SPECTROGRAPHIC METHODS OF STUDYING UNSTABLE COMPOUNDS. II.(1) THE AQUOTIZATION OF TRANS-DICHLORO-TETRAMMINE COBALTIC CHLORIDE IN AQUEOUS SOLUTIONS.

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Introduction. It is well known that trans-dichloro-tetrammine cobaltic salt undergoes a marked colour change(2) in aqueous solutions; its bright green colour fades rapidly away, passes a neutral tint and changes gradually to purple and finally to red. Quantitative measurement of light-absorption of this interesting compound, however, has scarcely been reported. R. Luther and A. Nikolopulos(3) have measured the absorption only in the visible region, and yet the authors themselves acknowledge the inaccuracy of their mearsurement owing to its instability. R. Samuel(4) published an absorption curves as

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(1) R. Tsuchida, this Bulletin, **10** (1935), 27.

(2) Y. Shibata, "Spectrochemistry", Vol. I. (1935), 327; *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2, 25.

(3) *Z. physik. Chem.*, **82** (1913), 367.

(4) *Z. Physik*, **70** (1931), 54.

that of $[Co(NH_3)_4Cl_2]Cl$(5), but the given absorption is almost identical with that of $[Co(NH_3)_4(H_2O)Cl_{\left\{\substack{(1)\\(2)}\right\}}]Cl_2$, i.e., an aquotization product of both the isomers of dichloro-tetrammine cobaltic chloride. Because of its high reaction velocity, there has been hardly any quantitative investigation on the change of this salt in aqueous solutions, except that of Prof. K. Matsuno(6), who showed the change in its valency effect on the coagulation of arsenious sulphide sol. The mechanism of the change, therefore, has been left to imagination from the analogy of this compound with trans-dichloro-diethylenediamine cobaltic chloride, which has also been investigated by Prof. K. Matsuno(7) by means of his ingenious method of coagulation of arsenious sulphide sol. The change was concluded to be due to the following reactions.

$$[Co\ en_2Cl_{2\left\{\substack{(1)\\(6)}\right\}}]Cl + H_2O \rightarrow [Co\ en_2Cl\ H_2O_{\left\{\substack{(1)\\(6)}\right\}}]Cl_2$$

$$[Co\ en_2Cl\ H_2O_{\left\{\substack{(1)\\(6)}\right\}}]Cl_2 + H_2O \rightarrow [Co\ en_2(H_2O)_{2\left\{\substack{(1)\\(2)}\right\}}]Cl_3\,.$$

The velocity constants have been given as 0.011 and 0.0031 referring to minute, i.e., 1.9×10^{-4} and 5.2×10^{-5} for second.

The reaction of $[Co(NH_3)_4Cl_{2\left\{\substack{(1)\\(6)}\right\}}]Cl$, however, is too rapid to follow quantitatively by means of the coagulation method or by measuring the electrolytic conductivity. Moreover, the aquotization takes place in the following scheme, as we shall see later.

$$\begin{tikzcd}
{[Co(NH_3)_4Cl_{2\left\{\substack{(1)\\(6)}\right\}}]Cl} \arrow[r] & {[Co(NH_3)_4ClH_2O_{\left\{\substack{(1)\\(6)}\right\}}]Cl_2} \arrow[d] & \\
& {[Co(NH_3)_4Cl\ H_2O_{\left\{\substack{(1)\\(2)}\right\}}]Cl_2} \arrow[r] & {[Co(NH_3)_4(H_2O)_{2\left\{\substack{(1)\\(2)}\right\}}]Cl_3}
\end{tikzcd}$$

It is obvious that the conductivity of the system is hardly affected by the second reaction and the valency of the ions remains the same during the isomeric change. Then both the conductivity measurement and the coagulation method would be inapplicable for this case. Spectrographic method could be more advantageously applied even for this rapid and complicated reaction. The present author photographed from time to time the absorption spectra of mixed solutions of the praseo-salt and its aquotization products as a whole, and analyzed the absorption at leisure in order to study the kinetics and at the same time to find the extinction coefficients which should belong to the praseo-salt.

Experimental. Trans-dichloro-tetrammine cobaltic chloride was prepared by the the method of S.M. Jörgensen(8). A weighed portion of this salt was

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(5) The configuration of the isomer used in the measurement has not been stated in the original.

(6) *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art. 11, 12.

(7) This Bulletin, **1** (1926), 133.

(8) *Z. anorg. Chem.*, **14** (1897), 416.

expeditiously dissolved in water to make a 0.0150 mol/l. solution, the moment of dissolution being taken as the starting point of the reaction. This solution was subject to spectrographic analysis by means of a spectrograph equiped with a sector-photometer. The first photographic recording was made 6 minutes after the time of dissolution with an aparture of the sector. Further recordings were made after successive intervals of 2, 4, 8,... minutes, i.e. after 8, 12, 20,.... minutes from the starting point, the aparture of the sector being kept at the same angle as in the first recording. Next, with a freshly prepared solution of the same concentration, the absorption spectra were photographed after 6, 8, 12, 20,.... minutes from the time of dissolution, the angle of the sector being kept constant throughout the second series of experiments, but different from that for the first. The process was repeated with many a portion, on the same conditions except the aparture of the sector which was varied for each portion. The room temperature was kept at about 17°C. throughout the experiment. The absorption of the mixed solutions were found by measuring the photographic plates, and a set of curves was obtained (Fig. 1).

