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

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β-$PtCl_2$ reacts with ammonia from the gas phase to form solid products of varying composition and structure. The products have the composition $PtCl_2 \cdot xNH_3$, 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 β-$PtCl_2$.

Recently, Pilbrow reported the preparation of clathrate adducts of β-$PtCl_2$ with several small molecules.[1] These adducts have the stoichiometry $Pt_6Cl_{12} \cdot nA$ (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 β-$PtCl_2$ by changing the unit cell geometry. The adducts all decomposed thermally to give the starting materials.

Results and Discussion

We effected reaction of β-$PtCl_2$ with ammonia at various ammonia partial pressures. At 1 atm of ammonia and 25 °C, β-$PtCl_2$ reacts very rapidly and exothermally to give metallic platinum and ammonium chloride:

$$3\beta\text{-}PtCl_2 + 8NH_3 \rightarrow 3Pt + 6NH_4Cl + N_2$$

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 β-$PtCl_2$ sorbs ammonia without decomposition. The quantity of ammonia sorbed was determined by weighing the solid phase. Samples with the composition $PtCl_2 \cdot NH_3$ were obtained. The X-ray diffraction pattern of this substrate is identical with that of β-$PtCl_2$.[2] Careful powder diffraction measurements of both the lattice parameters and intensities of the diffraction lines showed no change in position to ±0.01 Å or 5% in intensity.

Heating $PtCl_2 \cdot NH_3$ at 473 K for 16 h produced no change in composition or structure. Heating above 503 K results in decomposition according to the reaction

$$2PtCl_2 \cdot NH_3 \rightarrow 2Pt + N_2 + 4HCl + H_2$$

Exposing $PtCl_2 \cdot NH_3$ 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 $Pt(NH_3)_4Cl_2$.[5]

These observations indicate the $PtCl_2 \cdot NH_3$ still retains the basic Pt_6Cl_{12} structure found in β-$PtCl_2$, 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 $Pt(NH_3)Cl_2$ different from the earlier reported monoammine.[6] The water-insoluble material reported here is probably a cluster compound with the individual unit $Pt_6Cl_{12}(NH_3)_6$.

Upon further addition of ammonia to $PtCl_2 \cdot NH_3$ we have obtained solids which have the compositions $PtCl_2 \cdot 2NH_2$ and $PtCl_2 \cdot 3NH_3$.

The solid $PtCl_2 \cdot 2NH_3$ from all of our preparations is X-ray amorphous. We have tried without success to obtain crystalline products by heating the solid slightly and slurrying in water. This amorphous material represents a new structure for the composition $Pt(NH_3)_2Cl_2$, in addition to the known *cis*- and *trans*-diamminedichloroplatinum(II) complexes. The new compound with the empirical formula $Pt(NH_3)_2Cl_2$ 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 $PtCl_2 \cdot 3NH_2$ appears to be a mixture of crystalline $Pt(NH_3)_4Cl_2$ and another unidentified crystalline solid phase.[8]

Experimental Section

β-$PtCl_2$ was prepared from hydrated hexachloroplatinic acid (Matthey Bishop) as needed. The reactions were also observed on β-$PtCl_2$ (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 Cu Kα radiation. *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ were prepared by standard recipies.[10]

Registry No. $Pt(NH_3)Cl_2$, 66454-21-5; $Pt(NH_3)_2Cl_2$, 26035-31-4; $PtCl_2$, 10025-65-7; NH_3, 7664-41-7.

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