Chemistry

Academician A. A. Grinberg and Yu. N. Kukushkin

1962

SovietRxiv

Abstract

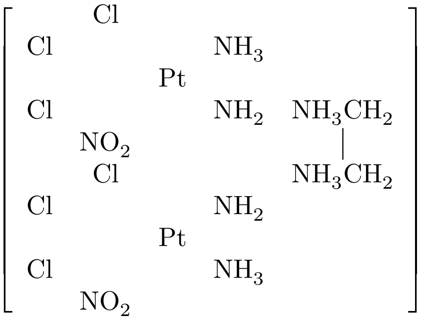
Full Text

Chemistry

Academician A. A. Grinberg and Yu. N. Kukushkin

On the question of the existence of salts of ammine complexes of tetravalent platinum

The acidic properties of ammine complexes of tetravalent platinum were discovered and characterized by one of us jointly with G. P. Faerman as early as 1930 (⁀1). Subsequently these investigations were extensively developed (⁀2, ⁀3). In 1932 one of us wrote that "these ammine complexes, being acids, should give salts and, what at first glance may seem especially striking, ammonium salts" (⁀4). In the same work it was indicated that one of the compounds of this type had already been described in the literature. It was synthesized by I. I. Chernyaev through the action of ethylenediamine on $[Pt(NH_3)_2NO_2Cl_3]$, and it may be assigned the structure



$$\left[\begin{array}{ccccc} & Cl & & & \\ Cl & & & NH_3 & \\ & & Pt & & \\ Cl & & & NH_2 & NH_3CH_2 \\ & NO_2 & & & | \\ & Cl & & & NH_3CH_2 \\ Cl & & & NH_2 & \\ & & Pt & & \\ Cl & & & NH_3 & \\ & NO_2 & & & \end{array}\right]$$

The acid-base interaction of ammine complexes and amides of tetravalent platinum was invoked by one of us (⁀5) to explain the very fact of formation of Rubinstein's salt, which is a product of the combination of Gros' salt $[Pt(NH_3)_4Cl_2]Cl_2$ and Chugaev' s amido salt $[Pt(NH_3)_4NH_2Cl]Cl_2$. However, aminates of tetravalent platinum in which the hydrogen of ammonia or of an amine would be replaced by a metal have not yet been described in the literature. The necessity of the existence of such compounds in solution was already pointed out in work (⁀1), and confirmation of this is the fact that $[Pt(NH_3)_6](SO_4)_2$ is soluble in caustic alkalis. Isolation from solution of a complex containing a coordinated molecule of sodium (or potassium) amide, which is extremely prone to hydrolysis, must undoubtedly be attended by great difficulties.

The bond between alkali-metal ions and the coordinated amido group is ionic in character. However, the amido group has a free electron pair, owing to which a covalent bond, characterized by greater strength, may be established with certain metal ions. Such metal ions should include the ions of silver, mercury, nickel, etc. In view of the great interest of the question, we undertook attempts to establish the actual existence of metallic derivatives (above all silver derivatives) of ammine complexes of tetravalent platinum. The interaction of Pt(IV) amido compounds with silver salts may proceed according to the reaction:

$$[\mathrm{Pt(NH_3)_5NH_2}]^{3+} + \mathrm{Ag}^{+} \rightleftarrows [\mathrm{Pt(NH_3)_5NH_2Ag}]^{4+}. \qquad (1)$$

The occurrence of such a reaction in solution should cause an increase in the solubility of silver salts, silver hydroxide, and silver oxide itself. Experiments showed that the solubility of freshly prepared silver hydroxide increases considerably in the presence of amido complexes of Pt(IV). We give a description of one of the experiments: 0.2726 g of $[\mathrm{Pt(NH_3)_6}](\mathrm{NO_3})_4$ $(0.50 \cdot 10^{-3}$ g-mole)