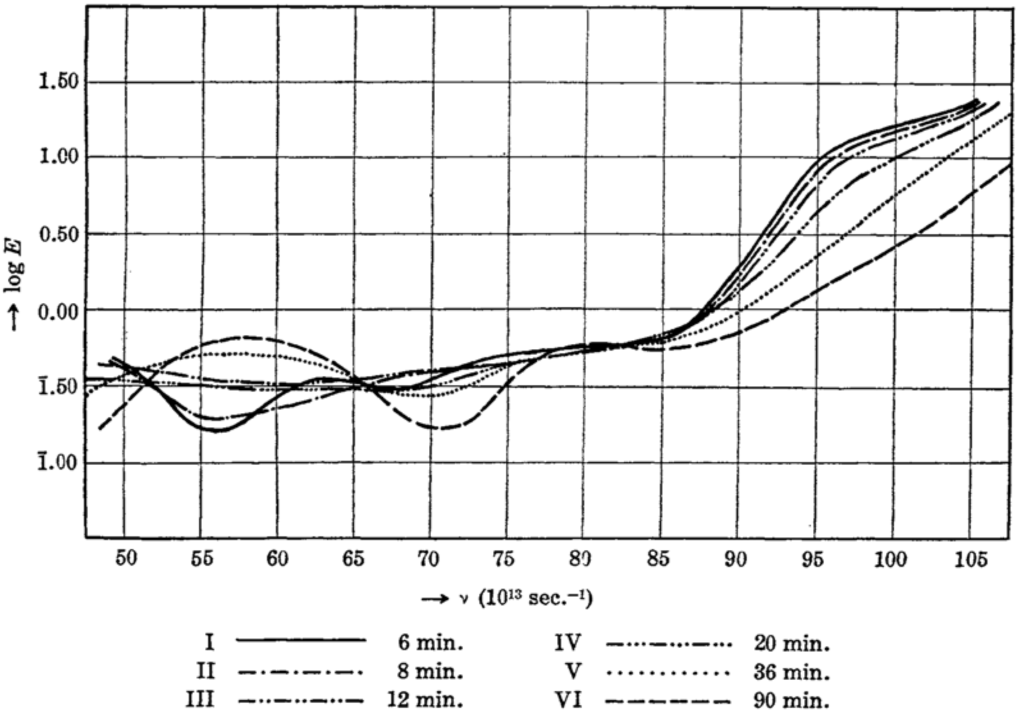

Fig. 1.

E represents $\Sigma\varepsilon c$ in $I = I_0 \times 10^{-d\Sigma\varepsilon c}$, where ε's are molar extinction coefficients, C's, concentrations and d, the thickness of layer. From these curves the following facts may be concluded.

(1) The curve VI, i.e., the absorption after 90 minutes, is almost identical with that of $[\mathrm{Co(NH_3)_4ClH_2O}_{\left\{{(1)\atop(2)}\right\}}]\mathrm{Cl_2}$ (Curve C(9) in Fig. 5), but considerably different from that of $[\mathrm{Co(N_3H)_4(H_2O)_2}_{\left\{{(1)\atop(2)}\right\}}]\mathrm{Cl_3}$ (Curve D(9) in Fig. 5). It can, therefore, be concluded that by this time the aquotization has so far proceeded that only one molecule of water has entered the complex radical and diaquotetrammine cobaltic chloride has not yet been produced in appreciable quantity.

(2) The praseo-salt and its aquotization products have equal molar extinction coefficients for two frequencies 66×10^{13} and 82.5×10^{13}.

(3) The bulges of the curves (I, II, III and IV) at about 96×10^{13} indicate the probable existence of an absorption band belonging to an unstable compound which changes gradually with the disappearance of the bulge.

Analysis and Discussion. Let X and Y be the compounds contained in mixed solutions and the molar extiction coefficients of X and Y for frequencies $\nu_1, \nu_2, \ldots.$ be $\varepsilon_1^{\mathrm{X}}, \varepsilon_2^{\mathrm{X}}, \varepsilon_1^{\mathrm{Y}}, \varepsilon_2^{\mathrm{Y}}, \ldots..$ Then the following relation exists among the concentrations of X in the mixed solutions, I, II, III, ...

$$\begin{vmatrix} \varepsilon_1^{\mathrm{X}} & \varepsilon_1^{\mathrm{Y}} \\ \varepsilon_2^{\mathrm{X}} & \varepsilon_2^{\mathrm{Y}} \end{vmatrix} = \frac{\begin{vmatrix} E_1^{\mathrm{I}} & \varepsilon_1^{\mathrm{Y}} \\ E_2^{\mathrm{I}} & \varepsilon_2^{\mathrm{Y}} \end{vmatrix}}{[\mathrm{X}]_{\mathrm{I}}} = \frac{\begin{vmatrix} E_1^{\mathrm{II}} & \varepsilon_1^{\mathrm{Y}} \\ E_2^{\mathrm{II}} & \varepsilon_2^{\mathrm{Y}} \end{vmatrix}}{[\mathrm{X}]_{\mathrm{II}}} = \frac{\begin{vmatrix} E_1^{\mathrm{III}} & \varepsilon_1^{\mathrm{Y}} \\ E_2^{\mathrm{III}} & \varepsilon_2^{\mathrm{Y}} \end{vmatrix}}{[\mathrm{X}]_{\mathrm{III}}} = \ldots.(1),$$

