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Abstract

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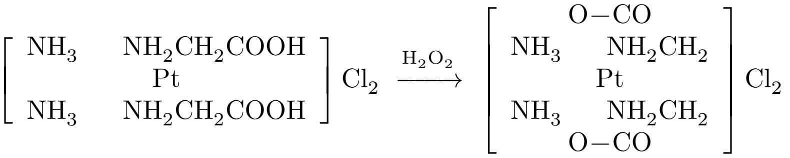
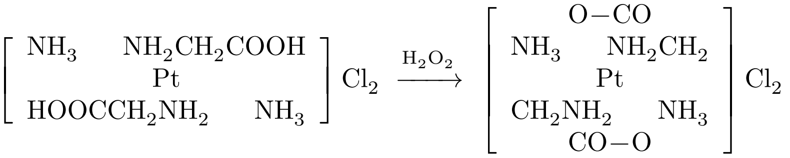
PROOF OF THE CONFIGURATION OF CIS-TRANS-ISOMERIC COMPOUNDS $[PtGl_2(NH_3)_2]Cl_2$*

Two of us succeeded in synthesizing isomeric forms of the composition $[PtGl_2(NH_3)_2]Cl_2$ (1) by oxidation with hydrogen peroxide of the previously described (2) cis-trans-tetramines $[Pt(GlH)_2(NH_3)_2]Cl_2$.

The oxidation reactions apparently proceed through the formation of trans-dihydroxo compounds $[Pt(GlH)_2(NH_3)_2(OH)_2]Cl_2$, which undergo intramolecular neutralization with formation of Pt–Gl rings. In the authors' opinion, no change in the relative positions of the ammine groups occurs in this process, and therefore to the oxidation products of cis-trans $[Pt(GlH)_2(NH_3)_2]Cl_2$ they assigned, respectively, the unsymmetrical cis- and the symmetrical trans-configurations:



$$\left[\begin{array}{ccc} NH_3 & & NH_2CH_2COOH \\ & Pt & \\ NH_3 & & NH_2CH_2COOH \end{array}\right]Cl_2 \xrightarrow{H_2O_2} \left[\begin{array}{ccc} & O-CO & \\ NH_3 & & NH_2CH_2 \\ & Pt & \\ NH_3 & & NH_2CH_2 \\ & O-CO & \end{array}\right]Cl_2 \qquad (1)$$



$$\left[\begin{array}{ccc} NH_3 & & NH_2CH_2COOH \\ & Pt & \\ HOOCCH_2NH_2 & & NH_3 \end{array}\right]Cl_2 \xrightarrow{H_2O_2} \left[\begin{array}{ccc} & O-CO & \\ NH_3 & & NH_2CH_2 \\ & Pt & \\ CH_2NH_2 & & NH_3 \\ & CO-O & \end{array}\right]Cl_2 \qquad (2)$$

In the present work, by the method of resolution into mirror isomers, the correctness of such an assignment of configurations was proved. Fractional crystallization of the *d*- and *l*-camphorsulfonates of the tetramine obtained according to equation (1) gave a clear separation into diastereoisomers. The less soluble of them had the signs Ld_2 and Dl_2. Fractional crystallization of the *d*-camphorsulfonate of the tetramine obtained according to equation (2) gave negative results—all fractions of the camphorsulfonate contained no optically active (o.a.) cation.

Figure 1 gives the rotatory-dispersion curves (r.d.) for the diastereoisomers Dl_2 and Ll_2 (a, a'). The form Dl_2 has an anomalous course of r.d. with a broadened maximum owing to the presence of two components with opposite signs of rotation. The r.d. curve of the form Ll_2 has a smooth course. Upon alkalization of solutions of the diastereoisomers there occurs the appearance, characteristic of an amido reaction, of a yellow coloration, which gradually disappears as the insoluble optically inactive dihydroxotetramine $[PtGl_2(NH_3)_2(OH)_2]$ separates from the solution. Therefore in the present case it is not possible to observe polarimetrically the phenomenon of imido inversion, which in o.a. amines (3) accompanies the amido reaction. However, it is possible to determine the presence of o.a. $[PtGl_2(NH_3)_2]^{2+}$ and the magnitude of its rotation from the difference between the initial rotation of the diastereoisomer (curves a, a') and the rotation of the filtrate after separation of the decomposition product corresponding to the rotation of the anion (curves b, b').

