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REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF PENTAAMMINE COBALT(III) COMPLEXES

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SUMMARY

The reversed-phase high-performance liquid chromatography of a variety of $[Co(NH_3)_5X]^{2+}$ cations including halo (X = F^-, Cl^-, Br^-, I^-), isomeric anionato (X = ONO^-, NO_2^-; NCS^-, SCN^-), anionato (X = NO_2^-, NO_3^-, N_3^-, Cl^-), carboxylato (X = $CH_3CO_2^-$, $CF_3CO_2^-$, $C_2H_5CO_2^-$, $C_3H_7CO_2^-$), isomeric toluato (X = $CH_3C_6H_4CO_2^-$), some $[Co(NH_3)_5X]^{3+}$ cations (X = H_2O, $(CH_3)_2SO$, NH_3) and $[Co(en)_3]^{3+}$ are reported. In general good separations are achieved using 25 mM toluenesulphonate ion-pairing reagent in water–methanol (isocratic or gradient) using a μBondapak C_{18} column. The efficiency and speed of the separations are superior to those obtained by ion-exchange chromatography.

INTRODUCTION

Although ion-exchange chromatography (IEC) has proved useful for separating isomeric cobalt(III) coordination complexes of increasing complexity and sophistication[1], and has allowed the "resolution" of certain enantiomeric complexes when used with optically active eluents[2], such separations are generally tedious. In most cases long columns and many hours are required to effect the complete or partial separation of related species bearing the same overall charge. Attempts by ourselves, and others, to use high-pressure ion-exchange chromatography (HPIEC) have in general been disappointing. Resolutions can be marginally improved over IEC but long elution times are still required. Also, the additional care and time required to set up the experiment has limited its usefulness for analytical and repetitive investigations. In our experience, this has been so with both a home-made low-pressure (*ca.* 600 p.s.i.) system and with commercial high-pressure (*ca.* 2000 p.s.i.) apparatus using Dowex- and Sephadex-based ion-exchangers.

High-performance liquid chromatography (HPLC) on inert supports such as silica has been largely reserved for the separation of uncharged coordination complexes[3], but the separations of *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ and $[Co(en)_2(OCOC_6H_5)_2]^+$ (ref. 4), and the Δ,Λ-diastereomers of $[Co(en)_2Glu]^+$ and $[Co(en)_2Asp]^+$ (ref. 5) and the *sym-cis* and *unsym-cis* geometric forms of $[Co(EDDA)en]^+$ (ref. 5) have been reported using programmed, mixed eluents. How-

ever, underivatized silica lacks the discriminatory power necessary for our purpose.

We have recently been introduced to the reversed-phase HPLC technique (RP-HPLC) and have found that by using low concentrations (< 25 mM) of n-hexanesulphonate, or with detection in the visible (> 400 nm) the less expensive toluene-p-sulphonate, in water–methanol solvents it is possible to achieve excellent separations of $[Co(en)_2AA]^{2+}$ cations (AA = Gly, Pro, Val, Leu, Phe) on a C_{18} stationary phase within 15 min of injection[6]. The ideal peak shapes and separations obtained, and the simplicity of the method, have encouraged us to explore it further as a general method for separating closely related, ionic, cobalt(III) complexes; our eventual aim being the rapid analysis of products arising from the induced and spontaneous hydrolyses of cobalt(III) and chromium(III) complexes in the presence of competing species.

Preliminary results have been most encouraging, and we report here the rapid and quantitative separations of a variety of simple pentaammine $[Co(NH_3)_5X]^{2+,3+}$ systems.

EXPERIMENTAL

Materials and instrumentation

Methanol (laboratory reagent) was purified by fractional distillation (64.5°C) following reflux over magnesium and iodine. Doubly distilled water was deionized (specific resistance 0.3 M Ω cm) with a Elgastat apparatus before use. AnalaR-grade sodium hydroxide (BDH) or orthophosphoric acid (BDH) were used to correct the eluent pH to 3.5 [measured using a Pye 292 pH meter fitted with a combined pH electrode (Radiometer)]. The ion-pairing reagent, toluene-p-sulphonic acid (BDH or Merck) was recrystallized from chloroform, characterized by ^{1}H nuclear magnetic resonance (NMR) and by elemental analysis (calculated for $CH_3C_6H_4SO_3H \cdot H_2O$: C, 44.20; H, 5.30. Found: C, 44.40; H, 5.18) and stored in a dessicator (calcium chloride). Preliminary filtering of solvents was done through glass filters (Whatman Microfibre GF/F, 4.7 cm). A Millipore solvent filter assembly (Waters Assoc.) fitted with either a cellulose nitrate membrane (Sartorius SM 11306, 0.45 μm, 47 mm, for aqueous solvents; SM 11807, 0.2 μm, 47 mm for non-aqueous solvents) or a polycarbonate filter (Nucleopore 111107, 0.4 μm, 47 mm, for aqueous and non-aqueous solvents) was used for the final filtering of the mobile phases.