where E's represent the measurable absorptions, the suffixes denoting the solutions and the frequencies. In our case two frequencies, $56 \times 10^{13} (= \nu_1)$ and $82.5 \times 10^{13} (= \nu_2)$ are chosen for practical analysis. For the former frequency, $[\mathrm{Co(NH_3)_4Cl\ H_2O}_{\left\{{(1)\atop(2)}\right\}}]\mathrm{Cl_3}$ has an extinction coefficient nearly equal to the maximum value in its first band, while $[\mathrm{Co(NH_3)_4Cl_2}_{\left\{{(1)\atop(6)}\right\}}]\mathrm{Cl}$ and $[\mathrm{Co(NH_3)_4Cl\ H_2O}_{\left\{{(1)\atop(6)}\right\}}]\mathrm{Cl_2}$ are supposed to have much smaller values approximately equal to each other. For the latter frequency, $[\mathrm{Co(NH_3)_4Cl_2}_{\left\{{(1)\atop(6)}\right\}}]\mathrm{Cl}$ and its aquotization products have equal coefficients. The analysis is as follows.

From (1)

$$\frac{E_1^{\mathrm{I}} - E_2^{\mathrm{I}} \dfrac{\varepsilon_1^{\mathrm{Y}}}{\varepsilon_2^{\mathrm{Y}}}}{[\mathrm{X}]_{\mathrm{I}}} = \frac{E_1^{\mathrm{II}} - E_2^{\mathrm{II}} \dfrac{\varepsilon_1^{\mathrm{Y}}}{\varepsilon_2^{\mathrm{Y}}}}{[\mathrm{X}]_{\mathrm{II}}} = \ldots\ldots\ldots\ldots = a\ . \qquad (2)$$

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(9) These complex salts were prepared and studied by Messrs. K. Fukui, S. Seki and M. Kobayashi in this laboratory.

From Fig. 1 we have

$$E_2^{\mathrm{I}} = E_2^{\mathrm{II}} = E_2^{\mathrm{III}} = \ldots\ldots\ldots\ldots \quad .$$

Assuming $[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(2)}]\mathrm{Cl_2}$ as Y, we have from Fig. 5

$$\log \varepsilon_1^{\mathrm{Y}} = 1.60 \quad \text{and} \quad \log \varepsilon_2^{\mathrm{Y}} = 1.56 \ ,$$

and from Fig. 1, $E_2 = \bar{1}.78$.

Therefore we get

$$\alpha[\mathrm{X}] = E_2 \frac{\varepsilon_1^{\mathrm{Y}}}{\varepsilon_2^{\mathrm{Y}}} - E_1 = 0.661 - E_1 \qquad (3)$$

The values of $\log \alpha [\mathrm{X}]_{\mathrm{I}}$, $\log \alpha [\mathrm{X}]_{\mathrm{II}}$, ... were calculated by (3) and plotted against time resulting a convex curve (Fig. 2).

The curve thus obtained was extrapolated to t_0, at which [X] was 0.0150 mol / l. From $\log \alpha [\mathrm{X}]_{t=0}$, we could estimate [X]'s for the solutions after 6, 8, 12, ... minutes from the time of dissolution.

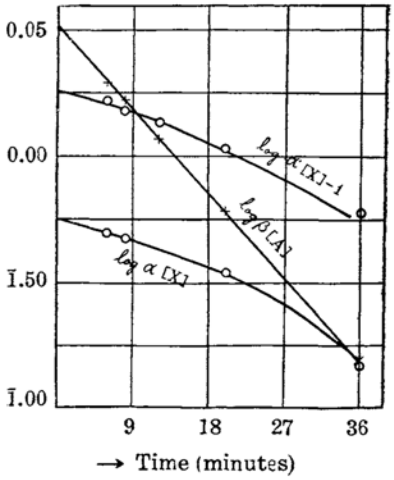


Fig. 2.

Table 1.

	Time (min.)	E_1	α[X]	log α[X]	[X]
I	6	0.159	0.502	$\bar{1}.701$	0.0134
II	8	0.187	0.474	$\bar{1}.676$	0.0126
III	12	0.329	0.332	$\bar{1}.521$	0.0088
IV	20	0.310	0.351	$\bar{1}.545$	0.0093
V	36	0.513	0.148	$\bar{1}.170$	0.0053
VI	90	0.617	0.004	$\bar{2}.643$	0.0012
	0	extrapol.	0.563	$\bar{1}.750$	0.0150

In order to confirm the results, another set of frequencies, $82.5 \times 10^{13} (= \nu_2)$ and $102 \times 10^{13} (= \nu_1)$ was taken for similar analysis. From Fig. 5 and Fig. 1,

$$\log \varepsilon_1^{\mathrm{Y}} = 2.16, \quad \log \varepsilon_2^{\mathrm{Y}} = 1.56 \quad \text{and} \quad \log E_2 = \bar{1}.78.$$

Therefore $$\alpha'[\mathrm{X}] = E_1 - E_2\frac{\varepsilon_1^{\mathrm{Y}}}{\varepsilon_2^{\mathrm{Y}}} = E_1 - 2.40\ . \qquad (3')$$

Log $\alpha'[\mathrm{X}]$ plotted against time (Fig. 2) gives another convex curve quite similar to log $\alpha[\mathrm{X}]$. Extrapolating the curve to t_0, we obtained log $\alpha'[\mathrm{X}]_{t=0}$ from which [X] could be calculated (Table 2).

