Thermoanalytical study of solid platinum(IV) pentammine complexes

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Abstract

The hydroxo pentammine complex of Pt(IV) (Chugaev–Chlopin salt) $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ (1) and its precursors were synthesized and characterized by X-ray diffraction and by TG/DTG. In argon, 1 loses H_2O below 170°C followed by the loss of $2NH_3$. A third decomposition step leads to metallic Pt as the end product above 350°C. Thermal degradation in oxygen produces PtO_2 as an intermediate before the formation of Pt above 430°C.

INTRODUCTION

In addition to being of theoretical interest for coordination chemistry, platinum complexes are technologically valuable in the preparation of supported catalysts. A widely used method to prepare industrial platinum catalysts is to impregnate a support, for instance alumina, with a solution of the complex and then use thermal treatment to yield supported metallic platinum. Another area where data on the thermal behaviour of platinum complexes are needed is the preparation of platinum metal films by chemical vapor deposition (CVD) and related techniques.

The existence of a pentammine series of Pt(IV) complexes had been originally predicted by Werner's theory but they were synthesized first in 1915 by the action of ammonia on ammonium hexachloroplatinate(IV) which leads to the formation of $[Pt(NH_3)_5Cl]Cl_3$ (Chugaev's salt) [1].

Probably owing to their relatively complicated and low-yield syntheses, the pentammine complexes have not been studied as frequently and thoroughly as the corresponding tetra- and hexammine series. This is especially true as regards their structural and thermal characterization where, for instance, thermal data are almost totally lacking [2].

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[1] Now deceased.

TABLE 1

Synthesis of the pentammine compounds according to Chugaev [5]

Starting materials and reactions	Product	Remarks
$(NH_4)_2[PtCl_6]$ (= 5) + Na_2HPO_4, $NH_3(aq)$	$[Pt(NH_3)_5Cl]PO_4$ (2)	Contains 2 moles of water
2 + HCl(aq)	$[Pt(NH_3)_5Cl]Cl_3$ (3)	White crystals
3 + $NH_3(aq)$	$[Pt(NH_3)_4NH_2Cl]Cl_2$ (4)	Yellow crystals
4 + NaOH(aq), neutralization with HCl	$[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ (1)	White crystals

In connection with an investigation into the preparation of platinum loaded catalysts on oxide supports using selective electrodeposition [3,4] we synthesized the hydrated monohydroxo complex $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ (Chugaev–Chlopin salt) and studied its properties by thermoanalytical and crystallographic techniques.

EXPERIMENTAL

Synthesis

The hydroxopentammine complex $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ (1) was synthesized using the improved synthesis of Chugaev [5] with slight modifications. The various intermediates were separated and characterized during the procedure. The outline of the synthetic route is given in Table 1. Total yield of 1 based on platinum content was 42% when 2 g of starting material (5) was used.

Characterization

X-Ray powder diffraction diagrams were recorded for the compounds 1–4 using a Philips MPD 1880 instrument and Cu Kα radiation. In the case of 1, single crystals large enough for X-ray crystallographic studies were obtained by slow cooling of the mother solution. In one case (2) the correct composition was ascertained by microanalysis.

Thermogravimetric experiments were carried out in a Perkin Elmer TGA-7 instrument using standard crucibles and sample sizes in the range 5–15 mg. The heating rate was usually 5°C min^{-1} and a dynamic gas flow (Ar, N_2 or air) was maintained during the heating.

RESULTS AND DISCUSSION

The Chugaev–Chlopin salt $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ (1) forms monoclinic crystals with $a = 7.614$, $b = 15.085$, $c = 9.230$ Å and $\beta = 92.03°$. A crystal

TABLE 2

Thermal degradation of pentammine (1–3) and related (4, 5) complexes. Heating rate is $5°C$ min^{-1} in dynamic argon atmosphere

Complex	DTG onset and end temperatures ($°C$)	Weight remaining (%)		Solid product [a]
		Obs.	Calc.	
1	100–170	95.0	95.5	$[Pt(NH_3)_5OH]Cl_3$
	170–250	87.0	86.5	$[Pt(NH_3)_3OH]Cl_3$
	260–330	46.5	46.3	Pt
2	90–140	92.0	91.9	$[Pt(NH_3)_5Cl]PO_4$
	220–270	84.0	84.3	$[Pt(NH_3)_3Cl]PO_4$
	270–320	65.0	65.0	$Pt_3(PO_4)_4$, Pt
	470–660	45.5	43.7	Pt
3	170–190	96.0	96.0	$[Pt(NH_3)_4Cl]Cl_3$
	210–240	93.0	92.0	$[Pt(NH_3)_3Cl]Cl_3$
	280–450	46.0	46.2	Pt
4	270–370	51.0	50.6	Pt
5	270–350	44.0	44.0	Pt