Solid samples were dissolved in doubly distilled, deionized water and filtered through a Swinney filter assembly fitted with a membrane filter (Millipore GSWP 01300, 0.22 μm, 13 mm) before injection (1–200 μl) with a Hamilton syringe (25 μl, 100 μl).

Separations were carried out on μBondapak C_{18} reversed phase (RP) columns (10 μm, 300 $\times$ 3.9 mm I.D., Waters Assoc.) or on Radial-Pak C_{18} cartridges (5 μm, 100 $\times$ 5 mm I.D., 10 μm, 100 $\times$ 8 mm I.D.) and a RCM-100 radial compression module (Waters Assoc.). A Varian 5000 microprocessor-controlled pump assembly was used to mix and deliver the two eluents, and samples were injected via a U6K universal injector assembly (Waters Assoc., 2.0-cm^3 capacity). Some experiments were carried out using a Partisil 10SCX ion-exchange column (Whatman). Detection was via a Varian UV-50 variable-wavelength detector (0.005–0.1 a.u.f.s., path length 1.0 cm) and chromatograms were recorded on a Varian Model 9176 strip chart recorder.

Procedure

The two eluent solutions were prepared as follows.

Water (50 cm^3) was added to toluene-*p*-sulphonic acid monohydrate (9.51 g, 50 mmol) and the solution adjusted to pH 3.50 $\pm$ 0.02. The volume was made up to 100 cm^3 with water and methanol added to a final volume of 2.0 dm^3 (95% methanol). The other eluent was similarly prepared to a volume of 2.0 dm^3 with water (100% water). The eluents were filtered through glass-fibre filters to remove large dust particles, and then through cellulose nitrate or polycarbonate membranes to remove the smaller particles (> 0.4 μm), and stored at 4°C prior to use.

The column was prepared by initially washing with methanol (40 cm^3) and then equilibrated with the 95% MeOH toluene-*p*-sulphonate (40 cm^3, 25 mmol dm^{-3}, pH 3.50) solution at a flow-rate of 2.0 cm^3 min^{-1}. Immediately before runs the column was brought to 100% aqueous toluene-*p*-sulphonate (25 mmol dm^{-3}, pH 3.50) over 30 min using a linear mixing gradient and allowed to equilibrate for a further 15 min. A sample of a standard [Co(en)$_2$Gly]I$_2$ solution was usually injected initially to check the column, detector (480 nm) and retention time.

The column was not thermostated (15–25°C) but it was found necessary to thermostat (20°C) the cell in the detector in order to maintain a stable baseline at high sensitivity (0.005 a.u.f.s.). Sample solutions (10–30 nmol μl^{-1}) were injected (10–200 μl) so that the total loading was less than 2000 nmol to avoid splitting of peaks (see below). Runs were carried out using either a constant eluent composition (isocratic) or a linear gradient mixing programme. On completion of the run the column was equilibrated with the initial mobile phase immediately (if the final composition was less than 50% methanol) or over a linear gradient (5–15 min, final composition greater than 50% methanol). When not in use the columns were thoroughly flushed with methanol and stored in a cool place.
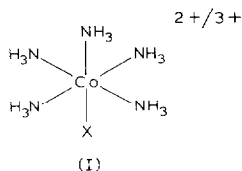
Complexes

