SovietRxiv

Soviet-era science, translated into English

COMPLEX COMPOUNDS OF DIVALENT PLATINUM WITH ϵ-AMINOCAPROIC ACID

1957

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195701.42118

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

CHEMISTRY

L. M. Volshtein and M. F. Mogilevkina

COMPLEX COMPOUNDS OF DIVALENT PLATINUM WITH ϵ-AMINOCAPROIC ACID

(Presented by Academician I. I. Chernyaev, January 9, 1957)

Recently we described compounds of divalent platinum (Pt^{2+}) with β- and γ-amino acids (with β-alanine ([1])—βH—and γ-aminobutyric acid ([2])—γH). The amino group and the carboxyl group in these amino acids are in the 1,3 and 1,4 positions. In the case of βH an inner-complex salt was obtained (six-membered rings); in the case of γH an inner-complex salt (which should have contained seven-membered rings) is not formed. Noncyclic compounds were obtained for βH and γH. It was shown ([2]) that the strength of the Pt—AH bond (AH = amino acid) in noncyclic compounds of the type $[Pt(AH)_2(NH_3)_2]Cl_2$ increases in the series: α-, β-, γ-amino acids.

Complex compounds with ϵ-aminocaproic acid $NH_2(CH_2)_5 \cdot CO_2H$ (the molecules and negative ions of the acid are denoted below, respectively, as ϵH and ϵ) were not known. In ϵH the groups $-NH_2$ and $-CO_2H$ are in the 1,6 position. The preparation of an inner-complex salt $[Pt\varepsilon_2]$, where the rings would be nine-membered, proved impossible, as was to be expected. Only noncyclic compounds were obtained:

$$[Pt(\varepsilon H)_4]X_2,\ [Pt(\varepsilon H)_2Cl_2],\ [Pt(\varepsilon H)_2(NH_3)_2]X_2,$$

$$[Pt(\varepsilon H)_2(Thio)_2]X_2, \quad (Thio = SCN_2H_4), \quad [Pt\varepsilon HNH_3Cl_2],$$

$$[Pt\varepsilon HNH_3(Thio)_2]X_2,\ [Pt\varepsilon_2(NH_3)_2],\ \text{where } X = \overline{Cl},\ \tfrac{1}{2}PtCl_4^{2-}.$$

The Pt—ϵH bond in compounds of the type $[Pt(\varepsilon H)_2(NH_3)_2]Cl_2$ proved even stronger than in analogous compounds with γ- and β-amino acids, and all the more so than in compounds with α-amino acids ([2]). In the case of α-amino acids, the product of Jørgensen cleavage (on boiling with concentrated HCl) of the compounds $(Pt(AH)_2(NH_3)_2)Cl_2$ is only $[PtCl_2(NH_3)_2]$. In the cases βH, γH, and ϵH, under analogous conditions a mixture of the compounds $[Pt(AH)_2Cl_2]$ and $[PtCl_2(NH_3)_2]$ is formed, decreasing from γH to ϵH.

It is especially interesting that we succeeded in obtaining the cis- and trans-isomers of the compound $[Pt(\varepsilon H)_2Cl_2]$ and platinates with isomeric (cis- and

trans-) cations $[Pt(\varepsilon H_2)(NH_3)_2]^{2+}$. All compounds $[Pt(AH)_2Cl_2]$ isolated up to the present time (9 are known ([1–5])) have the trans-configuration. The compounds $[Pt(AH)_2(NH_3)_2]Cl_2$ described in the literature also belong to the trans-series. Only in the case of glycocoll (GlH) were A. A. Grinberg and B. V. Ptitsyn ([3]) able to synthesize isomeric inner-complex salts $[PtGl_2]$ and from them obtain salts $[Pt(GlH)_2(NH_3)_2]X_2$ with isomeric cations (in the salt of one of the isomeric cations $X - Cl^-$, in the other $X = \frac{1}{2}PtCl_4^{2-}$).

We shall briefly describe the preparation of certain compounds with ϵH. By heating on a water bath a solution of K_2PtCl_4 with ϵH and KOH (molar ratio $1 : 4 : 4$) we obtained a pale-yellow transparent solution. The successive introduction of negative ϵ ions into the inner sphere should lead to the formation of complex anions: $[Pt\varepsilon Cl_3]^{2-}$, $[Pt\varepsilon_2Co_2]^{2-}$, $[Pt\varepsilon_3Cl]^{2-}$, $[Pt\varepsilon_4]^{2-}$. It is obvious (on the basis of Chernyaev' s trans-effect regularity) that the anion $[Pt\varepsilon_2Cl_2]^{2-}$ must have the cis-configuration. On addition of hydrochloric acid to the solution obtained, the complex anions add—

