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Abstract

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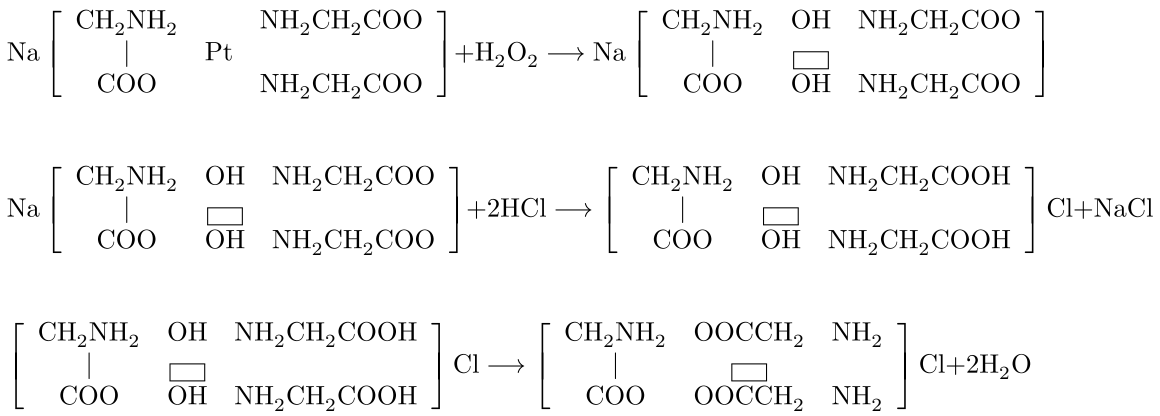
ON TRIGLYCOCOLLATES OF TETRAVALENT PLATINUM

As is known, the triglycocollates of cobalt and chromium, $Cogl_3$ and $Crgl_3$, were obtained long ago (^{1,2}); however, the derivative $[Ptgl_3]Cl$ has not been obtained up to the present time. The routes for its synthesis were unclear. The preparation of compounds with three glycocoll molecules for divalent platinum also presented difficulties, and only recently L. M. Volshtein and G. G. Motyagina (^{3}) synthesized $K[Ptglg_2^I]$ and $Ag[Ptglg_2^I]^*$.

On oxidation of $K[Ptglg_2^I]$ with hydrogen peroxide, the dihydroxo compound of tetravalent platinum $K[Ptglg_2^I(OH)_2]$ should be formed. Taking into account the reaction of inner-sphere neutralization (^{4}), it is natural to expect that this newly obtained product, having added, in the presence of acid, two hydrogen ions to the unclosed glycocoll residues, is capable of forming the compound $[Ptgl_3]Cl$. Considering that in the present work the sodium salt was taken instead of the potassium salt, the reactions may be represented by the following equations:



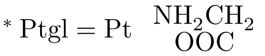
$$\mathrm{Na}\left[\begin{array}{ccc} \mathrm{CH_2NH_2} & & \mathrm{NH_2CH_2COO} \\ | & \mathrm{Pt} & \\ \mathrm{COO} & & \mathrm{NH_2CH_2COO} \end{array}\right] + \mathrm{H_2O_2} \longrightarrow \mathrm{Na}\left[\begin{array}{ccc} \mathrm{CH_2NH_2} & \mathrm{OH} & \mathrm{NH_2CH_2COO} \\ | & \square & \\ \mathrm{COO} & \mathrm{OH} & \mathrm{NH_2CH_2COO} \end{array}\right]$$

$$\mathrm{Na}\left[\begin{array}{ccc} \mathrm{CH_2NH_2} & \mathrm{OH} & \mathrm{NH_2CH_2COO} \\ | & \square & \\ \mathrm{COO} & \mathrm{OH} & \mathrm{NH_2CH_2COO} \end{array}\right] + 2\mathrm{HCl} \longrightarrow \left[\begin{array}{ccc} \mathrm{CH_2NH_2} & \mathrm{OH} & \mathrm{NH_2CH_2COOH} \\ | & \square & \\ \mathrm{COO} & \mathrm{OH} & \mathrm{NH_2CH_2COOH} \end{array}\right]\mathrm{Cl} + \mathrm{NaCl}$$

$$\left[\begin{array}{ccc} \mathrm{CH_2NH_2} & \mathrm{OH} & \mathrm{NH_2CH_2COOH} \\ | & \square & \\ \mathrm{COO} & \mathrm{OH} & \mathrm{NH_2CH_2COOH} \end{array}\right]\mathrm{Cl} \longrightarrow \left[\begin{array}{ccc} \mathrm{CH_2NH_2} & \mathrm{OOCCH_2} & \mathrm{NH_2} \\ | & \square & \\ \mathrm{COO} & \mathrm{OOCCH_2} & \mathrm{NH_2} \end{array}\right]\mathrm{Cl} + 2\mathrm{H_2O}$$

