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Abstract

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ON THE QUESTION OF ISOTOPIC EXCHANGE REACTIONS IN SALTS OF THE KOSS TYPE

In previous studies, the kinetics of isotopic-exchange reactions in complex bromides of Pt^II and Pt^IV (1–4), as well as in Zeise' s salt of composition $K[PtC_2H_4Cl_3]$ (5), were investigated. It was found that bromine ions coordinated to Pt^II exchange with free bromine ions in the surrounding medium at different rates depending on the composition of the inner sphere and the mutual influence of the coordinated groups. At the same time, both trans influence and cis influence affected the rate of exchange of bromine ions.

The effects of trans and cis influence were manifested especially clearly in the example of the isotopic-exchange reaction in Zeise' s salt. It could be expected that the chlorine ions in Koss' s salt $K[PtNH_3Cl_3]$ might likewise prove to be nonequivalent with respect to the rate of isotopic exchange. However, Elleman, Reischus, and Martin in 1959 (6), studying chlorine exchange in $K[PtNH_3Cl_3]$, came to the conclusion that the trans effect does not affect isotopic-exchange reactions. Undoubtedly, this discrepancy in the conclusions required additional verification.

In the present work we studied the isotopic exchange of chlorine in the systems $K[PtNH_3Cl_3]$ and $K[PtPyCl_3]$. The results obtained indicate the presence of functional nonequivalence of the chlorine ions in both complex ions studied.

Experimental Part

Koss' s ammonia salt and its pyridine analog were synthesized by the method of (7–9), and their composition was checked by analyses. The experimental procedure for the exchange experiments did not differ substantially from the procedure described in (5). The only difference was in the method of applying to the targets the isolated complexes $[Pt(NH_3)_4][PtNH_3Cl_3]_2$ and $[PtPy_4][PtPyCl_3]_2$, which were dissolved in 10% KOH solution with heating, and then the alkaline solutions were applied to the targets. It is important to note that, when working with the ammonia Koss salt, the yield of $[Pt(NH_3)_4][PtNH_3Cl_3]_2$ in individual

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experiments varied from ~ 90 to 75%, but was never below 75%. This indicates that, under the conditions of our experiments, monoammine ions were the predominant form in solution.

Exchange in the systems:

$K[PtNH_3Cl_3] + 3KCl^* \rightarrow$; $K[PtPyCl_3] + 3KCl^* \rightarrow$

was carried out at different concentrations of the complex salt (at constant ligand concentration), and at different concentrations of the ligand ion (at constant concentration of the complex ion). The results of the experiments are summarized in Tables 1, 2, and 3 and are presented graphically (Figs. 1, 2, 3). Tables 1 and 2 give experimental data for Koss' s salt and its pyridine analog at 25°. Table 3 presents two methods of calculating the exchange-rate constants k, based on experimentally found values of R and the concentration of chlorine in the complex. In one of these methods, the value R is divided by the concentration of slowly and rapidly exchanging chlorine ions, and in the other by the total concentration of chlorine ions in the complex. Both methods of calculation show that the rates of exchange of chlorine atoms at the coordinates Cl—Pt—Cl and NH_3—Pt—Cl differ by approximately an order of magnitude.

Fig. 1 gives the values of $\ln(1-F)$ for the system $K[PtNH_3Cl_3] + 3KCl^* \rightarrow$ as a function of time for all three concentrations listed in Table 1. The dotted lines denote the straight lines obtained by resolving the experimental curves.

Fig. 2 gives the same data for the system $K[PtPyCl_3] + 3KCl^* \rightarrow$. The experimental curves were resolved by the method indicated in work (2).

Fig. 1. Dependence of $\ln(1-F)$ on time at concentrations of the complex salt $K[PtNH_3Cl_3]$ (10^{-2} mol/l): 0.83 (1), 1.66 (2), and 3.32 (3)

We have established that, for the reactions of chlorine exchange in the complexes $K[PtNH_3Cl_3]$ and $K[PtPyCl_3]$, the dependence of the degree of exchange on time does not obey the law of simple exchange and is graphically expressed by curved lines (Figs. 1-3). These curves can be resolved into two straight lines, from which two half-exchange periods can be determined, corresponding to rapidly and slowly exchanging chlorine ions. Thus, as applied

Table 1

Fig. 2. Dependence of ln(1—F) on time at different concentrations of the complex salt K[PtPyCl3]

Figure 2: Fig. 2. Dependence of ln(1—F) on time at different concentrations of the complex salt K[PtPyCl3]