The following pentaammine complexes were prepared by standard procedures: [Co(NH$_3$)$_5$CO$_3$]NO$_3$ (ref. 7), [Co(NH$_3$)$_5$OH$_2$] (ClO$_4$)$_3$ (ref. 8), [Co(NH$_3$)$_5$F] (NO$_3$)$_2$ (ref. 7), [Co(NH$_3$)$_5$Cl]Cl$_2$ (ref. 9), [Co(NH$_3$)$_5$Br]Br$_2$ (ref. 10), [Co(NH$_3$)$_5$I]Cl$_2$ (ref. 7) following trituration of the iodide salt with AgCl, [Co(NH$_3$)$_5$OCOCH$_3$] (ClO$_4$)$_2$ (ref. 7), [Co(NH$_3$)$_5$DMSO] (ClO$_4$)$_3$ (ref. 11), [Co(NH$_3$)$_5$SCN]Cl$_2 \cdot 1.5$ H$_2$O (ref. 12), [Co(NH$_3$)$_5$NCS]Cl$_2$ (ref. 12), [Co(NH$_3$)$_5$ONO] (ClO$_4$)$_2$ (ref. 13), [Co(NH$_3$)$_5$NO$_2$] (NO$_3$)$_2$ (ref. 7), [Co(NH$_3$)$_5$NO$_3$] (NO$_3$)$_2$ (ref. 1), [Co(NH$_3$)$_5$N$_3$]Cl$_2$ (ref. 14), and [Co(NH$_3$)$_6$]Cl$_3$ (ref. 9). [Co(en)$_3$]Cl$_3$ was also prepared as described in ref. 9.

The propionate complex [Co(NH$_3$)$_5$OCOC$_2$H$_5$] (ClO$_4$)$_2$ was prepared by the method of Jackman[15] by treatment of [Co(NH$_3$)$_5$OH] (ClO$_4$)$_2$ (1 g) in water (17 cm^3) with propionic anhydride (0.73 g), and crystallization of the resultant red oil from hot water by addition of NaClO$_4$. (Analysis, calculated for CoC$_3$H$_{20}$N$_5$O$_2$ (ClO$_4$)$_2 \cdot 0.5$ H$_2$O: C, 8.47; H, 4.98; N, 16.47. Found: C, 8.46; H, 4.89; N, 16.57.) The *n*-butyrate complex, [Co(NH$_3$)$_5$OCOC$_3$H$_7$] (ClO$_4$)$_2 \cdot$ H$_2$O, was prepared from the reaction of excess *n*-butyric acid with [Co(NH$_3$)$_5$OH$_2$] (ClO$_4$)$_3$ in aqueous solution (80°C, pH *ca.* 6, 40 min). Following removal of unchanged butyric acid by ether extraction (three times), crystallization of the complex was induced by addition of HClO$_4$ (60%). (Analysis, calculated for CoC$_4$H$_{22}$N$_5$O$_2$ (ClO$_4$)$_2 \cdot$ H$_2$O: C, 10.72; H, 5.40; N, 15.63; Found: C, 10.52; H, 5.11; N, 14.99). The trifluoroacetate and *o*-, *m*- and *p*-toluate complexes were prepared in a similar fashion.

RESULTS AND DISCUSSION

The pseudo-octahedral pentaammine cobalt(III) complexes exist as cations in solution and most of them are relatively stable towards dissociation of the X group ($k_{aq} < 10^{-5}$ sec^{-1}, 25°C)[16]. However, some are more labile (*e.g.* X = OS(CH$_3$)$_2$, NO$_3^-$, I$^-$). Also, the ONO$^-$ and SCN$^-$ complexes isomerize to the NO$_2^-$ and NCS$^-$ species both in the solid state and in solution 12·17.

(I)

There has been no previous report on the LC of these complexes although it is well known that the 3+ ions (*i.e.* X = OH$_2$, NH$_3$) can be separated from the 2+ cations by IEC on Dowex-50 or SP-Sephadex resins.

In the absence of an ion-pairing reagent the [Co(NH$_3$)$_5$X]$^{2+/3+}$ ions showed no retention on the C$_{18}$-bonded phase, indicating that hydrophobic interactions between the two are insignificant compared with solvation of the complex by the aqueous mobile phase. Selective retention is however observed when large hydrophobic anions are added to the mobile phase, in much the same way as is found for amino acids and peptides[18]. Our studies[19] show that the pairing-ion capabilities follow the following pattern:

(1) Inorganic anions (SO$_4^{2-}$, HPO$_4^{2-}$) have little effect on the retention despite their excellent ion-pairing properties[20].

