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COLUMN-CHROMATOGRAPHIC STUDY ON THE ISOMERISM OF THE BIS(ETHYLENEDIAMINE)-SARCOSINATOCOBALT(III) ION WITH TWO ASYMMETRIC CENTERS

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A column-chromatographic method has been successfully applied to the separation of all the four possible isomers of $[Co(sar)(en)_2]^{2+}$ ($sar = CH_3NHCH_2COO^-$, $en = H_2NCH_2CH_2NH_2$), to the correlation of their absolute configuration, and to the determination of the difference in stability between the diastereomers(0.9 kcal/mol).

The isomerism of the $[Co(sar)(en)_2]^{2+}$ ion with two asymmetric centers, one at the cobalt and the other at the sarcosinate nitrogen atom, was originally studied by Meisenheimer *et al.*,[1)] who claimed to have isolated bromocamphorsulfonate of the [Co +, N -] isomer in pure form and to have identified two other isomers at least in impure state. However, Buckingham *et al.*[2)] were unsuccessful in their attempt to reproduce some of Meisenheimer's results, and obtained only two of the four possible isomers. Recently they carried out strain energy calculations, which suggested presence of the less stable Δ-$[Co(R\text{-}sar)(en)_2]^{2+}$ isomer in a detectable concentration(*ca.* 5 %).[3)] Nevertheless they thought the actual ΔG difference probably to exceed *ca.* 2 kcal/mol, since their careful ion-exchange experiments failed to show any isomer separation.

In view of the stereochemical significance of evaluating the actual ΔG difference between the isomers, we have performed another ion-exchange study of the complex with the intention of detecting and isolating the less stable isomers probably present as minor constituents in a reaction mixture.

A solution containing the $[Co(sar)(en)_2]^{2+}$ isomers was prepared according to

Liu and Douglas.[4)] After a preliminary chromatographic purification of the complex as a mixture of the isomers, the isomers were chromatographically separated with an SP-Sephadex column(ϕ2.7 × 139 cm) and a 0.11 M sodium L-tartrato-antimonate(III) eluent(pH 3.2). The elution curve given in Fig. 1 showed three bands, A, B, and C, with areas of an approximate ratio of 1.0 : 1.0 : 8.8. Similar results were also obtained with the complex prepared by a different method after Buckingham *et al.*[2)] Figure 2 shows circular dichroism(CD) spectra measured on the fractions, a, b, c_1, and c_2, indicated in Fig. 1. An approximate

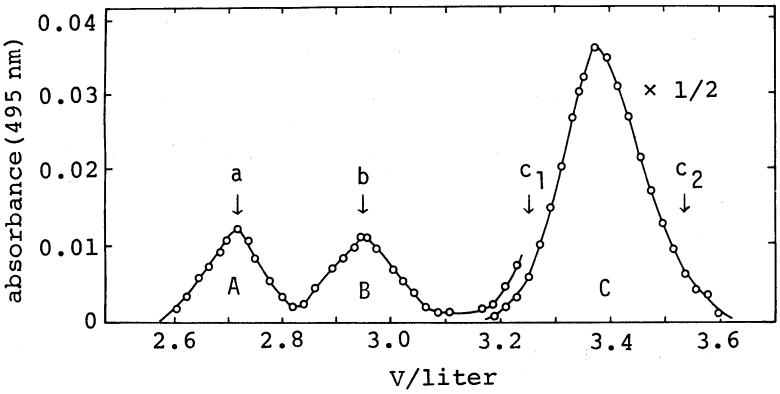

Fig. 1. The elution curve of $[Co(sar)(en)_2]^{2+}$.

