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## Note

### Paper electrophoretic study of ion-pair formation

#### XIV. Resolution of optically active cobalt(III) complexes

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Whereas particular attention has recently been paid to studies on the chromatography resolution of optical enantiomers, there have been few reports on the separation of this type of compounds by electrophoretic techniques. In our laboratory an electrophoretic method for resolving optical isomers in chiral media has been developed<sup>1-3</sup>. It consists in transforming the enantiomers into diastereoisomers by interaction (ion-pair formation) with an optically active counter-ion during the course of the electrophoresis and in the separation of the two diastereoisomers by the difference in their electrophoretic mobilities. So far this method has been used to separate optically active cationic and/or anionic complexes of Co(III), Cr(III), Fe(III) and Ni(II)<sup>1-3</sup>. High-voltage paper electrophoresis (HVE) and high-performance paper electrophoresis (HPPE) (a rapid electrophoretic method recently developed that yields good separations within a few minutes)<sup>4,5</sup> were utilized for those investigations. In the present paper we describe the electrophoretic resolutions obtained for some further racemic cobalt complexes with mixed ligands.

#### EXPERIMENTAL AND RESULTS

For HVE we used the Camag high-voltage paper electrophoresis apparatus

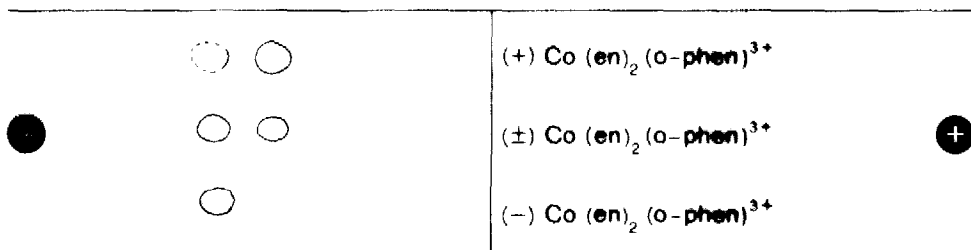


Fig. 1. Electropherogram of (+), (-) and ( $\pm$ )  $\text{Co}(\text{en})_2(\text{o-phen})^{3+}$  complexes. Separation of the optical isomers by high-voltage electrophoresis (3000 V for 45 min with Whatman No. 1 paper) in a 0.2 M solution of antimony potassium (+)-tartrate.

with Whatman No. 1 filter-paper. The cooling plate of the apparatus was kept at 6–8°C. The electrophoresis was run from 2000 to 3500 V; 0.1–0.3 M solutions of the electrolytes were used. The evaporation from the paper strips during the run is negligible.

The apparatus used for HPPE consisted of an LKB power supply (Model 337 IE), an electrophoretic cell without a cooling system and glass plates 10 cm long, 1–2 cm wide and 4 mm thick. Electric field applied: 120 V/cm; in the figure legends we give the values of the voltage applied, as the distance between the electrodes was always 10 cm. Whatman No. 1 paper strips were used.

The electroosmotic flow in HVE as well as in HPPE was measured by observing the movement of H<sub>2</sub>O<sub>2</sub>; the figures give distances already corrected for electroosmotic flow.

The samples were prepared and resolved into their optical isomers as described in the literature<sup>6–8</sup> or similarly. We placed the racemic mixture side by side with the two resolved optical isomers in the electropherograms (see Fig. 1). The spots of the cobalt(III) complexes were detected by spraying the paper sheets with Dragendorff reagent. A Camag TLC/HPTLC scanner was used for adsorption measurements directly on the electropherograms.

