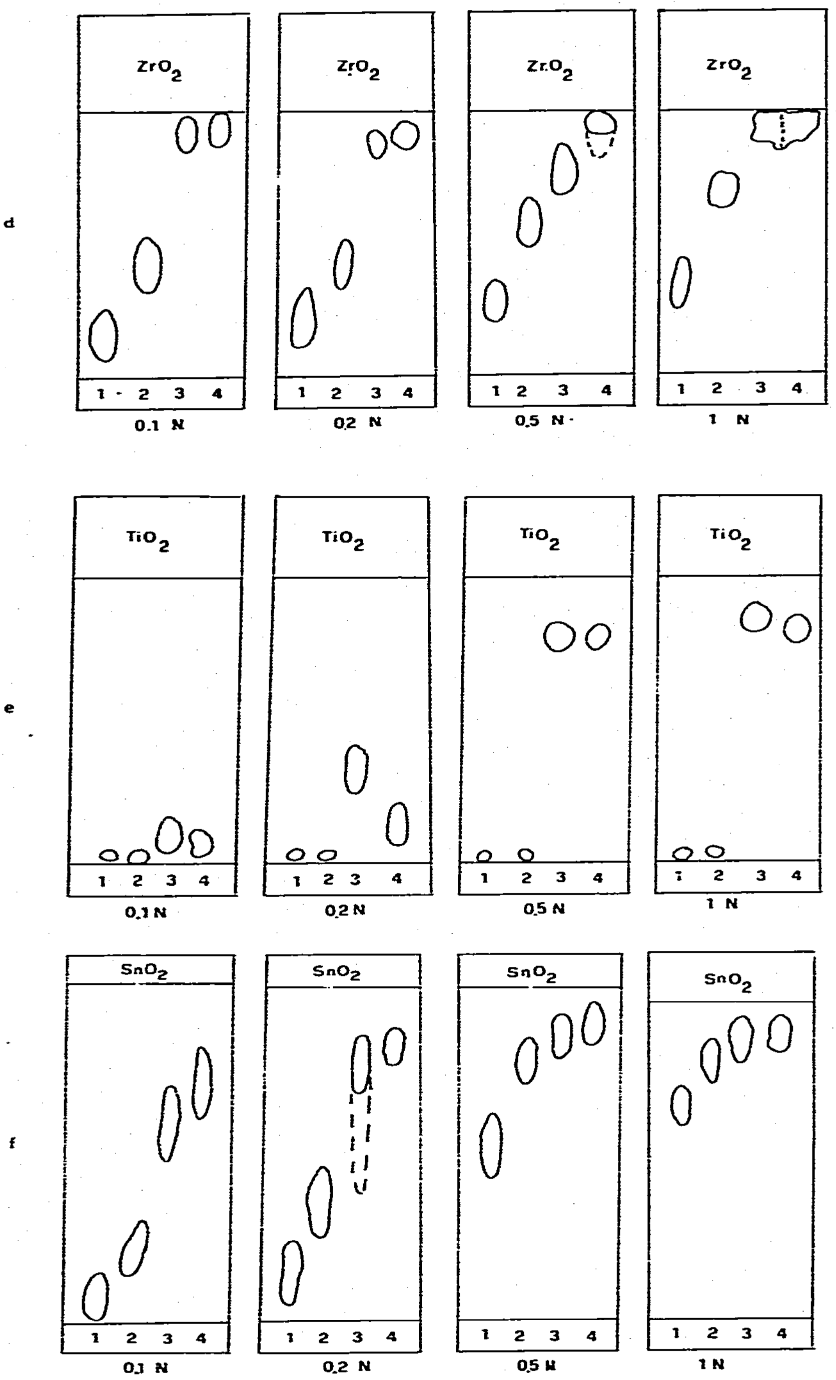

Fig. 1 *(continued)*.

