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STRUCTURAL AND MORPHOLOGICAL CHANGES IN THE COURSE OF THE THERMAL DECOMPOSITION OF $Ni(en)_3Pt(CN)_4 \cdot H_2O$ TO $NiPt(CN)_4$

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ABSTRACT

The compositional changes ocurring during the multi-step decomposition of the solid complex $Ni(en)_3Pt(CN)_4 \cdot H_2O$ (en = ethylenediamine) to $NiPt(CN)_4$ are determined by combined thermogravimetric / mass spectrometric measurements. In order to obtain detailed information of the mechanisms on a microscopic as well as on a macroscopic level for each step of the over-all decomposition, structural and morphological investigations have been carried out.

INTRODUCTION

In order to bring some light into the wide and generally still dark field of heterogeneous solid state reactions there is an absolute necessity to investigate well defined systems under accurately controlled experimental conditions. Thus systems of low complexity with even no apparent applications at the time have to be taken into consideration, whenever successful results are to be expected, which, in turn, may lead to a realistic interpretation of the processes occurring.

Solid state decompositions, in particular decompositions of complex compounds appear to be most promising for such kind of investigations, as a large number of solid complexes with characteristic structural features are available in single crystalline form. Moreover, these compounds usually decompose under formation of phases with well defined stoichiometry (refs. 1 and 2).

Correlations between the occurring structural, often topotactic reaction mechanisms, i.e. changes on a atomic, first coordination sphere level on one side, and concomitant macroscopic, in parti-

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cular morphological changes on the other side, lead finally to consistent descriptions of these complicated processes. Obviously such studies are affording an effective combination of results obtained by different, independent methods of investigation.

RESULTS

$Ni(en)_3Pt(CN)_4 \cdot H_2O$ undergoes a multi-step decomposition to $NiPt(CN)_4$ and – in oxidizing atmosphere – to nickel oxide and metallic platinum respectively. Combined thermogravimetric / mass spectrometric measurements give evidence for the formation of stoichiometrically well defined intermediates (fig. 1). Accordingly the compositional changes occurring in the course of the overall decomposition can be summarized as follows:

$$Ni(en)_3Pt(CN)_4 \cdot H_2O \rightarrow Ni(en)_3Pt(CN)_4 + H_2O$$

$$Ni(en)_3Pt(CN)_4 \rightarrow Ni(en)_2Pt(CN)_4 + (en)$$

$$Ni(en)_2Pt(CN)_4 \rightarrow Ni(en)Pt(CN)_4 + (en)$$

$$Ni(en)Pt(CN)_4 \rightarrow NiPt(CN)_4 + (en)$$

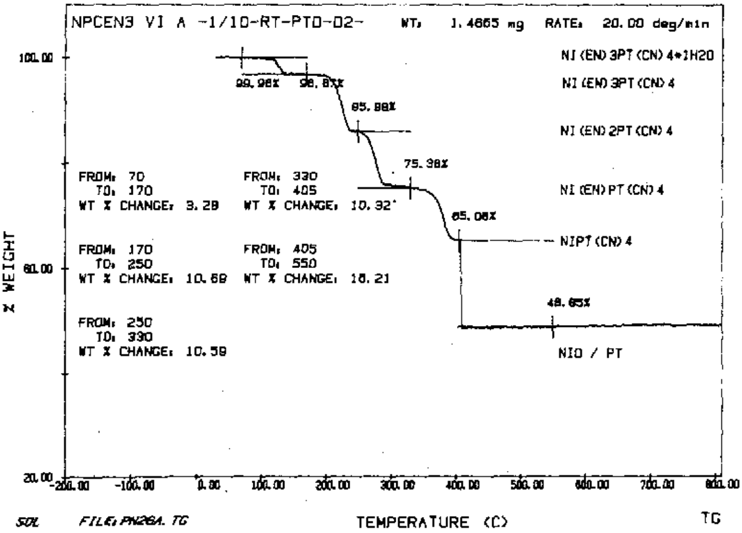


Fig. 1: Thermogravimetric curve of the decomposition of $Ni(en)_3Pt(CN)_4 \cdot H_2O$ in oxygen atmosphere.

