Journal of Chromatography, 318 (1985) 440–445
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,273

Note

Paper electrophoretic study of ion pair formation

XV*. Resolution of optically active cobalt(III)–cyclohexanediamine complexes

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(Received October 5th, 1984)

During work on the resolution of enantiomers by ion-pair formation in the liquid phase for metal complexes[1–4] using electrophoresis, we studied four catoptromers of Co(±)-$(chxn)_3^{3+}$, where chxn = *trans*-cyclohexane-1,2-diamine. The preparation and resolution of these complexes have already been reported[5,6]. A cation exchanger was used as a stationary phase in liquid column chromatography. In this work, paper electrophoresis was used because is a fast technique and gives a more direct insight into the nature of the complex–medium adduct.

EXPERIMENTAL AND RESULTS

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[7] were utilized. For HVE we used a Camag high-voltage apparatus with Whatman No. 1 paper. Usually 2000–3500 V were applied to the strips. Under the conditions normally used, the cooling arrangement is such as to remove the Joule heat produced in the paper during the passage of current. 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, 4–5 cm wide and 4 mm thick. The electric field applied was 80 V/cm. The figure legends indicate the voltage applied; the distance between the electrodes was always 10 cm. The electroosmotic flow in both HVE and HPPE was measured by observing the movement of H_2O_2; give distance already corrected for electroosmotic low are indicated in the Figures.

The samples were prepared and resolved into their isomers as described in the literature. We placed the mixture side-by-side with the resolved isomers in the electropherograms.

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* For Part XIV, see ref. 4.

0021-9673/85/$03.30

We used sodium (+)- and (−)-tartrate (Carlo Erba), ammonium (+)-tartrate (BDH), potassium antimonyl (+)-tartrate (BDH) and sodium arsenyl (+)-tartrate (prepared as reported in the literature) as electrolytes. When we used aqueous solutions of tartrate as the electrolyte, the spots of the cobalt(III) complexes were detected by spraying the electropherograms with aqueous ammonium sulphide; with antimonyl and arsenyl tartrate we used Dragendorff reagent. A Camag TLC/HPTLC scanners was used for adsorption measurements directly on the electropherograms.

Figs. 1–5 show the electrophoretic separations of the eight isomers of tris-cobalt(III)(*trans*-cyclohexane-1,2-diamine). As already reported, this complex consists of two series of isomers with the configuration Λ and Δ around the metal ion. For each configurational series the possible ligand conformations give rise to four diastereoisomers, which have been termed lel$_3$, lel$_2$ob, lel ob$_2$, ob$_3$. Fig. 1a and b show the electropherograms of a mixture of all isomers of cobalt(III)(chxn). It can be seen that using 0.2 *M* sodium phosphate as the electrolyte, in the electropherograms there

