

*Adsorbabilities of Diacidotetrammine Type Cobalt(III)
Complex Ions on a Cation Exchanger¹⁾*

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Since King and Walter²⁾ reported the separation of the cis and trans isomers of dinitrotetramminecobalt(III) ions by ion-exchange chromatography, the same kind of study has been extensively developed in our laboratory on other isomers of the diacidotetrammine type complex, and as a result it has been found that the trans isomers were, as a general rule, eluted faster than the corresponding cis isomers^{3,4)}. In the present work, some supplementary experiments for confirming the above rule are attempted by using the complexes which are relatively unstable in aqueous solutions. Furthermore, the adsorbabilities of all the complexes, including the previous ones, on a cation exchanger are compared.

Experimental

Complexes.—All the complexes were prepared according to the literatures⁵⁾, and their identity and purity were examined with the absorption

spectra in an alcoholic aqueous solution. The complexes used were as follows: the trans-cis and cis-trans isomers of $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$ and the trans and cis isomers of $[\text{Co en}_2\text{Cl}_2]$, $[\text{Co en}_2\text{Br}_2]\text{Br}$ and $[\text{Co en}_2(\text{NO}_2)\text{Cl}]\text{Cl}$.

Elution Methods.—A column (1×10 cm.) which contained 5 g. of Ammberlite IR-120 (50~100 mesh) in sodium form was used, and the sample solution was prepared in concentrations ranging from 0.01 to 0.06 M depending on the solubility of the complexes. Fifteen milliliters of each sample solution was applied to the column, and then the column was eluted with 0.15 M sodium chloride ethanol-water (1:1) solution. The velocity of elution was 0.5 ml./min. Examination of the eluted species was made by measuring the optical density of the eluted fraction at particular wavelengths. The ethanol-water solution was used as the eluant to minimize the aquation reactions of the complexes.

The measurement of the optical density was carried out with a Hitachi model EPU-2 spectrophotometer.

Results and Discussion

The elution curve of a mixture of the isomeric $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]^+$ is shown in Fig. 1, in which the measurement of the optical density was performed at an absorption maximum and a minimum of the trans-cis ion (460 and 560 mμ). As is seen in the figure, an elution maximum for the trans-cis ion appears in the fraction 10 and one for the cis-trans ion in the fractions 20 and 21. When only the trans-cis complex was applied to the

1) Separation of metal complex isomers by the ion-exchanger, Part III Partly presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

2) E. L. King and R. R. Walter, *J. Am. Chem. Soc.*, **74**, 4471 (1952).

3) M. Mori, M. Shibata and J. Azami, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **76**, 1003 (1955).

4) M. Mori, M. Shibata and M. Nanasawa, *This Bulletin*, **29**, 947 (1956).

5) J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940); A. Werner, *Ber.*, **34**, 1733 (1901); *Ann.* **386**, 48, 107, 111, 248 (1912).

column, the elution curve had its maximum in the fraction 9 and dropped to zero at the fraction 20. On the other hand, the *cis-trans* ion began to appear in the fraction 9 and showed the maximum elution at the fraction

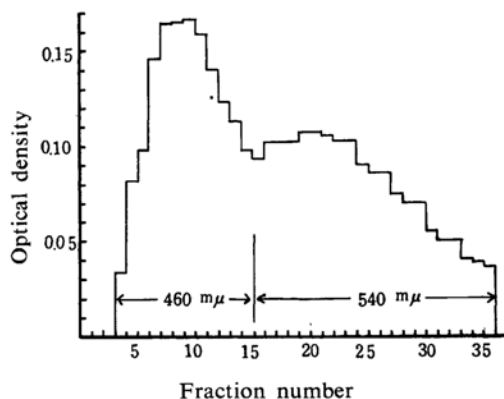


Fig. 1. Elution curve of $[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$ isomers.

