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Abstract

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NEW CONDITIONS FOR SYNTHESIS WITH THE PARTICIPATION OF $PtCl_4^{2-}$ IONS

(Presented by Academician A. A. Grinberg, 17 IV 1961)

It is known that, when certain free amines (ammonia, methylamine, ethylamine) are allowed to act on a solution of K_2PtCl_4 in order to obtain cis-diamines, a mixture of substances precipitates, consisting mainly of the desired diamine and the corresponding Magnus salt. The difficulty of separating the product of the interaction of K_2PtCl_4 with ammonia, and the fact that, when methylamine acts on K_2PtCl_4, the analogue of Magnus salt is the only reaction product, have led many investigators ($^{1-4}$) to seek synthesis conditions that exclude the action of these amines in the free state on platinite.

It should be emphasized that, when free hydroxylamine (^{5}) or its acetate salt (^{6}) is added to a solution of K_2PtCl_4, a brown substance separates out which does not contain the desired diamine and, according to A. V. Babaeva and co-workers (^{6}), is probably a polynuclear compound—the product of hydrolysis of $[Pt(HxCl)_2]$*.

They also, with known difficulty, isolated the hydroxylamine cis-diamine from the filtrate after separation of the aforementioned brown substance.

An analysis of the causes giving rise to the complications listed led to the idea that, if this reaction were carried out under conditions of a higher concentration of platinite than is possible when using K_2PtCl_4 (1 : 10), this could promote a more rapid saturation of the solution with the desired cis-diamine and, consequently, a more successful precipitation of it.

A sharp increase in the concentration of platinite (1 : 1) was achieved by replacing K^+ ions with Na^+ ions; experiments with free methylamine, which led to the isolation of $[(Pt(mCl)_2]$**, confirmed the correctness of our assumption.

The reaction of free hydroxylamine or its acetate salt with platinite under the indicated conditions led to the formation of a precipitate that was a large mixture of the cis-diamine and the analogue of Magnus salt. The brown substance did not form under these conditions.

Below are described methods for the synthesis of the methylamine and hydroxylamine analogues of Peyrone' s salt.

1. **Preparation of the initial solution of** Na_2PtCl_4**.** To 4 g of potassium platinite, 3 g of $NaClO_4$ in 4 ml of water are added. The excess $NaClO_4$ amounts to 30% relative to the theoretical amount. The mixture is vigorously stirred and heated on a boiling water bath for 5–10 min. After cooling, the $KClO_4$ precipitate is thoroughly suction-filtered and washed with 1-2 ml of water, which are combined with the filtrate. The resulting dark cherry-red solution of Na_2PtCl_4 is used for further syntheses.
2. **Synthesis of cis-dichlorodimethylamineplatinum** $[Pt(mCl)_2]$**.** To the solution of Na_2PtCl_4 obtained from 4 g of K_2PtCl_4, 1.8 ml of methylamine solution (2 mol of methylamine per 1 mol of K_2PtCl_4) is added dropwise with vigorous stirring. Almost immediately a precipitate begins to separate, and after 20–30 min the solution acquires a yellow color. During the synthesis, strong heating is observed. After 30 min the yellow-green precipitate is thoroughly suction-filtered and washed with a minimal amount of water, alcohol, and ether. The precipitate consists of methylamine analogs of Peyrone' s salt and Magnus' salt. The yield of the mixture is $\simeq$ 2 g. Separation of this mixture by the usual method proved very difficult, apparently because of the relatively close solubilities of $[Pt(mCl)_2]$ and $[Ptm_4][PtCl_4]$. A sharp decrease in the solubility of the Magnus' salt analog was achieved by separation from a solution of K_2PtCl_4 (the effect of the common ion). For this purpose, a solution of 0.4 g of K_2PtCl_4 in 10 ml of water acidified with two drops of HCl is added to the indicated mixture. The mixture is then heated on a boiling water bath with vigorous stirring for 5 min and rapidly suction-filtered. From the filtrate, on cooling (preferably with ice), light-yellow crystals of methylamine diamine precipitate. They are suction-filtered, and the filtrate is again added to the mixture of the diamine with the Magnus' salt analog. The operation is repeated 3 times. The resulting preparations are washed with alcohol and ether. The yield of methylamine diamine is 1 g, and that of the methylamine analog of Magnus' salt is 0.7 g. Analytical results:

For $[Pt(mCl)_2]$.	Found, %:	Pt 59.5; 59.6; 59.7;	Cl 21.70.
For $[Ptm_4][PtCl_4]$.	Found, %:	Pt 59.3; 59.2.	
	Calculated, %:	Pt 59.5	Cl 21.62

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* Hx —hydroxylamine.
** m —methylamine.

The values of the molecular electrical conductivity of methylamine diamine 15 min after the start of dissolution at $V = 1000$ and $t = 25^\circ$ were 5.36 $\Omega^{-1} \cdot \mathrm{cm}^2$ and 6.97 $\Omega^{-1} \cdot \mathrm{cm}^2$. The structure was proved by N. S. Kurnakov' s thiourea reaction and by the reaction of A. A. Grinberg and A. I. Dobroborskaya (^{7}).

