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Academician I. I. CHERNYAEV, A. V. BABKOV

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Abstract

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ON THE SYNTHESIS OF POTASSIUM CYANOPLATINATE

In the chemistry of cyanide complexes of transition metals, a characteristic gap is the absence of cyanoplatinates—$Me_2[Pt(CN)_6]$, where Me is a monovalent metal. Hexacoordinated cyanide complexes have been obtained for all elements of group eight of the periodic system except nickel, palladium, and platinum. In the case of platinum, the existence of cyanoplatinates is theoretically possible ([1]). Nevertheless, all attempts to obtain these salts have been unsuccessful. Hexacyanides of ruthenium, osmium, rhodium, and iridium were synthesized more than 100 years ago by K. K. Claus by fusing chloro compounds of these metals with potassium cyanide ([2]). However, when potassium cyanide acts on $K_2[PtCl_6]$ in the melt or in solution, platinum is reduced to the divalent state with formation of $K_2[Pt(CN)_4]$. The same result is produced by the interaction of potassium cyanide with $K_2[Pt(CN)_4Cl_2]$ and $K_2[Pt(CN)_4Br_2]$ or by the interaction of the corresponding barium salts ([3]). An obstacle to the normal replacement of halogen groups in Pt(+4) complexes by CN groups is the alkaline medium of potassium cyanide solutions, in which many Pt(+4) complexes are readily reduced. The undesirable action of alkali can be eliminated by carrying out the reaction between solid substances. In this case the reaction rate might prove too low, but heating the mixture to accelerate the reaction cannot be resorted to, since reduction of platinum must then occur. The only way out is to use for the reaction a complex with strongly trans-directing substituents. A suitable compound is potassium iodoplatinate. It was obtained according to the scheme:

$$K_2[PtCl_4] \xrightarrow{4KJ} K_2[PtJ_4] \xrightarrow{J_2} K_2[PtJ_6].$$

For the reaction, technical potassium cyanide dried over calcium oxide was used.

One and a half to two grams of $K_2[PtJ_6]$ were thoroughly ground in a porcelain mortar with an equal weight amount of KCN. The mixture was kept for five days in a desiccator. On dissolving the mixture in a small amount of water, an intensely yellow solution was formed. During slow evaporation of this solution, yellowish crystals of irregular shape first separated; these were filtered off and washed with alcohol. From the mother liquor, needle-shaped pale-violet crystals of $K_2[Pt(CN)_4] \cdot 3H_2O$ separated. The formation of this substance can be explained by reaction in solution between $K_2[PtJ_6]$ and KCN that had not

Fig. 1. Absorption spectrum of a solution of $K_2[Pt(CN)_6]$ (V = 4000 l/mol, l = 10 mm)

Figure 1: Fig. 1. Absorption spectrum of a solution of $K_2[Pt(CN)_6]$ (V = 4000 l/mol, l = 10 mm)

reacted in the solid state. On recrystallization of the yellowish substance from water, well-formed, almost colorless crystals separated in the form of hexagonal prisms terminating in pyramids. On slow cooling of the solution, the crystals reach a length of more than 1 cm. To remove the yellowish color completely, recrystallization must be repeated 4 times. The yield of the twice-recrystallized substance is about 20% of theoretical. The substance obtained contains no water of crystallization. Its composition corresponds to the formula $K_2[Pt(CN)_6]$, taking into account the circumst–

···that, in the analysis for carbon, 5 of the 6 carbon atoms are detected as a result of the reaction:

$$K_2[Pt(CN)_6] + 6\tfrac{1}{2}O_2 = Pt + K_2CO_3 + 3N_2 + 5CO_2.$$

Found, %: Pt 45.37, 45.56; K 18.00, 18.05; N 19.53, 19.79; C 14.12, 14.52
Calculated, %: Pt 45.44; K 18.21; N 19.57; C 13.99

A special test showed that, on ignition of the substance in a furnace, potassium carbonate is indeed formed.

To confirm the individuality of the substance obtained and the correctness of the formula $K_2[Pt(CN)_6]$, some of its physicochemical and chemical properties were investigated. The molar conductivity of the solution corresponds to a trivalent electrolyte (μ_{1000} = 274 cm^2/ohm); the pH of the solution is close to 6, whence it may be concluded that the salt is not hydrolyzed in solution. The solubility in water at 20°C is 7.91% and increases strongly with temperature. The solubility in alcohol is insignificant. The density of the substance ($d_4^{19.5}$), determined in toluene, is 2.02 g/cm^3. The crystals are optically uniaxial, with refractive indices $n_p = 1.483$ and $n_g = 1.510$.

In the absorption spectrum of the substance in the ultraviolet region (Fig. 1) there is a weak band with a maximum at 258 m . Absorption bands with maxima at 255 and 280 m , characteristic of cyanoplatinates ([4]), are absent.

Fig. 1. Absorption spectrum of a solution of $K_2[Pt(CN)_6]$ (V = 4000 l/mol, l = 10 mm)

The dry substance darkens on heating to a temperature of about 395°; it is stable on boiling aqueous solutions. It does not interact with ammonia. On boiling with hydrochloric acid it decomposes very slowly, with formation of a yellow amorphous precipitate. With copper salts it forms an almost colorless crystalline precipitate. With silver nitrate it gives a white amorphous precipitate,

apparently $Ag_2[Pt(CN)_6]$. Under the action of KI this precipitate is converted into yellow silver iodide, and $K_2[Pt(CN)_6]$ is again separated from the solution. With $H_2[PtCl_6]$ it forms a yellow crystalline precipitate of $K_2[PtCl_6]$.

Potassium cyanoplatinate supplements the series of cyano complexes of platinum metals: $K_4[Os(CN)_6]$, $K_3[Ir(CN)_6]$, $K_2[Pt(CN)_6]$. Study of this substance is of theoretical interest. Carrying out reactions between solid substances will apparently make it possible to obtain other cyano compounds of tetravalent platinum, as well as of tetravalent palladium.

Moscow State University
named after M. V. Lomonosov

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