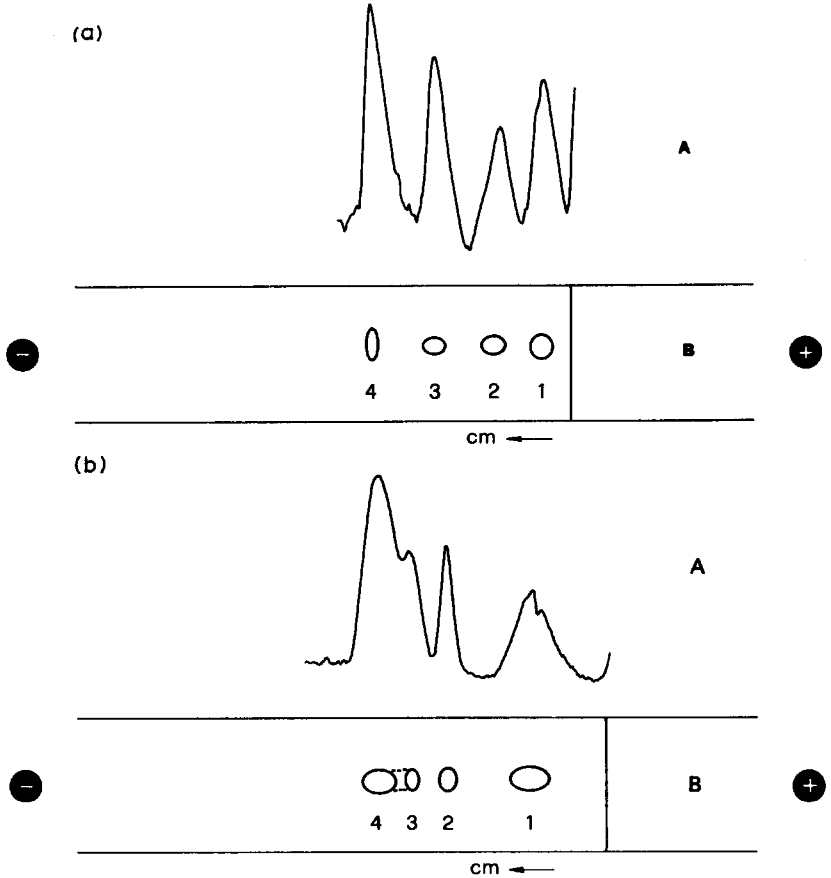


Fig. 1. Separation of four catoptromer complexes of cobalt(III)(±)-(chxn)$_3^{3+}$ by high-voltage electrophoresis on Whatman No. 1 paper at 1500 V for 60 min. (a) 0.2 *M* solution of sodium phosphate; (b) 0.2 *M* solution of sodium sulphate. B = Electropherogram; A = scan of the separate isomers in electropherogram B. Wavelength = 450 nm; slit length = 4 mm; slit width = 0.1 mm; V_p (plate travel) = V_c (recorder chart speed) = 1 mm/sec. 1 = Λ + Δ lel$_3$; 2 = Λ + Δ lel$_2$ob; 3 = Λ + Δ lel ob$_2$; 4 = Λ + Δ ob$_3$.

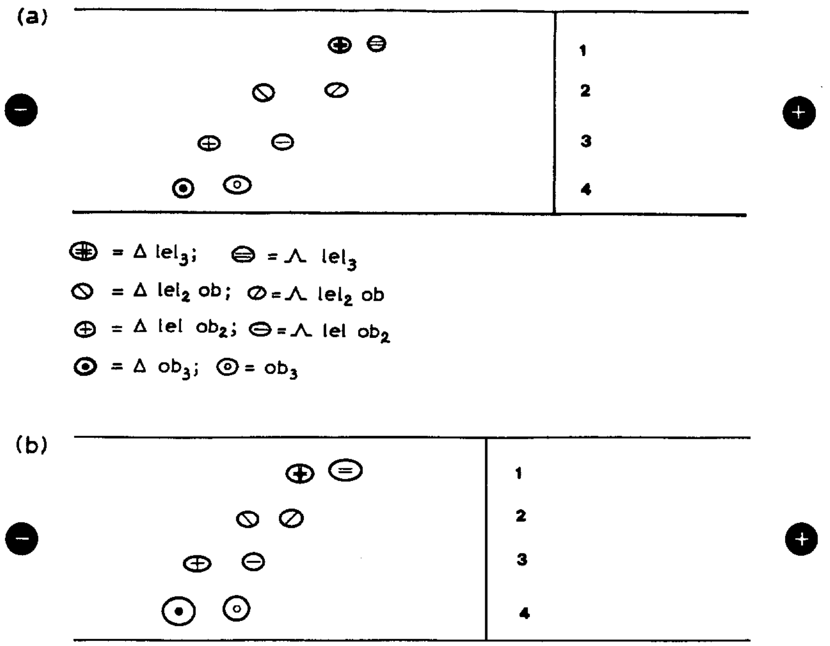


Fig. 2. Resolution of Λ and Δ forms of the four catoptromer complexes of cobalt(III)-*trans*-cyclohexane-1,2-diamine on Whatman No. 1 paper at 2000 V for 45 min by HVE (Camag apparatus). (a) Sodium (+)-tartrate, 0.2 M, pH = 6.8; (b) ammonium (+)-tartrate, 0.2 M, pH = 6.8.

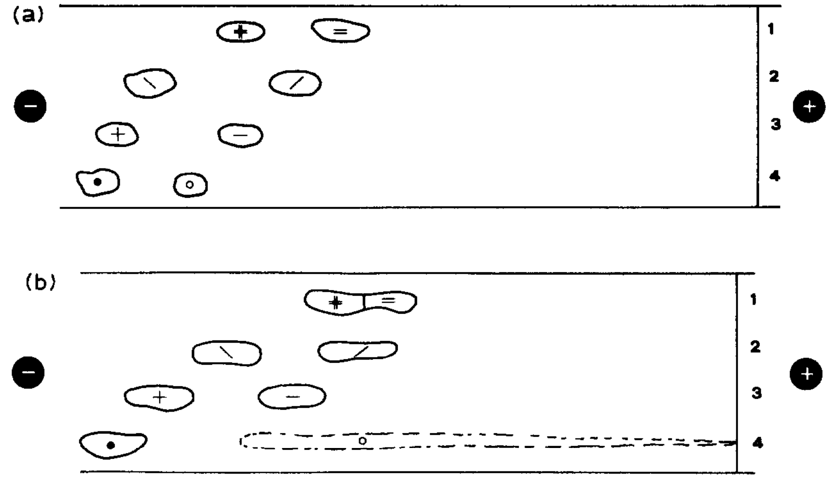


Fig. 3. Resolution of Λ and Δ forms of the four catoptromer complexes of cobalt(III)-*trans*-cyclohexane-1,2-diamine on Whatman No. 1 paper at 3500 V for 45 min by HVE (Camag apparatus). (a) Potassium antimonyl (+)-tartrate, 0.2 M; (b) sodium arsenyl (+)-tartrate, 0.2 M. Symbols as in Fig. 2.

