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Studies of Thin-layer Chromatography of Inorganic Salts. IV. Chromatographic Behavior of Square Planar Complexes in Comparison with that of Octahedral Complexes

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The chromatography of copper(II) and platinum(II) complexes on silica gel was investigated in comparison with that of cobalt(III) and nickel(II) complexes. Each complex showed various R_f values from zero to unity, when it was developed with aqueous solutions of various salts. This was interpreted to be due to different degrees of anionic association with the complex. The pattern of deversity of R_f values in copper(II) and platinum(II) complexes was found to be definitely different from that in cobalt(III) and nickel(II) complexes. Thus, different association mechanisms were proposed for both cases. In copper(II) and platinum(II) complexes, association occurs through the direct coordination of the anion to the metal ion, while, in cobalt(III) and nickel(II) complexes, association takes place at the outer-sphere of the complex.

We were interested in obtaining information concerning the behaviors and dissolved states of ions in solution through chromatographic studies. In a previous study[2] it was revealed that silica gel is charged negatively in contact with water and adsorbs cations so strongly that the R_f value of the complex cation is almost zero when developed with distilled water. Such strong adsorption is palliated and the increase of the R_f value is observed, when an aqueous solution of salts such as NaCl or Na_2SO_4 is used as a developer. The sample is eluted mainly through ionic association with anions contained in

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[2] T. Baba, H, Yoneda and M. Muto, This Bulletin, **41**, 1965 (1968).

the developer. In other words, such association reduces the apparent positive charge of the complex cation, which results in the decrease of the electrostatic attraction by the adsorbent and in the increase of the R_f value of the sample. Thus, we undertook to study the feature of ionic association by means of thin-layer chromatography. In the preceding paper[3] the effect of hydration of anions upon association was investigated using the crystal violet cation. In the present paper, we should like to report the characteristic features of association involving square planar complexes in compariosn with those involving octahedral complexes.

Experimental

Thin-layer Chromatography. As an adsorbent, Merck's silica gel H was used without further purification. This was spread on a glass plate with length 25 cm and thickness 0.25 mm.

The complexes used in this investigation were [Co en$_3$]Cl$_3$ [Co gly$_3$], [Cu en$_2$] (NO$_3$)$_2$, [Cu gly$_2$], [Pt en$_2$]Cl$_2$, [Ni en$_3$] (NO$_3$)$_2$ and [Ni gly$_2$ (H$_2$O)$_2$]. Each complex was dissolved in water to 1/50M, and 2.5μl of the solution was spotted at a starting point 5 cm above the lower edge of the plate.

The salts used in development were sodium salts of Cl^-, Br^-, I^-, NO_2^-, NO_3^-, $HCOO^-$, CH_3COO^-, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$, and potassium salts of OCN^-, SCN^- and $SeCN^-$. To obtain the best separation, different salt concentrations of developers were used, *viz.*, 0.2M for cobalt(III), 0.1M for nickel(II), 0.5M for copper(II) and platinum(II) complexes.

Development was carried out at room temperature (20—23°C). For detection of the developed spot an aqueous solution of potassium sulfide was sprayed on the cobalt(III) complex, while the alcoholic solution of rubeanic acid was sprayed on the other three complexes. For visualization of the platinum complex, a special procedure was necessary. Rubeanic acid must be acidified with a small amount of hydrochloric acid, and the sprayed plate must be heated to 100°C.

UV Spectral Measurement. The absorption spectra were recorded with a Hitachi Spectrophotometer Model 124.

Results and Discussion

The R_f values of the complexes are summarized in Table 1. In order to understand the characterisrics of the chromatography of square planar complexes, it is advantageous to discuss the chromatography of typical octahedral complexes first.

The tervalent complex cation is adsorbed so strongly on silica gel, that it can be eluted only through ionic association with anions contained in the developer. Thus, various R_f values of the [Co en$_3$]$^{3+}$ complex were obtained as shown in Table 1. This seems to reflect various degrees of anionic association. A marked feature of the chromatography of the [Co en$_3$]$^{3+}$ complex is that the difference in R_f values among univalent anions is not so marked, and that there is a definite difference in R_f values between univalent and bivalent anions. This seems to be the characteristics of octahedral complexes. In fact, the R_f value pattern of the

TABLE 1. R_f VALUES OF THE OCTAHEDRAL AND THE SQUARE PLANAR COMPLEXES DEVELOPED WITH SOLUTIONS OF VARIOUS SALTS

Anion	Complex					
	[Co en$_3$]$^{3+}$	[Co gly$_3$]^0	[Nien$_3$]$^{2+}$	[Cu en$_2$]$^{2+}$	[Cu gly$_2$]^0	[Pt en$_2$]$^{2+}$
H_2O	0.02	0.90	0.01	0.01	0.03	0.02
Cl^-	0.24	0.91	0.23	0.14	0.13	0.37
Br^-	0.23	0.92	0.23	0.16	0.08	0.39
I^-	0.26	0.94	0.21	0.44	0.81	0.52
NO_3^-	0.19	—a)	0.24	0.13	0.12	0.34
NO_2^-	0.18	—a)	0.24	0.27	0.49	0.29
$HCOO^-$	0.11	—a)	0.20	0.22	0.40	0.19
CH_3COO^-	0.07	—a)	0.19	0.15	0.39	0.13
OCN^-	0.12	—a)	0.13	0.63	0.95	0.27
SCN^-	0.32	—a)	0.32	0.67	0.88	0.58
$SeCN^-$	0.30	—a)	0.96	1.00	0.97	—c)
SO_4^{2-}	0.57	0.90	0.62	0.33	0.30	0.36
SO_3^{2-}	0.70	0.93	0.50	0.95	0.90	0.78
$S_2O_3^{2-}$	0.79	0.96	0.53	1.00	—b)	0.52

