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Studies of the Separation Mechanism in Ion-exchange Chromatography. III. Elution Order of *cis*-Bis(ethylenediamine)cobalt(III) and *cis*-*α*-Triethylenetetraminecobalt(III) Complexes on SP-Sephadex C-25 and IEX 510 Resins

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Chromatographic separation of *cis*-dianionobis(ethylenediamine)cobalt(III) and *cis*-α-dianionotriethylenetetraminecobalt(III) complexes has been investigated by using SP-Sephadex C-25 and IEX 510 cation-exchange resins. The elution order of the complex cations on both resins are rather similar to each other and the adjusted retention volumes of these complexes correlate very closely with the crystallographic volumes (the unit cell volumes divided by the number of molecules in a unit cell) of $[Co(X)(NH_3)_5]Cl_2$, where $X=CN^-$, Cl^-, NO_2^-, N_3^-, and NCS^-. This has been taken to indicate that the affinity of the complex cation to the functional group of the resins increases as the size of the cation, and hence the character of water-structure breaker of the cation, increases. Thus, the elution order obtained seems to be determined primarily by the difference in the affinities of the complex cations to the resins, rather than by the difference in the association constants for the ion-pairs formed between the complex cation and the eluent anion.

Ion-exchange chromatography has been used widely to separate metal complexes.[1] The mechanism of chromatographic separation of octahedral complexes with different charges or polarities on ion-exchange resins has been explained[2] mainly be electrostatic interactions between the complex ion and the functional group of the resin in the stationary phase and/or by those between the complex ion and the eluent ion in the moving phase. Our recent studies[3,4] were concerned with the inversion of the elution order of differently charged complexes and of geometrically isomeric complexes (*cis*/*trans*). The results pointed clearly to the importance of two processes in chromatographic separation; adsorption on the complex ion to the resin and elution by eluent ions. For example, the separation of the $[Co(N)_6]^{3+}$ type of complexes has been explained[5] by the difference in the strengths of the hydrogen bonding formed between the N–H hydrogen(s) of the complex cation and the eluent anions in the moving phase. Thus, the system can be considered to be a case of elution-governing.

Very few works[6] have, however, been made which discussed the mechanism of the separation of complexes with the same charge and geometric configuration, *e.g.*, the separation of a series of *cis*-$[Co(X)_2(en)_2]^+$ with various substituents X, where en stands for ethylenediamine. For univalent complex cations *cis*-$[Co(X)(Y)(en)_2]^+$ or *cis*-α-$[Co(X)(Y)(trien)]^+$ (trien=triethylenetetramine), if the eluent concentration is not so high, it may be expected that the interaction between the complex cation and the eluent anion is weak and therefore the separation is dominated by the difference in the affinities of the complex cations to the resin; the systems are adsorption-governed. Thus, a detailed mechanism of the adsorption to the resin might be clarified. With this idea in mind, we have measured the retention volumes of substitution-inert complexes, *cis*-$[Co(X)(Y)(en)_2]^+$ and *cis*-α-$[Co(X)_2(trien)]^+$, where X and Y stand for CN^-, NO_2^-, NCS^-, N_3^-, and Cl^-. The resins used were strongly acidic cation-exchangers, SP-Sephadex C-25 and IEX 510, both of which have the sulfonate group as the functional group.

Experimental

Materials. All the complexes used in this work were prepared by the literature methods and identified by UV/VIS absorption spectra, proton magnetic resonance spectra, and chemical analyses. The geometrically isomeric purity was checked by ion-exchange chromatography. All the complexes were confirmed to be stable against hydrolysis and isomerization during the chromatographic experiments.

The resins used were IEX 510 (Toyo soda Manufacturing Co., Ltd., Japan) and SP-Sephadex C-25 (Pharmacia Fine Chemicals, Sweden), which are strongly acidic ($-SO_3^-Na^+$) cation-exchangers based on silica gel and cross-linked dextran, respectively.

Apparatus. All the chromatographic experiments were carried out on a laboratory-built chromatographic apparatus. The sample solution and Blue Dextran 2000, which was used as a marker for the void volume measurement, was injected by a syringe. The detector, Shimadzu UV-140 double beam spectrophotometer, was operated at the first absorption band of each complex. The adjusted retention volume was obtained from the elution curve.

