Journal of Thermal Analysis, Vol. 17 (1979) 351—357

THERMAL PROPERTIES OF THE CLATHRATE COMPOUNDS OF BINARY CYANIDES

I. STOICHIOMETRY OF DECOMPOSITION OF CLATHRATE COMPOUNDS OF THE TYPE $Cd(en)Pd(CN)_4 \cdot 2\ G$

J. SKORŠEPA, ŠRAMKO* and E. JÓNA*

Department of Inorganic Chemistry, Faculty of Sciences, P. J. Šafarik University, Košice;
** Department of Inorganic Chemistry, Faculty of Chemical Technology, Slovak Technical University, Bratislava, Czechoslovakia*

(Received December 8, 1978)

The stoichiometry of thermal decomposition of a particular group of clathrate compounds, of the type $Cd(en)Pd(CN)_4 \cdot 2\ G$, with the same coordination component but different clathrate-enclosed components, was investigated. Irrespective of the experimental conditions, the liberation of the enclosed component *G* always proceeded in one step. Thermal investigation of the decomposition stoichiometry under identical experimental conditions showed that the temperature intervals in which the enclosed components are given off shift to lower temperatures in the order $C_6H_5OH > C_6H_6 > C_4H_5N > C_4H_4S$. Diffraction measurements indicated a considerable change in the structures of the original clathrate compounds after thermal release of the enclosed component *G*.

One of the groups of clathrate compounds of binary cyanides is represented by clathrates of the type $Cd(en)M(CN)_4 \cdot 2G$, where M is Ni'', Pd'' or Pt'' and G is phenol, benzene, thiophene, pyrrole or furan. The methods of preparation and identification [1], as well as the data concerning the structures [2] of these compounds have been published. As to their thermal properties, only some incomplete data [3, 4] are known. The selection of the investigated compounds resulted from an attempt to ascertain the stoichiometry of thermal decomposition for a series in which all compounds had identical coordination, i.e. in the host part, but the nature of the enclosed, i.e. the guest component, differed. The aim of this study is to elucidate the character of the decomposition in relation to the experimental conditions of the thermal study and the stoichiometry of thermal decomposition under fixed experimental conditions, as well as to study the structural changes in the coordination part of the compounds comprising the original clathrates and their intermediates produced by liberation of the enclosed component.

Experimental

Four clathrate compounds of the type $Cd(en)Pd(CN)_4 \cdot 2G$ were studied, where G is phenol, benzene, thiophene or pyrrole. The preparation and identification of these substances was published earlier [1]. They were sufficiently pure for further study. The thermal decompositions were investigated with a MOM (Hungary) derivatograph. A platinum crucible with 14 mm upper diameter, and a Pt/Pt-Rh thermocouple were used. The grain size of all specimens was under 0.06 mm.

The measurements were performed under the following conditions: weighed amounts 100 mg; heating 3°/min; air atmosphere.

The powder diffraction patterns were obtained on a GON III (Chirana) diffractograph, using CuKα radiation.

The infrared spectra were taken on a Perkin–Elmer Model 577 instrument, using the KBr technique.

Results and discussion

The thermal decompositions of clathrate compounds of binary cyanides containing benzene as the enclosed component have been investigated by several authors [3, 5–7]. It is obvious from the published results that the majority of the compounds give off the clathrate-bound benzene completely in the first stage of the thermal decomposition, while the subsequent decomposition is considerably differentiated from the liberation of benzene. However, results based on a comparison of the thermal properties of particular clathrate compounds of binary cyanides with identical coordination but containing different clathrate-enclosed components have not been reported hitherto.

