On the Separation of Cobalt(III) and Chromium(III) Ammines by Column Chromatography

ARNE JENSEN*, JANNIK BJERRUM and
FLEMMING WOLDBYE

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

A method is developed for the separation of cobalt(III) and other robust coordination complexes on columns of activated alumina with the aid of aqueous salt solutions of proper composition as eluents. The scope and applicability of the method are illustrated by a variety of separations which have been achieved. Some of the factors influencing and producing the separations are considered.

A problem of increasing importance in modern coordination chemistry is the separation and analysis of reaction mixtures of robust complexes, for example of Co(III) and Cr(III), a task which can be accomplished by classical and spectrophotometric methods only in special cases. It seems therefore desirable to attack problems of this kind from different angles, for example by adsorption methods. Ion exchange technique may be used for separations of this kind with good results, as shown *e.g.* by Gustavson[1] and King and coworkers [2]. Lederer [3] has made some experiments on the separation of cobalt-(III) nitroammines in non-aqueous solutions by means of paper chromatography, and Maki [4] has separated robust complexes, *e.g.* the chloroaquochromium(III) complexes in aqueous buffer solutions by means of electrochromatography on filter paper. In preliminary communications [5] we have described how robust complexes can be separated on columns of activated alumina using aqueous salt solutions as eluents. Sacconi [6] has obtained some qualitative results with pure aqueous solutions of cobalt(III) ammines, and Hein [7] has used columns of alumina for separating aqueous mixtures of phenylchromium compounds in a way which in principle is similar to the method used by us.

Chromatography on activated alumina is a very complex phenomenon as especially shown by Umland [8]. However, under specific conditions (proper composition and controlled pH of the solutions) we have developed this

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* Guest from: Dept. of Inorganic Chemistry, The Royal Danish School of Pharmacy, Copenhagen.

technique to a useful method for analyzing aqueous mixtures of robust complexes. Cation complexes are separated in basic solution, the anions on the other hand in weakly acidic buffers. As displacing agents were used relatively concentrated solutions of various colourless electrolytes with which the columns were also treated in advance. The separations are highly dependent on the salt applied, being in some cases limited to special kinds of electrolytes. Thus $Co(NH_3)_6^{+++}$ could be separated quantitatively from $Cr(NH_3)_6^{+++}$ with 0.01 M KOH, 1 M KCl as a displacing agent, with much better results than with basic solutions of NaCl or $N(C_2H_5)_4Cl$. On the other hand, alkaline $N(C_2H_5)_4Cl$ was necessary for separating mixtures of Co en_3^{+++} and Cr en_3^{+++} (see Table 2).

According to Tiselius [9] one can distinguish between displacement analysis and elution analysis. In the separations considered here the displacing electrolyte penetrates and separates the coloured zones of the complexes. The case seems, therefore, to correspond closely to what Tiselius and coworkers [10] denote as non-ideal displacement. Accordingly, our guiding principle was to look for salts whose cations or anions, respectively, were supposed to have an adsorption tendency comparable with that of the complex cations and anions. Added in a sufficiently high concentration the proper salts were found to separate completely very similar complexes such as the luteo ions mentioned. The displacing power of the various cations decreases with increasing ionic radius, i.e. in the sequence Li^+, Na^+, K^+, $N(C_2H_5)_4^+$ and $C_{16}H_{33}N(CH_3)_3^+$. It was found that Tl^+ enters this series before Na^+. On the other hand, very little difference was found between the displacing power of anions, such as Cl^-, Br^- and NO_3^-.

EXPERIMENTAL

The columns were prepared from Merck's alumina standardized according to Brockmann. The apparatus was constructed to permit continuous addition of solutions and eluating agents.

Technique. The adsorption tubes were made of Pyrex glass. Their normal dimensions were 11 by 250 mm, but larger columns with an internal diameter of 15 mm and a length of up to 500 mm were also used in special cases. The tubes were provided with a ground-glass joint which contained a removable sintered glass disc. The tubes and the ground-glass joints were held together with wire spirals.

