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The ammonium ion and the ammine ligand as internal reducing agents for platinum-group-metal complexes. A comment

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Abstract

Simultaneous thermal analysis–mass spectrometry and time resolved X-ray powder diffraction of the thermal behaviour of such platinum-group-metal complexes as $(NH_4)_2[PtCl_6]$, $[Pd(NH_3)_2Cl_2]$ or $(NH_4)_3[RhCl_6](H_2O)$, and preparative procedures, clearly reveal that the initial step to produce finely divided metal powder must be the internal redox reaction between the N^{3-} of the ammonium ion/ammine ligand and the noble-metal ion (M^{n+}; $n = 2, 3, 4$). It is certainly not the decomposition to binary components followed by their decomposition to the elements or reaction to oxides as has been reported quite recently.

The ammonium ion $(NH_4)^+$ is an excellent, versatile and unique tool for a large number of inorganic syntheses [1]. It is versatile because it contains, first, an active proton that may act as an acid or oxidant and, secondly, nitrogen in the oxidation state −3, which may act as a reductant and as a base as well. Furthermore, as a pseudo-alkali cation it may enter complexes as a counter-cation. It is excellent because such reactions may be carried out in the solid state at temperatures as low as 230°C. Reactions may take place as internal or external redox or acid–base reactions. Examples of external reactions are the reactions between, e.g., NH_4Cl and Y_2O_3, yielding $(NH_4)_3YCl_6$ ("ammonium chloride route"; acid–base) [2] or the reduction of NH_4ReO_4 with NH_4Cl to rhenium metal. Examples of internal reactions are those that take place, for example, in $(NH_4)_2[Pr(NO_3)_5(H_2O)_2] \cdot 2H_2O$ [3] or in such platinum-metal-group complexes as $(NH_4)_2[PtCl_6]$ [4].

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We have recently applied simultaneous thermal analysis (TG/DSC) coupled with mass spectrometry (MS) (Netzsch STA 429/Balzers QMS 511 mass spectrometer, courtesy of Dr. Emmerich of Netzsch, Selb, Germany) and X-ray powder diffractometry (Simon–Guinier, FR 553, Enraf-Nonius, Delft, Netherlands) and have followed all steps "seen" by these methods preparatively in that we have heated the starting materials or the intermediate products to the temperatures at which those reactions took place which were indicated by high-temperature X-ray patterns. Intermediate products were synthesized by independent methods and the properties of the products so obtained were compared with those of the intermediate by applying the above-mentioned methods [4].

Therefore, there can be no doubt that the thermal "decomposition" of $(NH_4)_2[PtCl_6]$ has to be described as an internal redox reaction between Pt^{4+} and N^{3-} (from $(NH_4)^+$) as we have reported [4]. Figure 1 shows the high-temperature X-ray pattern. Only the lines of $(NH_4)_2[PtCl_6]$ and, above 380–400°C, of Pt metal can be detected. The compound $PtCl_4$ does not appear as an intermediate. As a pure substance it decomposes to platinum and chlorine only at 480–500°C. The interpretation of the thermal behaviour of $(NH_4)_2[PtCl_6]$, i.e., decomposition to $PtCl_4$ and $NH_3 + HCl$ (NH_4Cl) first, followed by the decomposition of $PtCl_4$, recently restated by Matuschek et al. [5], does not therefore tell the true story.

Also, the interpretation of the thermal behaviour of $[Pd(NH_3)_2Cl_2]$ is erroneous. Rather, palladium(II) is reduced in one step directly by the N^{3-} of the ammine ligand according the equation

$$3[Pd(NH_3)_2Cl_2] = 3Pd + N_2 + 4NH_4Cl + 2HCl \qquad (1)$$

Ammonium cations that are reported to be released from $[Pd(NH_3)_2Cl_2]$ must stem from the NH_4Cl produced. The reaction starts at 270°C, as high-temperature X-ray patterns indicate. Thermal analysis gives a