Study of the stoichiometry of thermal decomposition of the compound $Cd(en)Pd(CN)_4 \cdot 2C_6H_5OH$ has shown (Fig. 1) that this substance is stable up

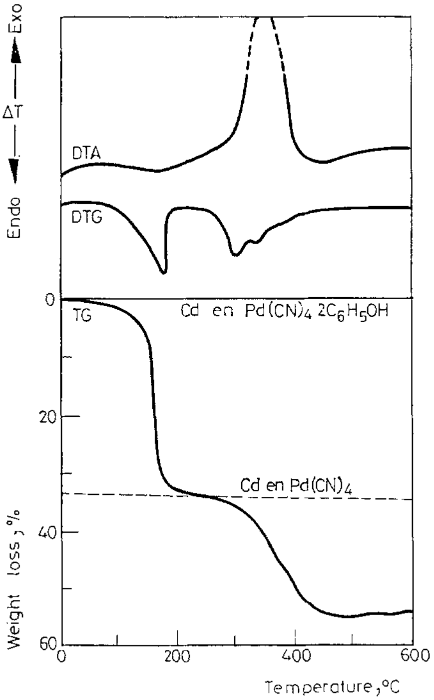

Fig. 1. Thermal curves of $Cd(en)Pd(CN)_4 \cdot 2\ C_6H_5OH$

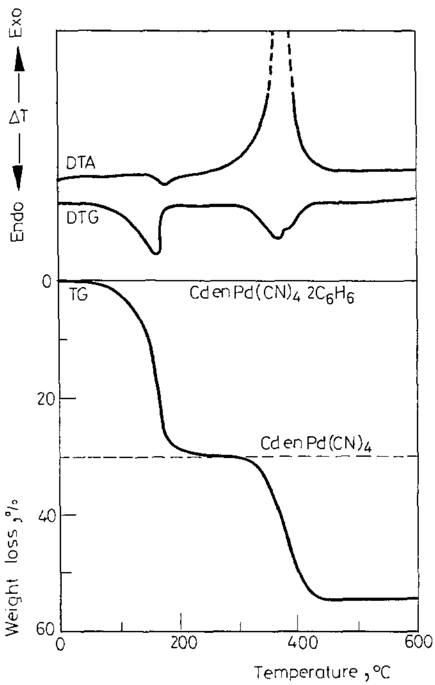

Fig 2. Thermal curves of $Cd(en)Pd(CN)_4 \cdot 2\ C_6H_6$

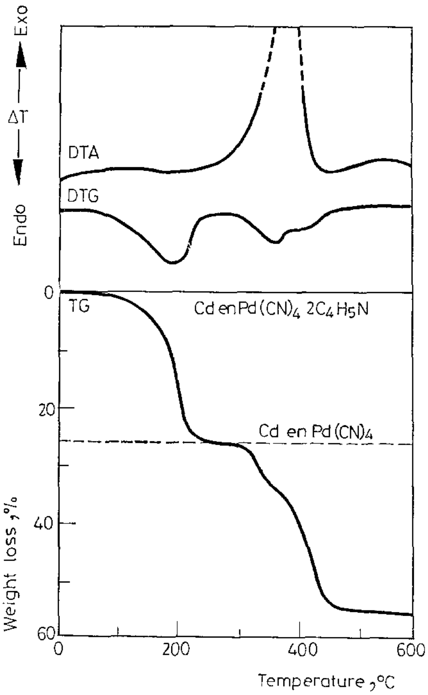

Fig. 3. Thermal curves of $Cd(en)Pd(CN)_4 \cdot 2\ C_4H_5N$

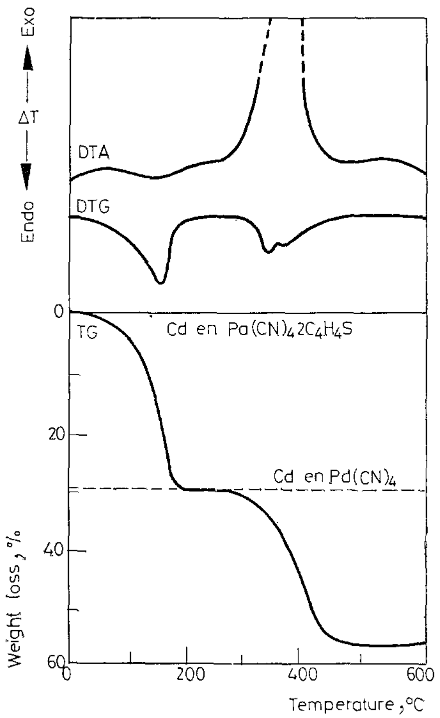

Fig. 4. Thermal curves of $Cd(en)Pd(CN)_4 \cdot 2\ C_4H_4S$

to approximately 70°, where the first weight loss appears. This weight loss comes to an end at about 200°. The loss is in good agreement with the calculated amount of phenol (32.9%) and is accompanied by a weak endothermic effect. On further heating, the coordination part of the clathrate starts to decompose, ethylenediamine being released in the first step; this is immediately succeeded by decomposition of cyanides. During this decomposition cyanogen was detected qualitatively. The final decomposition products at 600° are a mixture of metals and their oxides. The entire decomposition of the coordination part is accompanied by marked exothermic effects.