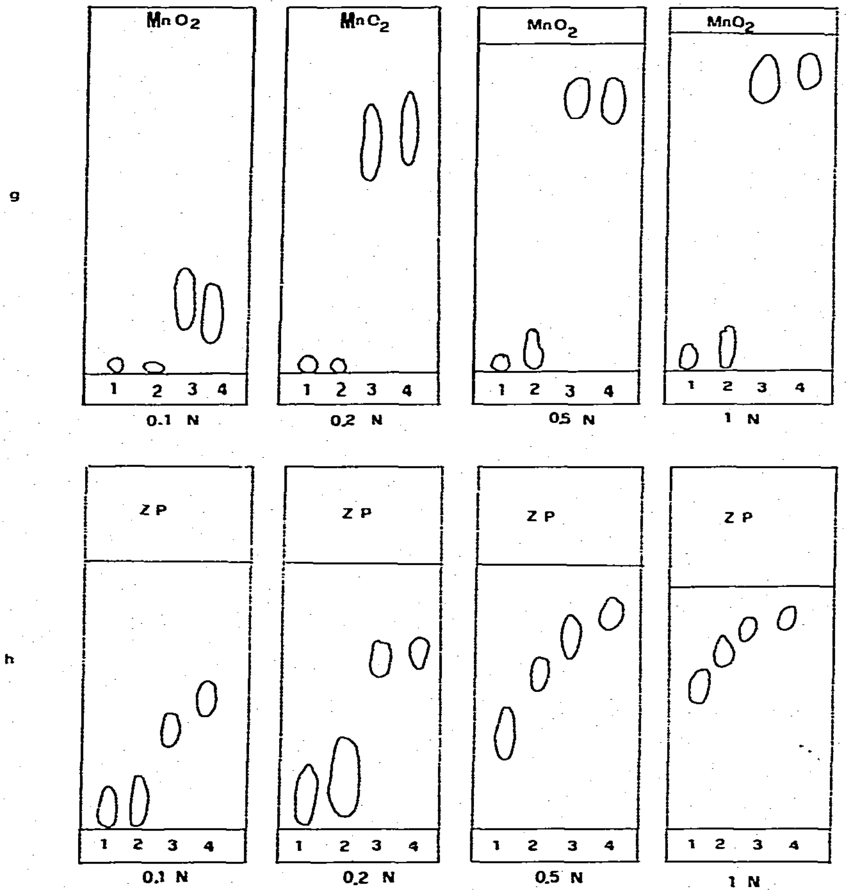

Fig. 1. Schematic chromatograms of 1, $Co(NH_3)_6^{3+}$; 2, $Co(en)_3^{3+}$; 3, $Co(dip)_3^{3+}$; and 4, $Co(phen)_3^{3+}$, developed with aqueous lithium chloride solutions (concentrations as marked) on papers impregnated with (a) Al_2O_3, (b) $Fe(OH)_3$, (c) ThO_2, (d) ZrO_2, (e) TiO_2, (f) SnO_2, (g) MnO_2 and (h) zirconium phosphate.

more strongly adsorbed than $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$. In addition to silica gel, which was discussed in a previous paper[2], we found only bismuth(III) oxide and ammonium phosphomolybdate in this group.

Adsorption of cobalt complexes on ion-exchange celluloses and resin papers

In order to make this survey complete, we compared inorganic exchangers with several substituted celluloses and resin papers. Fig. 3 shows the results obtained.

Substituted celluloses with either phosphoric or carboxylic groups showed the same selectivity towards all of the complexes as the alumina type of hydrous oxide. Sulphonated cellulose (reported previously[2]) also gave the same sequence. Resin papers gave rather inconclusive results, discussed below.