(2) The order of increasing retention, (D-(+)-arsenyltartrate (As -tart$_2^{2-}$(< D-(+)$_{589}$-antimonyltartrate (Sb$_2$-tart$_2^{2-}$) <tosylate < D-(+)$_{589}$-camphorsulphonate < *n*-hexanesulphonate, roughly follows the order of increasing hydrophobicity and, presumably, interaction with the non-polar surface of the stationary phase.

(3) The chiral anions camphorsulphonate, Sb$_2$-tart$_2^{2-}$, and As$_2$-tart$_2^{2-}$ fail to "resolve" enantiomers such as Δ,Λ-[Co(en)$_2$gly]$^{2+}$, and in general give no better resolution of diastereoisomers (such as Δ,Λ-[Co(en)$_2$(S)Pro]$^{2+}$) than do achiral anions.

(4) Tosylate is superior to hexanesulphonate or camphorsulphonate in separating diastereoisomers. This suggests a certain "column modifying" effect of the ion-pairing reagent.

Spectrophotometric determinations established the quantitative recovery of the cobalt(III) species from the reversed-phase stainless steel column.

From these studies it appears that for the relatively non-hydrophobic and structurally featureless [Co(NH$_3$)$_5$X]$^{2+/3+}$ ions the ability of the added anion to interact with the C$_{18}$ stationary phase is more important than its ability to form an ion pair with the complex, although the latter function is certainly required. Such interactions have recently been discussed by Bidlingmeyer *et al.*[21] in their "ion-interaction" model for RP-HPLC.

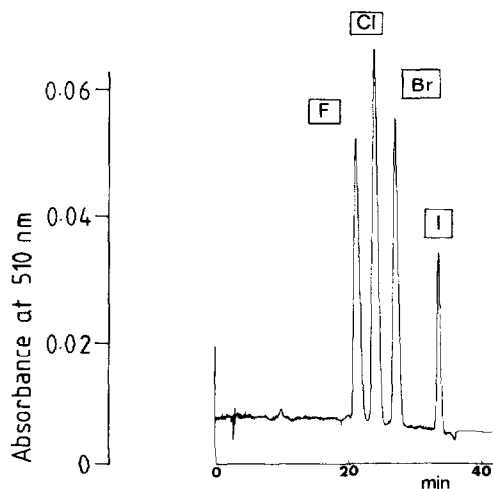Results using 25 m*M* tosylate as pairing ion (pH 3.50) are given below. The

Fig. 1. Chromatogram of a mixture of $[Co(NH_3)_5X]^{2+}$ complexes, $X = F^-$, Cl^-, Br^-, I^- (610 nmol in 25 μl). Gradient P-2; flow-rate, 2.0 cm^3 min^{-1}; chart speed, 0.25 cm min^{-1}.

solvent programmes used were as follows: (time (min), % eluent A): P-1 (isocratic, 71.5); P-2 (0, 100; 14, 99; 36, 85; 68, 70; 116, 40; 120, 100); P-3 (0, 100; 14, 99; 56, 0) with linear gradient between intervals (A = 100% aqueous tosylate; B = methanol-aqueous tosylate, 95:5).
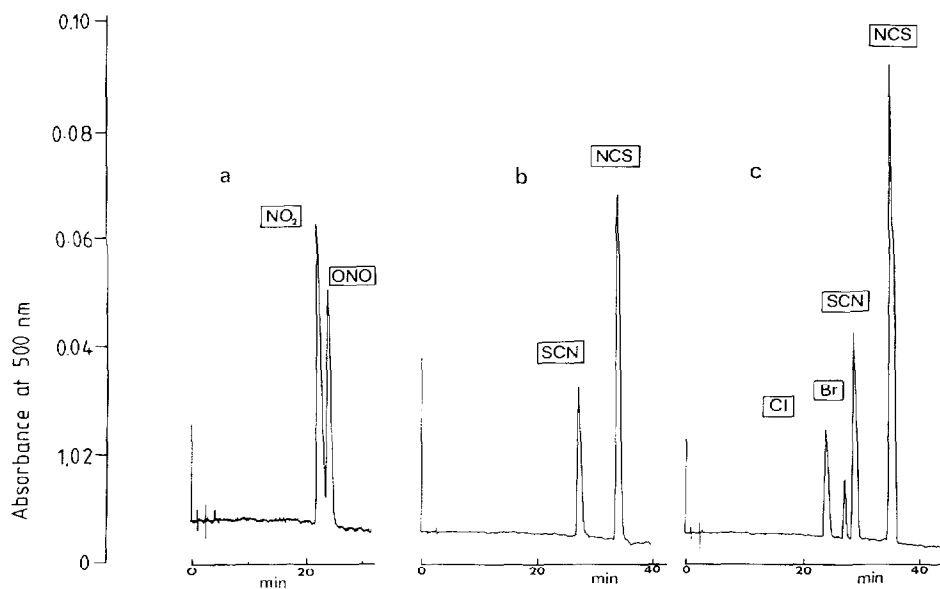