Table 2.

	Time (min.)	E_1	$\alpha'[\mathrm{X}]$	log $\alpha'[\mathrm{X}]$	[X]
I	6	19.1	16.7	1.223	0.0141
II	8	17.4	15.0	1.176	0.0126
III	12	15.9	13.5	1.130	0.0114
IV	20	13.2	10.8	1.033	0.0091
V	36	8.32	5.9	0.771	0.0050
VI	90	2.64	2.2	0.301	0.0002
	0	extrapol.	17.8	1.250	0.0150

From [X] the concentration of $[\mathrm{Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}}]\mathrm{Cl_2}$, [C], can be found by $[\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{X}]$.

Table 3.

The Concentration of $[\mathrm{Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}}]\mathrm{Cl_2}$.

	Time (min.)	From Table 1 (mol/l.)	From Table 2 (mol/l.)	Mean [C] (mol/l.)
	0	0.0000	0.0000	0.0000
I	6	0.0016	0.0009	0.0014
II	8	0.0024	0.0024	0.0024
III	12	0.0062*	0.0036	0.0036
IV	20	0.0057	0.0059	0.0058
V	36	0.0097	0.0100	0.0099
VI	90	0.0138	0.0148	0.0143

* This value is excluded from further calculation because of its deviation.

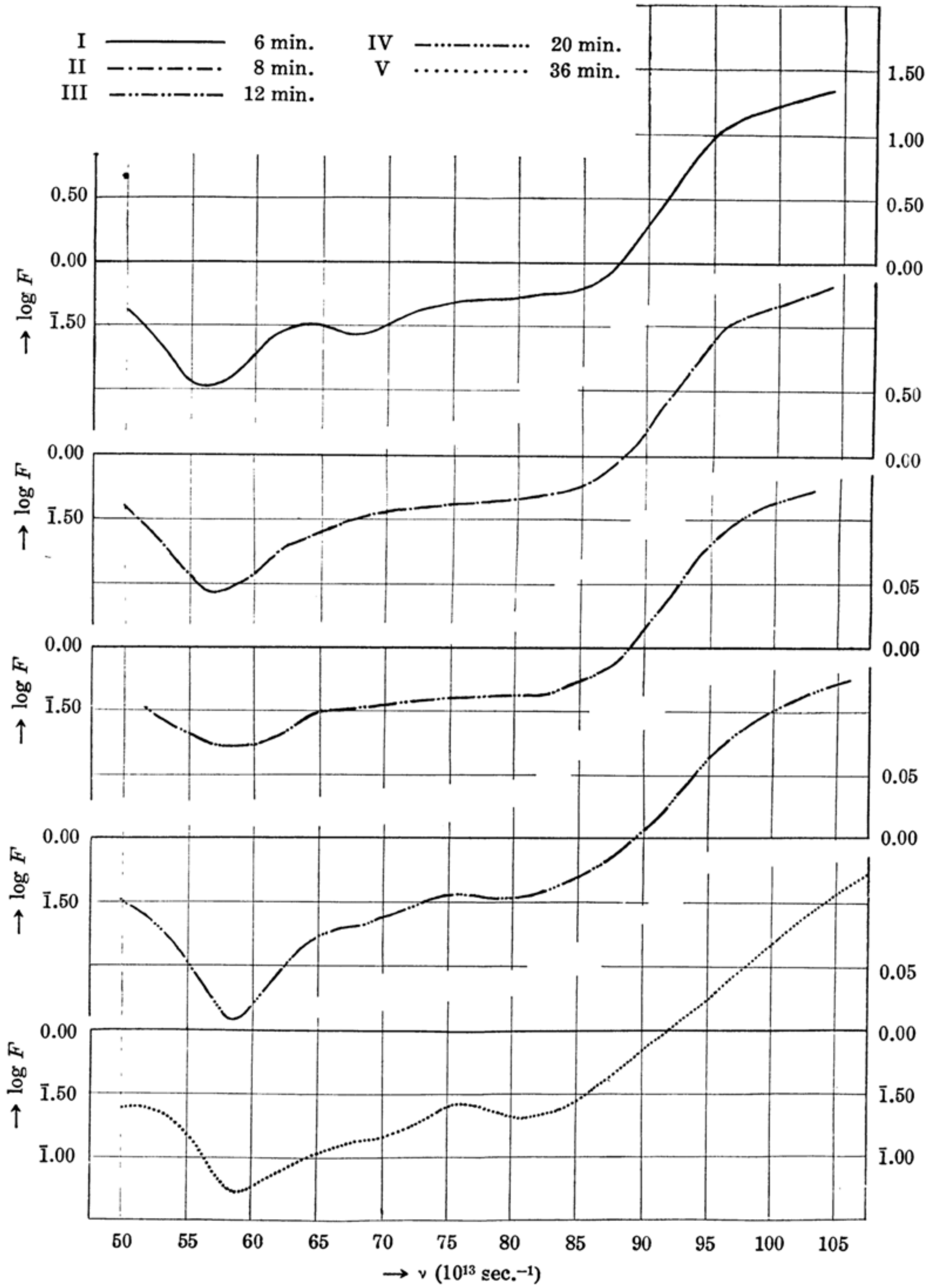
The concentration of $[\mathrm{Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}}]\mathrm{Cl_2}$ in each case being now known, the contribution of the salt to the light absorption of the reaction mixture can be calculated from the concentration (Table 3) and its extinction coefficients (Curve C in Fig. 5), and is subtracted from the absorption of the corresponding mixed solution. The residual absorption, i.e., the absorption, due to compounds other than $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ is shown in Fig. 3, where $E-\varepsilon^c[C]$ is represented by F.

