

CHROM. 3882

The study of ion pair formation

IV. Partition and ion-exchange studies of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$

The paper electrophoretic study of ion pair formation described in two previous communications yielded a good picture of the interaction of tri-positive Co(III) complexes with various anions^{1,2}. Therefore we thought that it might be interesting to examine the behaviour of such complexes in partition paper chromatography and ion-exchange paper chromatography. The results obtained are described in this note. Owing to the instability of the tris(dipyridyl) and the tris(*ortho*phenanthroline) complexes of Co(III) in most systems studied, the work deals only with the more stable $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$.

Partition chromatography

Fig. 1 shows the R_F values of the Co(III) complexes in butanol-HCl, butanol-HClO₄ and butanol-H₂SO₄. Little information can be obtained from these results. In butanol-HCl mixtures the R_F values increase continuously with the HCl concentration. Hydrated trivalent cations behave differently, *i.e.*, they reach a maximum

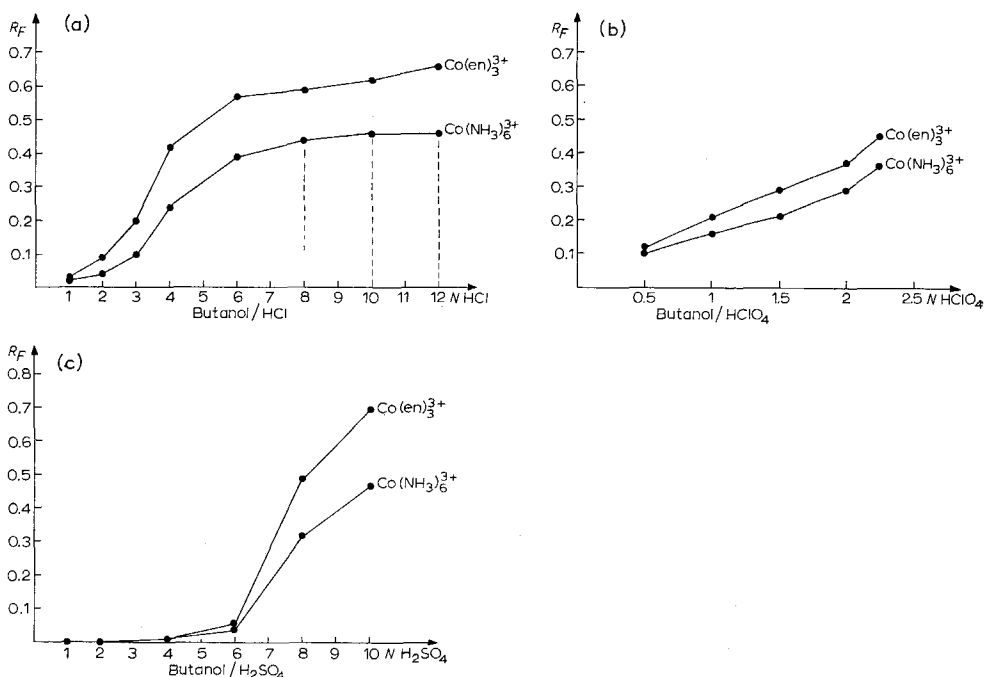
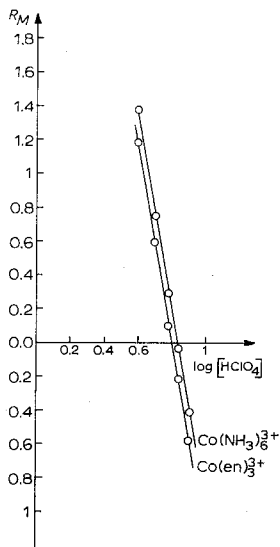
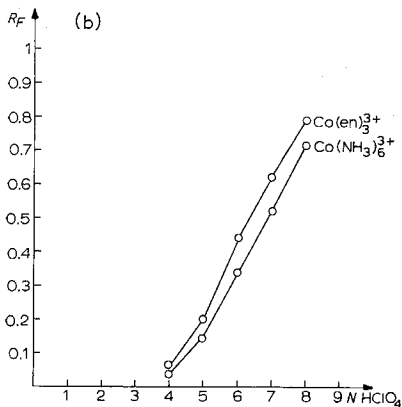
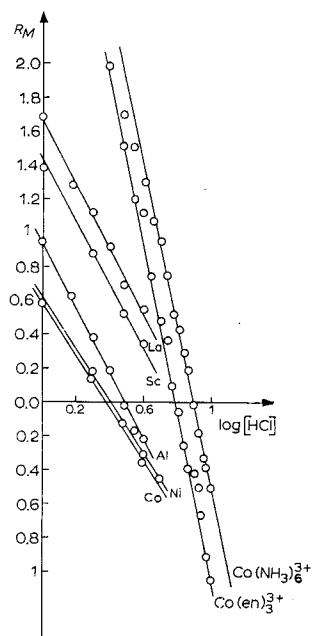
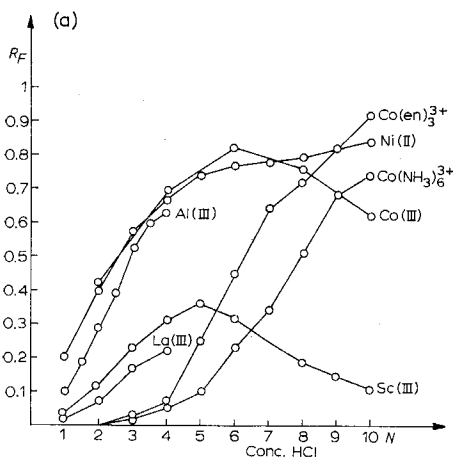