As is evident from the figure, the calculated r.d. curves for $[PtGl_2(NH_3)_2]^{2+}$ in the camphorsulfonate are very close to the experimentally found r.d. curves for the mirror-isomeric chlorides obtained from the diastereoisomeric forms (curves g, g'). Thus, measurement of the rotation of the diastereoisomers in aqueous and alkaline solutions makes it possible to judge the process of cation cleavage without replacing the active anion by an inactive one.

Table 1

Dispersion of the molecular rotation $[M]^0_\lambda$ of the *L*- and *D*-isomers $[PtCl_2(NH_3)_2]Cl_2$

λ, mμ	*L*-isomer, experiment No. 1	*L*-isomer, experiment No. 2	*L*-isomer, experiment No. 3	*D*-isomer, experiment No. 2	*D*-isomer, experiment No. 3
579	$c =$ 1.896−534	$c =$ 0.1516−346	$c =$ 0.3032−390	$c =$ 0.0758+375	$c =$ 0.1516398
546	−600	−398	−447	+439	456
491.6	–	−509	−579	+580	597
434	−1044	−700	−787	+784	800
405	−1229	−832	−930	+924	936
390.6	–	−889	−997	+998	999
365	−1434	−965	−1084	+1091	1092
395	$c =$ 0.0758−1465	–	–	+1129	–
334	−1748	–	–	1307	–
312.5	−2825	–	–	2437	–
302	$c =$ 0.01518−3780	–	–	2877	–
296	−4720	–	–	–	–

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* Gl = $NH_2CH_2COO^-$.

Fig. 1

Figure 1: Fig. 1

λ, mμ	*L*-isomer, experiment No. 1	*L*-isomer, experiment No. 2	*L*-isomer, experiment No. 3	*D*-isomer, experiment No. 2	*D*-isomer, experiment No. 3
289	−5890	–	–	–	–
275	−9760	–	–	–	–
$[M]_{365}:[M]_{579}$	2.68	2.78	2.77	2.90	2.74

Table 1 gives the dispersion data for the chlorides of the mirror isomers. The most complete cleavage occurred during fractional crystallization of *d*-camphorsulfonate (experiment No. 1); the chloride obtained from the first fraction has the maximum rotation. In the crystallization of the *l*-camphorsulfonates (experiments Nos. 2 and 3) the rotation of both mirror-isomeric chlorides isolated from the diastereoisomers proved to be somewhat lower than the rotation of the chloride of the *L*-isomer from experiment No. 1, despite additional recrystallizations or reprecipitation of the diastereoisomeric forms. The isolation of both diastereoisomers in one and the same experiment (see experiments Nos. 2 and 3) in approximately equal amounts indicates the stability of the mirror isomers of tetramine, owing to which, in the presence of the resolving reagent, no preferential synthesis occurs of the isomer giving the less soluble form. This is confirmed by the absence of inactivation over a long period of time of aqueous solutions of the chlorides at room and elevated temperature, especially in acidic solutions, which exclude hydrolysis.

Fig. 1. Dispersion curves: experiment No. 2, fraction I: *a*–*D*-$[PtCl_2(NH_3)_2](l\text{-}C_{10}H_{15}\cdot OSO_3)_2$; *b*–*D*-$[PtCl_2(NH_3)_2](l\text{-}C_{10}H_{15}OSO_3)_2$ + KOH; *v*–*D*-$[PtCl_2(NH_3)_2]Cl_2$ calculated; *g*–*D*-$[PtCl_2(NH_3)_2]Cl_2$ found. Experiment 3, fraction IV: *a′*–*L*-$[PtCl_2(NH_3)_2](l\text{-}C_{10}H_{15}\cdot OSO_3)_2$; *b′*–*L*-$[PtCl_2(NH_3)_2](l\text{-}C_{10}H_{15}OSO_3)_2$ + KOH; *v′*–*L*-$[PtCl_2(NH_3)_2]^{2+}$ calculated; *g′*–*L*-$[PtCl_2(NH_3)_2]Cl_2$ found.