A solution of $Na[Ptglg_2^I]$ was obtained by the method described by L. M. Volshtein and G. G. Motyagina. To 6 ml of a solution containing 1 g of $Na[Ptglg_2^I]$, 1.2 ml of 30% H_2O_2 (a fivefold excess) was added. At room temperature the reaction proceeds vigorously, with evolution of gas and formation of a light-yellow solution, from which two compounds can be obtained.

I. Preparation of $Na[Ptglg^{I}(OH)_2]$**.** After 4-5 hr, a dense flocculent white precipitate appears from the yellow solution, the amount of which gradually increases over the course of 10 hr. On the second day the precipitate is filtered off and washed with a minimum amount of water, alcohol, and ether. Yield 25-30%. The product dried over sulfuric acid contains two molecules of water, which are removed by drying at 100°.



* $Ptgl = Pt \begin{smallmatrix} NH_2CH_2 \\ OOC \end{smallmatrix}$; $PtglH = Pt{-}NH_2CH_2COOH$; $Ptgl^{I} = Pt{-}NH_2CH_2COO$.

Analysis results:

Found, %: H_2O 7.52. $Na[Ptglgl^{I}_{2}(OH)_2] \cdot 2H_2O$

Calculated, %: H_2O 7.05

Found, %: $Pt + \frac{1}{2}Na_2SO_4$ 55.88; 56.36; 55.95; N 8.46

$Na[Ptglgl^{I}_{2}(OH)_2]$. Calculated, %: $Pt + \frac{1}{2}Na_2SO_4$ 56.15; N 8.86

II. Preparation of $[Ptgl_3]Cl$. To a yellow solution that had stood for 3-4 hours at room temperature, without waiting for the appearance of a precipitate, 1.5 ml of concentrated hydrochloric acid (a fourfold excess) is added, and then alcohol (volume ratio 1 : 7). On stirring, a copious flocculent white precipitate immediately separates, which after 4 hours is filtered off and thoroughly washed with alcohol. Washing is carried out as follows: without allowing the wet precipitate to remain on suction for long, a fresh portion of pure alcohol is added. This is continued until the wash alcohol gives a neutral reaction to methyl orange. If the precipitate is left on suction for a long time, it may cake and gradually turn into a yellow viscous mass. This phenomenon is probably caused by absorption of moisture from the air. The precipitate, smelling of alcohol, is dried first over sulfuric acid, then at 90°. The yield is ~ 70%. The product obtained in this way is recrystallized: 0.5 g of $[Ptgl_3]Cl$ was dissolved in 2 ml of concentrated hydrochloric acid and then precipitated with 20 ml of alcohol.

Analysis results:

Found, %: Pt 42.84, 42.90; Cl 7.90, 7.75; Cl′ 7.55; N 9.11

$[Ptgl_3]Cl$. Calculated, %: Pt 43.10; Cl 7.65; N 9.28

The sparingly soluble derivative $[Ptgl_3]_2[PtCl_6]$ was obtained from $[Ptgl_3]Cl$ and $Na[Ptglgl^{I}_{2}(OH)_2]$. On addition of a solution of H_2PtCl_6 to a solution of $[Ptgl_3]Cl$, a finely crystalline yellow precipitate separates immediately. According to the analytical data, the product obtained corresponds to the composition $[Ptgl_3]_2[PtCl_6] \cdot 2H_2O$. The water of crystallization is not removed even at 130°. On addition of an excess of a solution of H_2PtCl_6 to a suspension of $\mathrm{Na[Ptglgl^{I}_{2}(OH)_{2}]}$, the latter compound dissolves completely. After some time $\mathrm{[Ptgl_3]_2[PtCl_6]\cdot 2H_2O}$ begins to precipitate from the solution; its amount increases rapidly on stirring. Yield $\sim 75\%$. Analysis results:

Substance obtained from $\mathrm{[Ptgl_3]Cl + H_2PtCl_6}$:

Found, %: Pt 45.52; Cl 16.29; N 0

Substance obtained from $\mathrm{Na[Ptglgl^{I}_{2}(OH)_{2}] + H_2PtCl_6}$:

Found, %: Pt 45.68; Cl 16.75; N 6.28

$\mathrm{[Ptgl_3]_2[PtCl_6]\cdot 2H_2O}$. Calculated, %: Pt 45.81; Cl 16.65; N 6.59

The preparation of the intermediate dihydroxo compound $\mathrm{Na[Ptglgl^{I}_{2}(OH)_{2}]}$ and its conversion under the action of acids into the corresponding derivatives with glycocol rings are important confirmation of the proposed mechanism for the oxidation by hydrogen peroxide of compounds of $\mathrm{Pt^{II}}$ containing glycocol molecules.