Comparative structural studies by means of temperature dependent X-ray diffraction on a Guinier-Lenne heating camera with CuK_α radiation confirm, that all the intermediates adopt individual structures. In order to obtain detailed informations about the structural changes on a first coordination sphere level the structures of initial material and the intermediates have been determined (ref. 3). As it is shown in figs. 2a and 2b, the structures of $Ni(en)_3Pt(CN)_4 \cdot H_2O$ as well as $Ni(en)_3Pt(CN)_4$ are made up of octahedral $[Ni(en)_3]^{2+}$ and square-planar $[Pt(CN)_4]^{2-}$ units. During the dehydration of the initial material the coordination polyhedra of both metal cations are preserved. During the decomposition of $Ni(en)_3Pt(CN)_4$ to $Ni(en)_2Pt(CN)_4$, however, the octahedral NiN_6 coordination is changed into a $NiN_4N'_2$ coordination (N: nitrogen of en; N': nitrogen of CN^-). This leads to a pronounced chain structure with cyanide as bridging ligand between Ni and Pt (fig. 2c).

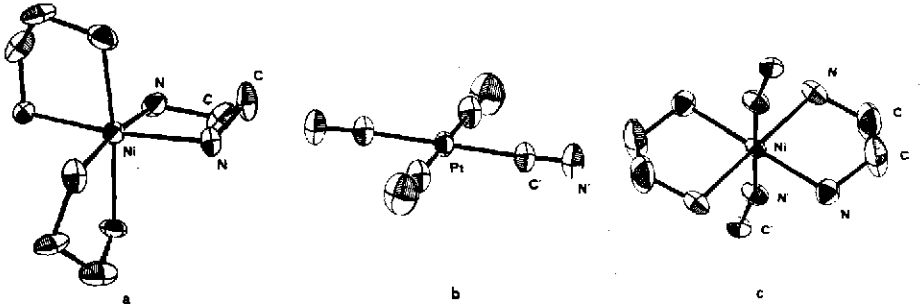
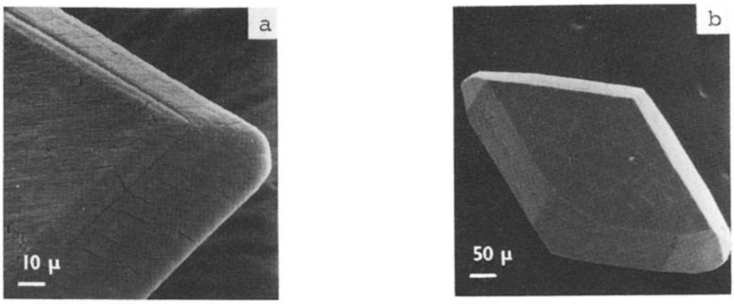


Fig. 2: Coordination polyhedra $[Ni(en)_3]^{2+}$ (a), $[Pt(CN)_4]^{2-}$ (b), and structural element $[Ni(en)_2(CN)_2]$ (c) found in $Ni(en)_3Pt(CN)_4 \cdot H_2O$, $Ni(en)_3Pt(CN)_4$ and $Ni(en)_2Pt(CN)_4$.

Based on the knowledge of the microscopic processes, the respective structural reaction mechanisms can be determined, which, in turn, have to be correlated with morphological observations of the concomitant macroscopic course of the over-all reactions by light and scanning electron microscopy. In fig. 3 scanning electron micrographs of pseudomorphous $Ni(en)Pt(CN)_4$ are presented. The different morphologies are due to the fact, that this intermediate was obtained by decomposing $Ni(en)_3Pt(CN)_4 \cdot H_2O$ (fig. 3a), $Ni(en)_3Pt(CN)_4$ (fig. 3b) and $Ni(en)_2Pt(CN)_4$ (fig. 3c) single crystals.



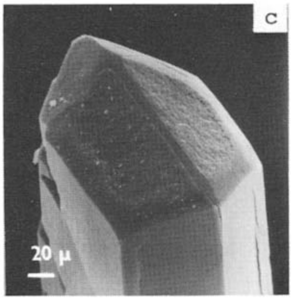


Fig. 3:
Scanning electron micrographs of pseudomorphous $Ni(en)Pt(CN)_4$ obtained from the decomposition of
$Ni(en)_3Pt(CN)_4 \cdot H_2O$ (a),
$Ni(en)_3Pt(CN)_4$ (b) and
$Ni(en)_2Pt(CN)_4$ (c).

CONCLUSIONS

From the correlation of comparative structural and morphological investigations valid contributions for the study of the mutual dependence respectively coherence between microscopic structural reaction mechanism and simultaneously occurring macroscopic changes can be obtained. Such kind of studies represent the indispensable base for the evaluation of specific kinetic data from thermogravimetric measurements.

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