The sulphonic resin paper Amberlite SA-2 adsorbed all complexes very strongly with 4 *N* lithium chloride solution. With lithium chloride solutions of higher

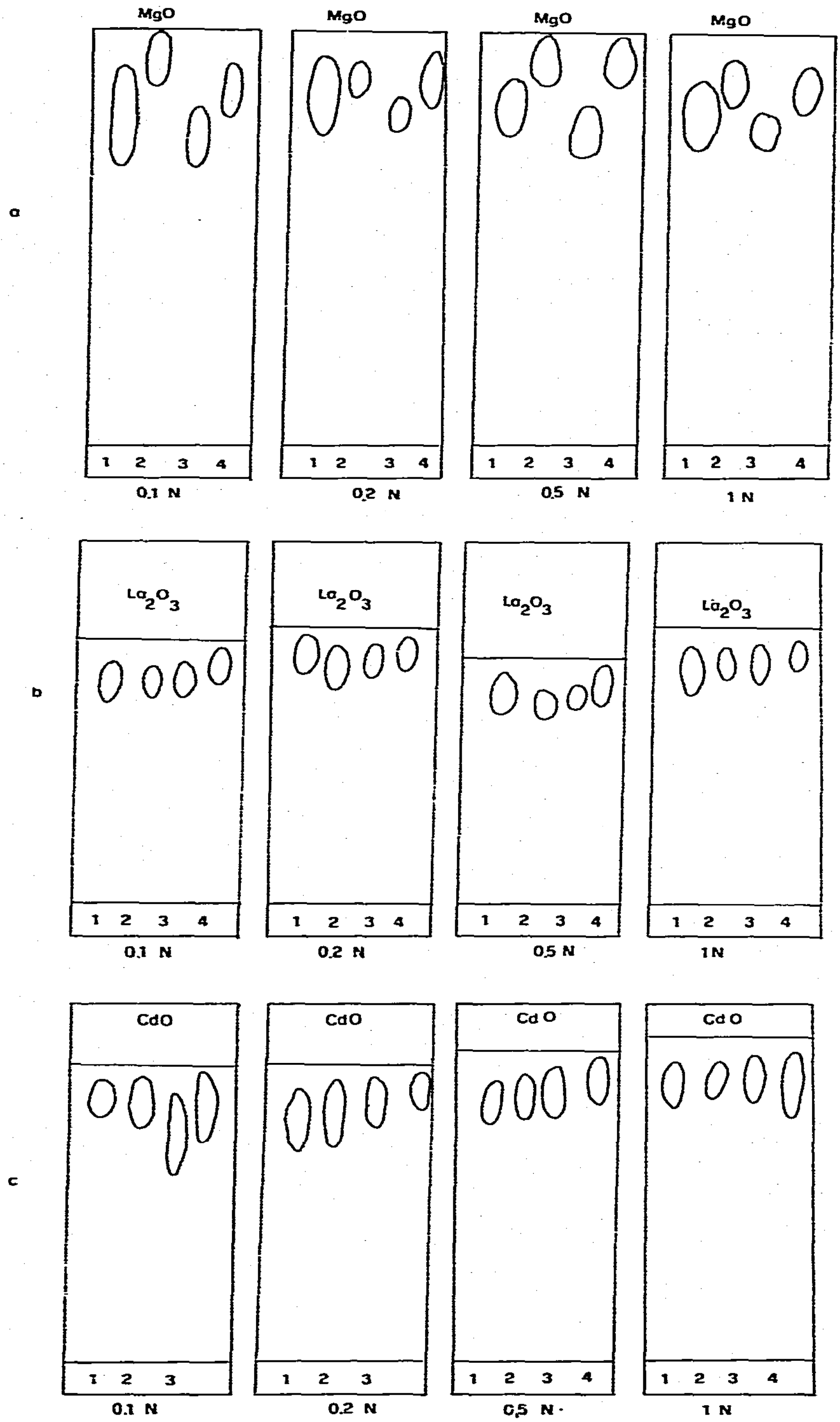
a
MgO
MgO
MgO
MgO
1 2 3 4
1 2 3 4
1 2 3 4
1 2 3 4
0.1 N
0.2 N
0.5 N
1 N
b
La2O3
La2O3
La2O3
La2O3
1 2 3 4
1 2 3 4
1 2 3 4
1 2 3 4
0.1 N
0.2 N
0.5 N
1 N
c
CdO
CdO
Cd O
Cd O
1 2 3
1 2 3
1 2 3 4
1 2 3 4
0.1 N
0.2 N
0.5 N
1 N

Fig. 2.