The columns were made by quickly pouring a thick aqueous slurry of the alumina [11] into the tubes. Especially with the normal size tubes columns made in this way lead to a uniform development of the zones. The tubes were usually filled to about three fourth of the volume, leaving the upper part of the volume for the addition of solutions. In order to save time the solutions were pressed through the columns by means of the pressure produced and regulated with the aid of two movable mercury reservoirs. The columns were equipped with a construction according to Sannie [12] which permits the introduction of eluating agents without releasing the pressure.

Procedure. Before an analysis the column was treated with the eluating solution to be used. Then 2 — 5 ml of the mixture of complexes were added to the column. The complex salts were sometimes but not necessarily dissolved in the eluating solvent. The eluating solution was added just at the moment when the complex mixture had passed into the column, but so quickly that the top of the column was not sucked dry. When an extra pressure of 0.5 — 1 atm. was applied, an experiment could usually be finished within 15 — 30 min. If no air bubbles happened to be evolved when the pressure was released, the same column could be used for other experiments.

The coloured effluents were collected in individual flasks, and in most cases the complexes could be separated and eluted completely. This could be done either with a

single eluent, or occasionally by the successive use of two eluents of increasing displacing power so that — in the ideal case — each component of the mixture was eluated by a specific eluent leaving the others for the following eluent.

For quantitative studies the collected samples of a given component were diluted to a known volume in a measuring flask, and the absorption curve of the solution measured with a recording Cary spectrophotometer. The absorption curve of the initial solution of the pure component diluted to the same extent was measured with the same instrument, and in this way information about the quality of the separations was obtained.

Various reagents were used to test the intermediate fractions. Sodium sulphide was an especially good reagent for testing traces of Co(III) complexes in mixtures of Co(III) and Cr(III) complexes.

Materials. The complex salts used were prepared according to prescriptions in the literature, or were from the laboratory collection of complex salts prepared by S. M. Jörgensen.

Basic alkali metal and quaternary ammonium salt solutions were used as eluating agents. Tetraethylammonium bromide and cetyltrimethylammonium bromide (technical pure) from Milton Industrial Chemicals (London) Ltd. gave colourless solutions and were sufficiently pure for the experiments. The bromides were converted to the corresponding hydroxides by means of an anion exchanger (Amberlite Resin IRA-400); in other cases we have applied mixed solutions of the quaternary ammonium salts and potassium hydroxide. The cetylammonium salt separated out on standing, but was easily dissolved before use by gentle heating.

In a few cases, *e. g.* for the separation of anion complexes, acidic solutions were used as eluents. To escape turbidity (due to colloidal dissolution of the alumina) acid-treated alumina was used. The alumina (Brockmann) was treated with 0.5 M HCl for a few minutes, washed with water and dried at 120°C.

RESULTS AND DISCUSSION

We have experimented with a single complex on the column in order to decide to what extent it can be recovered by displacement. Some examples are given in Table 1. 2 ml of a luteo salt solution were added to the columns and eluated with the basic salt solution mentioned in the table. The forerun was usually 10—15 ml, and the fraction containing the luteo salt had about the same volume. It was diluted to 25 ml in a measuring flask and the absorption curve compared with that of the initial solution diluted to the same extent. The losses (given in per cent) were somewhat variable especially in the case of $Co(NH_3)_6Cl_3$, which is bound so strongly to the alumina that the colour of the absorbed complex is distinctly more reddish than that of the solid salt. Here as for the chromium(III) ammines the loss is probably to some extent caused by decomposition of some of the luteo salt (not necessarily caused

Table 1. Experiments on the recovery of luteo salts. Loss in per cent.

Luteo salt sol.	Displacing sol.	0.1 M NaOH 1 M LiCl	0.1 M NaOH 5 M LiCl	0.1 M NaOH 1 M NaCl	0.01 M NaOH 1 M LiCl	1 M NH₃ 1M NH₄Cl
0.03 M [Co(NH₃)₆]Cl₃		av. 4.1				2.4
0.03 M [Co en₃]Cl₃		av. 3.6	3.5		0.5	
0.1 M [Co en₃]Cl₃		0.5				
0.03 M [Cr(NH₃)₆]Cl₃		2.7				
0.03 M [Cr en₃]Cl₃			3.0	3.0		

by the column). Thus a column which had been used for 10—15 determinations gave a cobalt reaction only near the top when developed with Na_2S.

