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Reaction of Ammonia with Platinum Dichloride: A Synthesis of Monoamminedichloroplatinum(II) and Diamminedichloroplatinum(II)

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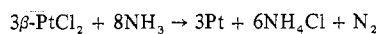
Received December 9, 1977

$\beta\text{-PtCl}_2$ reacts with ammonia from the gas phase to form solid products of varying composition and structure. The products have the composition $\text{PtCl}_2 \cdot x\text{NH}_3$, where x varies from 1 to 4. The reaction from $x = 0$ to $x = 1$ is highly exothermic, and the product has an X-ray diffraction pattern indistinguishable from that of $\beta\text{-PtCl}_2$.

Recently, Pilbrow reported the preparation of clathrate adducts of $\beta\text{-PtCl}_2$ with several small molecules.¹ These adducts have the stoichiometry $\text{Pt}_6\text{Cl}_{12} \cdot n\text{A}$ ($n = 1$ or 0.75) where A was reported as Br_2 , C_6H_6 , CS_2 , CCl_4 , CHCl_3 , or CH_2Cl_2 . The addition changed the X-ray diffraction pattern of the parent $\beta\text{-PtCl}_2$ by changing the unit cell geometry. The adducts all decomposed thermally to give the starting materials.

Results and Discussion

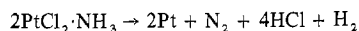
We effected reaction of $\beta\text{-PtCl}_2$ with ammonia at various ammonia partial pressures. At 1 atm of ammonia and 25 °C, $\beta\text{-PtCl}_2$ reacts very rapidly and exothermally to give metallic platinum and ammonium chloride:



The heat of the reaction is sufficient to vaporize the ammonium chloride from the platinum metal.

At ammonia pressures of 0.1 atm or less, the $\beta\text{-PtCl}_2$ sorbs ammonia without decomposition. The quantity of ammonia sorbed was determined by weighing the solid phase. Samples with the composition $\text{PtCl}_2 \cdot \text{NH}_3$ were obtained. The X-ray diffraction pattern of this substrate is identical with that of $\beta\text{-PtCl}_2$.² Careful powder diffraction measurements of both the lattice parameters and intensities of the diffraction lines showed no change in position to $\pm 0.01 \text{ \AA}$ or 5% in intensity.

Heating $\text{PtCl}_2 \cdot \text{NH}_3$ at 473 K for 16 h produced no change in composition or structure. Heating above 503 K results in decomposition according to the reaction



Exposing $\text{PtCl}_2 \cdot \text{NH}_3$ to NH_3 vapor up to 1 atm does not result in a strongly exothermic reaction. A slow addition of ammonia occurs, which ultimately yields $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$.⁵

These observations indicate the $\text{PtCl}_2 \cdot \text{NH}_3$ still retains the basic $\text{Pt}_6\text{Cl}_{12}$ structure found in $\beta\text{-PtCl}_2$, with the ammonia fitting into that structure. Since reaction of only one NH_3 per platinum is highly exothermic, we think one ammonia molecule is coordinated with each platinum(II) ion. This suggests that we have prepared a compound of empirical formula $\text{Pt}(\text{NH}_3)\text{Cl}_2$ different from the earlier reported monoamine.⁶ The

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water-insoluble material reported here is probably a cluster compound with the individual unit $\text{Pt}_6\text{Cl}_{12}(\text{NH}_3)_6$.

Upon further addition of ammonia to $\text{PtCl}_2 \cdot \text{NH}_3$ we have obtained solids which have the compositions $\text{PtCl}_2 \cdot 2\text{NH}_3$ and $\text{PtCl}_2 \cdot 3\text{NH}_3$.

The solid $\text{PtCl}_2 \cdot 2\text{NH}_3$ from all of our preparations is X-ray amorphous. We have tried without success to obtain crystalline products by heating the solid slightly and slurring in water. This amorphous material represents a new structure for the composition $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, in addition to the known *cis*- and *trans*-diamminedichloroplatinum(II) complexes. The new compound with the empirical formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ reacts with gaseous ammonia, which distinguishes it from the *cis* and *trans* isomers as these crystalline solids are inert in gaseous NH_3 .⁷

The solid $\text{PtCl}_2 \cdot 3\text{NH}_3$ appears to be a mixture of crystalline $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and another unidentified crystalline solid phase.⁸

Experimental Section

$\beta\text{-PtCl}_2$ was prepared from hydrated hexachloroplatinic acid (Matthey Bishop) as needed. The reactions were also observed on $\beta\text{-PtCl}_2$ (Alfa Inorganics) prepared by other methods. The reactions with ammonia were studied on a du Pont Model 950 thermogravimetric analyzer modified as described earlier.⁹ Larger quantities of products, up to 5 g, were prepared by reaction in a tube furnace. X-ray diffraction data were obtained with a Siemens powder diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. *cis*- and *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ were prepared by standard recipes.¹⁰

Registry No. $\text{Pt}(\text{NH}_3)\text{Cl}_2$, 66454-21-5; $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, 26035-31-4; PtCl_2 , 10025-65-7; NH_3 , 7664-41-7.

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