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Abstract

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CIS ISOMER OF THE INNER-COMPLEX SALT OF DIVALENT PLATINUM WITH α-ALANINE

(Presented by Academician A. A. Grinberg, 21 XI 1959)

Inner-complex salts of the general formula $[PtA_2]$*, obtained by the reaction:

$$K_2PtCl_4 + 2AH \rightarrow [PtA_2] + 2KCl + 2HCl, \qquad (1)$$

must exist in the form of two geometrical (cis and trans) isomers. In 1931 A. A. Grinberg and B. V. Ptitsyn showed (^{1}) that in the case of GlH reaction (1) leads to the isolation of both isomers $[PtGl_2]$ in the molecular ratio trans : cis $\simeq 3:1$. In 1934 it was shown (^{2}) that the reaction of K_2PtCl_4 with an excess of GlH, neutralized with alkali, proceeds according to the equation:

$$K_2PtCl_4 + 4GlH + 4KOH \rightarrow K_2[PtGl_4] + 4KCl + 4H_2O. \qquad (2)$$

From the soluble salt $K_2[PtGl_4]$, by adding the calculated amount of acid, a sparingly soluble compound H_2PtGl_4 was isolated:

$$K_2[PtGl_4] + 2HCl \rightarrow H_2PtGl_4 + 2KCl, \qquad (3)$$

It was shown (^{3}) that H_2PtGl_4, when heated with water, is almost quantitatively converted into the cis isomer of the inner-complex salt**:

$$H_2PtGl_4 \rightarrow 2GlH + \text{cis-}[PtGl_2]. \qquad (4)$$

In 1937 one of us, together with A. A. Grinberg, showed (^{4}) that reaction (1) in the case of AnH (in contrast to GlH) leads to the isolation only of the trans isomer $[PtAn_2]$. When K_2PtCl_4 reacts with an excess of AnH neutralized with alkali, the reaction proceeds according to an equation similar to (2); however, the compound H_2PtAn_4 did not precipitate upon addition of acid to the salt $K_2[PtAn_4]$ (the presence in solution of the anions $[PtAn_4]^{2-}$ was demonstrated (^{4}) by isolation of the compound $[Pt(AnH)_4Cl_2]Cl_2$, formed from $[PtAn_4]^{2-}$ as a result of oxidation of Pt(II) to Pt(IV) in an acidic medium). Cis-$[PtAn_2]$ not only was not detected among the products of reaction (1), but it also could not be obtained by a reaction similar to (4), since the compound H_2PtAn_4 was not isolated.

In 1957 one of us synthesized (^{5}) both isomers of the inner-complex salt $[PtM_2]$. However, in the case of MH (similarly to AnH), reaction (1) leads to the isolation only of trans-$[PtM_2]$. Cis-$[PtM_2]$ was synthesized from the compound H_2PtM_4, obtained from $K_2[PtM_4]$, i.e., reactions similar to (2), (3), and (4) were carried out. We note that a reaction of type (2), as proved (^{6}), is a general method for obtaining compounds $K_2[PtA_4]$. Thus, only in the case of AnH (of the three simplest members of the homologous of the series of α-amino acids) the cis-isomer of the inner-complex salt remained unknown. The assumption that there were any obstacles (for example, steric ones) preventing the formation of cis-$[PtAn_2]$ became unlikely after the synthesis of the cis-isomers $[PtGl_2]$ and $[PtM_2]$. Therefore we considered it fundamentally important to attempt again to synthesize this isomer.

Experimental Part

When acid was added to a solution of $K_2[PtAn_4]$, as noted above, the compound H_2PtAn_4 did not precipitate. However, the compound H_2PtAn_4 should be present in solution, and we assumed that, on heating the solution (by analogy with the behavior of the isolated solid H_2PtGl_4 and H_2PtM_4), H_2PtAn_4 would be converted into cis-$[PtAn_2]$. The experiment confirmed our assumption.

To 5 mmoles of K_2PtCl_4 were added 20 mmoles each of AnH and KOH; the total volume of the solution was $\sim$ 20 ml. The mixture was heated for about 1 hour on a water bath. To the almost colorless solution, 1 M HCl was added (calculated as 2 mmoles of HCl per 1 mmole of the initial K_2PtCl_4) and the mixture was heated for 2-3 hours on a water bath, maintaining the solution volume at 15-12 ml. On cooling the solution, a white precipitate separated in abundance; it was filtered off, washed with water, alcohol, and ether, and dried at 105°. The precipitate proved to be pure $[PtAn_2]$ (yield about 30%).