It is evident from this set of curves that the solutions are still mixtures, as we can easily point out at least three different absorption bands, of which one with the frequency of 65×10^{13} and another of about 10×10^{14} gradually disappear as the reaction proceeds, while the band at 75×10^{13} becomes more and more distinct. If $[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl$ and $[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ were the only constituents of the mixed solutions, such gradual change of F would never be seen, but a set of curves with an identical shape and different heights should result after the analysis. Moreover, if the praseo-salt were to change directly to the cis-aquochloro-salt as a reaction of the first, or of the higher, order, the curves of $\log\alpha[X]$ and $\log\alpha'[X]$ should be straight, or concave upwards. We have, however, seen that the curves are convex upwards (Fig. 2). This feature of the curves may be explained, if we assume that the praseo-salt, A, changes first to an intermediate compound, B, and then to the cis-aquochloro-salt, C. Then $\log([A]+[B])$ will give a curve convex upwards. Another fact also indicates that some compound must intervene between A and C; in spite that the colour of the praseo-salt had almost completely disappeared in 30 minutes, the absorption of the cis-aquochloro-salt alone was not seen till after 90 minutes. The absorption curves in Fig. 3, therefore, represent mixed solutions of $[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl$ and the intermediate compound. Whatever the constitution of the latter may be, the analysis of the curves may be done as follows. For this purpose the extinction coefficients of at least one of the salts must be known, but we know none of them: B is an unknown substance and A is the compound whose extinction coefficients are searched for. For practical purpose, however, we may assume without much risk that after 36 minutes from the time of dissolution the praseosalt had completely disappeared, as was shown by the colour of the solution.

Then
$$F_1^V \simeq \varepsilon^B[B] \quad . \tag{4}$$

Then frequencies $76\times10^{13}\,(=\nu_1)$ and $96\times10^{13}\,(=\nu_2)$ were chosen for analysis.

From (1)
$$\begin{vmatrix} \varepsilon_1^A & \varepsilon_1^B \\ \varepsilon_2^A & \varepsilon_2^B \end{vmatrix} = \frac{\begin{vmatrix} F_1^I & \varepsilon_1^B \\ F_2^I & \varepsilon_2^B \end{vmatrix}}{[A]_I} = \frac{\begin{vmatrix} F_1^{II} & \varepsilon_1^B \\ F_2^{II} & \varepsilon_2^B \end{vmatrix}}{[A]_{II}} = \cdots\cdots \tag{1'}$$


I 6 min.
II 8 min.
III 12 min.
IV 20 min.
V 36 min.
0.50
0.00
1̄.50
1.50
1.00
0.50
0.00
0.00
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1̄.50
1̄.00
→ log F
50
55
60
65
70
75
80
85
90
95
100
105
→ ν (10¹³ sec.⁻¹)

Fig. 3.

We get from (4) and Table 3,

$$F_1 \simeq 0.0051\,\varepsilon_1^B \quad \text{and} \quad F_2 \simeq 0.0051\,\varepsilon_2^B.$$

$$\therefore \quad \beta = \frac{F_1^{I}F_2^{V} - F_2^{I}F_1^{V}}{[A]_{I}} = \frac{F_1^{II}F_2^{V} - F_2^{II}F_1^{V}}{[A]_{II}} = \dots\dots\dots\dots\dots\dots \qquad (5)$$

When $\log \beta[A]$ thus calculated by (5) was plotted against time, a straight line was obtained (Fig. 2). This shows that the change of the praseo-salt into B is a reaction of the first order. Extrapolating this straight line, we obtain $\log \beta[A]_{t=0}$ which corresponds to the initial concentration of $[Co(NH_3)_4Cl_{2\binom{(1)}{(6)}}]Cl$, i.e., 0.0150 mol / l. Hence [A] in each of the mixed solutions can be calculated as in Table 4.

Table 4.

The Concentration of $[Co(NH_3)_4Cl_{2\binom{(1)}{(6)}}]Cl$.

