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Abstract

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PREPARATION OF VARIOUSLY SUBSTITUTED TRIACIDOTRIAMMINES OF TETRAVALENT PLATINUM

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In our previous papers ([1]-[4]) methods were described for the synthesis of five isomers (of the fifteen theoretically possible) of composition $[\mathrm{PyNH_3ClBrJNO_2Pt}]$.

The development of methods for obtaining other isomers of this composition is no longer of fundamental interest, although it may provide much new and interesting information on the mutual influence of atoms in a complex molecule.

At present, of considerably greater interest is the establishment of the existence of optical isomerism for compounds of the indicated type. However, the resolution into optical antipodes of nonelectrolyte complexes (and all compounds of this type obtained by us earlier are nonelectrolytes) presents great experimental difficulties. The method suitable in these cases–adsorption on finely divided quartz–has not yet found broad practical application. To achieve the aim, it was more expedient to synthesize soluble, variously substituted triacidotriammines of tetravalent platinum $[a_1a_2a_3x_1x_2x_3\mathrm{Pt}]x$ and subsequently attempt to resolve them by the usual method–the action of an optically active acid.

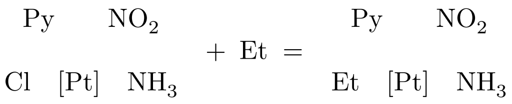
In the present brief communication, the results are set forth of experimental work on the synthesis of variously substituted triacidotriammines of tetravalent platinum.

The preparation of these compounds was carried out in three stages:

1. Preparation of variously substituted triammines of divalent platinum. 2. Conversion of them into triammines of tetravalent platinum. 3. Carrying out substitution in the third coordinate. In carrying out this synthesis, the data available in the literature on the preparation of asymmetric salts of divalent platinum of the Kleeve type ([5]) and on the preparation of methylamine and ethylamine compounds of platinum ([6], [7]) were taken into account.

We succeeded in synthesizing two variously substituted triacidotriammines of tetravalent platinum: $[\mathrm{PyNH_3EtNO_2ClBrPt}]\mathrm{Cl}^*$ and $[\mathrm{PyNH_3MeNO_2BrClPt}]\mathrm{Br}^{**}$.

To obtain the first of these, the triamminedivalent platinum [$PyNH_3EtNO_2Pt$]Cl was first prepared by the reaction:



$$\begin{array}{ccc} & Py \quad NO_2 & \\ Cl & [Pt] & NH_3 \end{array} + Et = \begin{array}{ccc} & Py \quad NO_2 & \\ Et & [Pt] & NH_3 \end{array}$$

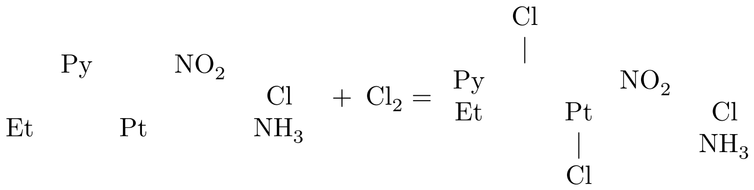
For this purpose a suspension of the salt [$PyNH_3ClNO_2Pt$] in water was heated with ethylamine until a colorless solution formed; ethylamine, in the form of a 50% solution, was added in small portions. After evaporation of the solution, there remained a colorless, slightly sticky, glassy mass, among which long needle-shaped crystals were present. After treatment with ether, a white crystalline powder was obtained.

Found, %: Pt 45.78; 45.48; Cl 8.56; H_2O 1.82

[$PyNH_3EtNO_2Pt$]Cl $\cdot \frac{1}{2}H_2O$ (mol. wt. 426.8).
Calculated, %: Pt 45.74; Cl 8.32; H_2O 2.11

By a similar method the triamine [$PyNH_3EtClPt$]Cl was also obtained.