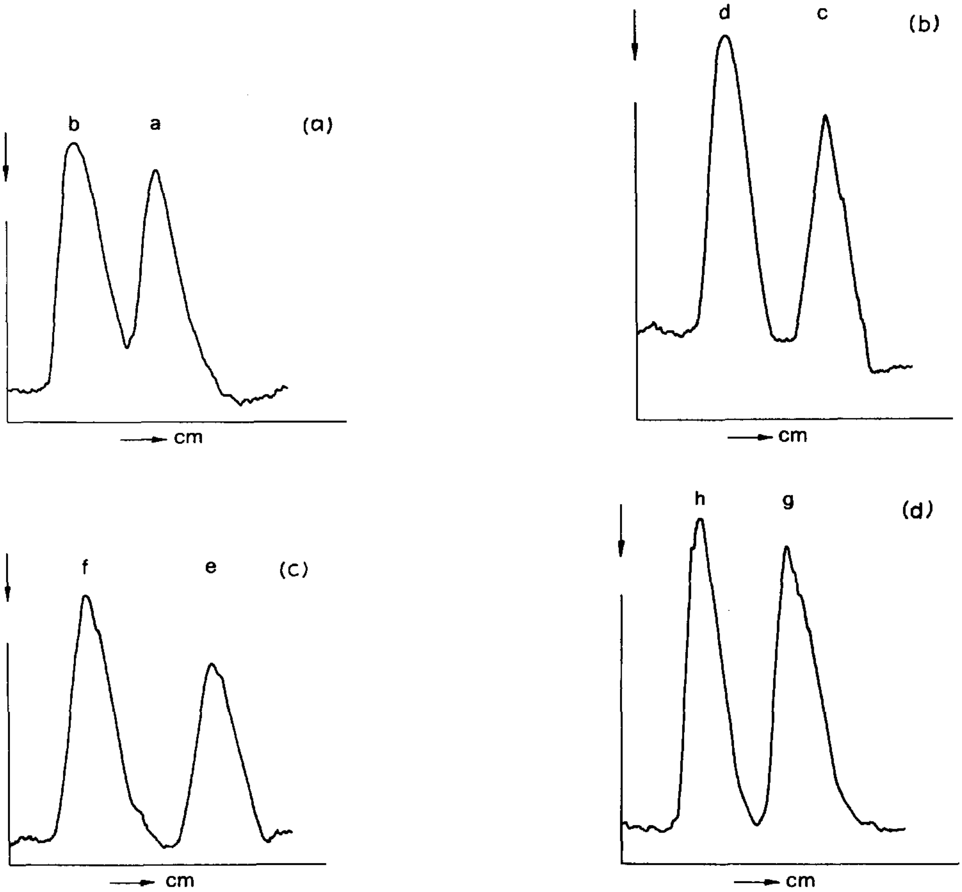


Fig. 4. Scan of the optical isomers of cobalt(III)-*trans*-cyclohexane-1,2-diamine separated by HVE (separations as in Fig. 3a). Wavelength = 525 nm; slit length = 4 mm; slit width = 0.1 mm; V_p = V_c = 1 mm/sec. Peaks: a = Λ lel$_3$, b = Δ lel$_3$, c = Λ lel$_2$ob, d = Δ lel$_2$ob, e = Λ lelob$_2$, f = Δlelob$_2$, g = Λ ob$_3$, h = Δ ob$_3$.

are four completely separated zones corresponding to (1) Λ + Δ lel$_3$, (2) Λ + Δ lel$_2$ob, (3) Λ + Δ lel ob$_2$ and (4) Λ + Δ ob$_3$; Fig. 1 (A) shows the scan of the electropherogram. With 0.2 *M* sodium sulphate as the electrolyte, zones 1 and 2 are better separated than in phosphate, but not the zones 3 and 4.

Figs. 2 and 3 show the resolution of optical isomers of the four fractions previously separated (1–4); the electrolytes used were aqueous solutions of sodium (+)- and (−)-tartrate, ammonium (+)-tartrate, potassium antimonyl (+)-tartrate and sodium arsenyl (+)-tartrate. In all the electrolytes it is possible to resolve the pair of isomers studied, the best results being obtained with potassium antimonyl (+)-tartrate. In this solution the distances between the spot centres were greater.

Fig. 4a–d show the scans of the separated isomers carried out with a Camag scanner directly on the electropherograms.