To decrease decomposition the hydroxyl ion concentration of the eluents should be as low as possible. Furthermore, it seems to be of some importance not to have too low a concentration of the salts to be displaced (*cf.* the experiments with Co en_3Cl_3).

Separation of luteo complexes

In Table 2 the results of some experiments on the separation of mixtures of luteo complexes are compared. About 0.03 M solutions of the luteo salts dissolved in the displacing solvent were mixed in equivalent amounts, and 2 (or 3) ml of the solution were analyzed. The coloured fractions of the two (or three) components diluted to 25 ml, were measured in 5 cm cells, and the absorption curve compared with that of the pure luteo salt solution at the same dilution.

Table 2. Separation of luteo complexes. Conc. (mole/l) in solution to be analyzed.

Salts separated	According to prep.	Chromatogr. found	Displacing solutions
Cr en_3Cl_3	0.0162	0.0155	0.1 M KOH, 1 M $(C_2H_5)_4NBr$
Co en_3Cl_3	0.0142	0.0139	
Co en_3Cl_3	0.0136	0.0136	0.1 M KOH, 1 M $(C_2H_5)_4NBr$
$Cr(NH_3)_6Cl_3$	0.0135	0.0135	0.1 M KOH, 1 M KCl
$Co(NH_3)_6Cl_3$	0.0138	0.0130	
Co en_3Cl_3	0.0158	0.0139	0.1 M KOH, 1 M $(C_2H_5)_4NBr$
$Cr(NH_3)_6Cl_3$	0.0160	0.0152	0.01 M KOH, 1 M KCl
Cr en_3Cl_3	0.0150	0.0147	0.01 M KOH, 1 M KCl
$Co(NH_3)_6Cl_3$	0.0150	0.0146	
$Cr(NH_3)_6Cl_3$	0.0160	0.0140	0.01 M KOH, 1 M KCl
$Co(NH_3)_6Cl_3$	0.0144	0.0132	

It will be seen that the tendency to adsorption increases in the series: Cr en_3^{+++} < Co en_3^{+++} < $Cr(NH_3)_6^{+++}$ < $Co(NH_3)_6^{+++}$. Quaternary ammonium salts were necessary in order to accomplish the separation of the two ethylenediamine complexes. The use of 0.1 M KOH, 1 M $(C_2H_5)_4NBr$ as a displacing agent gave a clear separation into two yellow fractions the first of which gave only a very weak reaction for cobalt with Na_2S. But already substitution of the quaternary ammonium salt with KCl gave no separation. Separation could also be performed with alkaline cetyltrimethylammonium salt solutions, but the eluates became more diluted, and the quasicrystalline character of the solvent also gave other difficulties in this case. In the table is given an example of the separation of a mixed solution of three of the luteo salts. Co en_3^{+++} was first displaced with 0.1 M KOH, 1 M $(C_2H_5)_4NBr$ after which

$Cr(NH_3)_6^{+++}$ and $Co(NH_3)_6^{+++}$ were separated and displaced with 0.1 M KOH, 1 M KCl. The three luteo fractions alternated with colourless runs, and the intermediate Cr(III)-fraction gave no reaction for cobalt.