As the starting material for the synthesis of the differently substituted triamine of tetravalent platinum we used the triamine containing a nitro group, [$PyNH_3EtNO_2Pt$]Cl, since on the basis of earlier investigations it was known that introduction of the nitro group into compounds of tetravalent platinum is extremely difficult. For this purpose the triamine [$PyNH_3EtNO_2Pt$]Cl obtained was oxidized with chlorine. The oxidation proceeds according to the equation:



$$\begin{array}{ccc} Py & & NO_2 \\ Et & Pt & \end{array} \begin{array}{c} Cl \\ NH_3 \end{array} + Cl_2 = \begin{array}{c} Py \\ Et \end{array} \begin{array}{c} Cl \\ | \\ Pt \\ | \\ Cl \end{array} \begin{array}{c} NO_2 \\ \\ \end{array} \begin{array}{c} Cl \\ NH_3 \end{array}$$

The oxidation is associated with a change in the color of the solution: from colorless it becomes yellow, and sometimes a small precipitate appears. On evaporation of the solution a yellow crystalline substance separated. As the analyses

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* Et–ethylamine $C_2H_5NH_2$.
** Me–methylamine CH_3NH_2.

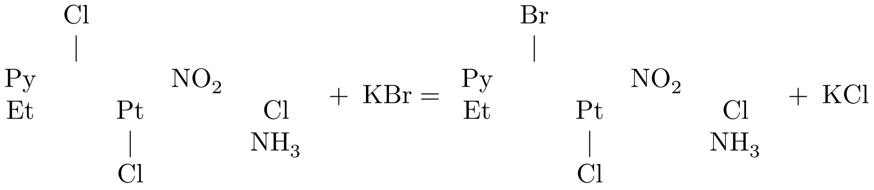
showed, this substance is the chloride $[PyNH_3EtNO_2Cl_2Pt]Cl$, containing water of crystallization, which it gradually loses on drying.

Analysis of the dry substance gave the following figures:

Found, %: Pt 39.66; 40.32; 40.11;
Cl 22.72; 22.54

$[PyNH_3EtNO_2Cl_2Pt]Cl$ (mol. wt. 488.8).
Calculated, %: Pt 39.94;
Cl 22.04

It was proposed to carry out the final stage of the synthesis according to the reaction:



$$\begin{array}{ccc} & \mathrm{Cl} & \\ & | & \\ \mathrm{Py} & & \mathrm{NO_2} \\ \mathrm{Et} & \mathrm{Pt} & \mathrm{Cl} \\ & | & \mathrm{NH_3} \\ & \mathrm{Cl} & \end{array} + \mathrm{KBr} = \begin{array}{ccc} & \mathrm{Br} & \\ & | & \\ \mathrm{Py} & & \mathrm{NO_2} \\ \mathrm{Et} & \mathrm{Pt} & \mathrm{Cl} \\ & | & \mathrm{NH_3} \\ & \mathrm{Cl} & \end{array} + \mathrm{KCl}$$

A weighed portion of the salt $[PyNH_3EtNO_2Cl_2Pt]Cl$ was dissolved in water and heated on a water bath for an hour and a half with potassium bromide, taken in the stoichiometric ratio. Gradually the color of the solution changed: from light yellow it became bright yellow. After evaporation and cooling of the solution, a bright-yellow precipitate separated from it; separated from the mother liquor, it was washed with several drops of cold water and thoroughly dried.

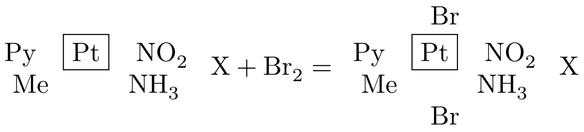
Found, %: Pt 36.99; 37.10; $\Sigma Cl + Br$ 27.99;
28.57; $Cl_{external}$ 7.03

$[PyNH_3EtNO_2ClBrPt]Cl$ (mol. wt. 533.2).
Calculated, %: Pt 36.62; $\Sigma Cl + Br$ 28.31;
$Cl_{external}$ 6.65

The second differently substituted triacidotriamine of tetravalent platinum, of composition $[PyNH_3MeNO_2BrClPt]Br$, was obtained as follows. To a weighed portion of the diamine $[PyNH_3NO_2BrPt]$ in hot water, a 10% solution of methylamine was added in an amount necessary to form a colorless solution. The solution was evaporated, and from it a white crystalline substance separated, the composition of which corresponded to the formula $[PyNH_3MeNO_2]Br$.