	Time (min.)	$\log F_1$	$\log F_2$	$F_1F_2^V - F_2F_1^V$	$\log \beta[B]$	[A] (mol/l.)
I	6	$\bar{1}.698$	1.057	1.92	0.283	0.0088
II	8	$\bar{1}.613$	0.996	1.68	0.225	0.0077
III	12	$\bar{1}.600$	0.902	1.21	0.082	0.0056
IV	20	$\bar{1}.547$	0.724	0.61	$\bar{1}.785$	0.0028
	0	extrapolated		3.27	0.515	0.0150
	36	,,		0.15	$\bar{1}.180$	0.0007

The concentration of B can be found by $[B] = [A]_0 - [A] - [C]$, from Tables 3 and 4.

As to the constitution of the intermediate compound B, there are two possible cases to be considered.

	A	B	C
(1)	$[Co(NH_3)_4Cl_{2\binom{(1)}{(6)}}]Cl$	$[Co(NH_3)_4Cl_{2\binom{(1)}{(2)}}]Cl$	$[Co(NH_3)_4Cl\ H_2O_{\binom{(1)}{(6)}}]Cl_2$
(2)	,,	$[Co(NH_3)_4Cl\ H_2O_{\binom{(1)}{(6)}}]Cl_2$	,,

Prof. Matsuno's research⁽¹⁰⁾ on $[Co\ en_2Cl_{2\binom{(1)}{(6)}}]Cl$ favours the second case, and as we shall see later, kinetic considerations and the absorption spectra also support the view.

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(10) *Loc. cit.*

The aquotization reaction of trans-dichlorotetrammine cobaltic chloride, therefore, can be shown by the following formulæ.

(1) $[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl + H_2O \rightarrow [Co(NH_3)_4Cl\ H_2O{}^{(1)}_{(6)}]Cl_2$.

(2) $[Co(NH_3)_4Cl\ H_2O{}^{(1)}_{(6)}]Cl_2 + H_2O \rightarrow [Co(NH_3)_4Cl\ H_2O{}^{(1)}_{(2)}]Cl_2 + H_2O$.

(3) $[Co(NH_3)_4Cl\ H_2O{}^{(1)}_{(2)}]Cl_2 + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2{}^{(1)}_{(2)}]Cl_3$.

As to the third reaction⁽¹¹⁾ it is not certain whether it proceeds in the sense of the arrow irreversibly or reversibly. Whichever the case may be, the above calculations are scarcely affected by the third reaction, because the two complex salts concerned in it have quite similar absorption curves (Fig. 5).

Kinetics. From the above calculations and discussions, the first and the second reactions may be expressed by the following equations.

$$\frac{d[B]}{dt} = k_1[A] \quad \text{and} \quad \frac{d[C]}{dt} = k_2[B].$$

Hence
$$[A] = [A]_0\, e^{-k_1 t}\ , \tag{6}$$

$$[B] = \frac{k_1[A]_0}{k_1 - k_2}(e^{-k_1 t} + e^{-k_2 t})\ , \tag{7}$$

and
$$[C] = \frac{[A]_0}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\ . \tag{8}$$

From [A] in Table 4, k_1 is calculated by means of (6) (Table 5).

Table 5.

The Velocity Constant k_1.

Time (sec.)	[A] (mol/l.)	k_1 at 17°C.
6×60	0.0088	1.48×10^{-3}
8× ,,	0.0077	1.39× ,,
12× ,,	0.0053	1.37× ,,
20× ,,	0.0028	1.40× ,,
36× ,,	0.0007	1.31× ,,
	Mean value	1.39×10^{-3}

Table 6.

The Velocity Constant k_2.

Time (sec.)	[B] (mol/l.)	k_2 at 17°C.
8×60	0.0049	8.1×10^{-4}
12× ,,	0.0058	10.5× ,,
20× ,,	0.0064	9.3× ,,
36× ,,	0.0044	8.3× ,,
	Mean value	9.05×10^{-4}

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(11) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 127; *ibid.*, **38** (1917), 696; J. N. Brönsted, *Z. physik. Chem.*, **122** (1926), 392; *J. Am. Chem. Soc.*, **49** (1927), 439.

The velocity constant k_2 is calculated by means of (7), k_1, [A] and [B] being now known (Tables 3, 4 and 5).

The concentrations of the three salts are calculated from (6), (7) and (8), substituting k_1 and k_2 thus found.

Table 7. Concentrations of the Compounds contained in the Mixed Solutions.

Time (min.)	$[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl$ (mol/l.)		$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(6)}Cl_2]$ (mol/l.)		$[Co(NH_3)_4Cl\ H_2O^{(1)}_{(2)}]Cl_2$ (mol/l.)	
	Found	Calc.	Found	Calc.	Found	Calc.
0	0.0150	0.0150	0.0000	0.0000	0.0000	0.0000
6	0.0088	0.0092	0.0048	0.0046	0.0014	0.0012
8	0.0077	0.0076	0.0049	0.0055	0.0024	0.0019
12	0.0056	0.0055	0.0058	0.0063	0.0036	0.0032
20	0.0028	0.0028	0.0064	0.0062	0.0058	0.0050
36	0.0007	0.0008	0.0044	0.0038	0.0099	0.0104
90	0.0000	0.0000	0.0007	0.0003	0.0143	0.0147