Results and Discussion

Tables 1 and 2 show the adjusted retention volumes of *cis*-$[Co(X)(Y)(en)_2]^+$ and *cis*-α-$[Co(X)_2(trien)]^+$ on IEX 510 and SP-Sephadex C-25, respectively, when eluted by 0.1 M ($1\ M=1\ mol\ dm^{-3}$) aqueous solution of sodium chloride. When IEX 510 was used, the difference in the adjusted retention volumes of these complexes is rather large and the degree of separation is high. With SP-Sephadex C-25, though the degree of separation is not so high as with IEX 510, almost the same elution order was obtained. The elution order of *cis*-$[Co(X)_2(en)_2]^+$ and *cis*-α-$[Co(X)_2(trien)]^+$, expressed in terms of the substituent X, is as follows.

$$CN > Cl > NO_2 > N_3 > NCS$$

It can be seen in Table 1 that the adjusted retention volume of *cis*-$[Co(X)(Y)(en)_2]^+$ with $X \neq Y$ falls midway between the retention volumes of *cis*-$[Co(X)_2(en)_2]^+$ and *cis*-$[Co(Y)_2(en)_2]^+$. This appears to be true also on SP-Sephadex C-25. Further, it will also be apparent

Table 1. The adjusted retention volumes (ml) of $[Co(X)(Y)(N)_4]^+$ on IEX 510 when eluted by 0.1 M aqueous solutions of sodium chloride

The column size was 4×300 mm, flow rate 0.30 ml min^{-1}, and void volume 1.38 ml.

(X)(Y)	*cis*-(en)$_2$	*cis*-α-trien
$(CN)_2$	8.07	8.01
$(Cl)_2$	10.78	11.21
$(Cl)(NO_2)$	12.31	
$(NO_2)_2$	12.80	12.60
$(N_3)(NO_2)$	13.41	
$(N_3)_2$	14.98	14.75
$(Cl)(NCS)$	16.29	
$(NO_2)(NCS)$	18.17	
$(NCS)_2$	32.00	30.09

Table 2. The adjusted retention volumes (ml) of $[Co(X)(Y)(N)_4]^+$ on SP-Sephadex C-25 when eluted by 0.1 M aqueous solution of sodium chloride

The column size was 6.5×52.5 mm, flow rate 0.69 ml min^{-1}, and void volume 0.72 ml.

(X)(Y)	*cis*-(en)$_2$	*cis*-α-trien
$(CN)_2$	6.93	6.52
$(Cl)_2$	8.20	8.26
$(Cl)(NO_2)$	8.71	
$(NO_2)_2$	8.75	8.44
$(N_3)_2$	8.77	8.79
$(N_3)(NO_2)$	8.81	
$(Cl)(NCS)$	9.09	
$(NO_2)(NCS)$	9.16	
$(NCS)_2$	9.70	9.40

Table 3. The adjusted retention volumes (ml) of *cis*-$[Co(X)_2(en)_2]^+$ on IEX 510 when eluted by 0.1 M aqueous solutions of various salts

The conditions are the same as in Table 1.

$(X)_2$	NaCl	$phSO_3Na$	$NaClO_4$	KCl
$(CN)_2$	8.07	8.05	7.94	6.06
$(Cl)_2$	10.78	10.91	10.90	8.83
$(NO_2)_2$	12.80	12.31	12.26	10.22
$(N_3)_2$	14.98	13.13	13.06	10.26
$(NCS)_2$	32.00	30.25	28.54	21.64

from these tables that the *cis*-α-$[Co(X)_2(trien)]^+$ ions show adjusted retention volumes similar in magnitude to those of *cis*-$[Co(X)_2(en)_2]^+$ on both resins (correlation coefficient 0.9995 on IEX 510 and 0.981 on SP-Sephadex C-25). These results imply that two series of complexes are separated on both resins by a similar mechanism and we may discuss collectively the results of two series of complexes on both resins.

We may first confirm that the retention volumes listed in Tables 1 and 2 are obtained under the adsorption-governed conditions. If the system is adsorption-governed, the complex cations will be eluted primarily according to the difference in the affinities of the complex cation and the eluent cation to the resin. Therefore, the adjusted retention volume will be influenced more strongly by the kind of the eluent cation than by the eluent anion which may associate with the complex cation in the moving phase. Thus, the adjusted retention volumes have been measured on IEX 510 by using several eluents. The results for *cis*-bis(ethylenediamine)cobalt(III) complexes are given in Table 3. The adjusted retention volumes obtained by various eluents are highly correlated (correlation coefficients$>$0.995) and more importantly the change in the adjusted retention volume brought about by changing the eluent cation is much larger than the change caused by changing the eluent anion. Thus, the eluent cation has a dominant effect upon the adjusted retention volumes, which supports the view that the degree of adsorption to the resin is mainly affecting the retention volumes obtained on both resins.