Figure 2 gives the dispersion curves for the antipodes in comparison with the absorption spectrum of the compound. Over the whole interval of wavelengths investigated, the dispersion curve has a smooth course with a very steep rise in the region close to the first absorption band (inflection at 270-280 mμ), which apparently is optically active. Unfortunately, it is not possible to measure the course of the dispersion below 275 mμ in order to determine the Cotton effect experimentally, because of intense absorption.

Tetramine $[PtCl_2(NH_3)_2]Cl_2$ is the first optically active complex of Pt(IV) containing a ring with glycol. Its analogue is cis-$[Pten_2Cl_2]Cl_2$ synthesized by

Cheneghan and Bailar$^{(4)}$. From the fore-

from the rotation values given in their work for the *D*-line of various fractions of α-bromo-*d*-camphorsulfonates and from the rotation of the active acid, we calculated the magnitude of the molecular rotation of the cation, which for the first fraction is −544°, i.e., coincides with the rotation of *L*-$[PtCl_2(NH_3)_2]Cl_2$. On comparing these data with the data for the rotation of Pt(IV) tetramines containing one Pt—en ring (^{3}), it is noteworthy that their rotation is an order of magnitude lower than the rotation of the dicyclic tetramines:

$$L\text{-}[\text{en } NH_3ClNH_3ClPt]Cl_2 \ [M]_{589} = -25.5^\circ;$$

$$D\text{-}[\text{en } NH_3NO_2NH_3ClPt]Cl_2 \ [M]_{589} = +14.4^\circ.$$

Fig. 2. O.r.d. curves: *a*—*L*-$[PtCl_2(NH_3)_2]Cl_2$ (experiment No. 1, fraction I); *b*—*D*-$[PtCl_2(NH_3)_2]Cl_2$ (experiment No. 2, fraction I); *v*—absorption curve of $[PtCl_2(NH_3)_2]Cl_2$

Experimental Part

Measurement of rotation

The rotation was measured on the first production model of a domestic Kudryavtsev photoelectric spectropolarimeter with automatic recording of the angle of rotation. The accuracy of recording the angle is ±0.0025°. The wavelength interval accessible to measurement is 600—250 mμ.

Fractional crystallization of cis-$[PtCl_2(NH_3)_2]d(l)(C_{10}H_{15}OSO_3)_2$

Experiment 1. To a solution of 5.0000 g of cis-$[PtCl_2(NH_3)_2]Cl_2$ in 100 ml of hot water was added a solution of 7.5672 g of Ag-*d*-$C_{10}H_{15}OSO_3$ in 30 ml of water. After 30 min the precipitate of AgCl was separated. From the filtrate (7% solution) white crystals of the form Ld_2 slowly began to separate. The first fraction, amounting to 1.5 g (15%), was separated on the following day.

Found %: Pt 22.73; H_2O 3.99
$[PtCl_2(NH_3)_2](C_{10}H_{15}OSO_3)_2 \cdot 2H_2O$. Calculated %: Pt 22.31; H_2O 4.10

The camphorsulfonate was ground in a mortar with conc. HCl. In this process the salt dissolves, and from the solution separates a finely crystalline tetramine chloride of white color.

Found %: Pt 43.22; Cl 16.31
$[PtCl_2(NH_3)_2]Cl_2$. Calculated %: Pt 43.53; Cl 15.82

The o.r.d. measurement data for the L-isomer are given in Table 1 and in Fig. 2. The second fraction of camphorsulfonate (10%) contained only an impurity of the L-isomer, while all subsequent fractions contained an increasing amount of the D-isomer. They were converted into the chloride and, for purification, fractional crystallization was repeated in the form of the l-camphorsulfonate. The Dl_2 chloride isolated from the first fraction (0.5 g, 20%) with sign D proved to be twice less optically pure: $[M]_{579} = +243°$, than the L-chloride: $[M]_{579} = -534°$.