were dissolved in 50 ml of water; to the resulting solution were added 7.70 ml of a 0.3254 N solution of KOH $(2.50 \cdot 10^{-3}$ gram-mole), and then 20 ml of a 0.1002 N solution of $\mathrm{AgNO_3}$ $(2.0 \cdot 10^{-3}$ gram-mole). The total volume was brought to 100 ml. The resulting solution with the precipitate of silver hydroxide was stirred at a temperature of 18° for 2.5-3 h. After this the solution was separated from the precipitate, and the silver content in it was determined gravimetrically as AgCl. From 100 ml of solution, 0.1445 g of AgCl was isolated, which corresponds to $1.01 \cdot 10^{-3}$ gram-ion of silver. Recalculated per liter, the solubility of silver hydroxide under these conditions is $1.01 \cdot 10^{-2}$ gram-mole/l, i.e., approximately 100 times greater than the solubility of AgOH in water. Thus, for each mole of amido complex in this experiment, about 2 gram-ions of silver passed into solution. When the experimental conditions are changed, and above all when the alkali concentration is increased, the transfer of silver into solution decreases.

As is known, Johnston and co-workers (^{6}), studying the amphoteric character of silver oxide, established that its solubility in weakly alkaline solutions decreases, reaching a minimum value in a 0.015 N alkali solution. With a further increase in alkalinity the solubility of silver oxide increases. In the same work it was shown that inert salts do not noticeably affect the solubility of silver oxide.

Such a large increase in the solubility of silver hydroxide gave grounds to expect an increase in the solubility even of silver chloride in the presence of amido complexes of Pt(IV). Qualitative experiments showed that the solubility of freshly prepared silver chloride increases in the presence of platinum amido complexes. For the quantitative determination of the solubility of AgCl in solutions of various amido complexes, the radioactive isotope of silver Ag^{110} was used. However, it was found that, when silver chloride dissolves in solutions of amido complexes, the solid phase changes owing to entrainment of the complex into the precipitate. Therefore the results of the entrainment of AgCl solubility also have a qualitative character. Since entrainment into the precipitate occurs to the least extent for Chugaev' s amide, we give one of the experiments for it. In a vessel for determining solubility, 0.1254 g of $[\mathrm{Pt(NH_3)_5Cl}](\mathrm{NO_3})_3$ $(0.25 \cdot 10^{-3}$ gram-mole) was dissolved in 15 ml of water, to which 1.45 ml of a 0.3462 N solution of KOH ($0.50 \cdot 10^{-3}$ gram-mole) had been added. Then 10 ml of a 0.1008 N solution of KCl ($1.01 \cdot 10^{-3}$ gram-mole) and 10 ml of a 0.07811 N solution of $AgNO_3$ ($0.78 \cdot 10^{-3}$ gram-mole) were successively introduced into the vessel. Stirring was carried out at a temperature of 20° for 2 h. After this the precipitate was separated from the solution, and the solubility of AgCl under the given conditions was judged from the radioactivity that had passed into the solution. The radioactivity was distributed as follows: 680 imp/min passed into solution, while 19720 imp/min remained in the precipitate. Consequently, $0.26 \cdot 10^{-4}$ gram-ion of silver passed into 36.45 ml of solution, and the concentration of silver ions in a liter of solution was $0.71 \cdot 10^{-3}$ gram-ion/l. As is known, the solubility of silver chloride at 20° is $1 \cdot 10^{-5}$ gram-mole/l.

Thus, the results of determining the solubility of silver hydroxide and of its chloride salt confirm the formation in solution of a Pt(IV) complex with a coordinated molecule of silver amide. Subsequently we proceeded to obtain compounds of this type in solution. The experimental procedure was as follows: $0.25 \cdot 10^{-3}$ gram-mole of the complex was dissolved in 50 ml of water, and $0.25 \cdot 10^{-3}$ gram-mole of KOH was added to the solution. The resulting solution was titrated with a 0.09968 N solution of $AgNO_3$. The presence of the reaction and the extent of its progress were judged from the change in the pH of the solution in the presence of a glass electrode.