Conductivity measurements showed that $\mathrm{[Ptgl_3]Cl}$ and $\mathrm{Na[Ptglgl^{I}_{2}(OH)_{2}]}$ are binary electrolytes, while $\mathrm{[Ptgl_3]_2[PtCl_6]}$ is a ternary electrolyte.

The compound $\mathrm{[Ptgl_3]Cl}$, as a triamine of tetravalent platinum, can split off a proton from a coordinated amino group and exhibit acidic properties

$$\mathrm{[Ptgl_3]Cl \rightleftarrows [Ptgl_2(gl-H)] + H^+ + Cl^-},$$

where $\mathrm{gl-H}$ represents the radical ion $\mathrm{^-NHCH_2COO^-}$ coordinated at the $\mathrm{Pt^{IV}}$ atom.

The acidic properties of the cation $\mathrm{[Ptgl_3]^+}$ were studied by potentiometric titration using a glass electrode. The dissociation constant

was calculated by the abbreviated formula $K = [\mathrm{H^+}]\frac{C_{\mathrm{NaOH}}}{C_{\mathrm{tot}} - C_{\mathrm{NaOH}}}$ for a monobasic acid. For the compound $\mathrm{[Ptgl_3]Cl}$, $K = 5.4\cdot 10^{-8}$; for $\mathrm{[Ptgl_3]_2(PtCl_6)}$, $K = 4.6\cdot 10^{-8}$. It should be noted that, judging by the dissociation constant, $\mathrm{[Ptgl_3]^+}$ is a stronger acid than the corresponding ammines and aminates of $\mathrm{Pt^{IV}}$. During titration of a solution of $\mathrm{[Ptgl_3]Cl}$ with the second equivalent of alkali, a noticeable change in pH with time was observed, owing to strong reduction of $\mathrm{Pt^{IV}}$ to $\mathrm{Pt^{II}}$.

When an equivalent amount of caustic soda (concentration $0.95\,N$) acts on $\mathrm{[Ptgl_3]Cl}$, a yellow precipitate $\mathrm{[Ptgl_2(gl-H)]}$ immediately separates, with a yield of $\sim 45\%$.

Found, %:	Pt 46.76, 46.76;	N 10.13
$\mathrm{[Ptgl_2(gl-H)]}$. Calculated, %:	Pt 46.88;	N 10.08

An aqueous solution of the derivative obtained shows an alkaline reaction and, in the presence of methyl orange, is titrated with hydrochloric acid, the consumption of which amounts to 74% of the theoretical value. The incomplete titration is explained by partial reduction of the compound $[\mathrm{Ptgl}_2(\mathrm{gl}-\mathrm{H})]$ to derivatives of divalent platinum.

To determine the degree of reduction of $[\mathrm{Ptgl}_3]\mathrm{Cl}$ in alkaline solutions, an accurately weighed sample was dissolved in different amounts of $0.385\,N$ NaOH solution. After standing for two hours, the divalent-platinum compound formed was titrated with a solution of potassium permanganate.

Molar ratio	1 : 1	1 : 2	1 : 4	1 : 10
Reduction, %	12	37	58	100

It follows from what has been described that, when $[\mathrm{Ptgl}_3]\mathrm{Cl}$ reacts with alkali, an imido reaction occurs, followed by reduction of $\mathrm{Pt}^{\mathrm{IV}}$ to $\mathrm{Pt}^{\mathrm{II}}$.