Experiment 2. To a solution of 3.3821 g of cis-$[PtCl_2(NH_3)_2]Cl_2$ in 50 ml of hot water was added a solution of 3.368 g of l-$HC_{10}H_{15}OSO_3$ in 30 ml H_2O. From an 8% solution

After two days the first fraction of crystals of camphorsulfonate separated (1.2 g, 18%) with sign Dl_2 (data on the ORD, see Fig. 1).

$$[PtCl_2(NH_3)_2](C_{10}H_{15}OSO_3)_2 \cdot 2H_2O.$$

Found, %: Pt 22.02
Calculated, %: Pt 22.31

For the chloride of the D-isomer obtained from them, ORD data are shown in Fig. 1 and Table 1.

After separation of two more fractions, amounting to 50% and containing a racemic cation with an admixture of the L-isomer, a fourth fraction was separated (0.7 g, 10%), having the sign Ll_2. The ORD data of the L-chloride isolated from it are given in Table 1. Within the limits of experimental error they coincide with the rotation of the D-isomer obtained in the same experiment.

Experiment 3. To a solution of 5.6261 g of cis-$[PtCl_2(NH_3)_2]Cl_2$ in 80 ml of H_2O was added a solution of 8.4815 g of Ag-l-$C_{10}H_{15}OSO_3$ in 30 ml of H_2O. After one hour the AgCl precipitate was separated. The filtrate concentration was 8.5%. The first fraction was 3.7 g (35%) and had cation rotation $[M]_{579} = +159°$. Repeated fractional crystallization was carried out from a 6.7% solution of $[PtCl_2(NH_3)_2]l\text{-}(C_{10}H_{15}OSO_3)_2$, obtained from the chloride of the first fraction. In the first fraction the cation rotation was $[M]_{579} = +315°$. It was converted to the chloride, unlike experiments Nos. 1 and 2, by fractional precipitation with hydrochloric acid from an aqueous solution of camphorsulfonate. The rotation of the first fraction was $[M]_{579} = +72°$, and the rotation of the more soluble second portion was $[M]_{579} = +398°$ and coincides with the rotation of the D-isomer obtained in experiment No. 2 (see Table 1). Apparently, purification of the D-isomer from the racemate during fractional precipitation of the chloride is associated with the phenomenon of configurational activity arising in the presence of an active anion. This phenomenon was first observed by Dwyer (^{5}).

From the main solution of $[PtCl_2(NH_3)_2]l\text{-}(C_{10}H_{15}OSO_3)_2$, two fractions (16%, 7%) containing a racemic cation and an admixture of the *L*-isomer were successively separated, and then a fourth fraction (10%), which is a fairly pure Ll_2 form. The results of the investigation of its ORD in aqueous and alkaline solutions and of the chloride isolated from it are presented in Figs. 1 and 2 and in Table 1.

Fractional crystallization of trans-$[PtCl_2(NH_3)_2]d\text{-}(C_{10}H_{15}OSO_3)_2$**.**

To a solution of 0.8154 g of trans-$[PtCl_2(NH_3)_2]Cl_2$ in 100 ml of hot water was added 1.2000 g of Ag-d-$C_{10}H_{15}OSO_3$. The precipitate was separated. From the filtrate of 1.5% concentration, after 6 days crystallization of the salt began. Three fractions were separated successively, whose composition, unlike that of the cis-isomer, corresponded to an anhydrous camphorsulfonate.

$$[PtCl_2(NH_3)_2](C_{10}H_{15}OSO_3)_2.$$

Found, %: Pt 23.88
Calculated, %: Pt 23.24

The ORD of chlorides obtained from camphorsulfonates lies within 0.003-0.01 in the interval 579-365 mμ ($c = 0.6080$), i.e., practically within the limits of error of measurement of the rotation angle.

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REFERENCES CITED

1. A. A. Grinberg, B. V. Ptitsyn, *Izv. Inst. po izuch. platiny*, issue 9, 55 (1932).
2. A. A. Grinberg, Yuan Kan, *ZhKhKh*, 7, issue 10, 2304 (1962).
3. I. I. Chernyaev, *Izv. Inst. po izuch. platiny*, issue 6, 32, 54 (1927).
4. L. F. Heneghan, J. C. Bailar, *J. Am. Chem. Soc.*, 75, No. 8, 1840 (1953).
5. F. P. Dwyer, E. C. Gyarfas, M. F. O' Dwyer, *Nature*, 167, 1036 (1951).

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