Investigation on Mixed Complexes. III[1]. *Spectrophotometric Studies on Platinum(II) Complexes*

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In general, mixed complexes are easily formed, but it appears that mixed cyano complexes are not easily formed. For instance, many species of mixed ammine complexes of cobalt(III) and platinum(II) are known, but mixed cyano complexes of cobalt(III) and platinum(II) known hitherto are few[2], and they have a strong tendency to become cyano complexes[3].

In the preceeding paper[1] of this series, it was demonstrated that no mixed cyano complexes are formed in the case of nickel(II) and copper(I). However, these are the cases where the parent complexes (for instance, $[\mathrm{Ni\,en_3}]^{2+}$ and $[\mathrm{Ni(CN)_4}]^{2-}$) have different configuration from each other. In this article an experiment has been carried out on platinum(II) complexes, which have the same configuration, in order to verify whether the mixed cyano complex is formed or not.

Results and Discussion

It has been known that chloride ions in tetrachloro platinate(II) ion are replaced by cyanide ions in solution at room temperature. Though no mixed cyano complex of platinum(II) has ever been known, a possibility of its formation in solution is still in question. The experiment was undertaken to solve this problem.

A potassium cyanide solution was added to a solution of potassium tetrachloro platinate(II) in the ratios as indicated in Table I, and extinction measurements were carried out on each of the mixed solutions. The results are shown in Fig. 1.

The extinction curves in Fig. 1 show that only the tetracyano platinate(II) and tetrachloro platinate(II) ions are present, no mixed complex ions such as $[\mathrm{Pt\,Cl_3CN}]^{2-}$, $[\mathrm{Pt\,Cl_2(CN)_2}]^{2-}$ and $[\mathrm{Pt(CN)_3Cl}]^{2-}$ being present; if any of the mixed complexes were formed, the absorption curve would be subject to deformation to some degree, or a new absorption maximum would appear correspondingly, in the region where tetracyano platinate(II) ion has no absorption.

TABLE I. THE COMPOSITION OF THE SOLUTIONS (cf. Fig. 1)

Solution number	(1)	(2)	(3)	(4)	(5)
0.03 F $K_2[\mathrm{Pt\,Cl_4}]$ and 3 F KCl*	8 ml.	8	8	8	8
0.1220 F KCN	0 ml.	2	4	6	8
Water	8 ml.	6	4	2	0

* KCl is added to supress hydrolysis of $[\mathrm{Pt.Cl_4}]^{2-}$.

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[1] Part II of this series: S. Kida, This Bulletin, 32, 981 (1959).

[2] J. C. Bailar, "The Chemistry of the Coordination Compounds", Reinhold Publ. Co., New York (1956), p. 87, "General Survey".

[3] This tendency can be seen when one compares the methods of preparation of the two complxes, $[\mathrm{Co(NH_3)_5 \cdot Cl}]^{2+}$ and $[\mathrm{Co(CN)_5Cl}]^{3+}$; the pentammine complex is readily prepared from cobaltous salt, ammonia and ammonium chloride in an aqueous solution, while the pentacyano complex is obtained only by substitution of the cyanide ion for ammonia of petammine complex under a very delicate condition.

