# TWO ISOMERS OF CHLOROAMMINEMETHIONINEPLATOCHLORIDE

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## Abstract

## Full Text

## CHEMISTRY

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# TWO ISOMERS OF CHLOROAMMINEMETHIONINEPLATOCHLORIDE

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Many isomeric pairs of cyclic compounds of divalent platinum of the type are known

$$\begin{bmatrix} & A & & A \\ B & & Pt & \\ & & & B \end{bmatrix} \text{ and } \begin{bmatrix} & A & & B \\ B & & Pt & \\ & & & A \end{bmatrix},$$

where the ligands AB are negative ions of amino acids $NH_2RCOO^-$ ($^{1-3}$). Compounds containing one ring and two different monodentate ligands should theoretically exist as two isomers of the type

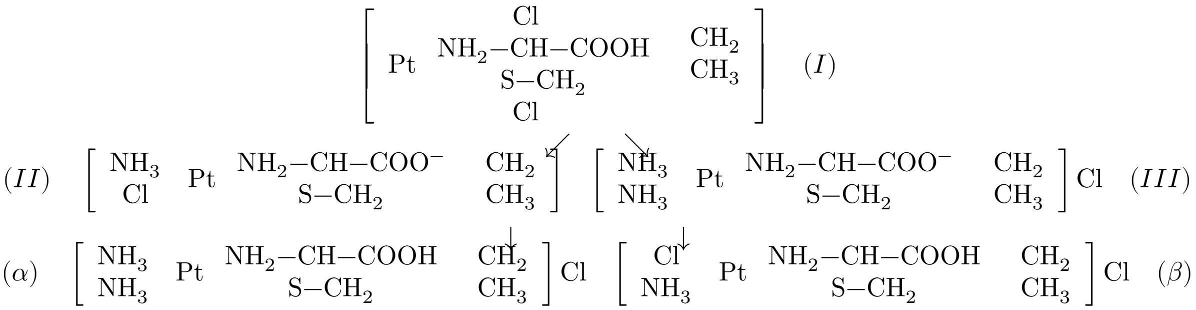
$$\begin{bmatrix} D & & A \\ & Pt & \\ E & & B \end{bmatrix} \text{ and } \begin{bmatrix} E & & A \\ & Pt & \\ D & & B \end{bmatrix}.$$

Isomerism of this kind, however, has not been described. To realize it, it is necessary to start from the compound

$$\begin{bmatrix} D & & A \\ & Pt & \\ D & & B \end{bmatrix}$$

and to be able to introduce ligand E into the inner sphere (in the position occupied by one of the D groups) in different positions with respect to the A and B groups of the bidentate ligand.

We succeeded in obtaining such isomers from the previously synthesized ($^{4,5}$) compound I (dichloromethionineplatinum). The coordinated molecule of methionine (= MtH) in I is bound to Pt(II) through the $NH_2$ and S groups, which differ sharply in the trans influence they exhibit ($S \gg NH_2$). This circumstance was the prerequisite that made it possible to predict a route for obtaining isomers of composition $[NH_3ClPtMtH]Cl$ according to the scheme:



$$\left[\mathrm{Pt}\begin{array}{cc}\mathrm{Cl} & \\ \mathrm{NH_2{-}CH{-}COOH} & \mathrm{CH_2} \\ \mathrm{S{-}CH_2} & \mathrm{CH_3} \\ \mathrm{Cl} & \end{array}\right] \quad (I)$$

$$(II)\quad \left[\begin{array}{c}\mathrm{NH_3}\\ \mathrm{Cl}\end{array}\ \mathrm{Pt}\ \begin{array}{cc}\mathrm{NH_2{-}CH{-}COO^-} & \mathrm{CH_2}\\ \mathrm{S{-}CH_2} & \mathrm{CH_3}\end{array}\right] \qquad \left[\begin{array}{c}\mathrm{NH_3}\\ \mathrm{NH_3}\end{array}\ \mathrm{Pt}\ \begin{array}{cc}\mathrm{NH_2{-}CH{-}COO^-} & \mathrm{CH_2}\\ \mathrm{S{-}CH_2} & \mathrm{CH_3}\end{array}\right]\mathrm{Cl}\quad (III)$$

$$(\alpha)\quad \left[\begin{array}{c}\mathrm{NH_3}\\ \mathrm{NH_3}\end{array}\ \mathrm{Pt}\ \begin{array}{cc}\mathrm{NH_2{-}CH{-}COOH} & \mathrm{CH_2}\\ \mathrm{S{-}CH_2} & \mathrm{CH_3}\end{array}\right]\mathrm{Cl} \qquad \left[\begin{array}{c}\mathrm{Cl}\\ \mathrm{NH_3}\end{array}\ \mathrm{Pt}\ \begin{array}{cc}\mathrm{NH_2{-}CH{-}COOH} & \mathrm{CH_2}\\ \mathrm{S{-}CH_2} & \mathrm{CH_3}\end{array}\right]\mathrm{Cl}\quad (\beta)$$