Fig. 2. Chromatograms of isomeric $[Co(NH_3)_5X]^{2+}$ complexes. (a) $X = NO_2^-$, ONO^- (480 nmol in 15 μl); (b) $X = SCN^-$, NCS^- (320 nmol, 10 μl); (c) $X = Cl^-$, Br^-, SCN^-, NCS^- (426 nmol, 20 μl). Gradient P-2; flow-rate, 2.0 cm^3 min^{-1}; chart speed, 0.25 cm min^{-1}.

Halo pentaammines, $[Co(NH_3)_5X]^{2+}$ $(X = F^-, Cl^-, Br^-, I^-)$

Retention times follow the order $F^- < Cl^- < Br^- < I^-$, (Fig. 1) which is the order of increasing size of the halo ion. However, the separation of $X = I^-$ from $X = Br^-$ seems large, and of $X = F^-$ from $X = Cl^-$ small, when a detailed comparison with the ionic radii is made (F^-, 136 pm; Cl^-, 181 pm; Br^-, 195 pm; I^-, 216 pm). This suggests that polarizability factors, including interactions of X with the stationary phase, are important. Clearly the separation of a mixture of these four complexes is easily achieved. This has never been previously reported by any technique.

Isomeric anionic pentaammines, $[Co(NH_3)_5X]^{2+}$ $(X = ONO^-, NO_2^-, NCS^-, SCN^-)$

Fig. 2a shows the nearly complete separation of the nitro (NO_2^-) and nitrito (ONO^-) isomers, with the yellow nitro isomer being preferentially eluted. No such separation by IEC has been reported, although we have observed some indication of a separation using a long (50-cm) Dowex 50W-X2 column. For the S- and N-bonded thiocyanate species separation is complete (Fig. 2b), and the elution order is the same
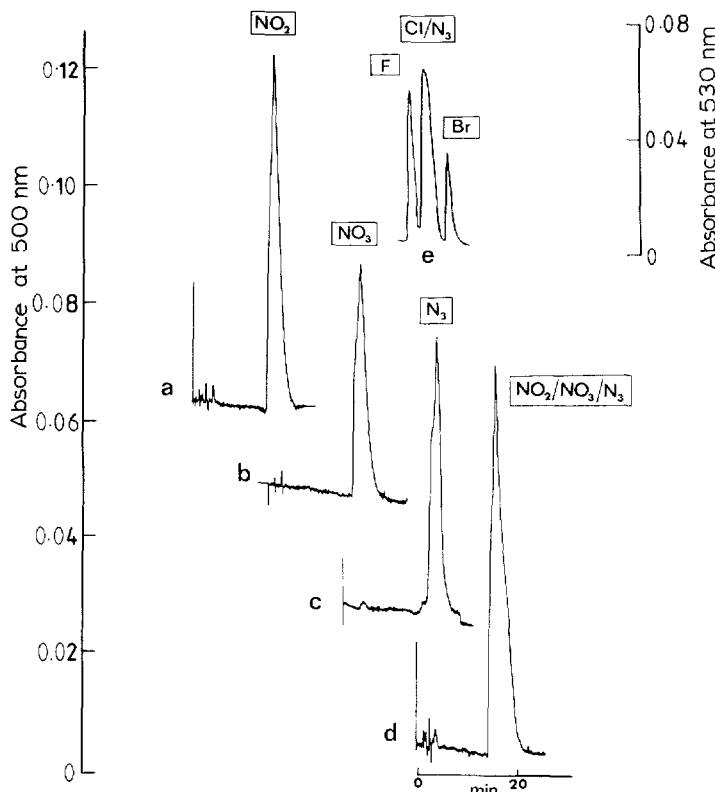