Study of the thermal decompositions of other three compounds points to an analogous course. However, there is a difference in the temperature at which the enclosed component is liberated. Benzene is released in the temperature interval 65–190° (Fig. 2), pyrrole in the interval 60–190° (Fig. 3) and thiophene in the interval 40–160° (Fig. 4).

The thermal decomposition intermediates obtained by liberating the clathrate-enclosed components were studied analytically by means of infrared spectra and X-ray diffraction. The compositions of all the intermediates correspond to the formula $Cd(en)Pd(CN)_4$ and, in contrast to the spectra of the original clathrate compounds, the infrared spectra of the intermediates do not exhibit any bands which could be assigned to clathrate-enclosed components. The diffraction patterns of the original clathrate compounds and intermediates obtained by liberating the enclosed components are represented in Figs 5–8.

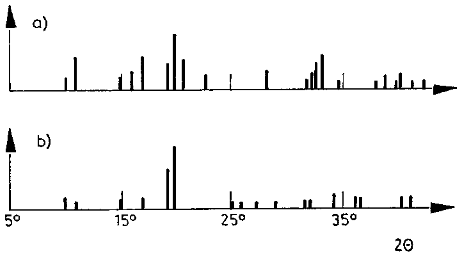

Fig. 5. Powder diffractograms; *a)* – $Cd(en)Pd(CN)_4 \cdot 2\,C_6H_5OH$, *b)* – $Cd(en)Pd(CN)_4$

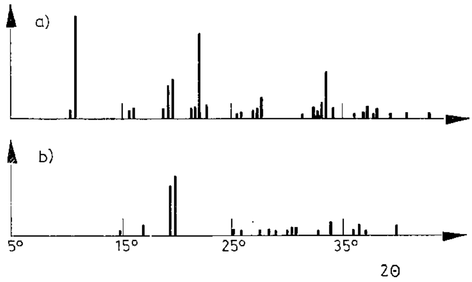

Fig. 6. Powder diffractograms: *a)* – $Cd(en)Pd(CN)_4 \cdot 2\,C_6H_6$, *b)* – $Cd(en)Pd(CN)_4$

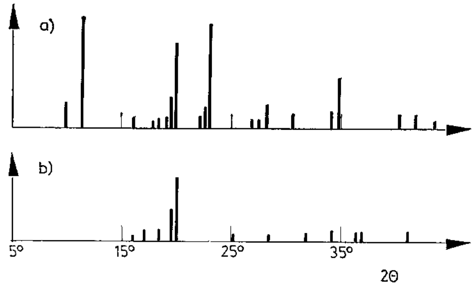

Fig. 7. Powder diffractograms: *a)* – $Cd(en)Pd(CN)_4 \cdot 2\,C_4H_5N$, *b)* – $Cd(en)Pd(CN)_4$