Fig. 1. R_F values of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ plotted against: (a) HCl concentrations in 1:1 mixtures of butanol and aqueous HCl. The dotted line indicates the comet formed with $[\text{Co}(\text{NH}_3)_6]^{3+}$. (b) HClO₄ concentrations in 1:1 mixtures of butanol and aqueous HClO₄. (c) H₂SO₄ concentrations in 1:1 mixtures of butanol and aqueous H₂SO₄. Whatman No. 3MM paper was used throughout.



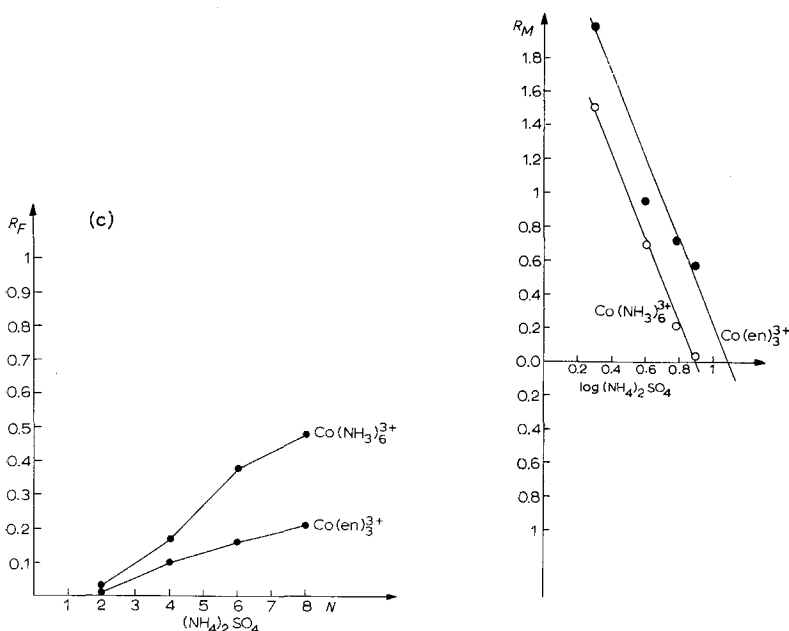


Fig. 2. (a) R_F vs. $[\text{HCl}]$ and R_M vs. $\log [\text{HCl}]$ plots for $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Al}(\text{III})$, $\text{Sc}(\text{III})$, $\text{La}(\text{III})$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{Co}(\text{en})_3]^{3+}$ on Amberlite SA-2 paper developed with aqueous HCl . The slopes of the R_M vs. $\log [\text{HCl}]$ plots are: $\text{Co}(\text{II}) = 1.7$, $\text{Ni}(\text{II}) = 1.6$, $\text{Al}(\text{III}) = 2.0$, $\text{Sc}(\text{III}) = 1.92$, $\text{La}(\text{III}) = 1.94$, $[\text{Co}(\text{en})_3]^{3+} = 4.6$, and $[\text{Co}(\text{NH}_3)_6]^{3+} = 4.75$. (b) R_F vs. $[\text{HClO}_4]$ and R_M vs. $\log [\text{HClO}_4]$ plots for $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ on Amberlite SA-2 paper developed with aqueous HClO_4 . The slopes of the R_M vs. $\log [\text{HClO}_4]$ plots are: $[\text{Co}(\text{NH}_3)_6]^{3+} = 5.3$ and $[\text{Co}(\text{en})_3]^{3+} = 5.6$. (c) R_F vs. $[(\text{NH}_4)_2\text{SO}_4]$ and R_M vs. $\log [(\text{NH}_4)_2\text{SO}_4]$ plots for $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ on Amberlite SA-2 paper developed with aqueous $(\text{NH}_4)_2\text{SO}_4$. The slopes of the R_M vs. $\log [(\text{NH}_4)_2\text{SO}_4]$ plots are: $[\text{Co}(\text{NH}_3)_6]^{3+} = 2.45$ and $[\text{Co}(\text{en})_3]^{3+} = 2.5$.

around 6 N HCl and then decrease slowly³. Using butanol- HClO_4 no difference in behaviour between trivalent metals such as Al^{3+} or La^{3+} (ref. 4) and the $\text{Co}(\text{III})$ complexes is noted; the R_F values increase with the HClO_4 concentration. For butanol- H_2SO_4 few data are available. However, $\text{Co}(\text{II})$ behaves much like the $\text{Co}(\text{III})$ complexes. Thus these partition systems do not give any marked indication of ion pair formation except possibly in high HCl concentrations in butanol- HCl mixtures.