A similar reduction reaction was found and explained by one of us together with Yu. N. Kukushkin (^{5}). In the present case it may be assumed that reduction occurs through transfer of an electron from the coordinated group $-\mathrm{NHCH}_2\mathrm{COO}^-$ to the central "ion" of tetravalent platinum. One can imagine two pathways for such a process. First, reduction of $\mathrm{Pt}^{\mathrm{IV}}$ through transformation of two initial $\mathrm{NH}_2\mathrm{CH}_2\mathrm{COO}$ residues into imido forms, followed by transfer of two electrons to $\mathrm{Pt}^{\mathrm{IV}}$, as a result of which $\mathrm{Pt}^{\mathrm{IV}}$ changes to $\mathrm{Pt}^{\mathrm{II}}$ with coordination number 4, accompanied by elimination of two $\mathrm{NHCH}_2\mathrm{COO}$ radicals. Second, one also cannot reject the possibility of transfer of two electrons from one imido group $-\mathrm{NHCH}_2\mathrm{COO}^-$, which is genetically related to hydrazine and therefore may possess reducing properties. The likelihood of the first mechanism is increased when one takes into account the acceleration of reduction with increasing amount of added alkali.

We, of course, do not have sufficient data for a confident judgment about the detailed mechanism of the reduction process described. If, nevertheless, we make the assumption that reduction proceeds mainly by the second mechanism, this gives some possibility of forming an idea of the relative amounts of geometrically isomeric diglycines that may be formed upon reduction. In this case, the indicated $\mathrm{NHCH}_2\mathrm{COO}$ radicals, in all probability, should be held more weakly than the glycine residues and therefore should most likely be eliminated when the coordination number changes from 6 to 4. If one further makes the quite plausible assumption that each of the three coordinated amino groups in the ion $[\mathrm{Ptgl}_3]^+$ is equally capable of eliminating a proton, then the following three variants of elimination of the $\mathrm{NHCH}_2\mathrm{COO}$ radical may be expected:

1) $\mathrm{NHCH}_2\mathrm{COO}$ is eliminated with subsequent rearrangement of the COO^- group from (b) into the place of NH. As a result, trans-$[\mathrm{Ptgl}_2]$ is obtained.
2) $\mathrm{NHCH}_2\mathrm{COO}$ is eliminated with subsequent rearrangement of the COO^- group from (c) into the place of NH. cis-$[\mathrm{Ptgl}_2]$ is obtained.

3) $NHCH_2COO$ is detached, with subsequent rearrangement of both COO groups to the positions freed by departure of the radical. The result is cis-[$Ptgl_2$].

Structural schemes (1), (2), and (3)

It follows from what has been said that the reduction products should contain one third trans-[$Ptgl_2$] and two thirds cis-[$Ptgl_2$]. In order to isolate the Pt^{II} products, the following experiments were carried out: a solution of 0.5 g of [$Ptgl_3$]Cl in 8 ml of 0.95 N NaOH (molar ratio 1 : 7) is heated on a water bath and left for one hour at room temperature. After addition of 3 ml of conc. HCl, the solution is heated on a water bath for 15 min. After cooling, a yellow precipitate separates from the solution and is filtered off. According to the analytical results, it corresponds to the composition [$Pt(glH)_2Cl_2$], whose trans configuration was proved by Kurnakov’ s thiourea reaction. When thiourea is allowed to act under ordinary conditions on the filtrate separated from trans-[$Pt(glH)_2Cl_2$], yellow crystals are obtained corresponding to the composition [$Pt(ThiO)_4$]Cl_2.

The data given are not in contradiction with the above-stated supposition concerning the probable course of the reduction mechanism. The preparation of trans-[$Pt(glH)_2Cl_2$] in 20-25% yield and of [$Pt(ThiO)_4$]Cl_2 in 40-45% yield is consistent with a larger yield of cis-[$Ptgl_2$] as the reduction product. However, direct proof of the presence specifically of cis-[$Ptgl_2$] in the reduction products is still lacking. Investigations aimed at further study of the reduction mechanism will be continued.

In conclusion, it may be said that the synthesis and study of the transformations of [$Ptgl_3$]Cl and its derivatives have, for the first time, made it possible to detect an imido reaction in glycocoll coordinated to Pt^{IV}, and a new type of bond between Pt^{IV} and $(gl - H)$. Thus it has been shown for the first time that glycocoll (and evidently its analogues as well) can, under appropriate conditions, function as a dibasic acid through elimination of a proton both from the carboxyl group and from the NH_2 group. At the same time it has been shown that the imido form of glycocoll is capable of reducing Pt^{IV}. Salts of the [$Ptgl_3$]Cl type will undoubtedly be an interesting object for resolution into optical antipodes.

It should be noted that, in addition to the form [$Ptgl_3$]Cl described here, it is theoretically possible to predict the existence of a geometrically isomeric form, which corresponds to the configuration

Proposed geometrically isomeric form of [$Ptgl_3$]Cl

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