If we look at Table 3 more closely, it can be seen that the adjusted retention volumes decrease, though slightly, as the eluent anion is changed from chloride through benzenesulfonate to perchlorate. This result indicates that the association between the complex cation and the eluent anion in the moving phase does have a contribution, though small, to the retention volumes. That the association between the complex cation and the eluent anion is important in ion-exchange chromatography will be most clearly appreciated by considering the optical resolution of metal complexes. For example, let us consider the case where a racemic complex cation is loaded on a resin and eluted by an aqueous solution containing some optically active anion, *e.g.*, *d*-tartrate or *d*-tartratoantimonate(III). Since in such a case the affinities of the Λ- and Δ-complex cations are exactly the same, we have to attribute the achievement of optical resolution by such a technique to the difference in the association constants of the Λ- and Δ-complex cations with the optically active anion.7) There are many reported examples8) of chromatographic optical resolution of metal complexes and it is apparent that retention volumes are more or less influenced by the association between the complex cation and the eluent anion in the moving phase. Note here, however, that the degree of optical resolution is always smaller than the degree of separation of different kinds of complexes, which suggests that the effect of elution is smaller than that of adsorption. This is also consistent with the view that our systems are adsorption-governed.

The data of Table 3 also indicate that the degree of ion association increases in the order $Cl^- <$ benzenesulfonate $<$ perchlorate. If we note that this order parallels the order of increasing character of water-structure breaker,9) it follows that the univalent complexes examined in this work bear the character of water-structure breaker, because a water-structure breaker associates more favorably with water-structure breakers rather than with water-structure makers.9) This inference gains some support from the works of Oh10) and Pethybridge and Spiers.11) Oh showed that for several ethylenediamine complexes of nickel(II), copper(II), and cobalt(III) with an overall charge of +1 or +2 the association of the complex cation with the iodide anion is favored over that with the chloride anion; the iodide ion is a well-known water-structure breaker while the chloride ion is a water-structure

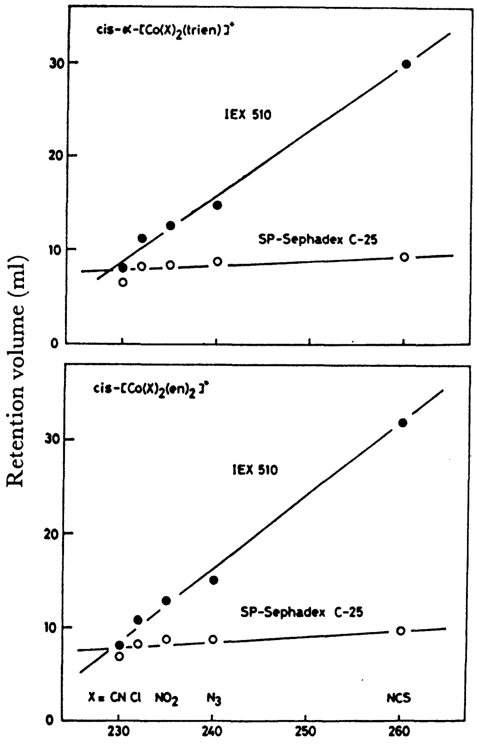

Fig. 1. The correlation between the adjusted retention volumes and the crystallographic volumes of $[Co(X)(NH_3)_5]Cl_2$.

maker.[12] Pethybridge and Spiers showed from conductance measurements that the association constants of $[Co(ox)(en)_2]X$ and *trans*-$[Co(NO_2)_2(en)_2]X$ in water increase in the order $X=Cl^- < Br^- < I^- < ClO_4^-$, where ox stands for the oxalate ion. Though they gave no explanation to these results, their results are most reasonably understood if we consider that univalent and bivalent complex cations bear the character of water-structure breaker.