[a] Based on observed weight losses and other evidence discussed in the text.

structure analysis using three-dimensional diffractometer data is in progress and the preliminary results indicate a rather regular octahedral arrangement of Cl^- and OH^- anions around the central ion [6].

Thermal stability

Thermal stability of **1** was studied by TG in argon, nitrogen and air. Similar experiments were also made with intermediate complexes **2–4**, and, for comparison, with $(NH_4)_2[PtCl_6]$ (**5**). Table 2 gives a summary of the experiments in argon indicating that in all cases the end product is metallic platinum but that there are considerable differences in reaction temperatures and mechanisms.

The TG/DTG curve of **1** shown in Fig. 1, shows a rather straightforward degradation in an inert atmosphere resulting in metallic Pt above $350°C$. The third reaction step from $[Pt(NH_3)_3OH]Cl_3$ to Pt involves most probably N_2 among the evolved gases as the nitrogen atmosphere has a clear influence on the reaction temperature (see. Fig. 1). Similarly, higher heating rate moves the decomposition temperatures upwards, in this case for all three steps (Fig. 2).

When the TG experiments were carried out in oxygen the only significant difference was the formation of PtO_2 as a transient intermediate above $350°C$ (Fig. 3). The observed and calculated weights (55.0% and 53.9%) agree reasonably well with each other as does the observed decomposition
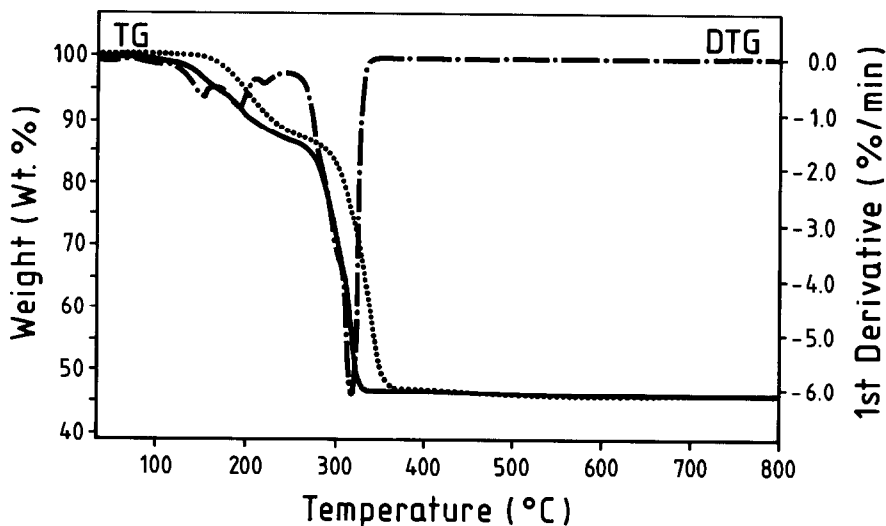
Fig. 1. TG (solid line) and DTG (broken line) curves in argon and TG curve in nitrogen (dotted line) for $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$. Heating rate is $5\,^\circ C$ min^{-1} and sample mass 7.5 mg.

temperature ($400\,^\circ C$) with the literature value for PtO_2 stability (up to $380-400\,^\circ C$) [7].

