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Note

Paper electrophoretic study of ion-pair formation

XIII. Survey of the ion-pair forming properties of monovalent inorganic anions

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In a series of studies¹⁻⁵ we have surveyed some aspects of the interaction between trivalent metal complexes and anions using paper electrophoresis. Many unexpected and interesting results have been obtained, such as the hydrophobic type of interaction of perchlorate and the hydrogen bonding type of interaction of many divalent anions. As we had not investigated many of the simple inorganic monovalent anions, in this work we studied the electrophoretic behaviour of trivalent Co(III) complexes in a wide range of monovalent anions as electrolytes, especially ClO_3^- , BrO_3^- , IO_3^- , IO_4^- , NO_2^- and CNS^- .

In previous work most results were obtained with four Co(III) complexes*, namely $\text{Co}(\text{NH}_3)_3^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{dip})_3^{3+}$ and $\text{Co}(o\text{-phen})_3^{3+}$. We have extended this range by a further four Co(III) complexes, namely $\text{Co}(\text{tn})_3^{3+}$, $\text{Co}(\text{pn})_3^{3+}$, $\text{Co}(4,7\text{-dimethyl-}o\text{-phen})_3^{3+}$ and $\text{Co}(5,6\text{-dimethyl-}o\text{-phen})_3^{3+}$.

EXPERIMENTAL

As in previous studies, high-voltage electrophoresis was carried out in a Camag apparatus with Whatman No. 1 paper. The spots of the Co(III) complexes were detected by spraying with aqueous ammonium polysulphide solution.

Preparation of the complexes

$\text{Co}(\text{tn})_3\text{Cl}_3$ and $\text{Co}(\text{pn})_3\text{Cl}_3$ were prepared by means of the synthesis used for $\text{Co}(\text{en})_3\text{Cl}_3$. $\text{Co}(\text{pn})_3\text{Cl}_3$ yields a mixture of isomers⁶, which are separable by chromatography with *n*-butanol-concentrated hydrochloric acid-water (6:1:3) into three fractions, the fastest being a mixture of D-Co(+)(pn)₃Cl₃ and L-Co(-)(pn)₃Cl₃, which was used in this work.

$\text{Co}(4,7\text{-dimethyl-}o\text{-phen})_3^{3+}$ and $\text{Co}(5,6\text{-dimethyl-}o\text{-phen})_3^{3+}$ were prepared by the method used for $\text{Co}(o\text{-phen})_3\text{Cl}_3$ (ref. 4). The other compounds were as described and employed previously.

* The following abbreviations are used: en = ethylenediamine; pn = propylenediamine; tn = trimethylenediamine; dip = dipyridyl; *o*-phen = *ortho*-phenanthroline; 4,7-dimethyl-*o*-phen = 4,7-dimethyl-*ortho*-phenanthroline; 5,6-dimethyl-*o*-phen = 5,6-dimethyl-*ortho*-phenanthroline.

RESULTS

The results are presented as schematic electropherograms in Fig. 1. Chloride and bromide as electrolytes yield essentially similar migration sequences, *i.e.*, the smallest complex moves fastest and the largest complex slowest. Nitrite, nitrate and thiocyanate also give about the same sequences. Thiocyanate produces tailing and double spots, which may be due to the occurrence of certain reactions, possibly reduction and complex formation.