Table I illustrates the agreement of the mobilities between the Δ and Λ forms of Cobalt(III) complexes in the various electrolytes used. Fig. 5 reports the results

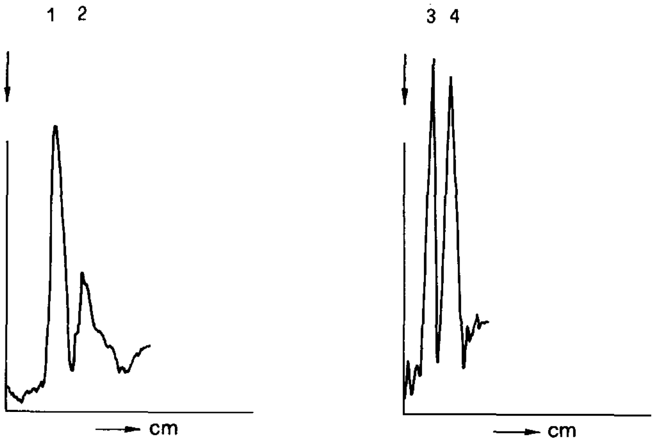


Fig. 5. Scans of some optical isomers of cobalt(III)-*trans*-cyclohexane-1,2-diamine complexes on Whatman No. 1 paper at 1000 V for 8 min with 0.1 *M* potassium antimonyl (+)-tartrate as electrolyte by HPPE. Wavelength = 525 nm; slit length = 4 mm; slit width = 0.1 mm; V_p = 1 mm/sec; V_c = 0.5 mm/sec. (1) Λ lel$_2$ ob; (2) Δ lel$_2$ ob; (3) Λ lel ob$_2$; (4) Δ lel ob$_2$.

obtained with the high-performance paper electrophoresis apparatus. With this technique it was possible to resolve only the optical isomers of Λ and Δ lel ob$_2$ and Λ and Δ lel$_2$ob.

DISCUSSION AND CONCLUSION

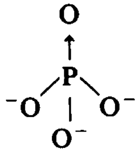
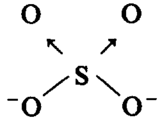
Separation of catoptromers

In electrophoresis the separation of a mixture is due to the different interactions between the conducting medium and the individual components, in this instance between PO$_4^{3-}$ or SO$_4^{2-}$ anions and the cation complexes. The stronger the interaction the less mobile is the ion-pair. Coulombic forces are in general responsible for the gross effect in ion-pair formation, but weaker forces are involved when a discriminating factor exists, as is apparent in this instance. $\Lambda(\delta\delta\delta)$ and $\Delta(\lambda\lambda\lambda)$, the lel$_3$ complexes, have D_3 symmetry,, $\Lambda(\lambda\lambda\lambda)$ and $\Delta(\delta\delta\delta)$, the ob$_3$ complexes, have pseudo-D_3 symmetry and the mixed complexes have approximate C_2 symmetry[8].

TABLE I

AGREEMENT OF MOBILITIES BETWEEN Δ AND Λ FORMS OF COBALT(III)(chxn)$_3^{3+}$ COMPLEXES

Electrolyte	*lel$_3$*	*lel$_2$ob*	*lel ob$_2$*	*ob$_3$*
Ammonium (+)-tartrate	1.20	1.35	1.27	1.17
Sodium (+)-tartrate	1.20	1.17	1.22	1.24
Potassium antimonyl (+)-tartrate	1.24	1.32	1.29	1.16
Sodium arsenyl (+)-tartrate	1.15	1.35	1.30	1.41

The several orientations of the cyclohexane ring with respect to the C_3 or pseudo-C_3 axis of symmetry give the net result of forcing the N–H bonds into differents orientations with respect to the same axis. The lel_3 conformations, as has been pointed previously for similar systems[8], have N–H bonds pointing in the same direction of the C_3 axis, which render the two opposite triangular faces of the octahedron prone to bi-capping by the tripodal  and less amenable to the  anions.

The ob_3 isomers have pseudo-D_3 symmetry with the N–H bonds twisted away from the three-fold axis direction with H–H distances greater by about 0.12 Å with respect to those found in the lel_3 isomers, thus rendering more difficult hydrogen bond formation with the anions. The behaviour of the mixed conformational complexes is easily explained as an intermediate case.

Separation of optical isomers

Here we can confirm a general trend outlined previously: although arsenyl (+)-tartrate is generally the most versatile resolving agent for metal complexes, whenever either hydrogen bonds are available or a more flexible counter ion is required, antimonyl (+)-tartrate is better suited to the conditions; this is the case with the optical isomers of cobalt(III) that we have tested so far.

ACKNOWLEDGEMENTS

Thanks are due to Mr. M. Viola for drawing the figures. This work was supported by the Chimica Fine e Secondaria project of the National Research Council.

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