For the two other pentammine complexes (**2** and **3**), which have Cl$^-$ instead of OH$^-$ in the inner coordination sphere, the end product after a
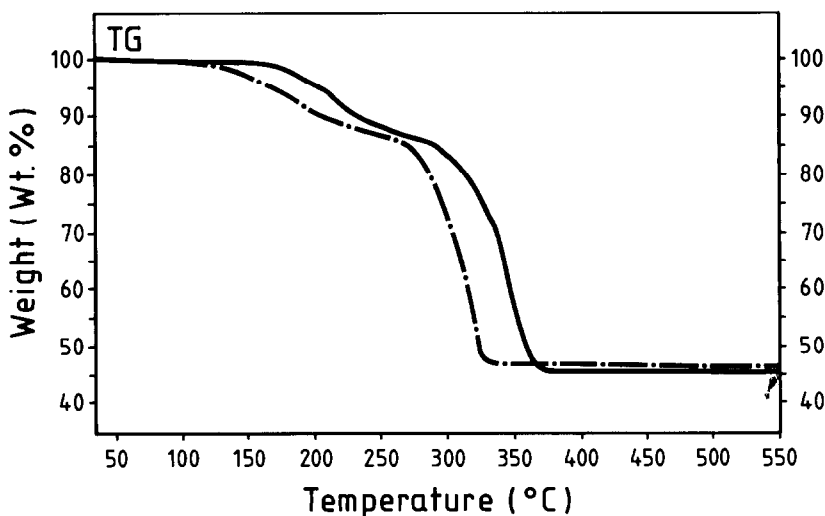

Fig. 2. The effect of heating rate on the thermal decomposition of $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ in argon. Solid line $25\,^\circ C$ min^{-1}, broken line $5\,^\circ C$ min^{-1}. Sample mass 7.5 mg.
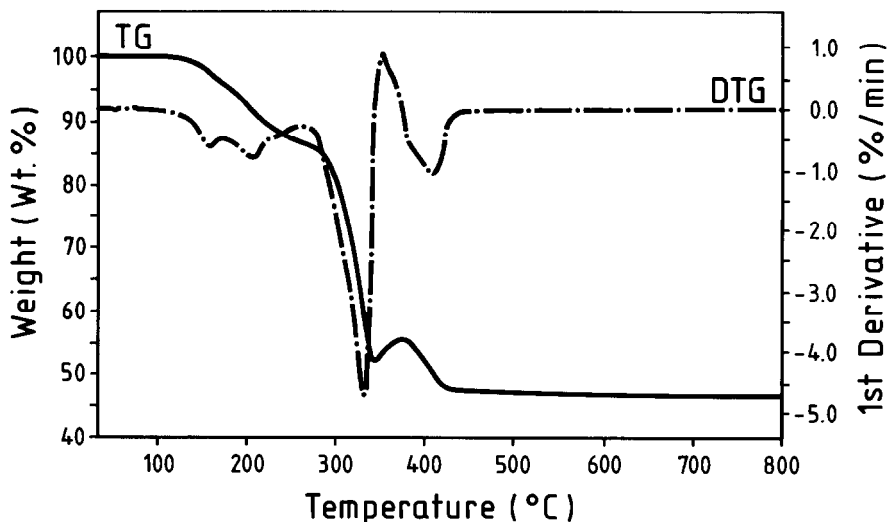
Fig. 3. TG and DTG curves for $[Pt(NH_3)_5OH]Cl_3 \cdot H_2O$ in oxygen. Heating rate is $5°C$ min^{-1} and sample mass 13.5 mg.

multistep degradation is metallic Pt as well. In the case of the phosphate compound (2) however, the reduction to metal takes place at much higher temperature (Table 2).

In contrast, the tetra- and hexammine complexes (4 and 5) decompose in a straightforward manner yielding metallic Pt in a single-step process at around $300°C$ (Table 2).

The present results on the thermal stability of the Pt(IV) pentammine complexes may be compared with the only available report in the literature. In their early DTA study Nikolaev and Rubinshtein [8] observed similar decomposition temperatures for the series $[Pt(NH_3)_5Cl]X_3$ where X_3 was $Cl_3(C_2O_4)_{3/2}$, $(NO_3)_3$ and SO_4Cl. The stabilities increased from $170°C$ to $360°C$, respectively.

The tetrammine series of platinum(II) has been studied much more frequently and recently. In an evolved gas analysis–mass spectroscopy (EGA–MS) study Richard and Pancirov [9] were able to establish that the decomposition of $Pt(NH_3)_4Cl_2$ takes place in two steps where the first one involves the loss of two NH_3 while the second step consists of simultaneous reduction of Pt(II) and oxidation of ammonia to yield metallic platinum and nitrogen. The mass spectrum ruled out the other obvious possibility, namely, simultaneous reduction of Pt(II) and oxidation of chloride to yield chlorine. In the case of the present pentammine complexes the formation of nitrogen also appears to be preferred route but in order to establish the details an EGA study is in progress.

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