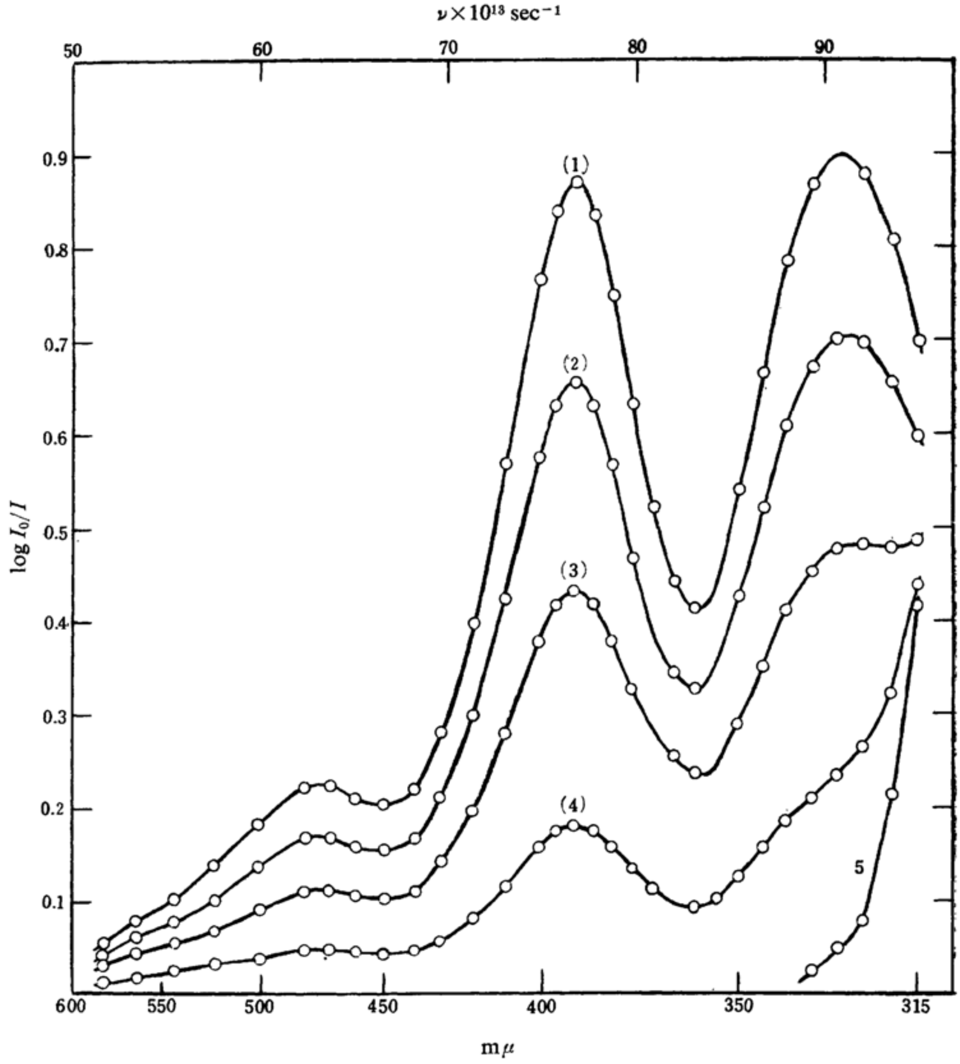

Fig. 1. (cf. Table I).

If it is assumed that all of the added cyanide ions are consumed to form the tetracyano platinate(II) ion, the calculated value of ([Pt] −1/4[CN])/[Pt] must accord with the experimentally obtainable value, D/D_1[4], where [Pt] and [CN] denote the total concentration of all platinum species and of the added cyanide ion in each solution shown in Table I and Fig. 1. Actually, a satisfactory agreement between the calculated and the experimental value can be found in Table II.

TABLE II

	(1)	(2)	(3)	(4)	(5)
([Pt]−1/4[CN])/[Pt]	1.00	0.746	0.492	0.237	0
D/D_1 for 470 mμ	1.00	0.748	0.496	0.207	0
for 400 mμ	1.00	0.751	0.492	0.208	0
for 390 mμ	1.00	0.753	0.499	0.209	0
for 380 mμ	1.00	0.759	0.505	0.212	0

Numbers in the first row denote solution numbers in Table I.

A potassium cyanide solution was added to a solution of potassium tetrabromo platinate(II), in order to examine the substitution of the cyanide ion for the coordinated bromide. The result was the same in the case of the potassium tetrachloro platinate(II); i.e. the absorption curves are not deformed in the region where the tetracyano platinate(II) ion has no absorption, and the calculated value, ([Pt] −1/4[CN])/[Pt] accords with the experimental value, D/D_6, as is shown in Fig. 2 and Table IV.

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[4] If the reaction, $[\text{Pt Cl}_4]^{2-}+4\,\text{CN}^-\rightarrow[\text{Pt(CN)}_4]^{2-}+4\text{Cl}^-$, takes place quantitatively, optical densities of the solutions are expressed as in the following:
$D=\varepsilon_1([\text{Pt}]-1/4[\text{CN}])+\varepsilon_2(1/4[\text{CN}])$, and for solution 1, $D_1=\varepsilon_1[\text{Pt}]$, where ε_1 and ε_2 are extinction coefficients of $[\text{Pt Cl}_4]^{2-}$ and $[\text{Pt(CN)}_4]^{2-}$, respectively. However, in the region of 330~600 mμ the ratio D/D_1 can be reduced to ([Pt]−1/4[CN])/[Pt], since in this region $\varepsilon_2=0$.