Ion-exchange paper chromatography

Fig. 2 shows the R_F vs. [eluent] and the R_M vs. \log [eluent] plots for $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ and some other ions developed with aqueous HCl , HClO_4 and $(\text{NH}_4)_2\text{SO}_4$ on Amberlite resin SA-2 paper (containing 45 % of a sulphonic resin).

The R_M vs. $\log [\text{HCl}]$ plot is analogous to the $\log K_d$ vs. $\log [\text{HCl}]$ plots given in column and equilibrium experiments (*e.g.*, by NELSON *et al.*⁵), and in both cases (column or paper) the slope of the line indicates the charge of the ion under study⁶. Plots of this kind are usually linear at low HCl or HClO_4 concentrations but become less "ideal" above approx. 3 N acid (see ref. 5). The trivalent metal ions exhibit a linear plot at low acidities, usually having a slope of less than 3 (2 to 2.5), which then curves upwards.

The cobalt complexes studied do not only give linear plots up to 10 *N* HCl and 8 *N* HClO₄, but the slopes of the linear plots are 4.7 for HCl and 5.3 for HClO₄, thus more than double the slope of trivalent metal ions such as La, Sc and Al.

We are tempted to explain the linearity of the plots at high acid concentration by the annulling of the usual "non-ideal" behaviour due to the increase in ion pair formation, but this explanation seems rather unlikely since paper electrophoretic data showed HClO₄ to form much stronger ion pairs than HCl. We have thus no satisfactory explanation for this behaviour at present. The slopes with values of approximately 5 instead of below 3 could only be explained by postulating rather strong ion pair formation between the sulphonic groups of the resin and the cobalt complexes, involving as many as three or more sulphonic groups. The slope of 2.5 obtained when developing with (NH₄)₂SO₄ seems to favour this explanation. Here the ion pairing with the resin and with the solution should be about equal, and the complexes should exhibit a "charge" of the order of the usual trivalent metal ions in HCl. The comparison is, however, limited because the exchanging cation was changed from H⁺ to NH₄⁺, and the latter is more extensively adsorbed than the former.

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