Hexammine, pentammine and tetrammine complexes

We have also used the method in the analysis of other kinds of mixtures of cobalt(III) and chromium(III) ammines. J. Bjerrum [13] has shown that if hexammine cobalt(III) nitrate is shaken with activated carbon in an ammonia-cal ammonium salt solution, an equilibrium mixture of hexammine, hydroxo-pentammine and dihydroxotetrammine is formed. Of the three complexes, dihydroxotetrammine is fixed very strongly to the column, while on the other hand hexammine is bound more strongly than hydroxopentammine. A mixture of pentammine and hexammine can be separated practically quantitatively using 0.01 M KOH, 1 M KCl as displacing agent (see Fig. 1). We have found that the separation is poor when K^+ is replaced by Na^+, but that a good separation is still obtained when Cl^- is replaced by F^-. Hexammine as well as hydroxopentammine can be displaced, but not separated with a less basic solution of the composition: 0.1 M NH_4Cl, 1 M NH_3, 1 M KCl. Dihydroxo-tetrammine has a much shorter lifetime than the two other complexes in alkaline solution, but is stable as a diaquo ion in acidic solution. These considerations lead to the procedure described in Table 2. The mixture of all three ions is introduced into column I, which preferably should be a short column, and the pentammine and hexammine are displaced from
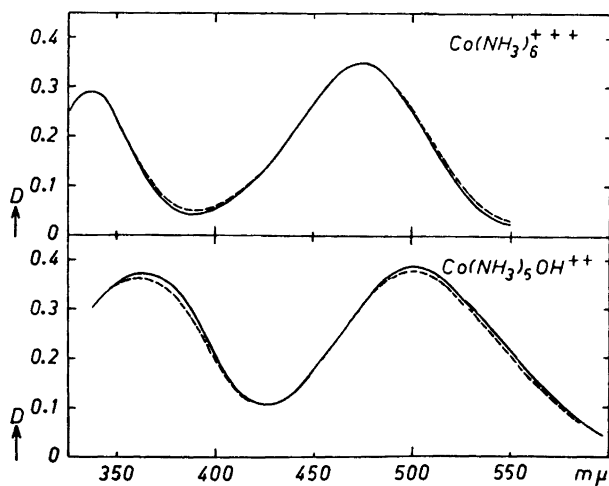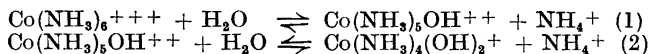

Fig. 1. Analysis of a mixture of $Co(NH_3)_6^{+++}$ and $Co(NH_3)_5OH^{++}$. 1 ml 0.030 M hex-ammine chloride and 1 ml 0.029 M pentammine nitrate were mixed, separated and dis-placed with 0.01 M KOH, 1 M KCl, and the fractions containing each component diluted to 25 ml. The optical density D was measured in 5 cm cells. Original mixture after dilution (0.0012 M $Co(NH_3)_6^{+++}$ and 0.00115 M $Co(NH_3)_5OH^{++}$): fulldrawn curves. Fractions after separation: dotted curves.

Table 3. Analysis of mixtures of: $Co(NH_3)_6^{+++}$, $Co(NH_3)_5OH^{++}$, $Co(NH_3)_4(OH)_2^+$. Equilibrium established with activated carbon as a catalyst.

$$Co(NH_3)_6^{+++} + H_2O \rightleftharpoons Co(NH_3)_5OH^{++} + NH_4^+ \quad (1)$$
$$Co(NH_3)_5OH^{++} + H_2O \rightleftharpoons Co(NH_3)_4(OH)_2^+ + NH_4^+ \quad (2)$$

	Column I Separation	Displacement	Column II Separation
Pentammine	0.1 M NH₄Cl, 1 M NH₃⎫		0.01 M KOH⎫
Luteo	+ 1 M KCl ⎬		+ 1 M KCl ⎭
Tetrammine		1 M HNO₃	

Sol. 1. Initial: 0.040 M $[Co(NH_3)_6](NO_3)_3$, 1.00 M NH₃

	$C_{Lut.}$	$C_{Pent.}$	$C_{Tetr.}$	$[NH_4^+]$	K(1)	K(2)
Chromatogr.	0.0081	0.0264	0.0018	0.036	0.117	0.0025
Classical methods	0.0097	0.0258	0.0023	0.034	0.091	0.0031

Sol. 2. Initial: 0.040 M $[Co(NH_3)_4(H_2O)_2](NO_3)_3$, 1.00 M NH₃, 0.1 NaOH

	$C_{Lut.}$	$C_{Pent.}$	$C_{Tetr.}$	$[NH_4^+]$	K(1)	K(2)
Chromatogr.	0.0028	0.0234	0.0062	0.0096	0.080	0.0025

the column with 0.1 M NH₄Cl, 1 M NH₃, 1 M KCl. Then the tetrammine is displaced as quickly as possible with 1 M HNO₃. The pentammine and hexammine are then separated on column II (of normal length, about 25 cm) by means of 0.01 M KOH, 1 M KCl.

The tetrammine could also be displaced with 0.1 M NaOH, 5 M LiCl and collected in dilute nitric acid, but due to fast decomposition in alkaline solution there is a considerably lower yield than when displaced with nitric acid. The use of nitric acid requires preliminary treatment of the alumina with acid as already described in the experimental section.