The first stage in obtaining the  -isomer consists in the action of ammonia on I under mild conditions (in the cold, dilute NH ). Substitution occurs in I only of that chlorine atom which is labilized by the methionine sulfur atom located in the trans position, and also detachment of H  from COOH (II is formed). In the second stage (action of HCl in the cold), the groups directly bound in II to platinum are not changed, but addition of H  to the COO  of methionine takes place.

The first stage in obtaining the  -isomer consists in the action of ammonia on I under severe conditions (heating, concentrated NH ), which leads to complete substitution of the inner-sphere chlorine and detachment of H  from COOH (III is formed). In the second stage (boiling with concentrated HCl), substitution by chlorine occurs only of that NH  molecule in III which is labilized by the sulfur atom located trans to it, and also addition of H  to COO .

The preparation of the isomers (  and  ) is somewhat reminiscent of the synthesis of the two isomers [$\mathrm{PtC_2H_4NH_3Cl_2}$], carried out by A. D. Gel'man by the action of NH  on Zeise's salt and by the action of C H  on Cossa's salt ( ); in this case the difference in the trans influence of three ligands was used ($\mathrm{C_2H_4} > \mathrm{Cl} > \mathrm{NH_3}$). The peculiarity of our synthesis consists in the fact that the difference in the trans influence of two functional groups of one and the same ligand (MtH), cyclically bound to platinum, is used.

## Experimental Part

The preparation of I and II has been described in ( ). For the synthesis of the  -isomer, to 1 mmol of II there were added, in the cold, 1 ml of conc. HCl and then ~5 ml of acetone. The precipitate obtained was washed with acetone and dried at 70° (yield ~90%). For the synthesis of the  -isomer, to 1 mmol of I there were added 3 ml of concentrated NH , and the mixture was heated for ~30 min on a water bath; a colorless solution of III was obtained (the isolation of the cation of compound III is described in ( )). Solution III was evaporated to dryness, 3 ml of concentrated HCl were added to the residue, and the mixture was boiled for 10 min (instead of boiling, the solution may be left for several hours at room temperature). The precipitate obtained was washed with concentrated HCl, alcohol, and ether, and dried at 70° (yield ~70%). Analyses of both isomers are given:

-Isomer. Found %: Pt 45.56; 45.17; 45.00; Cl 16.24; N 6.55
-Isomer. Found %: Pt 45.08; 45.33; 45.38; Cl 16.54; 16.63; 16.25; N
6.56; 6.45; 6.49
$[NH_3ClPtMtH]Cl$. Calculated %: Pt 45.15; Cl 16.40; N 6.48

Both isomers are almost white in color (with a yellowish tint, more noticeable in the -isomer), soluble in water, sparingly soluble in concentrated HCl, insoluble in acetone, alcohol, and ether; the -isomer forms needle-shaped crystals, the -isomer—elongated plates. Both isomers show an acid reaction with methyl orange (acidic properties of the COOH of coordinated MtH), and with Ag ions immediately give a precipitate of AgCl (outer-sphere chlorine).

The isomers are readily distinguished by adding a KOH solution; as a result of neutralization the -isomer forms a precipitate of compound II

Found %: Pt 49.39; N 7.01
II. Calculated %: Pt 49.32; N 7.08

yield ~70%; the -isomer under the same conditions does not form a precipitate.

Let us consider the properties of the isomers that confirm the structure of each of them. Weighed portions of both isomers were dissolved in water, and a titrated solution of Hg(NO ) was added in the presence of diphenylcarbazone indicator.

