CHEMISTRY

Academician A. A. GRINBERG, M. I. GELF' MAN

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. A. GRINBERG, M. I. GELF' MAN

ON THE QUESTION OF THE SEPARATION OF ISOMERIC DIAMINES OF DIVALENT PLATINUM AND THE PRODUCTS OF THEIR INTERACTION WITH THIOUREA

The conditions for the synthesis of isomeric diamines of divalent platinum are determined mainly by the regularities of Peyrone and Jørgensen. However, sometimes, depending on the nature of the coordinated groups, a partial or complete reversal of these regularities may be observed (1). In such cases the reaction product may be a mixture of isomers. It is important to have methods that make it possible to detect an admixture of one or another isomer, determine its quantity, and also carry out separation of the isomers.

The classical method for determining the geometrical configuration of diamines of divalent platinum is the thiourea reaction of N. S. Kurnakov. Along with this, another reaction was proposed, making it possible rapidly to detect traces of the cis-isomer in the trans-isomer, as well as an admixture of the trans-isomer to the cis-isomer (2). Finally, one of us, together with E. N. In' kova, recently succeeded in showing a characteristic difference in the behavior of cis- and trans-diamines of divalent platinum toward electrolyte solutions (3). In the present work we used this difference for the separation of mixtures of isomeric diamines. In addition, we developed two new methods for the detection and separation of the complexes $[Pt(thio)_4]Cl_2$ and $[Pt(NH_3)_2(thio)_2]Cl_2$, which, as is known, are products of the interaction of isomeric diamines of divalent platinum with thiourea.

Sulfate method. The product of the interaction of cis-isomers with thiourea—the ion $[Pt(thio)_4]^{2+}$—forms, in the presence of sulfuric acid or sulfates, the sparingly soluble compound $[Pt(thio)_4]SO_4$. Owing to this, the tetrathiourea complex can be quantitatively separated from solution. At the same time, the complex $[Pt(NH_3)_2(thio)_2]^{2+}$, even in the presence of a large excess of sulfate, remains in solution. A simple method for separating these products may be based on this. A mixture of thiourea products is dissolved in a small amount of water, and a saturated solution of sodium sulfate is added to the solution. A light-yellow precipitate of $[Pt(thio)_4]SO_4$ is thereby formed. The substance is separated, washed with cold water, alcohol, and ether. Its weight corresponds to the amount of cis-isomer in the mixture. When concentrated hydrochloric acid is added to the filtrate, a snow-white acicular precipitate of $[Pt(NH_3)_2(thio)_2]Cl_2$ falls out. The substance is separated from the solution and washed with alcohol and ether. From its weight, the amount of trans-isomer present in the mixture is determined.

A mixture consisting of 0.4 g of $[Pt(thio)_4]Cl_2$ and 0.2 g of $[Pt(NH_3)_2(thio)_2]Cl_2$ was dissolved in 25 ml of H_2O. After addition of Na_2SO_4, 0.42 g of $[Pt(thio)_4]SO_4$ was obtained, and from the filtrate 0.195 g of $[Pt(NO_3)_2(thio)_2]Cl_2$ was isolated with hydrochloric acid, i.e., the separation proved practically complete.

The method described makes it possible to detect and quantitatively determine both isomers even in those cases where the mixture contains less than 5% of one of the diamines.

Bromination of thiourea complexes. The second method is based on the different behavior of $[Pt(thio)_4]^{2+}$ and $[Pt(NH_3)_2(thio)_2]^{2+}$

during their oxidation with bromine in hydrochloric-acid solution. Whereas the second compound is converted into the sparingly soluble bromide $[Pt(NH_3)_2Br_4]$, the bromination product of the first compound remains in solution (if its concentration in the solution does not exceed a certain value).

In practice, the reaction was carried out as follows. A mixture of thiourea complexes was dissolved in water, the amount of which was taken on the basis of 15 ml per 0.1 g of mixture. To the solution were added 2 ml of conc. HCl and 1 ml of liquid bromine. The solution was heated on a water bath for 2 h. The precipitate that separated was filtered off and washed with water, alcohol, and ether. The amount of bromide obtained corresponded to the amount of the trans isomer in the mixture of diammines.

Thus, on bromination of a mixture consisting of 0.28 g of $[Pt(thio)_4]Cl_2$ and 0.14 g of $[Pt(NH_3)_2(thio)_2]Cl_2$, 0.16 g of $[Pt(NH_3)_2Br_4]$ was obtained, i.e., 94% of the theoretical amount.

Bromination of the products of the thiourea reaction thus makes it possible to determine the content of the trans isomer in a mixture of isomeric diammines.

Separation of isomeric diammines. The methods described above are based on the conversion of isomeric diammines into the corresponding thiourea products. However, in some cases it may become necessary to separate the isomers themselves. Such a separation may be based on the different solubilities of the diammines. The solubility of cis-$Pt(NH_3)_2Cl_2$ in water at 25° is 0.24 g per 100 ml, whereas the solubility of the trans isomer is 0.036 g per 100 ml of H_2O.

In work (3) it was shown that the solubilities of the isomeric diammines differ still more if, instead of water, a potassium chloride solution is used as solvent. With increasing KCl concentration, the solubility of Peyrone's chloride increases appreciably, whereas the solubility of Reiset' s second-base chloride decreases somewhat.

In 100 ml of saturated KCl solution at 25°, 0.385 g of Peyrone's chloride dissolves. The solubility of the trans isomer under the same conditions is 0.025 g.

If a mixture of diammines is treated with the appropriate amount of saturated KCl solution, complete dissolution of the cis isomer occurs, while the bulk of the trans isomer remains as the solid phase.

A mixture consisting of 0.155 g of trans-$Pt(NH_3)_2Cl_2$ and 0.32 g of cis-$Pt(NH_3)_2Cl_2$ was treated with 100 ml of saturated KCl solution. The solution was heated for 30 min on a water bath, then cooled and filtered. The precipitate was washed with water, alcohol, and ether. 0.11 g of trans-$Pt(NH_3)_2Cl_2$ was obtained. To check the purity of the trans isomer isolated from the mixture, the thiourea reaction was carried out. Addition of a Na_2SO_4 solution did not cause even turbidity in the solution containing the thiourea complex. On addition of HCl, a snow-white precipitate of $[Pt(NH_3)_2(thiO)_2]Cl_2$ separated; its amount proved to be 0.12 g.

We are checking the possibility of applying the indicated separation methods to isomeric diammines containing various amines in the inner sphere of the molecule.

Received
11 XI 1964

CITED LITERATURE

1. A. A. Grinberg, *Introduction to the Chemistry of Complex Compounds*, 1951.

2. A. A. Grinberg, A. I. Dobroborskaya, G. A. Shagisultanova, Publishing House of the Academy of Sciences of the USSR, Journal of General Chemistry, No. 6, 969, 1953.

3. A. A. Grinberg, E. N. In' kova, A. I. Dobroborskaya, Journal of Inorganic Chemistry, 7, 987 (1962).

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

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