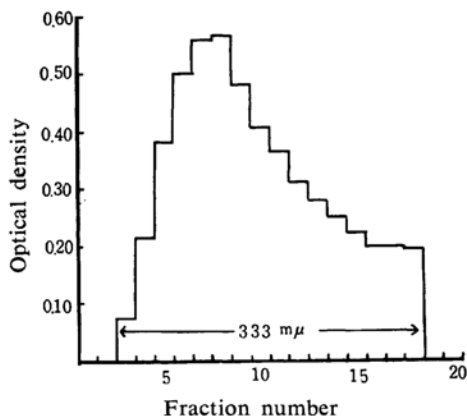


Fig. 2. Elution curve of *trans*- $[\text{Co en}_2\text{NO}_2\text{Cl}]\text{Cl}$.

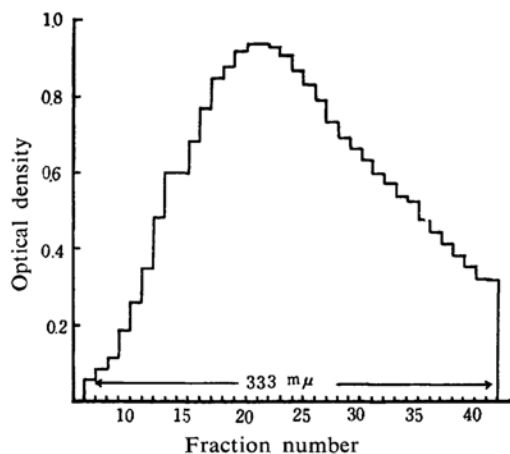


Fig. 3. Elution curve of *cis*- $[\text{Co en}_2\text{NO}_2\text{Cl}]\text{Cl}$.

21. It is, therefore, clear that each portion of the fractions 9–20 in Fig. 1 is, more or less, contaminated with both species.

The elution curves of *trans*- and *cis*- $[\text{Co en}_2\text{NO}_2\text{Cl}]^+$ are shown in Figs. 2 and 3. The maximum concentration of the *trans* compound is observed in the fraction 8, and that for the *cis* in the fractions 21 and 22. The elution of a mixture of these isomers was examined, but the elution curve is omitted because the absorption spectra of both isomers are quite similar, and hence no perceptible peak was obtained.

Figure 4 is the elution curve for *trans*- $[\text{Co en}_2\text{Br}_2]^+$ and shows the elution peak in the fraction 7. The experiment of the elution for the *cis* ion was unsuccessful because of the extremely low solubility of the complex.

The elution curve for the isomeric $[\text{Co en}_2\text{Cl}_2]^+$ in a mixed solution is shown in Fig. 5, where the elution maxima are in the fractions

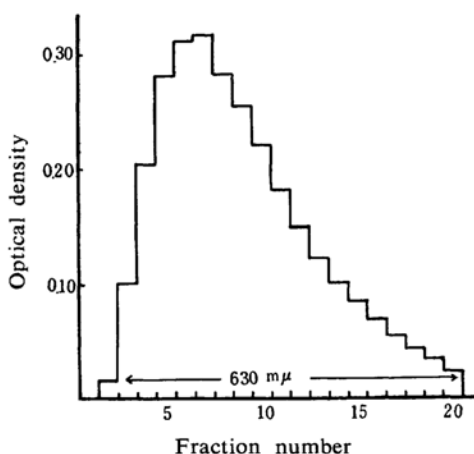


Fig. 4. Elution curve of *trans*- $[\text{Co en}_2\text{Br}_2]\text{Br}$.

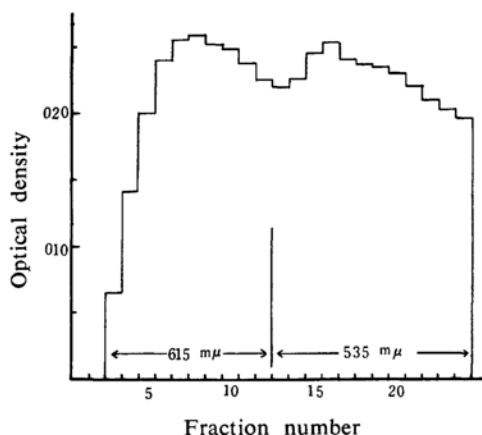
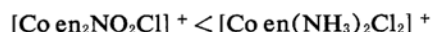
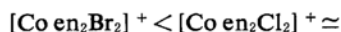


Fig. 5. Elution curve of $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ isomers.

