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Abstract

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Features of the Formation of Complex Compounds with Ring-Forming Substituents

(Presented by Academician A. A. Grinberg, December 19, 1960)

It is known that mixed tetrammines of composition $[\mathrm{Pt}2\mathrm{A}_1 2\mathrm{A}_2]\mathrm{X}_2$ can be obtained from two different diammines $[\mathrm{Pt}2\mathrm{A}_1\mathrm{X}_2]$ or $[\mathrm{Pt}2\mathrm{A}_2\mathrm{X}_2]$ by dissolving them in the corresponding other amine A_2 or A_1, and in the tetrammine obtained the spatial configuration of the original diammines is retained.

Such symmetrical behavior of two diammines differing in composition in the process of synthesis of one and the same mixed tetrammine is clearly expressed and is constantly observed. As a result, it has been used as one of the methods for identifying newly obtained diammines. The isomerism once proposed by S. M. Jørgensen (^{1}) for mixed tetrammines of composition* $[\mathrm{Pt(NH_3)Dma_2}]\mathrm{Cl}_2$ was, as is known, the subject of discussion and experimental verification in the works of L. A. Chugaev and B. P. Orelkin (^{2}) and K. Drew and G. Yutt (^{3}). The former showed that analogous isomers, using compounds with monoacetyl as an example, cannot be established, while the latter established the identity of both compounds obtained by S. M. Jørgensen.

In the course of an investigation of platinum compounds with diethanolamine, a compound of composition** $[\mathrm{Pt\,Detm_2Cl_2}]$ was obtained which, according to conductivity measurements, the result of N. S. Kurnakov' s thiourea reaction, and A. A. Grinberg' s reaction with KI and phenolphthalein, is undoubtedly a trans-isomer. It was decided to carry out two reactions:

$$[\mathrm{Pt(NH_3)_2Cl_2}] + 2\mathrm{Detm} \rightarrow \qquad (a)$$

$$[\mathrm{PtDetm_2Cl_2}] + 2\mathrm{NH_3} \rightarrow \qquad (b)$$

which, evidently, should have led to the same result and thereby once again confirmed the trans-structure of the diethanolamine derivative. It turned out that, whereas reaction (a) proceeds quite satisfactorily and the indicated trans-tetrammine can be isolated in the form of the chloride and of the tetrachloroplatinate, which is sparingly soluble in water, from the solution formed by reaction (b) it is not possible in an analogous manner to isolate the chloride, the tetrachloroplatinate does not precipitate, and upon vigorous acidification with hydrochloric acid the original diamine is isolated in unchanged form.

Thus, in this case, the nonequivalence of reactions (a) and (b) has been established, and this, evidently, must be associated with the properties of diethanolamine, which is capable of displaying a coordination capacity equal to one (bond through nitrogen) and to two (formation of cyclic compounds). The formation of a cyclic compound, using as an example the reaction mentioned above of [PtDetm$_2$Cl$_2$] with ammonia, may be represented by the following scheme:

[[structural scheme shown: trans- $[\text{PtDetm}_2\text{Cl}_2] + 2\text{NH}_3 \rightarrow$ cyclic platinum diethanolamine complex $+ 2\text{NH}_4\text{C}$

and the liberation of the starting diamine upon acidification with HCl is represented as follows:

$$[\text{structural scheme}] + 2\text{HCl} \longrightarrow [\text{structural scheme}]$$

Let us point out in this connection that, for the similarly constructed platinum compound with glycocoll* [Pt(GlH)$_2$Cl$_2$], both of the reactions described, with the successive action of amine until a colorless solution is formed and of hydrochloric acid to precipitate the substance, lead to the same result, namely (^{4,5}),

$$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] + 2\text{GlH} \rightarrow [\text{Pt}(\text{NH}_3)_2(\text{GlH})_2]\text{Cl}_2; \qquad (\ )$$

$$[\text{Pt}(\text{GlH})_2\text{Cl}_2] + 2\text{NH}_3 \rightarrow [\text{Pt}(\text{NH}_3)_2(\text{GlH})_2]\text{Cl}_2. \qquad (\ )$$

We emphasize that in reaction ( ), by analogy with reaction ( ), one might have expected the formation of the cyclic compound [PtGl$_2$].

Taking into account, moreover, that the monoethanolamine trans-diamine** [PtEtm$_2$Cl$_2$] behaves in this respect like the glycocoll analogue and quite differently from [PtDetm$_2$Cl$_2$], it is necessary to find an explanation for this phenomenon, anomalous as applied to [PtDetm$_2$Cl$_2$].