Fig. 3. Chromatograms of various anionato $[Co(NH_3)_5X]^{2+}$ complexes. (a) $X = NO_2^-$ (400 nmol in 25 μl); (b) $X = NO_3^-$ (300 nmol, 25 μl); (c) $X = N_3^-$ (320 nmol, 25 μl); (d) $X = NO_2^- + NO_3^- + N_3^-$ (420 nmol, 35 μl); (e) $X = F^- + Cl^- + N_3^- + Br^-$ (800 nmol, 25 μl). Gradient P-2; flow-rate, 2.0 cm³ min⁻¹; chart speed, 0.25 cm min⁻¹.

as observed using a long Dowex 50W-X2 column[12]. Since isomerizations in these ions occur, and can be catalysed[12,17], these rapid separations have obvious advantages. Fig. 2c is a chromatogram of a mixture of the Cl^-, Br^-, SCN^- and NCS^- complex ions. Each is clearly separated from the others, although the distinction between Br^- and SCN^- is not large.

Other anionic pentaammines, $[Co(NH_3)_5X]^{2+}$ $(X = NO_2^-, NO_3^-, N_3^-, Cl^-)$

These complexes show similar retention times and mixtures could not be resolved (Fig. 3). However, each could be separated from $X = F^-$ and Br^- and, by comparison with Fig. 2(c), from $X = SCN^-$ and NCS^-.
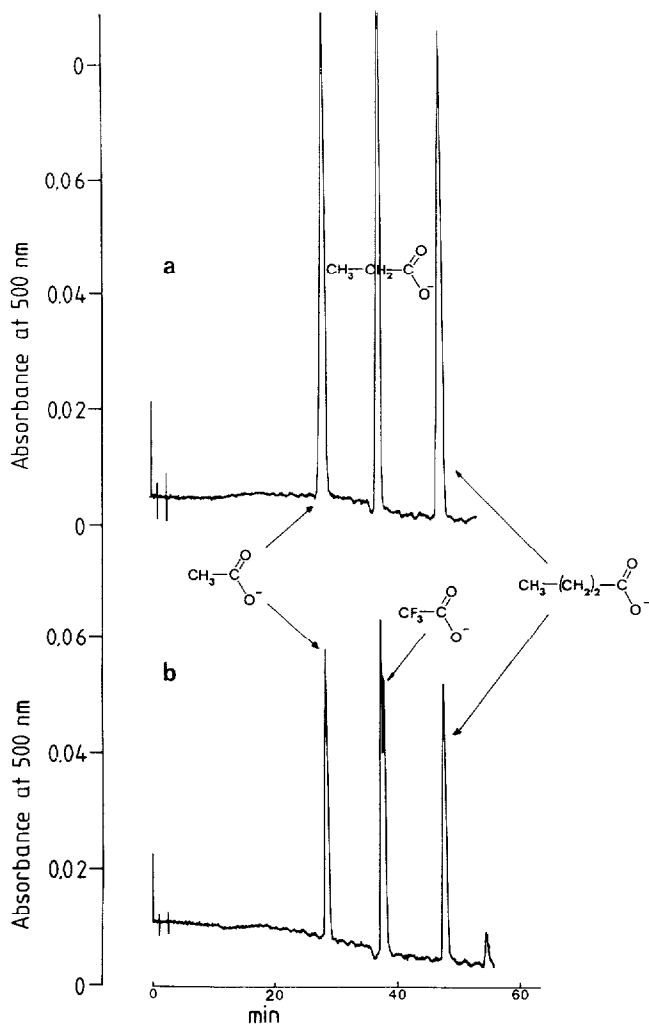