Found %: Pt 52.55; 52.59; 52.63; N 7.62; 7.72
$[PtAn_2]$. Calculated %: Pt 52.57; N 7.54

The properties of the $[PtAn_2]$ preparations isolated by the method described

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* AH denotes monobasic monoamino acids in the general form; GlH – α-aminoacetic acid (glycine), AnH –α-aminopropionic acid (alanine), MH – α-aminobutyric acid.

** It has recently been established that this reaction proceeds in two stages; in the first of them the compound $HPtGl_3$ is formed.

differ substantially from the properties of the trans-[$PtAn_2$] preparations (identical in composition) obtained(4) by reaction (1). The solubility of cis-[$PtAn_2$] in water (1.1% at 25°) is $\sim$ 14 times greater than the solubility of the trans-isomer. The trans-isomer forms plate-like crystals; the cis-isomer forms crystals of bar-like shape. The isomers differ especially sharply in their behavior toward hydrochloric acid. When concentrated HCl is added to the cis-isomer, even in the cold, the initial precipitate disappears instantaneously and completely, giving a bright-yellow solution; the trans-isomer under these conditions turns slightly yellow but does not go into solution. On gentle heating, the cis-isomer dissolves even in the theoretical amount of 1 M HCl (2 moles of HCl per 1 mole of cis-[$PtAn_2$]).

Previously(4), trans-dichloride [$Pt(AnH)_2Cl_2$] was obtained from trans-[$PtAn_2$] by boiling with an excess of concentrated HCl (10 ml per 1 g of the inner-complex salt). To obtain the cis-dichloride, we added only 2 ml of concentrated HCl to 1 g of cis-[$PtAn_2$] and heated for less than one minute on a water bath. After cooling, a yellow precipitate of cis-dichloride separated; the precipitate was transferred to a glass filter with concentrated HCl, washed with ether, and dried at 100°.

Found %: Pt 43.83; 43.76; N 6.22; 6.17
[$Pt(AnH)_2Cl_2$]. Calculated %: Pt 43.94; N 6.30

The cis-dichloride was obtained in yields up to 80%. Under the action of HCl on isomeric inner-complex salts, the alanine rings are opened:

$$[PtAn_2] + 2HCl \rightarrow [Pt(AnH)_2Cl_2].$$

Both dichlorides are dibasic acids, quantitatively titrated with alkali in the presence of phenolphthalein; the products of the reaction

$$[Pt(AnH)_2Cl_2] + 2KOH \rightarrow [PtAn_2] + 2KCl + 2H_2O$$

are isomeric inner-complex salts.

The isomeric dichlorides show a considerable difference in properties. The cis-dichloride is considerably more soluble in water than the trans-isomer (both are poorly soluble in concentrated HCl); conversely, in ether the trans-dichloride dissolves considerably better than the cis-dichloride.

The isomers differ in their behavior toward thiourea (Thio) and other reagents. Under the action of thiourea (under completely identical conditions), the cis-dichloride gives, in a yield of about 80%, a yellow precipitate [$Pt(Thio)_4$]Cl_2 (found: Pt—34.29; 34.02%; calculated: 34.21%), whereas from the trans-dichloride there is obtained[4] a white precipitate [$Pt(Thio)_2(AnH)_2$]Cl_2.

The absence of the cis isomer [$PtAn_2$] in the products of reaction (1) appears quite natural, since free HCl is present in the solution; in its presence cis-[$PtAn_2$] very readily passes into the readily soluble cis-dichloride. The same was observed in the interaction of K_2PtCl_4 with MH; the solubilities in water of cis-[$PtAn_2$] and cis-[PtM_2]^5 are almost identical. Cis-[$PtGl_2$] is appreciably less soluble in water (0.18% at 25°) than its analogs; therefore it is obtained, although in low yield, in the interaction of K_2PtCl_4 with GlH.

Thus, the cis- and trans-isomers [PtA_2] have now been obtained for all three of the simplest α-amino acids.

In conclusion, we note that the compound H_2PtAn_4, from which, as we suppose, cis-[$PtAn_2$] was obtained, has also very recently been isolated by us (as yet in low yield) and will be described later.

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