a) Development was not carried out, as no special difference of R_f values was expected.
b) The complex was reduced by the thiosulfate.
c) The developed spot was not identified, because red selenium appeared over the plate surface during the heating process for visualization of the spot.

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3) T. Baba, K. Sakushima, and H. Yoneda, This Bulletin, **43**, 931 (1970).

$[\mathrm{Ni\,en_3}]^{2+}$ complex is quite similar to that of the $[\mathrm{Co\,en_3}]^{3+}$ complex as seen in Table 1.

In the neutral $[\mathrm{Co\,gly_3}]^0$ complex, the R_f value is very large even with distilled water and is not affected much with salt solutions. This suggests that the octahedral neutral complex has little tendency towards association. A marked contrast to this can be seen in the R_f value pattern of the corresponding $[\mathrm{Cu\,gly_2}]^0$ complex. As shown in Table 1, the $[\mathrm{Cu\,gly_2}]^0$ complex is so strongly adsorbed on silica gel, it remains near the starting point when developed with distilled water. Such strong adsorption can not be explained by a simple electrostatic attraction between silica gel and the complex, because the complex as a whole is elecrically neutral. We must, therefore, assume that the adsorption of the complex takes place through the direct coordination of SiO_2 to the copper(II) ion. In other words, the oxygen atom of SiO_2 occupies the axial position of the square planar copper complex. Any kind of anion can make such direct coordination. Thus, a wide variety of R_f values were observed, when various salt solutions were used as a developer. This is considered to correspond to a wide variety of degree of coordination equilibrium between the complex and the anion. This makes a marked contrast to the case of the octahedral $[\mathrm{Co\,gly_3}]^0$ complex which has no more reserved coordination seat to be occupied by the anion. It should be noted that the R_f value of the copper complex seems to depend not on the ionic charge of anions but on the kind of anion, especially on the kind of donor atoms. Thus, the R_f value is definitely larger in the case of I^- than in the cases of Br^- and Cl^-, and the large R_f values in the cases of $S_2O_3^{2-}$, SO_3^{2-}, NCS^- and $NCSe^-$ can be regarded to result from the coordination through sulfur and selenium atoms. On the other hand, the R_f value is relatively small in the case of SO_4^{2-}, which can be understood by considering that the coordination is made through the oxygen atom. A quite similar pattern of R_f value variation is observed in the $[\mathrm{Cu\,en_2}]^{2+}$ complex too, as can be seen in Table 1. In this case the R_f value also depends not on the ionic charge of anions but on the kind of donor atoms. This is in contrast to the corresponding $[\mathrm{Co\,en_3}]^{3+}$ complex.

The characteristics of the chromatography of the typical square planar $[\mathrm{Pten_2}]^{2+}$ complex is quite similar to that of $[\mathrm{Cuen_2}]^{2+}$ complex. The R_f value is definitely larger in the case of I^- than in the cases of Br^- and Cl^-, and definitely smaller in the case of SO_4^{2-} than in the cases of SO_3^{2-} and $S_2O_3^{2-}$. Therefore, in the platinum(II) complex also, association of anions is presumed to occur not in an equatorial direction but along the axial direction of the complex. In the case of $[\mathrm{Ni\,gly_2(H_2O)_2}]^0$, though the complex has an octahedral configuration, the R_f value pattern appears to be similar to that of the square planar complex (R_f-value: 0.06 with H_2O, 0.82 with I^-, and 0.85 with SO_4^{2-}). Therefore, it is presumed that the water

