J. Synchrotron Rad. (1999). **6**, 468–470

Thermal decomposition of $(NH_4)_2[PtCl_6]$ – an *in situ* X-ray absorption spectroscopy study

Holger Rumpf,[ab] Josef Hormes,[a*] Angela Möller[c] and Gerd Meyer[c]

[a]*Physikalisches Institut, Universität Bonn, Nußallee 12, D-53115 Bonn, Germany*
[b]*Center for Advanced Microstructures and Devices, 6980 Jefferson Hwy., Baton Rouge Louisiana 70806, USA*
[c]*Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany.*
Email:hormes@physik.uni-bonn.de

The thermal decomposition of di-ammonium hexachloroplatinate ($(NH_4)_2[PtCl_6]$) to metallic platinum has been investigated by time-resolved *in situ* XAS measurements at the Cl K- and Pt L_{III}-edge. Spectra at the Cl K-edge were recorded utilizing an energy dispersive monochromator (EDM), while the Pt L_{III}-edge spectra were recorded using a double crystal monochromator. By analysing the energy shift of the Cl K-edge a reaction intermediate has been observed at about 310°C. Fingerprinting arguments indicate that this intermediate could be cis-platin or some other platinum amine complex.

Keywords: Pt L-III-XANES, Cl K-XANES, time-resolved, DEXAFS, in situ, chlorine, platinum, ammonium complex

1. Introduction

The $(NH_4)^+$ ion behaves in many ways like an alkali ion in the formation of polynaric compounds taking the role of a counterion. On the other hand, it formally consists of a N^{3-} and four H^+ ions. Therefore, redox reactions may take place and acid-base reactions can also occur in the solid state. Investigations of the thermal decomposition of ammonium compounds have been reported earlier (Möller 1994, Meyer 1994). Thermolyses of noble metal compounds have shown that in chloro complexes like $(NH_4)_2[PtCl_6]$ or $(NH_4)_3[RhCl_6]$ the N^{3-} is oxidized to yield N_2 while the metal cation (e.g. Pt^{4+}, Rh^{3+}) is reduced to form the metal powder. The total reaction can be described as follows:

$$(NH_4)_2[PtCl_6] \rightarrow Pt + 2/3\ N_2 + 16/3\ HCl + 2/3\ NH_4Cl \qquad (1)$$

In the case of $(NH_4)_3[RhCl_6]$, an intermediate could be observed by DTA/TG and was identified as $(NH_4)_2[RhCl_5(NH_3)]$ by powder diffraction. This gives strong evidence of the mechanism of these reactions in respect of forming an amine complex as a result of ligand exchange evolving HCl. With the previously used investigative methods (thermal analysis, X-ray Guinier technique, preparative methods) no intermediate for $(NH_4)_2[PtCl_6]$ could be detected (Meyer 1991). Therefore, a further study of these reactions with techniques that allow *in situ* observations on a much shorter time scale than the above mentioned techniques is of interest (Epple 1996, Tröger 1997, Ressler 1997).
Time-resolved XAS experiments, especially those using the energy dispersive mode, enable the acquisition of spectra in less then a second. Thus, this technique was applied in the here reported investigation to prove the evidence of intermediate(s) and to give further information about the proposed reaction(s).

2. Experimental

Time-resolved XANES measurements were performed at the Bonn Electron Storage Ring ELSA (2.3 GeV) (Althoff 1990) at beamline BN1, which is equipped with an energy dispersive monochromator (EDM) utilizing a bent Si<111> crystal. The experimental description of this set-up can be found elsewhere (Blank 1992). It allows the recording of two XAS-spectra within a time interval of less than 100 milliseconds depending on the concentration of the sample. In order to obtain a reasonable signal to noise ratio, 12 Cl K-XANES spectra (665 ms per spectrum) have been averaged. Therefore, the actual time interval between two spectra was 10 seconds.
The *in situ* measurements were carried out by means of water-cooled heating cells. The EDM cell permits temperatures up to 450°C, whereas the DCM cell is designed for temperatures higher than 1000°C.
Pt L_{III}- and Cl K-XANES measurements were carried out at the DCM-beamline (Lemmonier 1978) of the Center for Advanced Microstructures and Devices (CAMD) (Scott 1992). For the chlorine K-edge, InSb<111> crystals were used, while the CAMD storage ring was operated at 1.3 GeV. The Pt L_{III}-XANES spectra were recorded using a pair of Si<400> crystals and a storage ring energy of 1.5 GeV.
Due to the low energy, the measurements at the chlorine K-edge (2833 eV) (Sugiura 1972) were carried out under helium flow, because the absorption coefficient of helium is relatively low. The Pt L_{III}-edge spectra were recorded under a nitrogen flow to assure an inert gas atmosphere. The programmed temperature ramps were 9 K/min (EDM) and 2.3 K/min (DCM).
Many compounds are known containing Pt^{2+} and chloride or amine as ligands. Therefore, these might be possible intermediate(s) in the first step of a redox reaction in which the final product is platinum metal powder. For reference purposes the cis-platin complex was used for the XAS experiments.
The reference samples were prepared on self-adhesive Kapton foils, while the $(NH_4)_2[PtCl_6]$ was distributed on thin fiberglass foils since the glue on the Kapton foil evaporates at temperatures above 200°C.
Data analysis was performed in the following way. First, a linear background was subtracted before normalizing the spectra to the edge jump. Finally, an energy calibration was carried out (Pt L_{III}-edge of Pt-foil to 11564eV and the Cl K-edge of NaCl to 2833eV).