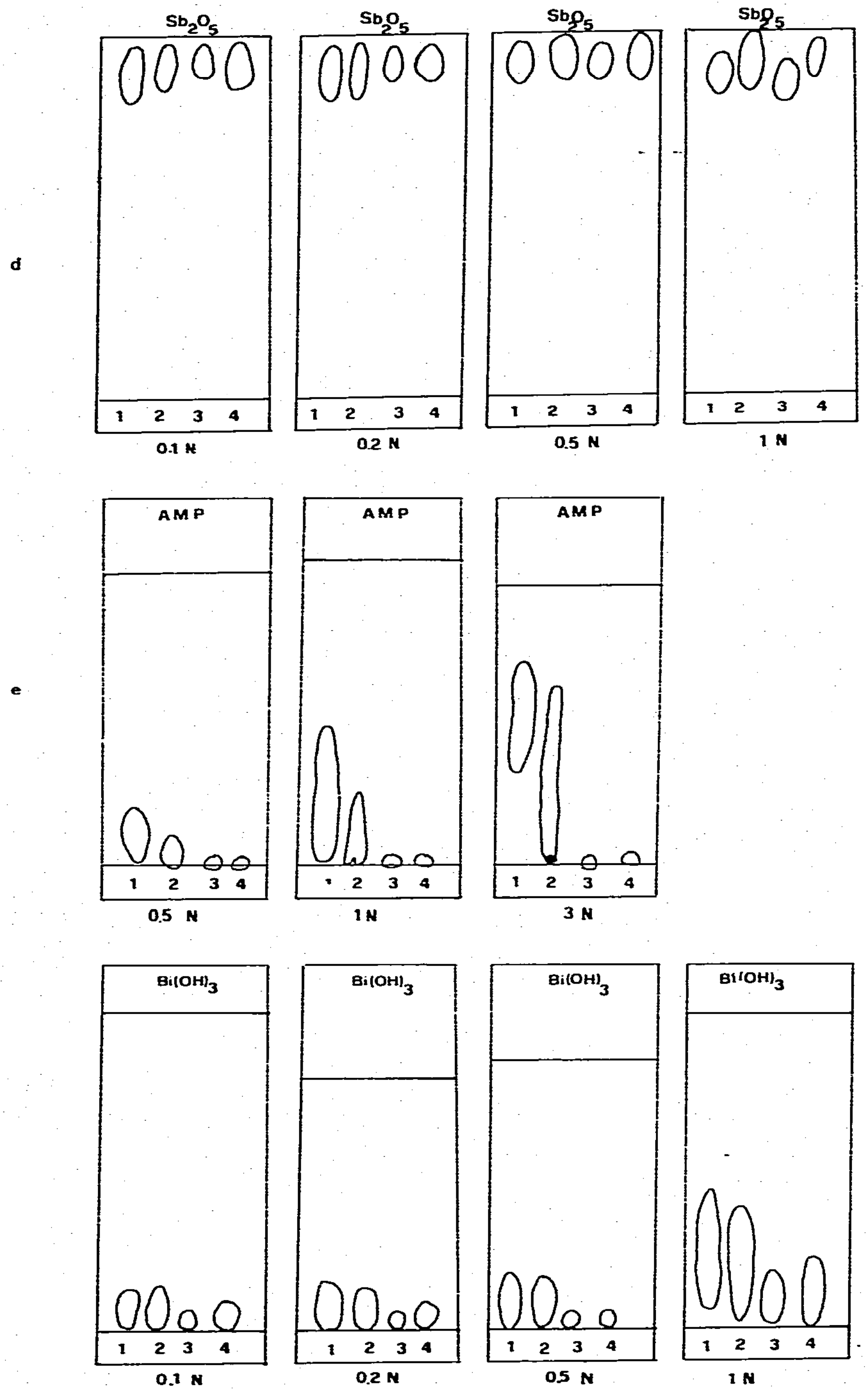

Fig. 2. Schematic chromatograms of 1, $Co(NH_3)_6^{3+}$: 2, $Co(en)_3^{3+}$: 3, $Co(dip)_3^{3+}$: and 4, $Co(phen)_3^{3+}$, developed with aqueous lithium chloride solutions (concentrations as marked) on papers impregnated with (a) MgO, (b) La_2O_3, (c) CdO, (d) Sb_2O_5, (e) ammonium molybdophosphate and (f) bismuth hydroxide.