replace H^+ and form: $[Pt\varepsilon HCl_3]^-$, $[Pt(\varepsilon H)_2Cl_2]$, $[Pt(\varepsilon H)_3Cl]$, $[Pt(\varepsilon H)_4]^{2+}$. In this process the poorly water-soluble cis-dichlorides $[Pt(\varepsilon H)_2Cl_2]$ and $[Pt(\varepsilon H)_4]Cl_2$ precipitate. The latter compound is considerably more soluble in warm water than the former. After treating the mixture of $[Pt(\varepsilon H)_2Cl_2]$ and $[Pt(\varepsilon H)_4]Cl_2$ with warm water, the yellow precipitate, which proved to be pure cis-dichloride $[Pt(\varepsilon H)_2Cl_2]$, was filtered off. An acidified solution of platinite was added to the cooled filtrate, and a pink precipitate $[Pt(\varepsilon H)_4][PtCl_4]$ was obtained.

The trans-dichloride is formed if concentrated HCl is added to a solution obtained by the interaction of K_2PtCl_4 with εH and KOH, and boiling is carried out, causing Iørgensen cleavage of the tetra derivative:

$$[Pt(\varepsilon H)_4]Cl_2 \quad \text{trans-}[Pt(\varepsilon H)_2Cl_2] + 2\varepsilon H.$$

However, the precipitate formed in this case is a mixture of both isomers (the cis-dichloride, as already noted, is formed from the anions $[Pt\varepsilon Cl_2]^{2-}$). Since both isomers are very poorly soluble in water, their separation by fractional crystallization is difficult. To obtain pure trans-dichloride we used the different behavior of the isomers toward ammonia. On boiling a mixture of dichlorides with concentrated NH_3, the trans-dichloride is converted into the very poorly soluble trans-$[Pt\varepsilon_2(NH_3)_2]$, and the cis-dichloride into the readily soluble cis-$[Pt\varepsilon_2(NH_3)_2]$. Trans-$[Pt\varepsilon_2(NH_3)_2]$ is a white precipitate, a nonelectrolyte, readily soluble in acids with formation of the cation $[Pt(\varepsilon H_2)(NH_3)_2]^{2+}$. The filtered, washed, dried, and analyzed preparation trans-$[Pt\varepsilon_2(NH_3)_2]$ was boiled with concentrated HCl. The Iørgensen cleavage proceeds according to the scheme:

SovietRxiv

$$2\varepsilon H+\begin{bmatrix} Cl & NH_3 \\ & Pt \\ NH_3 & Cl \end{bmatrix} \xleftarrow{HCl+} \begin{bmatrix} \varepsilon & NH_3 \\ & Pt \\ NH_3 & \varepsilon \end{bmatrix} \xrightarrow{+HCl} \begin{bmatrix} \varepsilon H & Cl \\ & Pt \\ Cl & \varepsilon H \end{bmatrix} +2NH_4^{\cdot}$$

A mixture of the chloride of Reiset' s second base with the trans-dichloride precipitates; the latter product greatly predominates (the yields are respectively 15-20 and 40-45%). The mixture was titrated with alkali; in this process the acid $[Pt(\varepsilon H_2Cl_2]$ passed into the soluble salt $K_2[Pt\varepsilon_2Cl_2]$ (closure of the amino-acid rings, as noted above, does not occur here), while $[PtCl_2(NH_3)_2]$ remained in the precipitate. After filtering off $[PtCl_2(NH_3)_2]$, HCl was added to the filtrate; from the salt $K_2[Pt\varepsilon_2Cl_2]$ the acid $[Pt(\varepsilon H)_2Cl_2]$ was obtained again. The precipitated solid was pure trans-dichloride.

It was noted above that, as a result of the action of NH_2 on the mixture of dichlorides, a precipitate of trans-$[Pt\varepsilon_2(NH_3)_2]$ was separated, while the soluble cis-$[Pt\varepsilon(NH_3)_2]$ remained in the filtrate. Boiling the filtrate with concentrated HCl should lead to Iørgensen cleavage:

$$\begin{bmatrix} \varepsilon & NH_3 \\ & Pt \\ \varepsilon & NH_3 \end{bmatrix} + 3HCl \rightarrow \begin{bmatrix} \varepsilon H & Cl & \\ Cl & Pt & NH_3 \end{bmatrix} + NH_4Cl + \varepsilon H$$

In this case a yellow precipitate is obtained; analyses showed that its composition indeed corresponds to the formula $[Pt\varepsilon HNH_3Cl_2]$; its configuration was confirmed by the action of Thio on it (the compound $[Pt\varepsilon HNH_3(Thio)_2]Cl_2$ was obtained). The preparation of $[Pt\varepsilon HNH_3Cl_2]$ proved the cis structure of the soluble $[Pt\varepsilon_2(NH_3)_2]$.