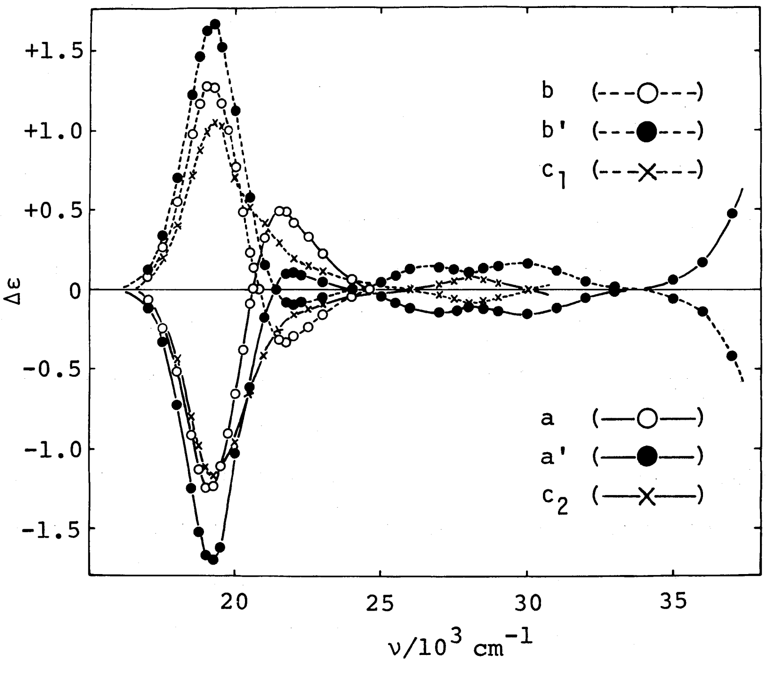

Fig. 2. The circular dichroism spectra of the solutions.

mirror-image relationship was observed between the spectra of c_1 and c_2, which are very similar to the spectra reported for Λ-$[Co(\mathit{R}\text{-sar})(en)_2]^{2+}$ and Δ-$[Co(\mathit{S}\text{-sar})(en)_2]^{2+}$, respectively, by Buckingham *et al.*[3,5,6] On the other hand, only an unsatisfactory mirror-image relationship was observed between the spectra of a and b, probably because of diastereomeric interactions of the isomers with L-tartratoantimonate(III) ions. Therefore solutions containing no optically active ions other than the complex ions were prepared for the measurement of the CD spectra. Such hydrochloric acid solutions, a' and b', were obtained from the portions of the eluate belonging respectively to the A and B bands by means of ion-exchange technique. These solutions, a' and b', showed mirror-image spectra of each other, as can be seen from Fig. 2. Thus it was presumed that the complexes contained in a' and b' would be the less stable isomers, Δ-$[Co(\mathit{R}\text{-sar})(en)_2]^{2+}$ and Λ-$[Co(\mathit{S}\text{-sar})(en)_2]^{2+}$, respectively.

In order to obtain conclusive evidence for this presumption and to collect further information about the relative stabilities of the isomers, equilibrium mixtures of the isomers were examined for composition. After the C-band portion of the eluate was diluted with water, the contained complexes were sorbed on a small amount of SP-Sephadex and then eluted with a 0.4 M sodium acetate solution of pH 7.6. The resulting solution was allowed to stand for 48 hours at room temperature to reach the isomerization equilibrium, and then the equilibrated isomers were chromatographically separated in the way described above. The elution curve was very similar to that given in Fig. 1. A similar treatment of the combined A- and B-band portions of the eluate (Fig. 1) also gave a similar elution curve. A separate treatment of the A-band portion of the eluate gave the elution curve given in Fig. 3, where an SP-Sephadex column of a smaller size (ϕ1.2 × 77 cm) was used. The measurement of CD spectra showed that the isomers eluted in the first and second bands of this experiment correspond to those contained in a and c_2, respectively

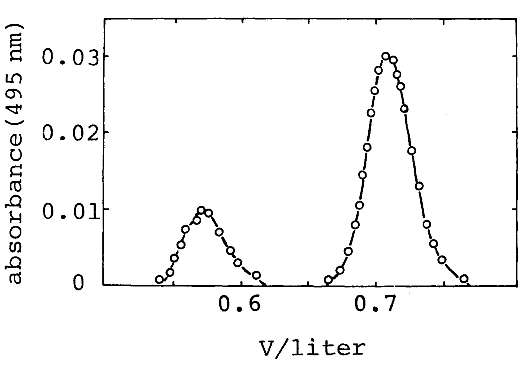

Fig. 3. The elution curve of the equilibrium mixture resulting from the complex contained in the A band of Fig. 1.

(Fig. 1). This draws the conclusion that the A-band portion of the eluate contained Δ-$[Co(R\text{-sar})(en)_2]^{2+}$, which on equilibration partly isomerized into Δ-$[Co(S\text{-sar})(en)_2]^{2+}$, the isomer contained in c_2. As deduced from the ratio of areas of the A, B, and C bands of the elution curve (1.0 : 1.0 : 8.5, as average), the Δ-$[Co(R\text{-sar})(en)_2]^{2+}$ and Λ-$[Co(S\text{-sar})(en)_2]^{2+}$ isomers giving the A and B bands are only 0.9 kcal/mol less stable than the more stable isomers giving the C band. This experimental value of the ΔG difference is about half the value(*ca.* 1.7 kcal/mol) estimated by Buckingham *et al.*$^{3)}$ from strain energy calculations.

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