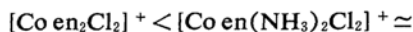
8 and 16. In the case of the individual solution, the trans ion was eluted with the maximum in the fraction 7 and finished its elution at the fraction 15, while the cis ion began to elute in fraction 5 and showed the maximum in the fraction 16.

From these results, it is again found that the trans ion is eluted faster than the cis ion. Furthermore, it is possible to predict the relative adsorbabilities as follows:

For the trans ions,



For the cis ions,



Now, we are in a position to discuss the relative adsorbabilities of all the complex ions studied in the present and previous papers^{3,4}.

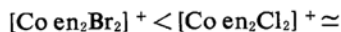
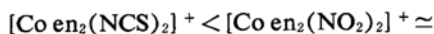
TABLE I. COMPARISON OF ELUTION MAXIMA

Complex ion	Eluant	Fraction no. of elution max.	
		trans	cis
$[\text{Co en}(\text{NH}_3)_2\text{Cl}_2]^+$	0.15 M NaCl alcoholic aqueous soln.	10	21—22
$[\text{Co en}_2\text{Cl}_2]^+$		8	16
$[\text{Co en}_2\text{NO}_2\text{Cl}]^+$		8*	21—22*
$[\text{Co en}_2\text{Br}_2]^+$		7*	—
$[\text{Co en}_2\text{Cl}_2]^+$	0.5 M NaCl aqueous soln.	7	12
$[\text{Co en}_2(\text{NO}_2)_2]^+$		6	17
$[\text{Co en}_2(\text{NCS})_2]^+$		5	14
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	0.5 M NaCl aqueous soln.	13	35
$[\text{Co en}_2(\text{NO}_2)_2]^+$		11	31

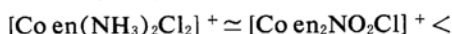
* Fraction number in individual solution.

Unfortunately, it was impossible to perform all of the elutions under identical conditions. It is, therefore, difficult to derive a definite adsorbability order directly, but it is possible to predict such an order from a comparison of the elution maxima (Table I).

For the trans ions,



For the cis ions,



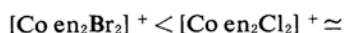
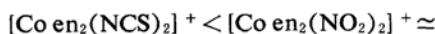
For the trans ions of the diacido-bisethylene-diamine complexes, the adsorbabilities increase in the order of the dithiocyanato-, the dinitro-, the dibromo- and the dichloro-complexes; this trend may be attributed to the differences of the ionic radii of the complex ions since the distance between the cobalt and the ligand ion increases in the order Cl^- , Br^- , NO_2^- and NCS^- . On the other hand, such a trend was not observed for the cis ions. It must, however, be said that the ammine-complexes always have a stronger affinity for a cation exchanger than the corresponding ethylenediamine-complexes; this also be due to the differences of size between ammonia and ethylenediamine molecules.

In the present work, we wanted to study many complexes of the diacido-type, but we were limited by the solubility of the complexes. However, through all the experiments it is to be noted that this kind of technique is useful for distinguishing isomeric forms of complexes, apart from the practical separation of the isomers.

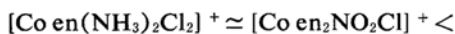
Summary

Additional elution experiments for confirming the fact that the trans ions of the diacido-tetrammine-type complexes are always eluted faster than the corresponding cis ions have been performed by using several diacido-type complexes which are relatively unstable. By comparing the elution maxima for the whole complex ions which have been used to date, the relative adsorbabilities of the isomeric ions on a cation exchanger have been predicted as follows:

For the trans ions,



For the cis ions,



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