Addition to a solution of cis-$[Pt\varepsilon_2(NH_3)_2]$ of a solution of K_2PtCl_4 acidified with HCl led to the formation of a dark-green precipitate of platinite:

$$[Pt\varepsilon_2(NH_3)]_2 + 2HCl + K_2PtCl_4 \rightarrow [Pt(\varepsilon H)_2(NH_3)_2][PtCl_4] + 2KCl.$$

To obtain the isomeric platinite, trans-$[Pt\varepsilon_2(NH_3)_2]$ was dissolved in dilute HCl and a solution of K_2PtCl_4 was immediately added; a gray-green precipitate formed.

The size of the article does not permit us to dwell on the description of all the compounds obtained; we shall briefly describe the isomeric compounds.

Cis-dichloride

Found, %: Pt 36.66; 36.82; 37.03; N 5.16

SovietRxiv

Trans-dichloride

Found, %: Pt 36.86; 37.03; Cl 13.65; N 5.35

$$[Pt(H)_2Cl_2].$$

Calculated, %: Pt 36.94; Cl 13.42; N 5.30

Platinate with a cation of cis-structure

Found, %: Pt 47.09; 47.27; Cl 17.17; N 6.70; H^+ 0.25

Platinate with a cation of trans-structure

Found, %: Pt 47.01; 47.17; Cl 17.48; N 6.60; H^+ 0.25

$$[Pt(H)_2(NH_3)_2][PtCl_4].$$

Calculated, %: Pt 47.12; Cl 17.12; N 6.76; H^+ 0.24.

The cis- and trans-dichlorides differ in shade of color (yellow and light yellow), in the form and refractive indices of the crystals, and in solubility in water (at 14°: 0.00089 and 0.00025 mol/l). Both dichlorides are soluble in alcohol; they should be washed with water and ether and dried at 80°. On heating the cis-dichloride with water to boiling, the solution becomes brown; a solution of the trans-dichloride under the same conditions remains yellow. The isomers differ sharply in their behavior toward Thio. When thiourea was allowed to act on the isomers under exactly identical conditions, from the cis-dichloride a yellow precipitate of the tetra-thio derivative $[Pt(Thio)_4]Cl_2$ was obtained, and from the trans-dichloride a white precipitate of the dithio derivative $[Pt(H)_2(Thio)_2]Cl_2$. The formation of these compounds (both are obtained in pure form and in high yield) confirms, in accordance with Kurnakov' s regularity, the configuration of the initial dichlorides. Under the action of NH_3, the cis-dichloride, as noted, gives no precipitate, while the trans-dichloride gives a precipitate of $[Pt_2(NH_3)_2]$ in a yield $> 90°$.

The platinate with a cation of trans-configuration forms, like Magnus' salt $[Pt(NH_3)_4][PtCl_4]$, two differently colored modifications. When washed with dilute HCl or with water, the gray-green precipitate becomes lilac; on drying, the precipitate again becomes gray-green, etc. The isomeric dark-green platinate does not change color on addition of water. The precipitates of both isomers were washed on the filter with dilute HCl, alcohol, ether, and dried at 60°.

Very sharp and quite striking is the difference between the isomeric platinates in their behavior toward alkali. Both isomers are quantitatively titrated with alkali.

SovietRxiv

$$[Pt(H)_2(NH_3)_2][PtCl_4] + 2KOH \rightarrow [Pt_2(NH_3)_2] + K_2PtCl_4 + 2H_2O.$$

As titration proceeded, the initial colored precipitates disappeared; in both cases pink solutions of $[K_2PtCl_4]$ were obtained. From the platinate with a cation of cis-structure a clear solution was obtained (cis-$[Pt_2(NH_3)_2]$ is soluble), while from the trans-isomer a white precipitate of trans-$[Pt_2(NH_3)_2]$ was obtained. We note that both isomers $[Pt(H)_2(NH_3)_2][PtCl_4]$ are dimers of the above-mentioned monomeric compound $[Pt\,HNH_3Cl_2]$.

Dnepropetrovsk Chemical-Technological Institute
named after F. E. Dzerzhinsky

Received
24 XII 1956

CITED LITERATURE

1. L. M. Volshtein, M. F. Mogilevkina, DAN, 104, 418 (1955).
2. L. M. Volshtein, M. F. Mogilevkina, DAN, 110, 83 (1956).
3. A. A. Grinberg, B. V. Ptitsyn, Izv. Platin. inst., 9, 55 (1932).
4. A. A. Grinberg, L. M. Volshtein, Izv. AN SSSR, ser. khim., No. 4, 885 (1937).
5. L. M. Volshtein, N. S. Velikanova, Zhurn. neorg. khim., 1, 48 (1956).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.