3. Results and Discussion

In Figure 1, some of the Pt L_{III}-XANES spectra recorded during the *in situ* reaction are shown. Below 270°C, no change in the spectra could be observed. In the spectra at 310°C and 380°C, the white-line intensity is lowered about 5% and stays at this level. Thus, the white-line decreases rapidly. The spectrum at 490°C closely resembles the spectrum of metallic platinum shown in Figure 1. Also, there is little difference between the XANES spectrum of cis-platin $[PtCl_2(NH_3)_2]$ and that of metallic platinum. Therefore, no statement about the intermediate at ca. 300°C is possible from the Pt L_{III}-spectra. Probably, the resulting XANES spectrum is a linear combination of the XANES of $(NH_4)_2[PtCl_6]$ and an intermediate.

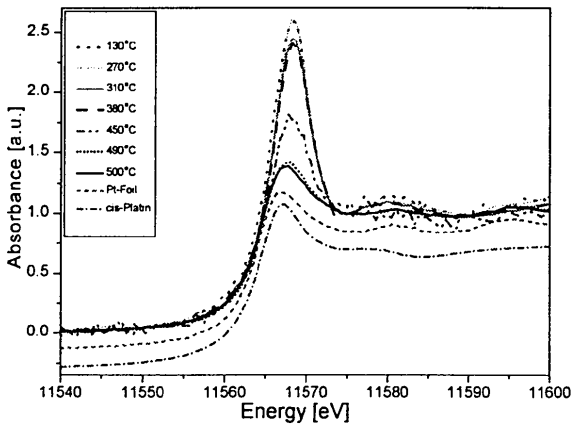

Figure 1
Pt L_{III}-XANES taken during the thermal decomposition of $(NH_4)_2[PtCl_6]$ together with reference spectra

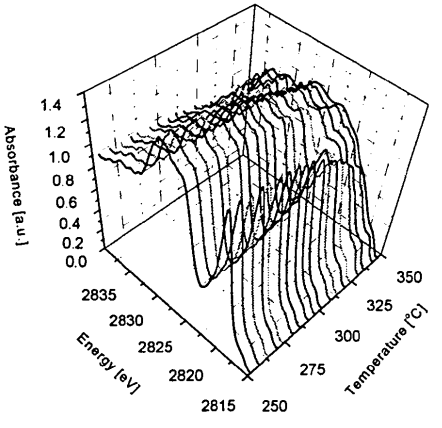

Figure 2
Time-resolved *in situ* Cl K-XANES of $(NH_4)_2[PtCl_6]$ taken at the EDM while heating with a constant temperature ramp

More information can be obtained from the chlorine K-edge-XANES spectra shown in Fig. 2. A temperature interval between 250°C and 350°C has been chosen and only every fifth spectrum is displayed. Below 300°C no changes in the spectra could be observed but at about 310°C a second pre-edge structure at 2822 eV emerges and at about 2825.5 eV a new feature appears (cf. Fig. 4). Above 330°C, these spectral indications of an intermediate disappear. This can be attributed to a further decomposition of the platinum complex into the pure metal and gaseous chlorine compounds (cf. Eq. (1)).

To obtain further confirmation of this interpretation, the complete set of 280 XANES spectra were analysed regarding the edge shift by a modified integration method first published by Capehart *et al.* (Capehart 1995).

The analysis is based on a simple integration of the edge jump. The first spectrum of the time-resolved series (the spectrum of $(NH_4)_2[PtCl_6]$) defines the reference point of the energy axis. The upper limit of the integral of this spectrum is the absorption value one. The reference area is 80% of this integral and defines the reference energy value. The energy shift is then calculated as the difference between the upper integral borders having the same area as the reference.

The result is shown in Fig. 3. This graph indicates very clearly the emergence of an intermediate starting around 255°C (arrow in Fig. 3). The formation of this intermediate ends at 310°C and, finally, it further decomposes at higher temperatures.

It is difficult to record reasonable Cl K-XANES spectra in this temperature range. This is due to the fact that only a small quantity of NH_4Cl is captured in the sample and the final spectra are too noisy to identify these reaction products. Mass spectroscopic investigations have already shown that this decompositon occurs yielding NH_4Cl and HCl as reaction products (Möller 1994).