-Isomer. Found %: Cl 8.34; 8.40;
-Isomer. Found %: Cl 16.63; 16.54; 16.25

for $[NH_3ClPtMtH]Cl$, 16.40% total chlorine and 8.20% outer-sphere chlorine were calculated. Thus, in the $\alpha$-isomer only the outer-sphere chlorine is titrated, whereas in the $\beta$-isomer all the chlorine is titrated. It is evident that the inner-sphere chlorine in the $\beta$-isomer is labilized and is in the trans position to the S atom of methionine, while in the $\alpha$-isomer it is in the trans position to the amino group MtH. The results of titration of the isomers with alkali agree with these data. Titration of the $\alpha$-isomer proceeds clearly; 1 equiv of KOH is consumed per 1 mole of isomer (found 0.22 and 0.24% $H^+$; calculated 0.233% $H^+$). Meanwhile, in titration of the $\beta$-isomer, $> 1.5$ equiv of KOH is consumed per 1 mole of isomer; the end point of the titration is indistinct. Evidently, the labilized inner-sphere chlorine in the $\beta$-isomer is partially replaced by hydroxyl from the added alkali. In one experiment, KCl was added to the $\beta$-isomer before titration (20 mmoles per 1 mmole); a large excess of $Cl^-$ ions in the solution stabilizes the inner-sphere chlorine, and in this case the titration proceeds normally (found 0.25% $H^+$; calculated 0.233% $H^+$).

The results of measuring (at 25°) the molecular electrical conductivity ($\mu$) of solutions of the isomers also reflect the difference in their structures. For the $\beta$-isomer, $\mu_{100} = 220$ and $\mu_{1000} = 360\ \Omega^{-1} \cdot cm^2$ were found, with both $\mu$ values remaining completely unchanged with time. As is known, compounds containing inner-sphere chlorine usually show an increase of $\mu$ with time. However, in those cases where the chlorine atom is opposite a group with a strong trans effect (in the present case, opposite the S atom), a value of $\mu$ is established at once, due to more or less appreciable replacement of chlorine by water, and does not change with time (for example, in the case of trans-$[(NH_3)_2PtClNO_2]$, see (8)). We note that the comparatively large $\mu$ values of both isomers (especially $\mu_{1000}$) are due to a considerable extent to the acid properties of the COOH group of coordinated MtH. In the case of the $\alpha$-isomer, $\mu_{100} \sim 210$ and $\mu_{1000} \sim 340\ \Omega^{-1} \cdot \mathrm{cm}^2$ were found, but, in contrast to the $\beta$-isomer, the $\mu$ values slowly decrease with time, reaching after 12–14 days approximately constant values equal, respectively, to $\sim 120$ and $\sim 200\ \Omega^{-1} \cdot \mathrm{cm}^2$. It would seem that the $\mu$ values of the $\alpha$-isomer should increase with time as a result of replacement of chlorine by water. However, apparently, this effect is considerably outweighed by the effect of gradual replacement by water of $NH_3$ molecules labilized by the trans position to the S atom. The liberated $NH_3$ binds the protons split off from the COOH group into $NH_4^+$ ions and thereby sharply lowers the $\mu$ of the solutions.

**Table 1**

**Comparison of the properties of the isomers**

| Properties | $\alpha$-Isomer | $\beta$-Isomer |
|---|---|---|
| Crystal form, refractive indices* | Needles$n_g = 1.711$; $n_m = 1.708$;$n_p = 1.701$ | Plates$n_g = 1.718$; $n_m = 1.692$;$n_p = 1.668$ |
| Titration with $Hg(NO_3)_2$ solution | 50% of chlorine is titrated | 100% of chlorine is titrated |
| Titration with alkali | 1 equiv of KOH is consumed; a precipitate is formed | $> 1.5$ equiv of KOH is consumed; no precipitate is formed |
| Electrical conductivity of solutions | Considerably decreases with time | Does not change with time |
| Boiling with conc. HCl | Converts into I | Does not change |

* The refractive indices were determined by E. D. Ruchkin, to whom we express our gratitude.

The sharply differing mobility of $NH_3$ in the isomers (coordinates $NH_3$–S and $NH_3$–$NH_2$) is directly confirmed by comparison of their behavior toward heating with concentrated HCl. It was noted above that the $\beta$-isomer is obtained in good yield by boiling a solution of the compou-

III with concentrated HCl. Meanwhile, the $\alpha$-isomer, as experiment showed, after only 2 min of heating on a water bath with concentrated HCl is converted in a yield of more than 70% into compound I (i.e., substitution of $NH_3$ by chlorine occurs). For a visual comparison, 3 ml of concentrated HCl was added to equal weighed portions (0.5 mmole each) of the $\alpha$- and $\beta$-isomers and they were boiled for 10 min. Both isomers went into solution. On cooling, a yellow precipitate I separated from the first solution

Found, %: N 3.54
I. Calculated, %: N 3.37

and from the second—a precipitate of the initial $\beta$-isomer

Found, %: N 6.79
Calculated, %: N 6.48

Thus, the totality of the experimental data confirms the structure of the isomers (see Table 1).

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

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