In Table 3 is given the result of an analysis of two equilibrium solutions of different composition. The ammonium ion concentration in the equilibrium solutions was determined by glass electrode measurements against a standard solution with known concentrations of ammonia and ammonium ion. It will be seen that the estimated hydrolysis constants corresponding to eqns. (1) and (2) agree satisfactorily for the two solutions, and that there is also a fair agreement with the data previously obtained by J. Bjerrum [13] for one of the solutions. In the case of solution 1 J. Bjerrum determined the hexammine gravimetrically as luteo oxalate, the pentammine as chloropentammine, and the tetrammine indirectly by titration of the amount of cobalt which was reduced to Co(II) when boiled with 20 % HCl. Mixtures of only hexammine and pentammine were analyzed spectrophotometrically [13], but the contents of these ions can also be estimated polarographically in 0.1 M H₂SO₄ as found by R. A. Vasadeva Murthy *. As a rule, however, polarography is not a good method for analyzing mixtures of related complexes with the same central ion.

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* Visitor from The Indian Institute of Science, Bangalore, India.

In a study on the decomposition of chromium(III) ammines Jørgensen and Bjerrum [14] have used a procedure for separating hexammine, hydroxopentammine and dihydroxotetrammine, which in principle is similar to that described here for the corresponding cobalt(III) complexes. Hexammine and pentammine are first displaced leaving the tetrammine on the column, and then separated on another column.

Separation of *cis* and *trans* complexes

The chromatographic method is also suitable for the separation of *cis* and *trans* complexes. Thus we have analyzed an alkaline equilibrium mixture of the *cis* and *trans* dihydroxobis(ethylenediamine)cobalt(III) ion prepared from a solution of the composition: 0.02 M *cis*-[Co en$_2$(H$_2$O)$_2$](NO$_3$)$_3$,0.1 M NaOH, 1 M NaNO$_3$. At room temperature equilibrium is reached in about a week [15]. We used a column of the larger type. The *trans*-compound was first displaced by means of 0.1 M NaOH, 1 M NaCl, and the *cis*-compound afterwards by means of the stronger displacing agent 0.1 M NaOH, 1 M LiCl. In this way it was found that $C_{cis}/C_{trans} = 0.57$. When calculating this ratio from the absorption spectrum of the mixture we found $C_{cis}/C_{trans} = 0.65$ in fairly good agreement. It should be mentioned that Woldbye [16] similarly has determined the *cis-trans* equilibrium constant for the dihydroxobis(ethylenediamine)chromium(III) ions, using 0.1 M KOH, 1 M KCl as eluating agent.

The hydroxyl group is a strongly polar group, and there is much evidence that the complex with the two strongest polar groups in *cis* position is more strongly bound than the corresponding *trans* compound. This rule was also confirmed in case of the dinitrotetrammines.

Separation of nitroammines

Systematically we have examined the wellknown series of nitroammines of the type Co(NH$_3$)$_{6-x}$(NO$_2$)$_x$$^{3-x}$ for x = 0, 1, 2, 3 and 4, and we have established conditions under which they can be separated in the case that two or three of the complexes are present simultaneously. *Tr.*-Co(NH$_3$)$_4$(NO$_2$)$_2$$^+$ and Co(NH$_3$)$_2$(NO$_2$)$_4^-$ form a slightly soluble salt, but otherwise all combinations are possible. The results are summarized in Table 4. Some of the complexes, especially Erdmann's salt Co(NH$_3$)$_3$(NO$_3$)$_3$ are considerably decomposed in alkaline solution, and for this reason the recovery of the complexes was not complete. It will be seen that the adsorption tendency in basic solution decreases in the series:Co(NH$_3$)$_6$$^{+++}$>Co(NH$_3$)$_5NO_2$$^{++}$>*cis*-Co(NH$_3$)$_4$(NO$_2$)$_2$$^+$>Co(NH$_3$)$_3$(NO$_2$)$_3$->*tr.*-Co(NH$_3$)$_4$(NO$_2$)$_2$$^+$, and inversely in acidic solution the anion complex Co (NH$_3$)$_2$(NO$_2$)$_4^-$ is more strongly adsorbed than Co(NH$_3$)$_3$(NO$_2$)$_3$ and the cation complexes. In the example given *cis*-Co(NH$_3$)$_4$(NO$_2$)$_2$$^+$ and Co(NH$_3$)$_3$(NO$_2$)$_3$ are displaced from Co(NH$_3$)$_2$(NO$_2$)$_4^-$ with a weak acetic acid buffer while a 1 M LiCl-acetic acid buffer is necessary to eluate the anion complex from the column. The *cis* and *trans* complexes Co(NH$_3$)$_4$(NO$_2$)$_2^+$ have previously been separated by King and Walters [2] by the ion exchange method. Table 4 shows that the separation of these two isomers can be accomplished just as well, and more conveniently, by the chromatographic method. On the other