For this purpose let us first consider the reactions of trans-[PtEtm$_2$Cl$_2$] with ammonia, monoethanolamine, and diethanolamine, which were carried out under identical conditions over a fairly wide range of concentrations. They are of interest to us because the molecule of monoethanolamine contained in [PtEtm$_2$Cl$_2$]

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* Dma –dimethylamine.
** Detm –diethanolamine.

can in principle form a ring, while the reacting molecules of ammonia, monoethanolamine, and diethanolamine obviously have different rates of penetration into the inner sphere of the diamine.

The results of the reactions are represented by the equations:

$$\begin{aligned}
&1.\ [\mathrm{PtEtm_2Cl_2}] + 2\mathrm{NH_3} \rightarrow [\mathrm{PtEtm_2(NH_3)_2}]\mathrm{Cl_2}.\\
&2.\ [\mathrm{PtEtm_2Cl_2}] + 2\mathrm{Etm} \rightarrow [\mathrm{PtEtm_4}]\mathrm{Cl_2}.\\
&3.\ [\mathrm{PtEtm_2Cl_2}] + 2\mathrm{Detm} \rightarrow [\mathrm{Pt(Etm-H)_2}] + 2\mathrm{DetmHCl},
\end{aligned}$$

i.e., in processes 1 and 2 the expected tetramines were formed, whereas in the last case a cyclic compound was isolated

[cyclic platinum structural formula]

On the basis of these reactions one may conclude that the ratio of the rates of ring formation by the monoethanolamine molecule from $[\mathrm{PtEtm_2Cl_2}]$ and of penetration of the corresponding reacting amine into the sphere of the diamine is such that in the first and second cases penetration predominates, and in the third, ring formation. It may also be said that the indicated amine molecules, in terms of their rate of penetration into the inner sphere of the diamine under consideration, are arranged in the series

$$\mathrm{Detm} < \mathrm{NH_3},\ \mathrm{Etm}.$$

The latter relationship is clearly confirmed by the reactions given below with the glycocoll trans-diamine, reactions 1 and 2, like reactions ( ) and ( ), consisting of the successive action of amine and hydrochloric acid:

$$\begin{aligned}
&1'.\ [\mathrm{Pt(GlH)_2Cl_2}] + 2\mathrm{NH_3} \rightarrow [\mathrm{Pt(GlH)_2(NH_3)_2}]\mathrm{Cl_2}\ (^5).\\
&2'.\ [\mathrm{Pt(GlH)_2Cl_2}] + 2\mathrm{Etm} \rightarrow [\mathrm{Pt(GlH)_2Etm_2}]\mathrm{Cl_2}.\\
&3'.\ [\mathrm{Pt(GlH)_2Cl_2}] + 2\mathrm{Detm} \rightarrow [\mathrm{PtGl_2}] + 2\mathrm{DetmHCl}.
\end{aligned}$$

A comparison of the reactions described above:

$$\begin{aligned}
&1''.\ [\mathrm{Pt(GlH)_2Cl_2}] + 2\mathrm{NH_3} \rightarrow [\mathrm{Pt(GlH)_2(NH_3)_2}]\mathrm{Cl_2};\\
&2''.\ [\mathrm{PtDetm_2Cl_2}] + 2\mathrm{NH_3} \rightarrow [\mathrm{Pt(Detm-H)_2}] + 2\mathrm{NH_4Cl}
\end{aligned}$$

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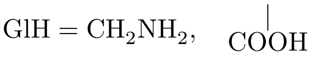
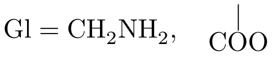
* 
$\mathrm{GlH} = \mathrm{CH_2NH_2},\ \underset{\mathrm{COOH}}{|}$

$\mathrm{Gl} = \mathrm{CH_2NH_2},\ \underset{\mathrm{COO}}{|}$

** Etm –monoethanolamine.

leads to the conclusion that, in the diethanolamine molecule, the rate of ring formation is greater than in the glycol molecule.

In light of the developing idea that the result of the reaction of a diamine with a free amine depends on the ratio of the rates of ring formation by the inner-sphere amine and of substitution by the external one, let us consider the reactions of K_2PtCl_4 with an excess of monoethanolamine and diethanolamine. After the first act of the process,

$$K_2PtCl_4 + Etm \rightarrow K[PtEtmCl_3] + KCl,$$

which leads to the formation of a monoamine, the further course depends on the ratio just mentioned and may lead to the formation of a tetramine or of a cyclic diamine according to the schemes:

$$1''. \quad K[PtEtmCl_3] + 3Etm \rightarrow [PtEtm_4]Cl_2 + KCl.$$

$$2''. \quad K[PtDetmCl_3] + Detm \rightarrow K[Pt(Detm - H)Cl_2] + DetmHCl.$$

$$K[Pt(Detm - H)Cl_2] + Detm \rightarrow [PtDetm(Detm - H)Cl] + KCl.$$

$$[Pt(Detm - H)DetmCl] + Detm \rightarrow [Pt(Detm - H)_2] + DetmHCl.$$

The fact that the reaction with monoethanolamine actually proceeds according to the first equation is proved by the formation of the tetramine $[PtEtm_4Cl_2]Cl_2$ upon chlorination of the resulting solution in hydrochloric acid medium. The course of the reaction with diethanolamine according to the second scheme is supported by the interesting fact that, upon simple acidification of the resulting solution with hydrochloric acid in the cold, a precipitate of the above-mentioned $[PtDetm_2Cl_2]$ separates almost immediately. The same can be proved by measuring the pH in solutions of $K_2PtCl_4 + Etm$ and $K_2PtCl_4 + Detm$, which were prepared as follows: 0.5 g of K_2PtCl_4 in 5 ml of water was mixed, respectively, with 5 ml of a 4.7 M solution of monoethanolamine and 5 ml of a 4.25 M solution of diethanolamine; after 3 days the solutions were diluted to 50 ml and examined the following day.

In parallel, analogous operations were carried out with 4 ml of a 4.7 M solution of monoethanolamine ($K = 3.46 \cdot 10^{-5}$) and 4 ml of a 4.25 M solution of diethanolamine ($K = 9.6 \cdot 10^{-6}$), which correspond to the possible excess of amine after formation of the tetramine.

If the interaction of the platinite with the amine proceeds according to the first scheme, the pH of the solution under study should approximately correspond to the value obtained in the solution of the corresponding free amine. If the process proceeds according to the second scheme, which in sum may be expressed by the equation

$$K_2PtCl_4 + 4Detm \rightarrow [Pt(Detm - H)_2] + 2DetmHCl + 2KCl,$$

the pH should decrease under the influence of the $DetmHCl$ formed.

It turned out that, in the system K_2PtCl_4 with diethanolamine, the pH is considerably lower than in the solution of free diethanolamine (respectively 9.87 and 11.11) and practically coincides with the theoretical value that corresponds to the formation of the cyclic diamine (9.89). In the system with monoethanolamine the corresponding values are much closer (11.0 and 11.51) and indicate that the predominant direction in this reaction is the formation of the tetramine. Thus, for monoethanolamine the process of substitution into the inner sphere is more characteristic; for diethanolamine, on the contrary, the tendency toward ring formation is more clearly expressed.

From the point of view under discussion, it is interesting to compare the results of the reactions of $[Pt(NH_3)_2Cl_2]$ and $[PtDetm_2Cl_2]$ with an excess of ethylenediamine, taking into account that, upon cleavage of the mixed tetramine $[Pt(NH_3)_2Detm_2]Cl_2$ in hydrochloric acid medium, analytically pure $[Pt(NH_3)_2Cl_2]$ is formed. Knowing that the interaction of $[Pt(NH_3)_2Cl_2]$ with ethylenediamine leads to the formation of $[PtEn_2]Cl_2$, one should expect that the reaction of $[PtDetm_2Cl_2]$ with ethylenediamine should give an analogous result. However, the greater rate of ring formation in the diethanolamine molecule prevents substitution by ethylenediamine, and the reaction proceeds according to the scheme

$$[PtDetm_2Cl_2] + 2En \rightarrow [Pt(Detm - H)_2] + 2EnHCl.$$

Upon acidification of the solution with hydrochloric acid, unchanged $[\mathrm{PtDetm_2Cl_2}]$ is precipitated.

It is clear that from $[\mathrm{PtDetm_2Cl_2}]$, as the starting product, one can obtain the triamine and tetramine by reaction with an amine whose rate of entry exceeds the rate of ring formation in the diethanolamine molecule. This amine proved to be pyridine, which is consistent with the data of A. A. Grinberg and Yu. N. Kukushkin [6] on the rates of entry of ammonia and pyridine into $\mathrm{K_2PtCl_4}$.

In conclusion, we note that the above-mentioned ratio of the rates of ring formation and entry is maintained under certain reaction conditions (pH, temperature, etc.).

Thus, in the well-known reaction of A. A. Grinberg [4] concerning configuration,

$$\mathrm{[Pt(NH_3Cl)_2] + GlH_{excess} \rightarrow [Pt(NH_3)_2GlCl] + HCl},$$

$$[Pt(NH_3)_2GlCl] \rightarrow [Pt(NH_3)_2Gl]Cl$$

the process proceeds in an acidic medium, and the rate of ring formation predominates.

When the pH is raised, which can be achieved by neutralization of glycol, the ratio of rates changes in the opposite direction, and the reaction proceeds according to the scheme

$$[Pt(NH_3Cl)_2] + 2GlH + 2NaOH \rightarrow [Pt(NH_3Gl)_2] + 2NaCl + 2H_2O,$$

and upon acidification with HCl, the tetramine $[Pt(NH_3GlH)_2]Cl_2$ precipitates.

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Note: Figure translations are in progress. See original paper for figures.