Fig. 4. Separation of carboxylato $[Co(NH_3)_5X]^{2+}$ complexes. (a) $CH_3CO_2^-$, $C_2H_5CO_2^-$, $C_3H_7CO_2^-$ (960 nmol in 15 μl); (b) $CH_3CO_2^-$, $C_2H_5CO_2^-$, $CF_3CO_2^-$, $C_3H_7CO_2^-$ (640 nmol, 10 μl). Gradient P-2; flow-rate, 2.0 cm³ min⁻¹; chart speed, 0.25 cm min⁻¹.
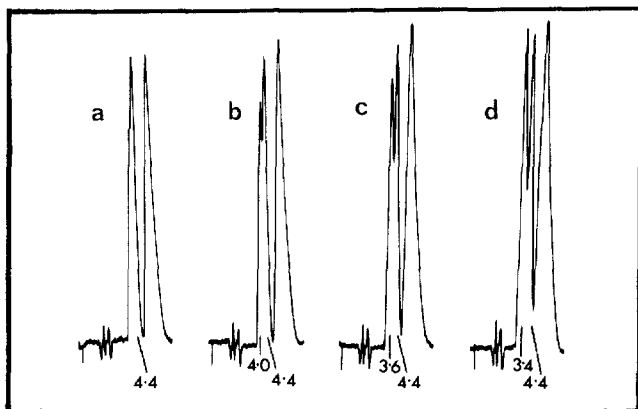
Fig. 5. Chromatograms depicting pairing-ion deficient splitting of $[Co(NH_3)_5OCOCH_3]^{2+}$ in the presence of $[Co(NH_3)_5OCOC_2H_5]^{2+}$. Samples: (a) 759 nmol in 30 μl; (b) 886 nmol, 35 μl; (c) 1012 nmol, 40 μl; (d) 1265 nmol, 50 μl. Eluent, methanol–water (2.5:97.5) (isocratic); flow-rate 2.0 cm^3 min^{-1}; 5 mM tosylate; chart speed, 0.25 cm min^{-1}. With increasing loadings the peak at 4.4 min (t_R (normal)) is preceded by an abnormal peak at progressively earlier times (t_R (abnormal)).

Carboxylato pentaammines, $[Co(NH_3)_5OCOR]^{2+}$ $(R = CH_3, CF_3, C_2H_5, C_3H_7)$

The acetate, propionate and butyrate complexes can be easily separated, the order being that expected for increasing interaction with the stationary phase (Fig. 4a). Fig. 4b shows that the acetato and trifluoroacetato ions are completely resolved but that the latter overlaps the propionato complex.
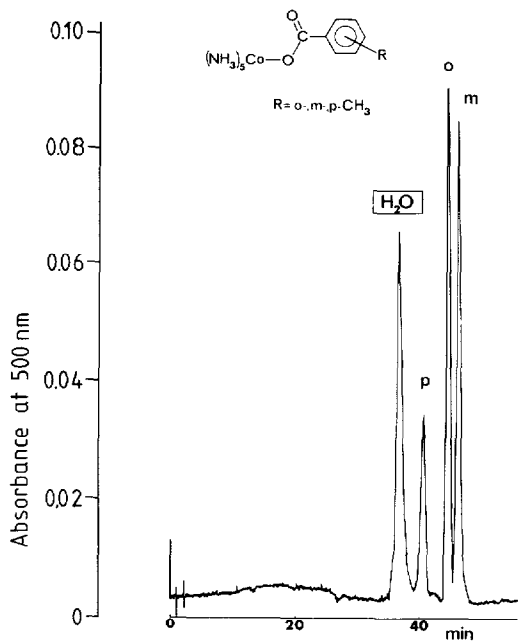

Fig. 6. Separation of *o*-, *m*- and *p*-isomers of the toluic acid complexes $[Co(NH_3)_5toluate]^{2+}$ in the presence of $[Co(NH_3)_5H_2O]^{3+}$ (960 nmol in 15 μl). Gradient P-3; flow-rate, 2.0 cm^3 min^{-1}; chart speed, 0.25 cm min^{-1}.

A note of warning must be given when larger loadings are used. A peak-splitting phenomenon occurs which is related to the total loading, and preferentially splits the least retained species. Fig. 5 shows this for a 1:1 mixture of the R = CH_3 and C_2H_5 complexes under isocratic conditions (2.5% methanol, 5 mM tosylate), and it can be seen how the acetato peak splits into two with the leading component being eluted with progressively shorter retention times and the other peak remaining constant. This phenomenon was noted earlier[6] during chromatography of a mixture of $\varDelta$-[Co(en)$_2$Gly]$^{2+}$ and $\varDelta$-[Co(en)$_2$Pro]$^{2+}$ ions, and was found to be due to interactions between the different complexes, the ion-pairing reagent, and the stationary phase. It limits the loadings that can be used, but can be avoided by increasing the ion-pairing reagent concentration.