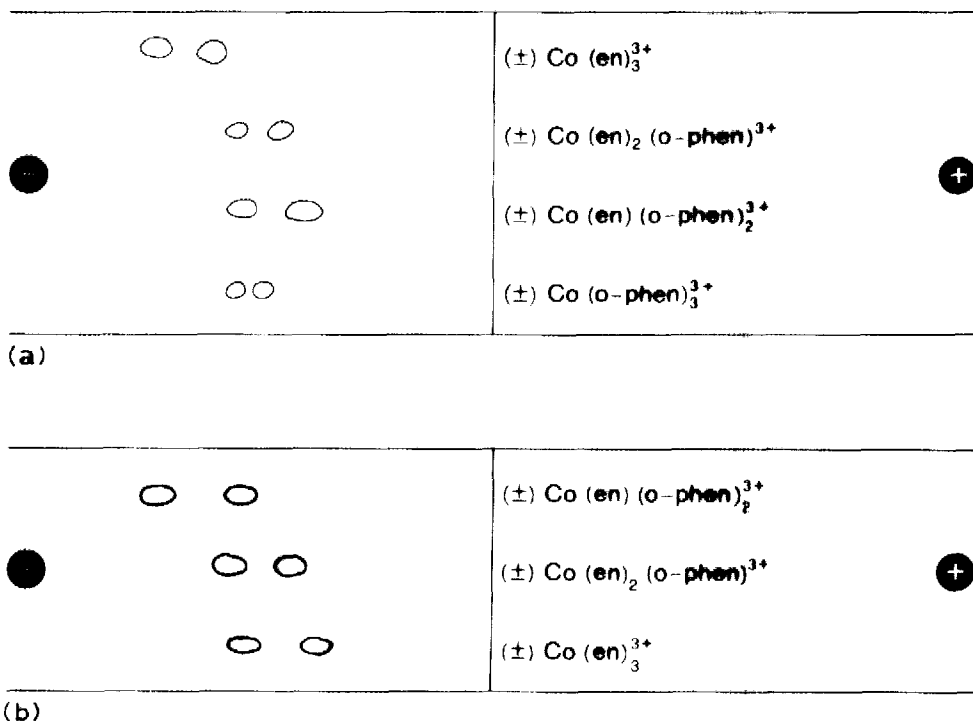


Fig. 2. (a) Separation of the optical isomers of cobalt(III) complexes with mixed ligands by HVE (2500 V for 1 h with Whatman No. 1 paper) in 0.3 M arsenic sodium (+)-tartrate. (b) Electropherogram of cobalt(III) complexes with mixed ligands on Whatman No. 1 paper at 3000 V for 45 min in 0.2 M antimony potassium (+)-tartrate (Camag HVE apparatus).

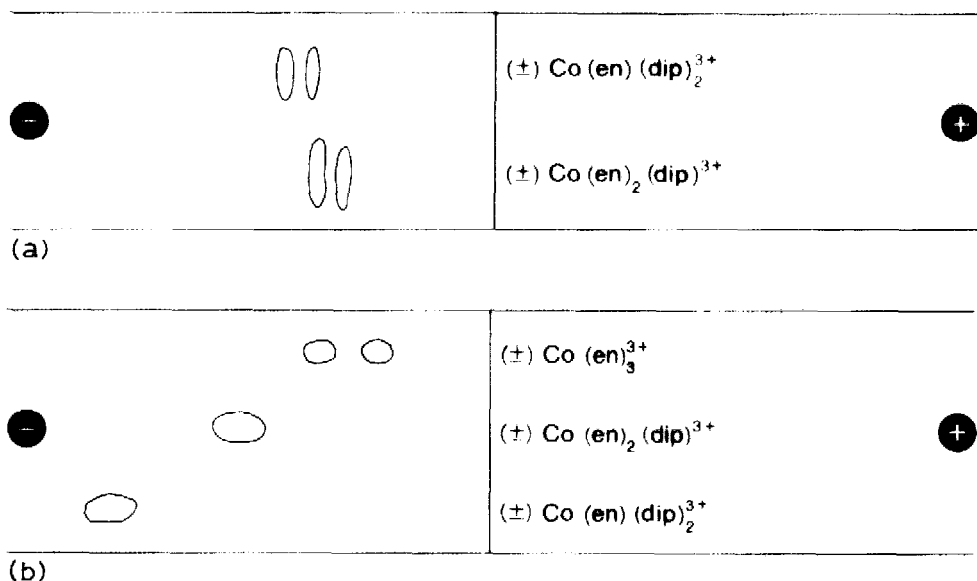


Fig. 3. (a) Separation of the optical isomers of  $\text{Co}(\text{en})(\text{dip})_2^{3+}$  and  $\text{Co}(\text{en})_2(\text{dip})^{3+}$  by HVE (2000 V for 1 h with Whatman No. 1 paper) in a 0.25 M solution of arsenic sodium (+)-tartrate. (b) Electropherogram of cobalt(III) complexes on Whatman No. 1 paper at 3000 V for 45 min by HVE (Camag apparatus) in 0.2 M antimony potassium (+)-tartrate.

Figs. 1-4\* show the HVE electropherograms of racemic cobalt(III) complexes with mixed ligands in solutions of arsenic sodium (+)-tartrate and antimony potassium (+)-tartrate. Good separations were achieved with all the solutions used for racemic  $\text{Co}(\text{en})_2(o\text{-phen})^{3+}$  and  $\text{Co}(\text{en})(o\text{-phen})_2^{3+}$  (Fig. 2). Although the separation is better in antimony tartrate solution (Fig. 2b), the arsenic tartrate solution permits also the resolution of racemic  $\text{Co}(o\text{-phen})_3^{3+}$  (Fig. 2a). Fig. 3 shows the electropherograms of  $\text{Co}(\text{en})_2(\text{dip})^{3+}$  and  $\text{Co}(\text{en})(\text{dip})_2^{3+}$ ; it is possible to separate the optical isomers of these complexes in arsenic potassium (+)-tartrate; in antimony tartrate solution no resolutions are obtained.