Table 4. Separation of mixtures of $Co(NH_3)_{6-x}(NO_2)_x{}^{3-x}$ for x = 0, 1, 2, 3, 4. Conc. (mole/l) in solution to be analyzed.

Salts separated	According to prep.	Chromatogr. found	Displacing solutions $(R = C_{16}H_{33}(CH_3)_3N)$
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0062	0.0060	0.1 M KOH, 1 M (C$_2$H$_5$)$_4$NBr
[Co(NH$_3$)$_5$(NO$_2$)](NO$_3$)$_2$	0.0065	0.0062	0.1 M KOH, 1 M KCl
[Co(NH$_3$)$_6$](NO$_3$)$_3$	0.0067	0.0064	0.1 M NaOH, 1 M LiCl
tr-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0075	0.0067	0.01 M ROH, 0.02 M RBr
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0105	0.0105	0.01 M KOH, 1 M KCl
tr-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0050	0.0048	0.01 M ROH, 0.02 M RBr
[Co(NH$_3$)$_3$(NO$_2$)$_3$]	0.0056	0.0031	
[Co(NH$_3$)$_3$(NO$_2$)$_3$]	0.0071	0.0062	0.01 M ROH, 0.02 M RBr
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0051	0.0051	0.01 M ROH, 0.02 M RBr, 0.8 M KCl
[Co(NH$_3$)$_3$(NO$_2$)$_3$]	0.0046	0.0023	0.01 M HAc, 0.001 M NaAc
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$	0.0054	0.0043	further sep., see above
Rb[Co(NH$_3$)$_2$(NO$_2$)$_4$]	0.0049	0.0049	0.09 M HAc, 0.01 M NaAc, 1 M LiCl

hand, the corresponding ethylenediamine complexes are more difficult to separate chromatographically, and we have obtained only partial separation of *cis* and *trans* [Co en$_2$(NO$_2$)$_2$]NO$_3$ using our longest column (55 cm) and 0.01 M C$_{16}$H$_{33}$N(CH$_3$)$_3$OH, 0.02 M C$_{16}$H$_{33}$N(CH$_3$)$_3$Br as displacing solvent. Experiments with mixed solvents of water, dioxan or *tert.*-butanol gave no better results. The complexes were fixed more strongly to the column and were more difficult to displace, but the separations were not improved.

In general cations are easily eluated and poorly separated in acidic solution. Inversely anions are easily eluated and poorly separated in basic solution. However, we have established the following adsorption tendency in solutions buffered with NaHCO$_3$: $Co(CO_3)_3{}^{---} > Co$ enta$^- > Fe(CN)_6{}^{---} > Fe(CN)_6{}^{--}$. In acidic solution the highest charged anions are relatively much more strongly adsorbed. Thus in acetic acid buffers $Fe(CN)_6{}^{---}$ is more strongly adsorbed than the ethylenediaminetetraacetatocobalt(III) ion, and $Co(NH_3)_2NO_2)_4^-$ much more weakly than $Co(NO_2)_6{}^{---}$. This last ion can be removed from the column with 0.09 M HAc, 0.01 M HAc, 1 M LiCl, but more easily when 1 M LiCl is replaced by 1 M Na$_2$SO$_4$.

In conclusion it may be said that the chromatographic method developed here for separation of robust complexes seems to have a considerable range of application and offers several advantages over the ion exchange method. Thus, contrary to what is the case for ion exchange resins, even trivalent complexes can easily be removed from the column, and the coloured zones of the complexes are much more easily seen on the white alumina than on the resins.

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