$K[PtNH_3Cl_3]$, 10^2 mol/l	$K[PtNH_3Cl_3]$, 10^2 g-at Cl/l	KCl, 10^2 g-at Cl/l	$Cl_{(1-3)}$ in complex salt, 10^2 g-at Cl/l	Cl_2 in complex salt, 10^2 g-at Cl/l	$\tau_{1/2}(1)$, h	$\tau_{1/2}(2)$, h	R_1, g-at Cl/l	R_2, g-at Cl/l $\cdot$ sec
0.83	2.49	4.98	1.66	0.83	5	45	$4.78 \cdot 10^{-7}$	$3.0 \cdot 10^{-8}$
1.66	4.98	4.98	3.32	1.66	4.5	31.5	$8.50 \cdot 10^{-7}$	$7.6 \cdot 10^{-8}$
3.32	9.96	4.98	6.64	3.32	2.5	28	$21.8 \cdot 10^{-7}$	$13.7 \cdot 10^{-8}$

to chlorinated salts of the Koss type, the kinetic nonequivalence of ligands is shown. The curvature of the straight line is manifested especially clearly in the region corresponding to the exchange of approximately 2/3 of the chlorine contained in the complex ion. This gives us grounds to consider that rapid exchange is characteristic of chlorine ions on the coordinate Cl—Pt—Cl, and slow exchange on the coordinate NH_3—Pt—Cl. It is further seen that exchange on the coordinate Py—Pt—Cl proceeds more slowly than on the coordinate NH_3—Pt—Cl (Tables 1, 2). These data agree well with the fact that the trans influence of chlorine is greater than that of ammonia, and the latter is greater than the trans influence of pyridine. On the other hand, the greater exchange rate of two chlorine atoms in the ion $[PtPyCl_3]^-$ compared with the ion $[PtNH_3Cl_3]^-$ confirms the greater cis influence of pyridine compared with the cis influence of ammonia. This fact has been established in a number of other works from our laboratory (10-12). Our

the data agree well with the results on the kinetics of isotopic exchange in the bromide analogs of Koss's salt, with data on the kinetics of substitution reactions in Pt^II complexes, with the results of our work on isotopic exchange in Zeise' s salt, and also with the well-known Peyrone regularity.

As regards the correspondence of the data from our laboratory with the results of work by the American authors of Martin' s group ($^{13-16}$), it may be said that

Fig. 2. Dependence of $\ln(1-F)$ on time at different concentrations of the complex salt $K[PtPyCl_3]$ (10^{-2} M/l): 0.83 *(1)*, 1.66 *(2)*, and 3.32 *(3)*

the strongest discrepancy consists in the fact that the rates of aquation of chlorine ions in Koss' s salt, situated at the coordinates Cl—Pt—Cl and NH_3—Pt—Cl, differ, according to our data, by approximately an order of magnitude, whereas according to the Americans they differ only by a factor of 1.4.* The data of Martin and others concerning the ion $[PtNH_3Cl_3]^-$ do not agree with the generally known fact of the practical absence of a trans-isomer in the synthesis of salts of the Peyrone type. They also contain a certain internal contradiction: they indicate that the instability constant corresponding to elimination of cis-chlorine according to the equation

Table 2

$K[PtPyCl_3]$, M/l 10^2	$K[PtPyCl_3]$, GAC/l 10^3	KCl, 10^2 GAC/l	$Cl_{(1-3)}$ in the complex salt, 10^2 GAC/l	Cl_2 in the complex salt, 10^2 GAC/l	$\tau_{1/2}(1)$, h	$\tau_{1/2}(2)$, h	R_1, GAC/l· s	R_2, GAC/l· s
0.83	2.49	4.98	1.66	0.83	4	54.6	$6.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-8}$
1.66	4.98	4.98	3.32	1.66	3.2	54.3	$12.0 \cdot 10^{-7}$	$4.45 \cdot 10^{-8}$
3.32	9.96	4.98	6.64	3.32	2	41	$27.4 \cdot 10^{-7}$	$9.35 \cdot 10^{-8}$

$$[PtNH_3Cl_3]^- + H_2O \rightleftharpoons [PtNH_3H_2OCl_2]^0 + Cl^-$$

at 25° and $\mu = 0.318$ is equal to $1.4 \cdot 10^{-2}$, while the corresponding constant for trans-chlorine is less than $0.2 \cdot 10^{-2}$. With nearly equal rates of the aquation reaction, such a situation can arise only at the expense of a higher rate of reverse entry of the chloride ion into the place of water situated in the trans-position to the ammonia molecule. But this is unlikely, and such a conclusion can be drawn only with an unjustified underestimation of the rules of trans-influence as applied to derivatives of Pt^II. Meanwhile, the data we obtained, in combination with the higher rate established by a number of authors for the interaction of trans-$[Pt(NH_3)_2Cl_2]$ with water and ammonia (as compared with the cis-isomer), make it possible to explain the practical absence of a trans-isomer impurity in the synthesis of cis-diammine Pt^II (^{17}).

