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Abstract

Full Text

Chemistry

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On the Difference in Reactivity of Geometrically Isomeric Compounds of Composition $[PtA_2X_4]$

Geometrically isomeric salts of composition $[PtA_2X_2]$, where A is an ammonia or amine molecule, and X is a monovalent acid residue, can be rapidly distinguished from one another both by means of N. S. Kurnakov’s well-known reaction and by the reaction with KJ in the presence of phenolphthalein that we described earlier ([1]). As for the corresponding derivatives of tetravalent platinum, they can be distinguished from one another either by reduction to derivatives of Pt^{II}, with subsequent determination of the configuration by one of the above-mentioned methods, or by the method of I. I. Chernyaev, which is based on a principle analogous to Werner’ s principle ([2]).

In the present work it has been possible to show that isomeric salts of composition $[Pt(NH_3)_2Cl_4]$ can readily and rapidly be distinguished by means of the reaction with KJ. Indeed, when an excess of KJ acts, with heating, on a suspension of trans-$[Pt(NH_3)_2Cl_4]$ in water, the formation of a precipitate of trans-$[Pt(NH_3)_2J_4]$ proceeds rapidly. The solution above the precipitate becomes almost colorless (with a faint yellowish tint).

Procedure for the Determination

A certain amount of $[Pt(NH_3)_2Cl_4]$ is placed in a test tube or in a beaker, and several milliliters of water are added. The solution is heated, and an excess of a concentrated solution of potassium iodide is added to it.

In the case of the trans isomer $[Pt(NH_3)_2Cl_4]$, the solution at first acquires a brown color, and at the same time a black precipitate, insoluble in alcohol, separates.

As the solution cools, the brown color rapidly disappears, and the solution above the precipitate becomes, as indicated, almost colorless. Experiments showed that trans-$[Pt(NH_3)_2J_4]$ precipitates practically completely from the solution. In one experiment, 0.3350 g of the initial trans-$[Pt(NH_3)_2Cl_4]$ was taken, and 0.6306 g of a black precipitate of trans-$[Pt(NH_3)_2J_4]$ was obtained, which is in agreement with the theoretical yield.

The composition of the precipitate was checked by gravimetric determination of platinum. For $[Pt(NH_3)_2J_4]$, the theoretical platinum content is 26.49%. Found: Pt 26.44; 26.58%.

The solution above the precipitate obtained has a practically neutral reaction (pH 6.7).

When the reaction of potassium iodide with the cis isomer is studied under the same conditions, an intense red coloration of the solution appears instantaneously. The red solution, obtained by the action of an excess of KJ on cis-$[Pt(NH_3)_2Cl_4]$, shows a clearly alkaline reaction, owing to partial displacement of ammonia by iodide ions from cis-$[Pt(NH_3)_2Cl_4]$. Thus, for example, on interaction with 0.5 M KJ of cis-$[Pt(NH_3)_2Cl_4]$ at $C = 2.48 \cdot 10^{-4}$ M, a pH of 9.40 was obtained.

With amounts of cis-$[Pt(NH_3)_2Cl_4]$ on the order of 0.04 g or somewhat smaller, a noticeable black precipitate of cis-$[Pt(NH_3)_2J_4]$ separates from the red solution; this precipitate, unlike the corresponding trans isomer, dissolves in alcohol.

From 0.3 g of cis-$[Pt(NH_3)_2Cl_4]$, 0.28 g of cis-$[Pt(NH_3)_2J_4]$ was obtained, which corresponds to ∼ 47% of the starting salt.

Analysis of the black precipitate cis-$[Pt(NH_3)_2J_4]$:

Found, %:	Pt 26.88; N 3.87, 4.01.
$[Pt(NH_3)_2J_4]$. Calculated, %:	Pt 26.49; N 3.80.

With very small amounts of cis-$[Pt(NH_3)_2Cl_4]$ (traces), the separation of a black precipitate in an intensely red solution is practically not observed.

The reaction with KJ recommended above, by means of which it is possible to distinguish the isomeric salts of composition $[Pt(NH_3)_2Cl_4]$, may also be applied to analogous platinum compounds in which aliphatic amines are present instead of ammonia.

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