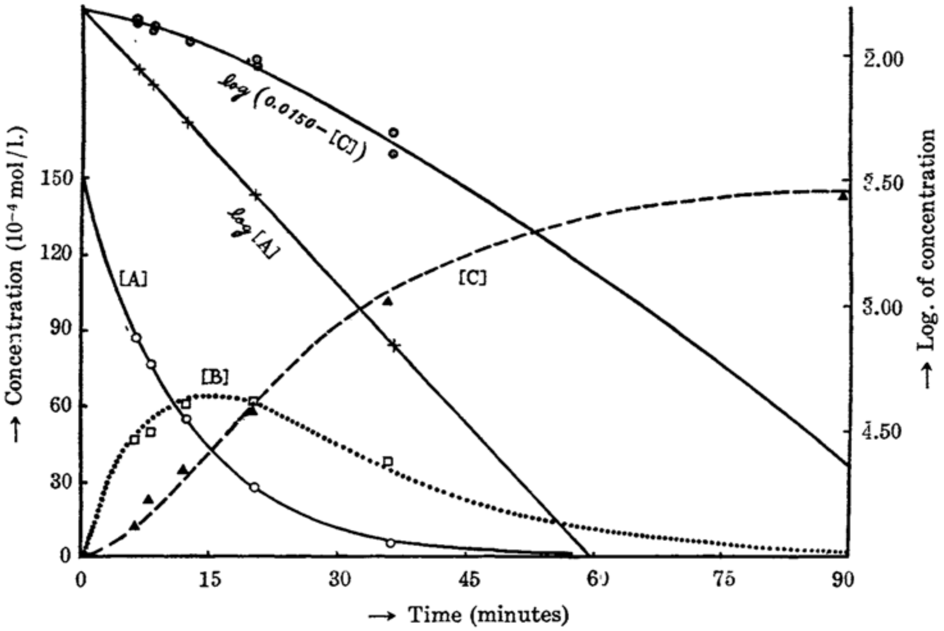


Fig. 4.

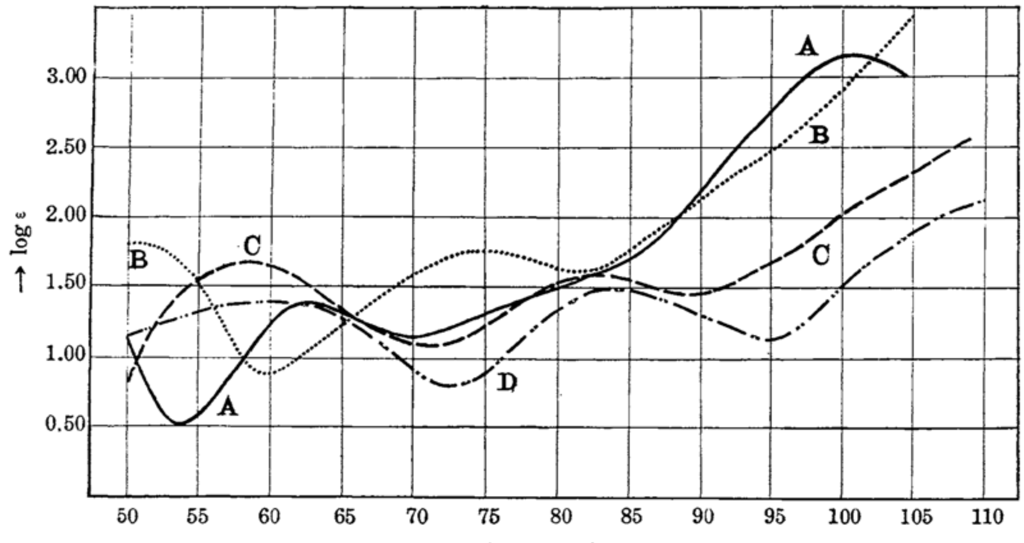
The results are summarized in Fig. 4 in which the smooth curves show the calculated values.

The maximum value of [B] is attained at

$$t_{\max.} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \; . \tag{10}$$

The results of the analysis show that the maximum value is attained at a point between 12 and 20 minutes, while the calculation by (10) gives 15 minutes.

Absorption Curves of $[\mathrm{Co(NH_3)_4Cl_2}{}^{(1)}_{(6)}]\mathrm{Cl}$ and $[\mathrm{Co(NH_3)_4Cl\ H_2O}{}^{(1)}_{(6)}]\mathrm{Cl_2}$. Trans-aquochloro-tetrammine cocaltic salt has never been reported. Trans-dichloro-tetrammine cobaltic saltic salt can never exist alone in aqueous solutions and consequently its absorption has never been observed without superposition of those of its aquotization products. In order to find molar extinction coefficients of these very unstable complex compounds, the curves I and V in Fig. 1 were again analysed making use of the calculated concentrations in Table 7. The results are shown in Fig. 5, together with the absorption curves of $[\mathrm{Co(NH_3)_4Cl\ H_2O}{}^{(1)}_{(2)}]\mathrm{Cl_2}$ and $[\mathrm{Co(NH_3)_4(H_2O)_2}{}^{(1)}_{(2)}]\mathrm{Cl_3}$.