Nevertheless, we tried to identify the intermediate by comparing the Cl K-XANES at 310°C with those of reference spectra. Linear combination of the spectra of cis-platin and $(NH_4)_2[PtCl_6]$ resulted in a XANES spectrum which strongly resembled the spectrum of the intermediate. We calculated a ratio of 55% $(NH_4)_2[PtCl_6]$ and 45% cis-platin as the best fit (cf. Fig. 4). Therefore, we can conclude that the Cl K-XANES of cis-platin corresponds very well with the intermediate. Despite this agreement we cannot not completely exclude the possibility of another amine complex like trans-platin or $(NH_4)[PtCl_5(NH_3)]$ as the intermediate. Here, further measurements are necessary.

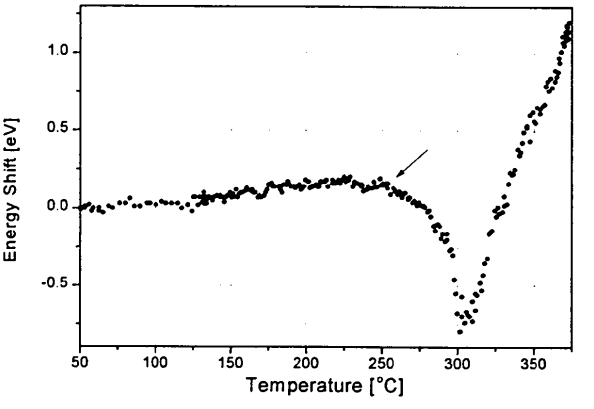

Figure 3
Energy shift of the Cl K-edge determined by the integration method (cf. text)

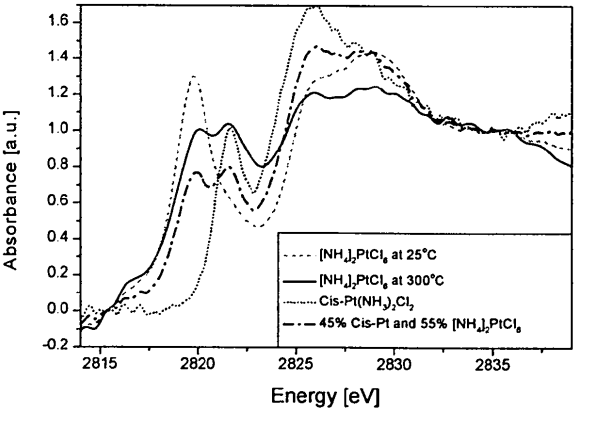

Figure 4
Cl K-XANES of $(NH_4)_2[PtCl_6]$ and cis-platin

4. Conclusion

We have shown that time-resolved XAS is a powerful tool for investigating solid state reactions *in situ* and that the employed energy dispersive monochromator (DEXAFS) is very useful for discovering short-lived intermediates of these reactions.
In agreement with our hypothesis concerning the course of the thermal decomposition of di-ammonium hexachloroplatinate ($(NH_4)_2[PtCl_6]$), a Pt amine complex, probably cis or trans-platin, was observed as a reaction intermediate. This means that the ammonium ion has undergone an internal redox reaction.

The project has been supported by the *Deutsche Forschungsgemeinschaft* (DFG) and the Federal Ministry of Research and education (Germany) (contract No. 05SG8PDA9). The hospitality of the CAMD staff is gratefully acknowledged.

References

Althoff, K.H., v. Drachenfels, W., Dreist, A., Husmann, D., Neckening, M., Nuhn, H.D., Schauerte, W., Schillo, M., Schittko, F.J., Wermelskirchen, C. (1990). *Part. Accel.* **27**, 101.
Blank, H., Neff, B., Steil, S., Hormes, J. (1992). *J. Rev. Sci. Instrum.*, **63**(1), 1334-1337.
Capehart, T.W., Herbst, J.F., Mishra, R.K., Pinkerton, F.E. (1995). *Phys. Rev.* **B51**, 7907.
Epple, M., Sazama, U., Reller, A., Hilbrandt, N., Martin, M., Tröger, L. (1996). *Chem. Commun.*, 1755-1756.
Lemmonier, M.,Collet, O., Depautex, C., Esteva, J.M., Raoux, D. (1978). *Nucl. Instr. And Meth.* **152**, 109-111.
Meyer, G., Möller, A. (1991). *J. Less-Common Met.* **170**, 327-331.
Meyer, G. (1994). *Advances in the Synthesis and Reactivity of Solids*, Vol.2, 1-26.
Möller, A., Meyer, G. (1994). *Z. anorg. u. allg. Chem.* **122**, 1185-1190.
Ressler, T., Hagelstein, M., Hatje, U., Metz, W. (1997). *J. Phys. Chem.* **B101**, 6680-6687.
Scott, J.D., Bluem, H.P., Craft, B.C., Marceau-Day, L., Mihil, A., Morikawa, E., Saile, V., Vladimirsky, Y., Vladimirsky, O. (1992). *SPIE* **1736**, 117-128.
Sugiura, C (1972). *Phys. Rev.* **B6**, 1709-1713.
Tröger, L., Hilbrandt, N., Epple, M. (1997). *SRN* **10**(6), 11-17.

(*Received 10 August 1998; accepted 26 November 1998*)