* Quite recently, from a private communication by Martin, corrected values of the rate constants for the aquation of Koss' s ammoniacal salt, obtained on the basis of spectrophotometric studies, have become known.

Table 3

Fig. 3. Dependence of $\ln(1-F)$ on time at ligand-ion concentrations (10^{-2} mol/l): 4.98 (1) and 14.94 (2)

Figure 3: Fig. 3. Dependence of $\ln(1-F)$ on time at ligand-ion concentrations (10^{-2} mol/l): 4.98 (1) and 14.94 (2)

K[PtNH$_3$Cl$_3$]	K[PtNH$_3$Cl$_3$]	K[PtNH$_3$Cl$_3$]	K[PtNH$_3$Cl$_3$]	K[PtPyCl$_3$]	K[PtPyCl$_3$]	K[PtPyCl$_3$]	K[PtPyCl$_3$]
Cl_{(1)} –Pt– Cl_{(3)} $K_1 = \frac{R_1}{C\mathrm{Cl}_{(1-3)}}$	NH$_3$–Pt– Cl_{(2)} $K_2 = \frac{R_2}{C\mathrm{Cl}_{(2)}}$	Cl_{(1)} –Pt– Cl_{(3)} $K_1 = \frac{R_1}{C3\mathrm{Cl}}$	NH$_3$–Pt– Cl_{(2)} $K_2 = \frac{R_2}{C3\mathrm{Cl}}$	Cl_{(1)} –Pt– Cl_{(3)} $K_1 = \frac{R_1}{C\mathrm{Cl}_{(1-3)}}$	Py–Pt – Cl_{(2)} $K_2 = \frac{R_2}{C\mathrm{Cl}_{(2)}}$	Cl_{(1)} –Pt– Cl_{(1)} $K_1 = \frac{R_1}{C3\mathrm{Cl}}$	Py–Pt – Cl_{(2)} $K_2 = \frac{R_2}{C3\mathrm{Cl}}$
$2.88 \cdot 10^{-5}$	$3.65 \cdot 10^{-6}$	$1.94 \cdot 10^{-5}$	$1.22 \cdot 10^{-6}$	$3.62 \cdot 10^{-5}$	$3.12 \cdot 10^{-6}$	$2.41 \cdot 10^{-5}$	$1.04 \cdot 10^{-6}$
$2.57 \cdot 10^{-5}$	$4.6 \cdot 10^{-6}$	$1.71 \cdot 10^{-5}$	$1.53 \cdot 10^{-6}$	$3.62 \cdot 10^{-5}$	$2.68 \cdot 10^{-6}$	$2.41 \cdot 10^{-5}$	$0.894 \cdot 10^{-6}$
$3.3 \cdot 10^{-5}$	$4.12 \cdot 10^{-6}$	$2.21 \cdot 10^{-5}$	$1.37 \cdot 10^{-6}$	$4.12 \cdot 10^{-5}$	$2.82 \cdot 10^{-6}$	$2.74 \cdot 10^{-5}$	$0.938 \cdot 10^{-6}$
$2.91 \cdot 10^{-5}$	$4.16 \cdot 10^{-6}$	$1.95 \cdot 10^{-5}$	$1.37 \cdot 10^{-6}$	$3.82 \cdot 10^{-5}$	$2.87 \cdot 10^{-6}$	$2.52 \cdot 10^{-5}$	$0.98 \cdot 10^{-6}$

The practical absence of an influence of the concentration of external chloride ions (Fig. 3) on the rate of isotopic exchange in the monoamines studied agrees with the idea that in these systems also the principal mechanism of exchange is reversible aquation.

Fig. 3. Dependence of $\ln(1-F)$ on time at ligand-ion concentrations (10^{-2} mol/l): 4.98 (1) and 14.94 (2)

The exchange rates were calculated as indicated in paper (5). From the tables it is seen that the exchange rate is directly proportional to the concentration of the complex salt and is practically independent of the concentration of the external ligand. Therefore the exchange-rate constants were calculated by us according to the formula $R = kC_{\text{complex}}$ and are given in Table 3. The investigations are continuing.

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