In this way complexes containing silver amide were obtained, starting from $[Pt(NH_3)_5Cl](NO_3)_3$, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)_5OH]Cl_3$, and $[Pt(NH_3)_6]Cl_4$. Figure 1 presents the characteristic course of the titration curves of these salts. It is evident from the figure that, in the case of $[Pt(NH_3)_5Cl](NO_3)_3$, upon addition of the first drops of $AgNO_3$ solution there is a sharp decrease in the pH of the solution being titrated. At the end of the titration the pH value practically remains···

constant. For complexes having outer-sphere chloride ions, silver is first consumed in binding the chloride ions in the form of AgCl. The change in pH in this section of the titration curve is small. A sharp jump in pH begins after all the outer-sphere chloride ions have been bound. It should be noted that, for complexes with outer-sphere chloride ions, at the initial moment of titration a delay is observed in the precipitation of AgCl from the solution, which agrees with the results of the solubility determination. The reactions occurring with the complex compounds, using $[Pt(NH_3)_5Cl](NO_3)_3$ as an example, may be represented schematically as follows:

$$\begin{gathered}[Pt(NH_3)_5Cl]^{3+} + OH' \rightleftarrows \\ \rightleftarrows [Pt(NH_3)_4NH_2Cl]^{2+} + H_2O, \end{gathered} \tag{2}$$

$$[Pt(NH_3)_4NH_2Cl]^{2+} + Ag^{+} \rightleftarrows$$

Fig. 1. Titration curves with AgNO3 solution. 1 —solution of Pt(NH3)5Cl3 upon addition of 1 equiv. of alkali; 2 —solution of [Pt(NH3)5Cl]Cl3 upon addition of 1 equiv. of alkali.

Figure 1: Fig. 1. Titration curves with AgNO3 solution. 1 —solution of Pt(NH3)5Cl3 upon addition of 1 equiv. of alkali; 2 —solution of [Pt(NH3)5Cl]Cl3 upon addition of 1 equiv. of alkali.

$$\rightleftarrows [\mathrm{PtNH_2Ag(NH_3)_4Cl}]^{3+}. \tag{3}$$

It is important to note that in the course of the titrations no precipitation of silver hydroxide was observed. On the contrary, when $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ was titrated under the corresponding conditions, after the chloride ions had been bound by silver, silver hydroxide began to precipitate from the solution.

Fig. 1. Titration curves with $\mathrm{AgNO_3}$ solution. 1 —solution of $[\mathrm{Pt(NH_3)_5Cl}](\mathrm{NO_3})_3$ upon addition of 1 equiv. of alkali; 2 —solution of $[\mathrm{Pt(NH_3)_5Cl}]\mathrm{Cl_3}$ upon addition of 1 equiv. of alkali.

If the complexes with silver amide obtained in solution are titrated with NaCl solution, processes occur that are the reverse of reactions (2) and (3). This is manifested in an increase in the alkalinity of the solutions and in the restoration of pH values close to the initial ones. Along with the preparation in solution of complexes containing silver amide, a number of compounds have been isolated in the solid phase. The investigations of the isolated compounds are being completed, and their results will be published shortly.

The complex formation of silver ions with amines and the associated increase in the solubility of its salts and oxide hydrate are well known. In the present case, the amido compounds of Pt(IV) behave toward silver ions similarly to amines.

In conclusion, it should be said that, probably, the silver-containing products obtained by Dixon[7] may be assigned to the category of compounds described in the present article. However, Dixon' s conception of the structure of these compounds cannot be considered satisfactory.

Received
10 IV 1962

REFERENCES

1. A. A. Grinberg, G. P. Faerman, *Izv. Inst. platiny*, **8**, 115 (1931).

2. A. A. Grinberg, Kh. I. Gildengershel, *Izv. AN SSSR, OKhN*, 1948, No. 5, 479.

3. A. A. Grinberg, L. V. Vrublevskaya et al., *ZhNKh*, **5**, 1018 (1959).

4. A. A. Grinberg, *Izv. Inst. platiny*, **10**, 47 (1932).

5. A. A. Grinberg, *Introduction to the Chemistry of Complex Compounds*, 1945, p. 349.

6. H. L. Johnston, F. Čúta, A. B. Garrett, *J. Am. Chem. Soc.*, **55**, 2311 (1933).

7. B. E. Dixon, *J. Chem. Soc.*, 1932, 2948.

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