In an analogous manner, from the diamines $[PyNH_3(NO_2)_2Pt]$ and $[PyNH_3Br_2Pt]$, the triamines $[PyNH_3MeNO_2Pt]NO_2$ and $[PyNH_3MeBrPt]Br$, respectively, were obtained.

As starting substances for further work, the triamines $[PyNH_3MeNO_2Pt]Br$ and $[PyNH_3MeNO_2Pt]NO_2$ were taken. Solutions of these salts were oxidized with bromine. The oxidation reaction proceeded according to the equation:



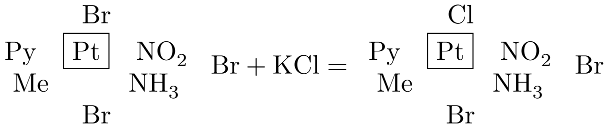
$$\begin{matrix} \mathrm{Py} & \boxed{\mathrm{Pt}} & \mathrm{NO_2} \\ \mathrm{Me} & & \mathrm{NH_3} \end{matrix}\,\mathrm{X} + \mathrm{Br_2} = \begin{matrix} & \mathrm{Br} & \\ \mathrm{Py} & \boxed{\mathrm{Pt}} & \mathrm{NO_2} \\ \mathrm{Me} & & \mathrm{NH_3} \\ & \mathrm{Br} & \end{matrix}\,\mathrm{X}$$

The outer-sphere anion in the starting compound has practically no effect on the composition of the oxidation product; since a considerable concentration of bromide ions is formed in solution, upon crystallization from the solution the bromide $[PyNH_3MeNO_2Br_2Pt]Br$ separates. Its composition was confirmed by analyses.

Found % : Pt 32.67; 32.61; 32.90; Br_{total} 39.11;
Br_{outer} 13.45.

$[PyNH_3MeNO_2Br_2Pt]Br$ (mol. wt. 607.9). Calculated % : Pt 32.11; Br_{total} 39.43;
Br_{outer} 13.14.

The last stage of the synthesis consisted in replacing, in the compound obtained, one of the bromines in the coordinate Br—Pt—Br by chlorine. On the basis of previously observed facts, we assumed that, because of the greater coordination strength of bromine, carrying out this reaction would be more difficult than the above-described reaction of replacing chlorine in the coordinate Cl—Pt—Cl. This indeed proved to be the case. In order to obtain the required triacidotriamine, according to the equation it was necessary to take potassium chloride



$$\begin{matrix} & \mathrm{Br} & \\ \mathrm{Py} & \boxed{\mathrm{Pt}} & \mathrm{NO_2} \\ \mathrm{Me} & & \mathrm{NH_3} \\ & \mathrm{Br} & \end{matrix}\,\mathrm{Br} + \mathrm{KCl} = \begin{matrix} & \mathrm{Cl} & \\ \mathrm{Py} & \boxed{\mathrm{Pt}} & \mathrm{NO_2} \\ \mathrm{Me} & & \mathrm{NH_3} \\ & \mathrm{Br} & \end{matrix}\,\mathrm{Br}$$

in more than the stoichiometric amount and to conduct the reaction at a higher temperature. As a result of the reaction, a bright-yellow crystalline substance was obtained.

Found % : Pt 34.57; 34.44; $\Sigma Cl + Br$ 34.55;
34.27; Br_{outer} 14.73

$[PyNH_3MeNO_2BrClPt]Br$ (mol. wt. 563.5). Calculated % : Pt 34.64; $\Sigma Cl + Br$ 34.66; Br_{outer} 14.18

The preparation of triamines of composition $[PyNH_3EtNO_2ClBrPt]Cl$ and $[PyNH_3MeNO_2BrClPt]Br$ makes it possible to proceed with the realization of the coordination-theory prediction of the resolution of heterosubstituted tetravalent platinum compounds into optical antipodes.

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

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