The yield of methylamine diamine can be increased considerably, and that of the corresponding Magnus' salt decreased, if the synthesis is carried out while cooling the reaction mixture with ice. In this case the reaction proceeds slowly, and it is recommended that the mixture be filtered after 4 h. Its yield is $\simeq$ 2 g, and $[\mathrm{Pt(mCl)_2}]$ 1.6 g. It may be expected that combining the acetate method (^{2}) with synthesis from Na_2PtCl_4 will lead to an even greater increase in the yield of methylamine diamine.

3. **Synthesis of cis-dichlorodihydroxylamineplatinum** $[\mathrm{Pt(HxCl)_2}]$. The synthesis is carried out by the action on sodium platinites of an aqueous solution of hydroxylamine, which is prepared as follows: 1.5 g of hydroxylamine hydrochloride are dissolved in 2 ml of water, and 1 ml of a 50% NaOH solution is added to it. The resulting NH_2OH solution is added dropwise, with vigorous stirring, to the sodium chloroplatinite solution described above (2 mol NH_2OH per 1 mol K_2PtCl_4). After 5 min (if the synthesis is conducted at room temperature) or after 15-20 min (with ice cooling), a precipitate begins to form. Accordingly, after 2 or 4-6 h, the precipitate is thoroughly suction-filtered and washed with 2 ml of ice water. It is a mixture of violet needle-shaped crystals of the hydroxylamine analog of Magnus' salt and yellow needle-shaped crystals of the corresponding diamine. To separate these salts, the precipitate, after suction filtration and washing with 1-2 ml of ice water, is transferred to a small beaker, and 5 ml of the indicated K_2PtCl_4 solution acidified with a drop of conc. HCl are added to it. The resulting mixture is heated with vigorous stirring on a boiling water bath for one minute and rapidly suction-filtered. From the filtrate, on cooling with ice, a voluminous pale-yellow needle-shaped precipitate of hydroxylamine diamine forms. The crystals of the diamine are suction-filtered, and the filtrate is added to the mixture and again heated on the water bath. The operation is repeated 2-3 times. The resulting preparations are washed with alcohol and ether. The yield of diamine is 0.3-0.5 g, and the yield of the Magnus' salt analog is 0.7-1.0 g. The yield of diamine increases somewhat, and that of the Magnus' salt analog decreases, if the synthesis is carried out using hydroxylamine acetate (acetate method). For this purpose, to the solution of sodium chloroplatinite in 7 ml of water, 1.7 g of hydroxylamine hydrochloride are successively added until dissolution—

amine and 1.9 g of sodium acetate (calculated as 2.2 mol of NH_2OH per 1 mol of K_2PtCl_4). After 30 min, a precipitate begins to separate from the resulting solution, and after 4-6 h the reaction is complete. The resulting mixture is separated as described above. The yield of diamine is 0.5-0.6 g; that of the Magnus-salt analogue is also 0.5-0.6 g. In the acetate synthesis, an additional amount of diamine can be obtained from the mother liquor if its acidity is reduced by neutralizing the excess acetic acid with 0.3–0.4 g of Na_2CO_3.

The resulting preparation $[Pt(HxCl)_2]$ consists of light-yellow crystals that do not require further recrystallization from acetone (6). When carrying out analyses both for platinum (heating with sulfuric acid) and for chlorine (fusion with soda), large samples should be avoided and heating should be performed cautiously, owing to the energetic decomposition of the dynamite. Results of analyses:

For $[Pt(HxCl)_2]$. Found, %: Pt 58.6; 58.5; 58.5; Cl 21.45; 21.60; 21.70
For $[PtHx_4][PtCl_4]$. Found, %: Pt 58.7; 58.8
Calculated, %: Pt 58.8; Cl 21.35

The values of the molecular conductivity 15 min after the start of dissolution at $V = 1000$ and $t = 25°$ were 11.62 and 11.25 $\Omega^{-1} \cdot cm^2$. The structure of $[Pt(HxCl)_2]$ was confirmed by the thiourea reaction of N. S. Kurnakov. Analysis of the yellow thiourea derivative obtained gave the following results:

$[Pt(ThiO)_4]Cl_2$. Found, %: Pt 34.5; 34.4
Calculated, %: Pt 34.2

Thus, a new method of synthesis from Na_2PtCl_4 has been proposed, associated with a tenfold increase in the concentration of $PtCl_4^{2-}$, by means of which it is possible: 1. Under the action of free methylamine, to obtain successfully the corresponding cis-diamine and thereby to eliminate in principle the "methylamine anomaly." 2. To obtain with great ease $[Pt(HxCl)_2]$, which precipitates together with the Magnus-salt analogue without hydrolysis products.

It should be noted that, on the basis of the greater solubility of $Na[PtPyCl_3]$* as compared with $K[PtPyCl_3]$, it was possible to accelerate the synthesis considerably and to increase the yield of the mixed diamine $[PtNH_3PyCl_2]$, first obtained by A. D. Gel' man (8).

It may be supposed that the principle of the method (increasing the specific concentration of the salt by replacing K^+ ions with Na^+ ions) will find application in other syntheses.

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* Py—pyridine.

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

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