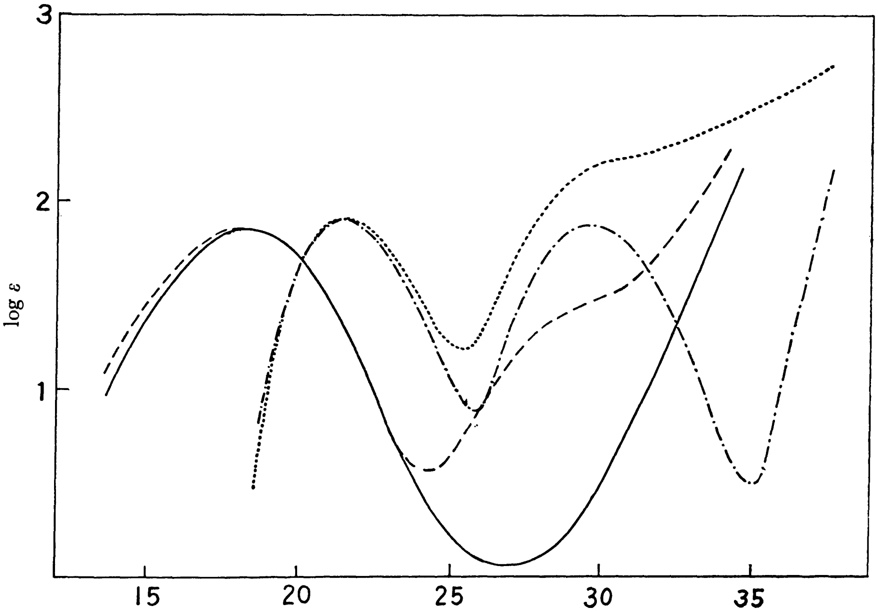

Fig. 1. Electronic spectra of $[\mathrm{Cu\,en_2}]](\mathrm{ClO_4})_2$ and $[\mathrm{Co\,en_3}](\mathrm{ClO_4})_3$.
——— $[\mathrm{Cu\,en_2}]^{2+}$ in distilled water
– – – – – – $[\mathrm{Cu\,en_2}]^{2+}$ in 1 M Na_2SO_3 aqueous solution
–·–·–·– $[\mathrm{Co\,en_3}]^{3+}$ in distilled water
··········· $[\mathrm{Co\,en_3}]^{3+}$ in 1 M Na_2SO_3 aqueous solution

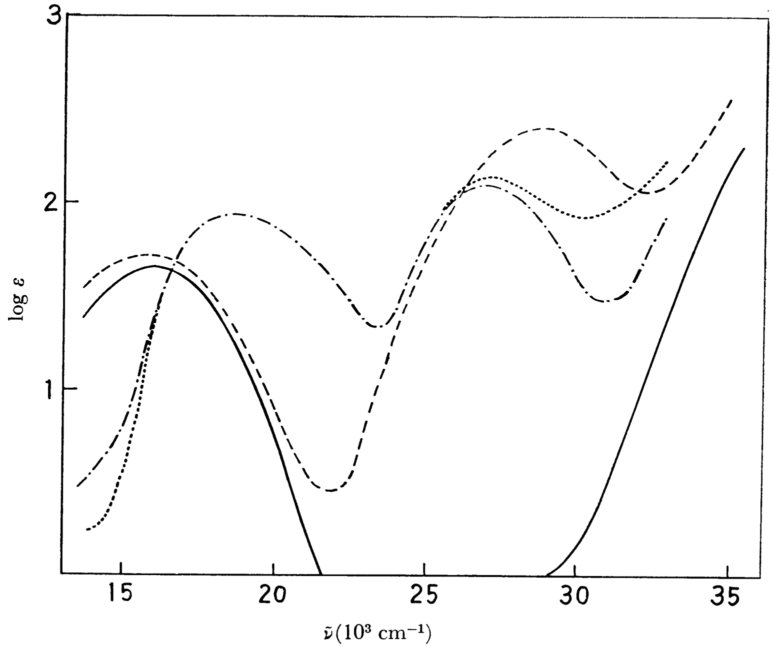

Fig. 2. Electronic spectra of [Cu gly$_2$]^0 and [Co gly$_3$]^0.
——— [Cu gly$_2$]^0 in distilled water
------ [Cu gly$_2$]^0 in 1 M Na_2SO_3 aqueous solution
—·—·— [Co gly$_3$]^0 in distilled water
·········· [Co gly$_3$]^0 in 1 M Na_2SO_3 aqueous solutions

molecules at the axial positions can be replaced by the anion.

The above-mentioned ionic association can be supported from the spectral data of the complex. As can be seen in Fig. 1, the UV spectra of the [Coen$_3$]$^{3+}$ and [Cuen$_2$]$^{2+}$ complexes dissolved in 1 M Na_2SO_3 solution show a new band in the near ultraviolet region, which is not observed in water. Such a band can be regarded as a charge-transfer band due to ionic association. A similar charge-transfer band was also observed in the [Cugly$_2$]^0 complex (See Fig. 2). It should be noted that the intensity of the charge-transfer band in the [Cu gly$_2$]^0 complex is much larger than that in the [Cu en$_2$]$^{2+}$ complex. Thus a greater interaction is presumed between SO_3^{2-} and [Cugly$_2$]^0 than between SO_3^{2-} and [Cuen$_2$]$^{2+}$.[4] On the contrary, the absorption spectrum of [Cogly$_3$]^0 is almost the same both in water and in 1 M Na_2SO_3 solution, which suggests no marked interaction between the complex and SO_3^{2-}.

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[4] The association constant for [Cu alanin$_2$]^0 and SO_3^{2-} is 240, while that for [Cu en$_2$]$^{2+}$ and SO_3^{2-} is only 25. H. Yoneda, This Bulletin, **29**, 68 (1956); *ibid.*, **29**, 319 (1956).