Isomeric toluic acid pentaammines, $[Co(NH_3)_5OCOC_6H_4CH_3]^{2+}$

These complexes are firmly retained on the stationary phase as might be ex-

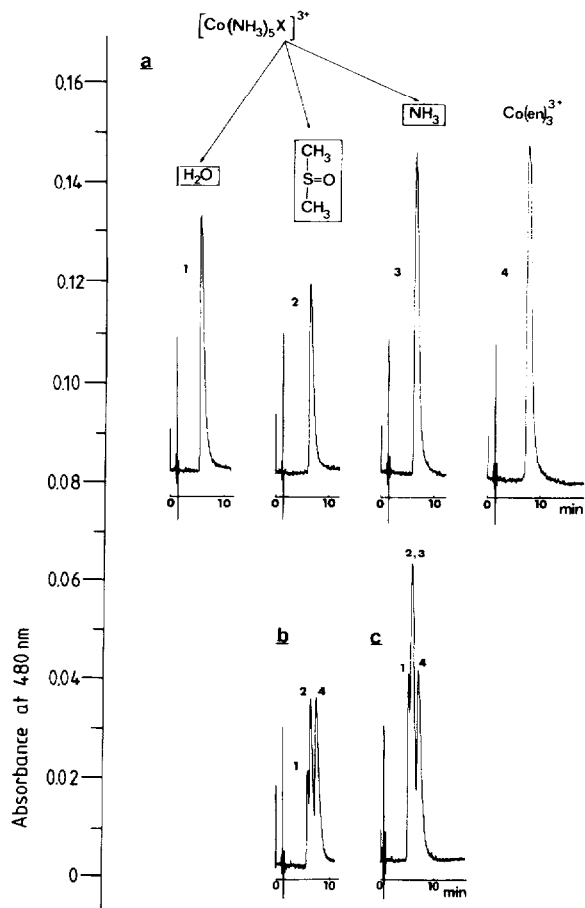Fig. 7. Chromatograms of various [Co(NH$_3$)$_5$X]$^{3+}$ complexes. (a1) X = H$_2$O (400 nmol in 10 μl); (a2) X = (CH$_3$)$_2$SO (320 nmol, 10 μl); (a3) X = NH$_3$ (640 nmol, 10 μl); (a4) [Co(en)$_3$]$^{3+}$ (640 nmol, 10 μl); (b) 640 nmol, 10 μl and (c) 960 nmol, 10 μl are of mixtures. Eluent, P-1; flow-rate, 2.0 cm^3 min^{-1}; chart speed, 0.25 cm min^{-1}.

pected from the presence of the phenyl group. Fig. 6 shows that they are retained more firmly than the more highly charged $[Co(NH_3)_5OH_2]^{3+}$ ion. The unusual elution order $p > o > m$ is difficult to rationalize on steric, ion-pairing, or stationary-phase-interaction grounds, and a complex set of parameters probably combine.

Tervalent pentaammine complexes $[Co(NH_3)_5X]^{3+}$ $(X = OH_2, OS(CH_3)_2, NH_3)$ and $[Co(en)_3]^{3+}$

Increasing the positive charge from 2 to 3 results in enhanced retention. This might be anticipated on ion-pairing grounds: for the pentaammine $3+$ ions with $1-$ species the ion-pair constant $K_{ip} = ca.$ 30 M^{-1} while for the $2+$ ions $K_{ip} \approx 5–8\ M^{-1}$ (ref. 22). Good peak shapes are observed (Fig. 7a) for each $3+$ ion under isocratic solvent conditions (28.5 % methanol), but the distinction between them is less dramatic than for the $2+$ ions (Fig. 7b and c). Only the $[Co(NH_3)_5OH_2]^{3+}$ and $[Co(en)_3]^{3+}$ ions are fully resolved under these conditions. Clearly a more discriminating ion-pairing reagent and/or a more carefully modified solvent programme is required to separate these species.

CONCLUSION

The above results show that RP-HPLC has considerable potential for the routine analysis of pentaammine-cobalt(III) ions of the same charge. The method is characterized by rapid separations with excellent peak shapes and high column efficiencies. Loadings must be small with conventional stainless steel μBondapak C_{18} columns (less than 1 mg of complex) but can be significantly larger (10–100 mg) with radial-compression columns[23]. For precise analytical work the method has three clear advantages over conventional IEC: (1) it is capable of separating $[Co(NH_3)_5X]^{2+}$ complexes with a high degree of differentiation; (2) it is relatively rapid (*ca.* 20 min); (3) it is ideal for handling microgram amounts. These advantages are critical for the competition studies alluded to in the introduction.

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