Since the character of water-structure breaker is expected to get prominent as the volume of the complex cation increases,[9] we have plotted the adjusted retention volumes of *cis*-$[Co(X)_2(en)_2]^+$ and *cis*-α-$[Co(X_2)(trien)]^+$ on both resins against the crystallographic volumes of corresponding anionopentaamminecobalt(III) chlorides, $[Co(X)(NH_3)_5]Cl_2$, all of which are anhydrous and were analysed previously by X-ray diffraction.[13] The abscissa of Fig. 1 is thus the crystallographic volume of $[Co(X)(NH_3)_5]Cl_2$, namely, the unit cell volume divided by the number of molecules in a unit cell. As seen from Fig. 1, the correlation between the two quantities is very good; the correlation coefficients are 0.996 and 0.878 for *cis*-$[Co(X)_2(en)_2]^+$ on IEX 510 and SP-Sephadex C-25, respectively, and 0.995 and 0.754 for *cis*-α-$[Co(X)_2(trien)]^+$ on IEX 510 and SP-Sephadex C-25, respectively. This correlation, in conjunction with the system being adsorption governed, indicates that the complex cation is more tightly bound to the resin function as the crystallographic volume of the cation increases. The correlation in Fig. 1 seems to be quite reasonable in view of the previously reported trend in the association constants of various metal salts. For example, Pethybridge and Spiers[14] reported that the association constants of most 1 : 1 salts in water, including those forming outer-sphere complexes, are primarily determined by the combined size of the two ions; the association constants gets larger as the sum of the crystallographic radii of the two ions increases. It is very interesting to note that the quantity which is correlated with the association constants or the retention volumes is the crystallographic volume of the complex cation, not the hydrodynamic volume of the cation as estimated from, *e.g.*, conductance measurements. In fact, we could find no correlation between the retention volumes and the effective ionic radii of *cis*-$[Co(X)_2(en)_2]^+$, which we have estimated from conductance measurements in water.[15]

Finally, it will be pertinent to point out that the dipole moments of the complex cations do not contribute significantly to the observed retention volumes. This statement follows from the observation that the *trans*-$[Co(X)_2(en)_2]^+$ ions exhibited the same elution order as the corresponding *cis* complexes and the retention volume of *trans*-$[Co(X)(Y)(en)_2]^+$ $(X \neq Y)$ fell midway between the retention volumes of *trans*-$[Co(X)_2(en)_2]^+$ and *trans*-$[Co(Y)_2(en)_2]^+$.[15] Clearly the *trans*-$[Co(X)(Y)(en)_2]^+$ ion can have a dipole moment but the parent complexes can not. Therefore, we conclude that the univalent cations, *cis*-$[Co(X)(Y)(en)_2]^+$ and *cis*-α-$[Co(X)_2(trien)]^+$, assume more and more the character of water-structure breaker and hence get adsorbed to the resins more strongly as the crystallographic volume of the complex cation increases.

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References

1) Part II: H. Yoneda, C. E. Oh, and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, **53**, 2403 (1980).

2) See, for a review; L. F. Druding and G. B. Kauffman *Coord. Chem. Rev.*, **3**, 409 (1968).

3) H. Yoneda and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, **52**, 1859 (1979).

4) H. Yoneda, C. E. Oh, and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, **53**, 2403 (1980).

5) See, for example: G. H. Searle, *Aust. J. Chem.*, **30**, 2625 (1977); K. Sakakibara, Y. Yoshikawa, and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **52**, 2725 (1979).

6) See, for example: M. Mori, M. Shibata, and K. Hori, *Bull. Chem. Soc. Jpn.*, **34**, 1809 (1961); M. Mori, M. Shibata, M. Nanasawa, *ibid.*, **29**, 947 (1956); Y. Yoshikawa, M. Kojima, M. Fujita, M. Iida, and H. Yamatera, *Chem. Lett.*, **1974**, 163; K. Kobayashi and M. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 2561 (1975).

7) H. Nakazawa and H. Yoneda, *J. Chromatogr.*, **160**, 89 (1978); S. Yamazaki and H. Yoneda, *ibid.*, **177**, 227 (1979); H. Yoneda, *J. Liq. Chromatogr.*, **2**, 1157 (1979).

8) See, for a review: Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, **28**, 205 (1979).

9) See, *e. g.*: B. G. Cox and A. J. Parker, *J. Am. Chem. Soc.*, **94**, 3674 (1972); C. M. Criss and M. J. Mastroianni, *J. Phys. Chem.*, **75**, 2532 (1971); H. Yoneda, M. Muto, T. Baba, and T. Miura, *Bull. Chem. Soc. Jpn.*, **44**, 689 (1971).

10) C. E. Oh, *J. Sci. Hiroshima Univ., Ser. A*, **44**, 145 (1980).

11) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Faraday Trans. 1*, **72**, 64 (1976).

12) See, *e.g.*: K. Miyoshi, T. Taura, C. Shimada, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **44**, 783 (1975).

13) Y. Kushi, Ph. D. Thesis, Osaka City University (1968); W. Ozbirn and R. A. Jacobson, *Inorg. Chim. Acta*, **4**, 377 (1970).

14) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Chem. Commun.*, **1974**, 423; A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Faraday Trans. 1*, **72**, 64 (1976).

15) S. Wakida, U. Sakaguchi, and H. Yoneda, unpublished.