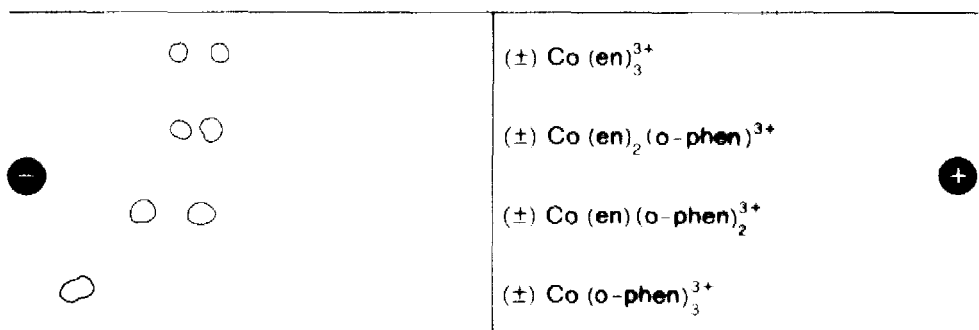


Fig. 4. Separation of the optical isomers of cobalt(III) complexes by (HPPE) at 1200 V for 5 min with Whatman No. 1 paper in 0.1 M antimony potassium (+)-tartrate solution.

\* en = Ethylenediamine; o-phen = 1.10-phenanthroline.

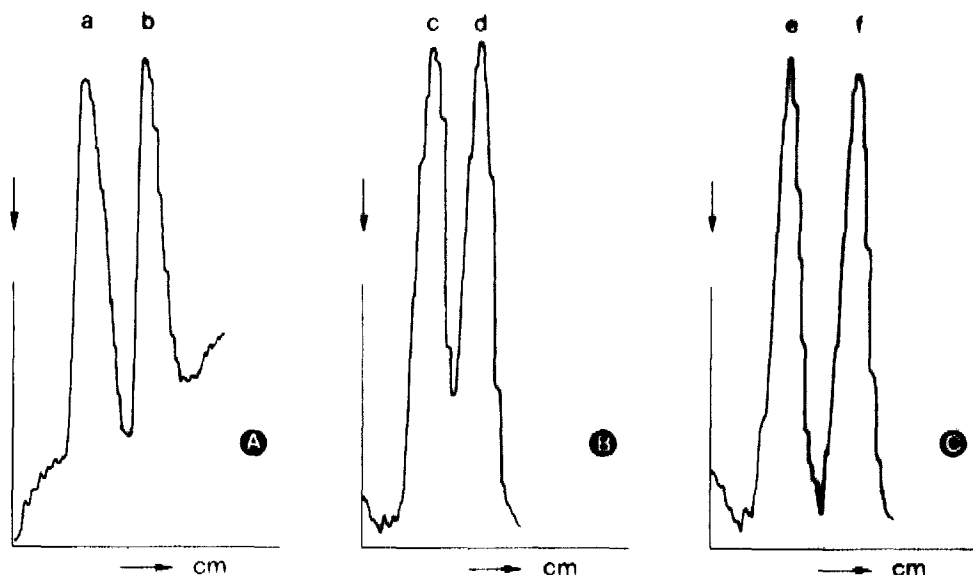


Fig. 5. Scans of some optical isomers of cobalt(III) complexes separated by HVE (separations as in Fig. 2b). Wavelength 525 nm. Slit length: 5 mm. Slit width: 0.2 mm.  $V_p = 0.5$  mm/sec.  $V_s = 0.4$  mm/sec. A,  $(\pm)\text{-Co(en)}_3^{3+}$ ; B,  $(\pm)\text{-Co(en)}_2(o\text{-phen})^{3+}$ ; C,  $(\pm)\text{-Co(en)}(o\text{-phen})_2^{3+}$ .

Fig. 4 shows the results obtained with the high-performance paper electrophoresis apparatus. With this technique it is possible to resolve the optical isomers of  $\text{Co(en)}_2(o\text{-phen})^{3+}$  and  $\text{Co(en)}(o\text{-phen})_2^{3+}$ , but no separations are obtained with the cobalt(III) complexes with en and dip ligands. Finally, in Fig. 5 we report the scans of some separated complexes carried out with a Camag scanner directly on the electropherograms. With this measurement it is possible to control the separations obtained and also to determine the ratios of the isomers separated.

From all the experiments reported, the arsenic potassium (+)-tartrate was found to be the best separating agent among the chiral anions normally used although the antimonyl (+)-tartrate gives the best separations with the complexes containing en and *o*-phen.

As discussed previously<sup>1</sup>, for effective separations of optical isomers it is not sufficient that a racemic mixture of a complex is in an optical environment, but that outer-sphere complexes are formed; the results obtained confirm that supposition. Until now the best separations were obtained when hydrogen bonding was involved. A comparison of the results obtained by HVE and HPPE leads us to conclude that for this type of compounds HVE is the most versatile; when it is possible to use the HPPE apparatus there is the great advantage of shortening the resolution time ( $\leq 5$  min).

We would like to stress that electrophoretic methods are very useful for this type of resolution. There is the advantage that it is possible to study the interactions in solution since the paper does not interfere during the separation processes. Moreover, the use of the scanning apparatus allows control of the separations obtained directly on the paper.

A part of these results has been presented previously<sup>9</sup>.

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