The main feature of the results is that the sequences are different in chlorate,

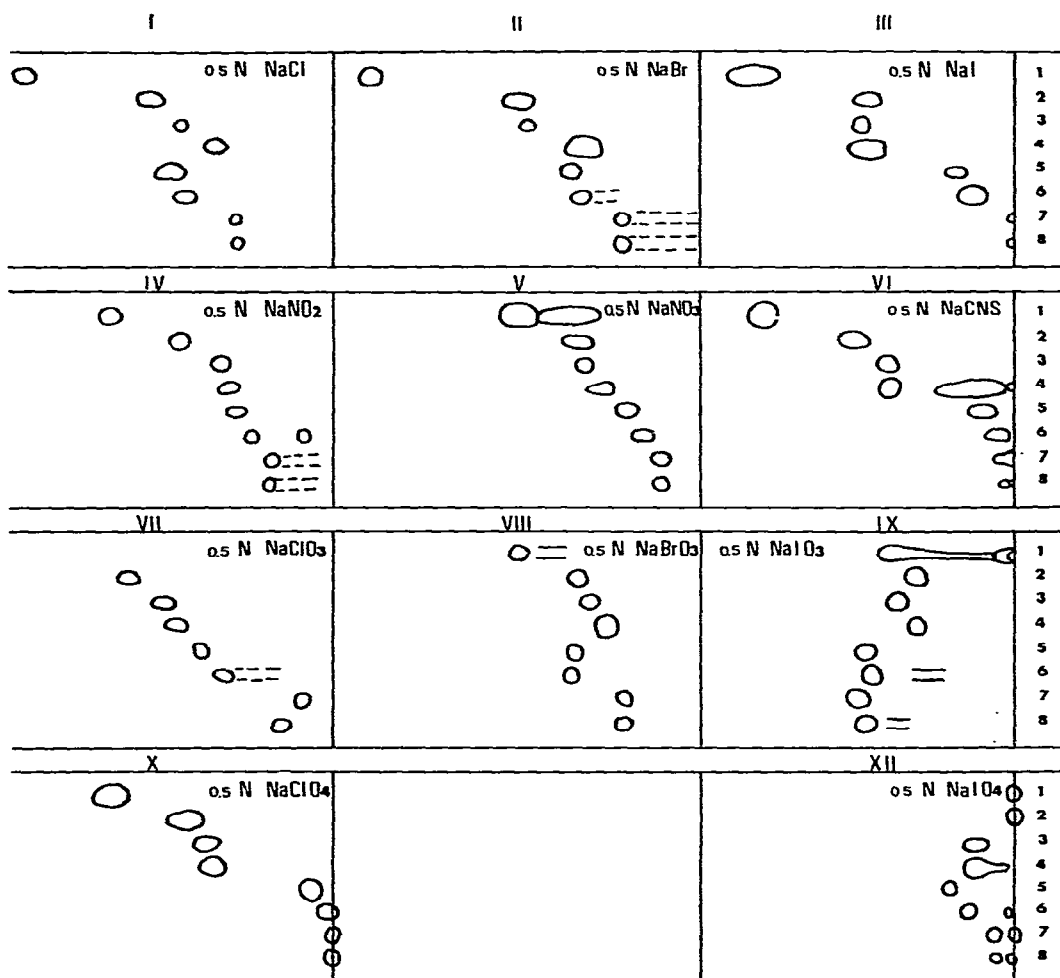


Fig. 1. Schematic electropherograms of cobalt complexes on Whatman No. 1 paper in a Camag high-voltage apparatus in 0.5 *N* sodium salt solutions. Voltage, 1500 V; temperature, 6–8°; time, 30 min. Complexes (from top to bottom) in each electropherogram: 1 = $\text{Co}(\text{NH}_3)_3^{3+}$; 2 = $\text{Co}(\text{en})_3^{3+}$; 3 = $\text{Co}(\text{tn})_3^{3+}$; 4 = $\text{Co}(\text{pn})_3^{3+}$; 5 = $\text{Co}(\text{dip})_3^{3+}$; 6 = $\text{Co}(\text{o-phen})_3^{3+}$; 7 = $\text{Co}(\text{4,7-dimethyl-o-phen})_3^{3+}$; 8 = $\text{Co}(\text{5,6-dimethyl-o-phen})_3^{3+}$.

bromate and iodate (which have not been studied previously). The latter two give the same sequences as divalent anions such as sulphate and chromate. The tendency of iodate to form hydrogen bonds with trivalent aquo complexes, *e.g.*, $\text{Al}(\text{H}_2\text{O})_3^{3+}$, is already known⁷. Our results seem to indicate that this is a general phenomenon, not restricted to aquo complexes and also for BrO_3^- and not only for IO_3^- .

Perchlorate, as reported previously¹⁻⁵, interacts much more strongly with large cations while periodate produces almost the same sequence as sulphate, *i.e.*, a hydrogen bonding type of interaction. As periodate is probably a polyvalent anion under the conditions used here, this result is not surprising. Iodide gives a sequence similar to perchlorate.

There is little difference in electrophoretic movement between $\text{Co}(4,7\text{-dimethyl-}o\text{-phen})_3^{3+}$ and $\text{Co}(5,6\text{-dimethyl-}o\text{-phen})_3^{3+}$, but both move much more slowly than $\text{Co}(o\text{-phen})_3^{3+}$ in most electrolytes. This result is unexpected if one considers that $\text{Co}(o\text{-phen})_3^{3+}$ and $\text{Co}(\text{dip})_3^{3+}$ have much smaller differences in electrophoretic movement, *e.g.*, 0.5 *N* sodium chloride solution. A similar effect due to projecting methyl groups can be seen in 0.5 *N* sodium chloride solution (but only in this solution) for the sequence of movement of $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{tn})_3^{3+}$ and $\text{Co}(\text{pn})_3^{3+}$. In all other electrolytes the differences in outer-sphere complexing seem to be more important. The effect due to addition of methyl groups to the complexant is more striking in partition chromatography with *n*-butanol-water-acid mixtures.

TABLE I

R_F VALUES OF Co(III) COMPLEXES ON POLYGRAM CEL 400 THIN LAYERS

Complex	Solvent	
	<i>n</i> -Butanol-HClO ₄ -water (7:1:2)	<i>n</i> -Butanol-HCl-water (6:1:3)
$\text{Co}(\text{NH}_3)_3^{3+}$	0	0.07
$\text{Co}(\text{en})_3^{3+}$	0.32	0.21
$\text{Co}(\text{tn})_3^{3+}$	0.53	0.24
$\text{Co}(\text{pn})_3^{3+}$ (symmetrical)	0.83	0.61
$\text{Co}(\text{dip})_3^{3+}$	~0.4	0.07
$\text{Co}(o\text{-phen})_3^+$	0.50	0.07
$\text{Co}(4,7\text{-dimethyl-}o\text{-phen})_3^{3+}$	1.0 + comet	0.27
$\text{Co}(5,6\text{-dimethyl-}o\text{-phen})_3^{3+}$	1.0 + comet	0.30

Table I gives the R_F values of all of the complexes mentioned above in one solvent containing perchloric acid and another containing hydrochloric acid. In both solvents there is a small difference in R_F values between $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{tn})_3^{3+}$ but a large difference between these and $\text{Co}(\text{pn})_3^{3+}$. Also, the complexes $\text{Co}(4,7\text{-dimethyl-}o\text{-phen})_3^{3+}$ and $\text{Co}(5,6\text{-dimethyl-}o\text{-phen})_3^{3+}$ always move much faster than $\text{Co}(o\text{-phen})_3^{3+}$, while $\text{Co}(\text{dip})_3^{3+}$ usually moves with the same R_F value as $\text{Co}(o\text{-phen})_3^{3+}$. Thus, in non-aqueous solvents the additional methyl group(s) have a much larger effect than differences in ring structure such as those between $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{tn})_3^{3+}$ and $\text{Co}(o\text{-phen})_3^{3+}$ and $\text{Co}(\text{dip})_3^{3+}$.

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