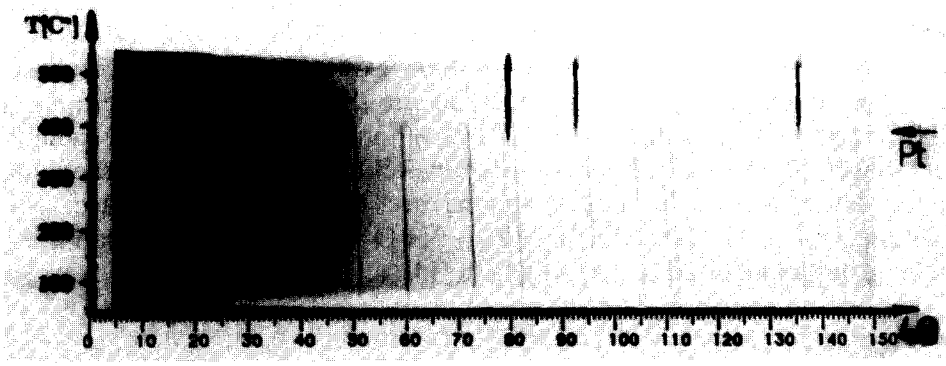

Fig. 1. High-temperature X-ray powder pattern of $(NH_4)_2[PtCl_6]$ (Simon camera, FR 553, Enraf-Nonius, Cu Kα_1 radiation; heating rate 10 K h^{-1}; film speed 1 mm h^{-1}).

somewhat higher decomposition temperature (300°C), in consequence of the different heating rates: $10\,K\,h^{-1}$ (X-ray) vs. $10\,K\,min^{-1}$ (TA–MS). If the reaction is carried out in air, PdO is indeed formed through the reaction of finely divided palladium metal and oxygen at temperatures above 350°C.

This is also true by analogy for the third compound, $(NH_4)_3[RhCl_6]$ (most certainly the monohydrate, if the common literature procedure for its synthesis was used; see for example ref. 6), investigated by the above-mentioned authors [5]. Rhodium oxide Rh_2O_3 is indeed produced finally if the reaction is carried out in air. But it is not the reaction between $RhCl_3$ and oxygen, rather that between oxygen and the finely divided rhodium metal previously produced by internal reduction of Rh^{3+} through the inner-sphere ammine ligand of $(NH_4)_2[Rh(NH_3)Cl_5]$. The true "fragmentation pathway" of $(NH_4)_3[RhCl_6](H_2O)$ has been reported recently [4].

A number of additional ternary ammonium halides and chloro-ammine complexes of palladium, platinum and rhodium all follow principally the same pattern (Table 1): it is always formally N^{3-} that reduces the central cation of the complex. Not in many cases were we able to show that an ammine complex is formed as an intermediate from the ternary ammonium halide. But $(NH_4)_3[RhCl_6](H_2O)$ is an excellent example. In

TABLE 1

Thermal behaviour of some selected palladium, platinum and rhodium complexes: reaction temperatures and products (from simultaneous TA–MS and X-ray diffraction experiments)

Educt	Temperature (°C)	Products
$(NH_4)_2PtCl_6$	390–410	$Pt + HCl + N_2 + NH_4Cl$
$[Pt(NH_3)_4][PtCl_4]$	260–280	*trans*-$[Pt(NH_3)_2Cl_2]$
	290–310	$Pt + N_2 + HCl + NH_4Cl$
$[Pt(NH_3)_4]Cl_2$	210–230	$[Pt(NH_3)_2Cl_2]$ [a] $+ NH_3$
	240–250	*trans*-$[Pt(NH_3)_2Cl_2]$
	300–320	$Pt + N_2 + HCl + NH_4Cl$
$(NH_4)_2PdCl_6$	250–280	$(NH_4)_2PdCl_4 + Cl_2$
	310–370	$Pd + N_2 + HCl + NH_4Cl$
$(NH_4)_2PdCl_4$	300–310	$Pd + N_2 + HCl + NH_4Cl$
$[Pd(NH_3)_4]Cl_2$	280–310	$(NH_4)_2PdCl_4 + Pd$
	310–360	$Pd + N_2 + HCl + NH_4Cl$
$[Pd(NH_3)_2Cl_2]$	270–300 [b]	$Pd + N_2 + HCl + NH_4Cl$
$[Pd(NH_3)_4][PdCl_4]$	220–240 [b]	*trans*-$[Pd(NH_3)_2Cl_2]$
	280–300 [b]	$Pd + N_2 + HCl + NH_4Cl$
$(NH_4)_3[RhCl_6](H_2O)$	60–160	$(NH_4)_3[RhCl_6] + H_2O$
	320–380	$(NH_4)_2[RhCl_5(NH_3)] + HCl$
	410–440	$Rh + N_2 + HCl + NH_4Cl$

[a] Of unknown structure. [b] See ref. 7.

other cases where no intermediate could be detected, the internal redox reaction at temperature is so fast that the intermediate once formed reacts simultaneously, at least judging on the time scale of the "analytical" methods applied.

It is certainly true that a combination of methods for the investigation of the thermal behaviour of complex compounds helps a great deal with the interpretation of the reactions involved. However, thermoanalytical results, even when combined with mass spectrometry, may easily be misinterpreted. Therefore it is strongly recommended that such investigations always be combined with the identification of the product(s) and intermediates through X-ray powder diffractometry and also preparative procedures.

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