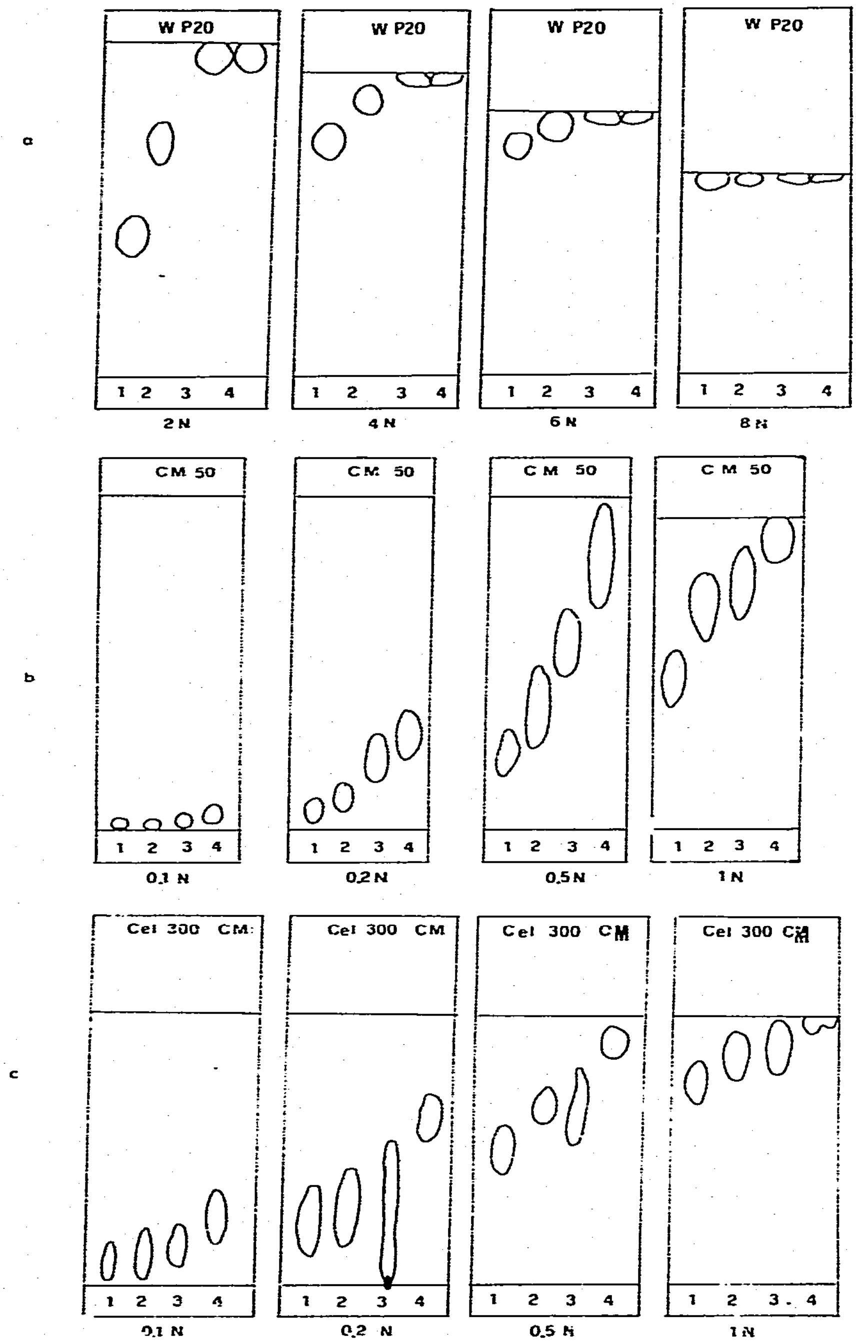

Fig. 3. Schematic chromatograms of 1, $Co(NH_3)_6^{3+}$; 2, $Co(en)_3^{3+}$; 3, $Co(dip)_3^{3+}$; and 4, $Co(phen)_3^{3+}$, developed with aqueous lithium chloride solutions (concentrations as marked) on the following ion-exchange celluloses: (a) Whatman WP-20 paper (with phosphoric acid groups); (b) Whatman carboxymethylcellulose paper CM-50; (c) Polygram Cel 300 CM thin layers consisting of carboxymethylcellulose.

concentrations, $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ were desorbed and moved as distinct spots, while the dipyridyl and *o*-phenanthroline complexes yielded indistinct trails, which we previously thought to be due to decomposition[4]. We believe that the lack of decomposition on so many other supports now indicates that rather some type of irreversible adsorption occurs, perhaps a hydrophobic interaction between the ring systems of the complexant and the resin matrix. In any case, it was not possible to establish a selectivity sequence. The results on the carboxylic resin paper Amberlite WA-2 were equally difficult to interpret. If employed in the sodium form only long trails were formed. When converted into the lithium form, there was a stronger adsorption and in 1 *N* lithium chloride solution perhaps more rapid elution of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, but the elongated trails make us hesitate to draw conclusions from these results.

Elution with acetate buffers of various pHs did not clarify the situation.

DISCUSSION

It had been suggested earlier that the high affinity of ions such as Cu^{2+} and Ni^{2+} towards hydrous zirconium(IV) oxide is due to ion-pair or complex formation[6]. We were able to show[2] that two opposite selectivity sequences can be obtained with a series of cobalt(III) complexes which resemble the sequences obtained in paper electrophoresis. In the present paper we have attempted to classify inorganic exchangers according to this selectivity sequence.