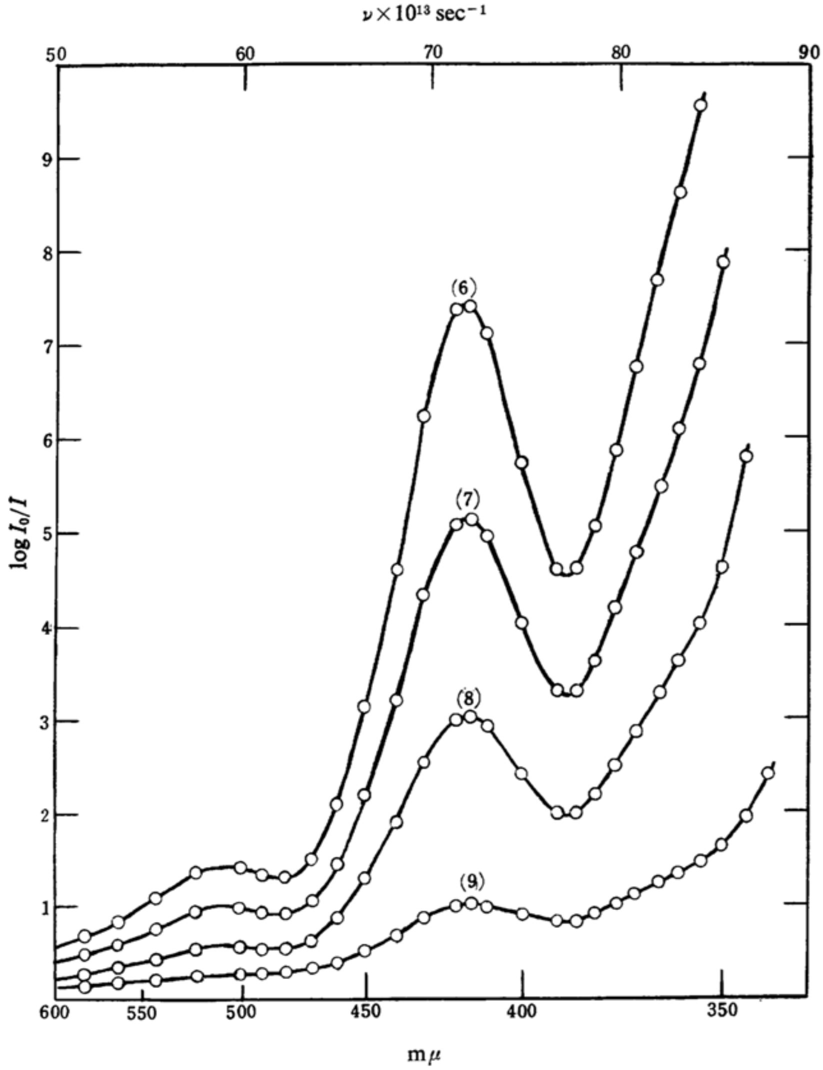

Fig. 2. (cf. Table III).

TABLE III. THE COMPOSITION OF THE SOLUTIONS (cf. Fig. 2)

Solution number	(6)	(7)	(8)	(9)	(10)
0.015 F $K_2[PtBr_4]$ and 1 F KBr**	8 ml.	8	8	8	8
0.0703 F KCN	0 ml.	2	4	6	8
Water	8 ml.	6	4	2	0

** KBr is added to supress hydrolysis of $[PtBr_4]^{2-}$.

TABLE IV

		(6)	(7)	(8)	(9)	(10)
$([Pt]-1/4[CN])/[Pt]$		1.00	0.707	0.414	0.121	0
D/D_6	for 520 mμ	1.00	0.691	0.403	0.187	0
	for 420 mμ	1.00	0.690	0.407	0.137	0
	for 410 mμ	1.00	0.697	0.411	0.140	0

Numbers in the first row denote solution numbers in Table III.

These results are the first example which evidently shows that no mixed complex is formed between the complexes of the same configuration. The cause of this phenomenon will be discussed in the last paper of this series⁵⁾.

Further experiments on the other compounds, especially on cobaltic complexes, to find further similar examples, are desirable. Unfortunately, however, it has been found difficult to find appropriate compounds to be examined for the present purpose.

When a potassium cyanide solution is added to a solution of hexammine cobalt(III) chloride, the coordinated ammonia is replaced by the cyanide ion, and the only product obtained is not easily soluble crystals, $[Co(NH_3)_6]\cdot[Co(CN)_6]$. From the above fact alone, one

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5) S. Kida, to be published.

can not deduce a conclusion, because there are two probable cases; i.e. 1) the mixed complex is not formed because of its comparatively less stability, 2) although the mixed complexes are easily formed in solution, the least soluble compound, $[Co(NH_3)_6]\cdot[Co(CN)_6]$, separates out, and the equilibrium shifts to produce the crystals, $[Co(NH_3)_6]\cdot[Co(CN)_6]$.

Experimental

Extinction measurements were made by the Beckman DU Spectrophotometer using 1 cm. qualtz cells at room temperature.

Potassium tetrachloro platinate(II), $K_2[PtCl_4]$, and potassium tetrabromo platinate(II), $K_2[PtBr_4]\cdot 2H_2O$, were prepared according to the literatures[6,7], and their purity was checked by analyzing their quantity of halogen. The concentration of potassium cyanide was determined by a titration with a standard solution of silver nitrate.

Summary

The spectrophotometric investigation has shown that in the substitution reactions of cyanide ion for halogens(X^-) of the complexes, $[PtX_4]^{2-}$, (X=Cl and Br) in solution, no mixed complex is formed.

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[6] W. C. Fernelius, "Inorganic Syntheses", Vol. II, McGraw-Hill Book Co., Inc., New York (1954), p. 87.

[7] E. Billmann and A. C. Anderson, *Ber.*, 36, 1566 (1903).