A ——————— $[\mathrm{Co(NH_3)_4Cl_2}{}^{(1)}_{(6)}]\mathrm{Cl}$ C – – – – – – $[\mathrm{Co(NH_3)_4H_2O\ Cl}{}^{(1)}_{(2)}]\mathrm{Cl_2}$

B ………… $[\mathrm{Co(NH_3)_4H_2O\ Cl}{}^{(1)}_{(6)}]\mathrm{Cl_2}$ D –··–··–··– $[\mathrm{Co(NH_3)_4(H_2O)_2}{}^{(1)}_{(2)}]\mathrm{Cl_3}$

Fig. 5.

The selective absorption bands of these complex salts are given in Table 8.

Table 8.

	The first band		The second band		The third band	
	ν	log ε	ν	log ε	ν	log ε
$[Co(NH_3)_4Cl_{2\substack{(1)\\(6)}}]Cl$	$< 50\times 10^{13}$	1.2	62.5×10^{13}	1.37	10×10^{14}	3.16
$[Co(NH_3)_4Cl\ H_2O_{\substack{(1)\\(6)}}]Cl_2$	50 ,,	1.3	74.5 ,,	1.76	—	—
$[Co(NH_3)_4Cl\ H_2O_{\substack{(1)\\(2)}}]C\ l$	58.5 ,,	1.67	82.5 ,,	1.59	—	—
$[Co(NH_3)_4(H_2O)_{2\substack{(1)\\(2)}}]Cl_3$	60 ,,	1.40	84 ,,	1.49	—	—

The first and the second band of $[Co(NH_3)_4Cl\ H_2O_{\substack{(1)\\(6)}}]Cl_2$ is of higher frequency than the corresponding band of $[Co(NH_3)_4Cl_{2\substack{(1)\\(6)}}]Cl$. In other words, the substitution of the Cl ion in the co-ordination by H_2O molecule shows a hypsochromic effect. Similar effect is observed when Cl in $[Co(NH_3)_4Cl\ H_2O_{\substack{(1)\\(2)}}]Cl_2$ is substituted by H_2O.

One of the most remarkable features of the absorption curve of the praseo-salt is that it has three absorption bands, of which the third is of interest. Generally speaking, most complex salts have two selective absorption bands in the visible and the near-ultraviolet regions and it has been known that only a few trans-dinitro-complex compounds such as $[Co(NH_3)_4(NO_2)_{2\substack{(1)\\(6)}}]Cl$(12), $[Co(NH_3)_3(NO_2)_3]$(12), $[Co(NH_3)_2(NO_2)_4]NH_4$(12), $[Co(NH_3)_3(NO_2)_2Cl]$(13) and $[Co(NH_3)_3(NO_2)_2Br]$(13), and some rhodanatoammine complex salts(14) show the third absorption bands. The author should like to predict that the third band is one of the general characteristics of those complex compounds which have at least one pair of ions co-ordinated in trans-position to each other. In order to confirm this view, Mr. S. Kashimoto(15) in this laboratory has recently examined $[Co(NH_3)_4NO_2Cl]Cl$ and $Na_3[Co(NO_2)_6]$ and found that they have also the third absorption bands.

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(12) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(13) M. Kobayashi, A. Hagitani, and I. Mita, *ibid.*, **57** (1936), 500.

(14) Y. Shibata and K. Matsuno, *J. Coll. Sci.*, *Imp. Univ. Tokyo*, **41** (1921), Art. 9.

(15) The results shall soon be published.

Summary.

(1) A new complex compound $[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(6)}]\mathrm{Cl_2}$ was found by the spectrographic analysis.

(2) Trans-dichloro-tetrammine cobaltic chloride in aqueous solutions changes in the following scheme:

$$\begin{tikzcd}
{[\mathrm{Co(NH_3)_4Cl_2}{}^{(1)}_{(6)}]\mathrm{Cl}} \arrow[r] & {[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(6)}]\mathrm{Cl_2}} \arrow[d] & \\
 & {[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(2)}]\mathrm{Cl_2}} \arrow[r] & {[\mathrm{Co(NH_3)_4(H_2O)_2}]\mathrm{Cl_3}}
\end{tikzcd}$$

(3) The velocity constants of the first two reactions were found to be 1.39×10^{-3} and 9.05×10^{-4} respectively.

(4) The absorption curves were found for the unstable complex salts $[\mathrm{Co(NH_3)_4Cl_2}{}^{(1)}_{(6)}]\mathrm{Cl}$ and $[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(6)}]\mathrm{Cl_2}$, both of which can never exist in acqueous solutions without contamination of related compounds.

(5) The praseo-salt shows a third absorption band of the same type as that of $[\mathrm{Co(NH_3)_4(NO_2)_2}{}^{(1)}_{(6)}]\mathrm{Cl}$.

(6) The third absorption band is supposed to be one of the general characteristics of those complex salt which have in the co-ordination at least one pair of ions in trans-positions to each other.

(7) Substitution of Cl in $[\mathrm{Co(NH_3)_4Cl_2}{}^{(1)}_{(6)}]\mathrm{Cl}$ or $[\mathrm{Co(NH_3)_4Cl\ H_2O}^{(1)}_{(2)}]\mathrm{Cl_2}$ by $\mathrm{H_2O}$, has hypsochromic effect.

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