There seems to be a tendency, on strongly acidic exchangers such as silica gel and ammonium molybdophosphate to give one sequence and metal oxides to give another. It is doubtful, however, whether the sequence depends on the acidity because, according to Abe and Ito[7], silica and manganese dioxide have about the same acidities yet the opposite selectivity sequences were found.

In the case of bismuth(III) oxide, the titration curves show an extremely high chloride ion capacity and it seems that a surface chlorobismuthate anion is formed during elution with lithium chloride solution which exhibits properties different from those of the oxyanion that is believed to exist on the surface of most hydrous oxides.

Zirconium phosphate, zirconium oxide and cellulose phosphate all give the same sequence, namely that of the hydrous oxides. In paper electrophoresis, this sequence is typical for anions such as SO_4^{2-} that form hydrogen bonds with the amino groups of the complexant. The selectivity sequence observed therefore seems to suggest the type of surface anion (if indeed it is really a surface anion) available to the complexes, and this property may still prove useful in other aspects of the chemistry of hydrous oxides.

REFERENCES

1 M. Lederer and C. Polcaro, *J. Chromatogr.*, 84 (1973) 379.
2 M. Lederer and M. Battilotti, *J. Chromatogr.*, 89 (1974) 380.
3 M. Mazzei and M. Lederer, *J. Chromatogr.*, 31 (1967) 196.
4 M. Mazzei and M. Lederer, *J. Chromatogr.*, 40 (1969) 197.
5 G. Alberti and G. Grassini, *J. Chromatogr.*, 4 (1960) 423.
6 C. B. Amphlett and J. Kennedy, *Chem. Ind. (London)*, (1958) 1200.
7 M. Abe and T. Ito, *J. Chem. Soc. Jap.*, 86 (1965) 1259.