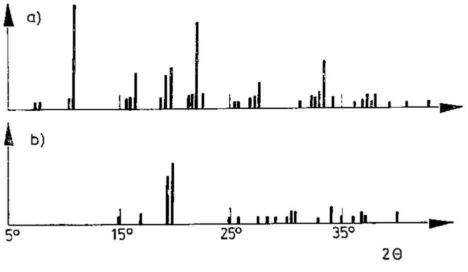

Fig. 8. Powder diffractograms; *a)* – $Cd(en)Pd(CN)_4 \cdot 2\,C_4H_4S$ *b)* – $Cd(en)Pd(CN)_4$

The clathrate compounds of binary cyanides exist only in the solid state, and their study therefore demands the application of methods suitable for investigating solid substances. Thermoanalytical examinations combined with the study of infrared spectra and X-ray diffraction yield an idea of the changes in the investigated clathrate compounds in the course of decomposition. It results from this study that the liberation of the enclosed component is always a one-step process. The infrared spectra and X-ray diffraction patterns show that the liberation of the enclosed component is accompanied by a profound change in structure of the intermediate when compared with the structure of the original clathrate compound. The change in structure brings about irreversibility with respect to entrapping the enclosed component again.

In spite of the relative importance of the initial temperatures of decomposition, these temperatures show a tendency to decrease under identical experimental conditions, in the following order of the enclosed components:

$$C_6H_5OH > C_6H_6 > C_4H_5N > C_4H_4S.$$

According to present knowledge, this order is related to the molecular size of the individual enclosed components. Bhatnagar and Iwamoto et al. [9, 10] state that the maximum value of the molar volume for a component to fit into the cavities is 90 cm^3 $mole^{-1}$. Components with molar volumes near to 90 $cm^3 \cdot mole^{-1}$ make more compact clathrates, and their release requires higher temperatures than for components with lower molar volumes. The molar volumes of the components used (C_6H_5OH: 88.8; C_6H_6: 88.6; C_4H_4S: 78.5; C_4H_5N: 72.0) are in good correlation with this assumption. An exception is pyrrole, which has a lower molar volume than thiophene, but starts to be freed at a higher temperature. This may explained by the presence of the lone electron pair on the nitrogen atom, which is certainly not able to form a coordinate bond, but may produce a partial interaction with the coordination part of the clathrate and thus, in spite of the lower molar volume, shift the start of the decomposition (under identical experimental conditions) to higher temperatures.

These conclusions are supported by a kinetic study of the thermal decompositions of this series of clathrate compounds, which will be the topic of a subsequent paper.

References

1. J. Skoršepa, J. Chomič and E. Matejčíkova, Monatsh. Chem., 107 (1976) 297.
2. T. Miyoshi, T. Iwamoto and Y. Sasaki, Inorg. Nucl. Chem. Letters, 6 (1970) 21.
3. A. Sopková, J. Chomič, E. Matejčiková and J. Skoršepa, Proc. 13th ICCC, Krakow–Zakopane, Poland, 1970.
4. J. Skoršepa and J. Chomič, Zborník VI. ČSSR konferencie, Termanal 73, Vysoké Tatry ČSSR, 1973.
5. J. Leicester and J. K. Bradley, Chem. Ind., (1968) 208.
6. Y. Mathey and C. Mazières, Bull. Soc. Chim. France, 11 (1973) 2918.

7. J. Skoršepa, E. Matejčiková and J. Chomič, J. Thermal Anal., 12 (1977) 69.
8. T. Miyoshi, T. Iwamoto and Y. Sasaki, Inorg. Chim. Acta, 6 (1972) 59.
9. V. M. Bhatnagar, Clathrate Compounds, S. Chand. Company, 1968.
10. T. Iwamoto, T. Miyoshi and Y. Sasaki, Acta Cryst., B 30 (1974) 292.

Résumé — Dans cette étude on a établi la stoechiométrie de la décomposition thermique d'un groupe particulier de clathrates du type $Cd(en)Pd(CN)_4 \cdot 2\,G$, avec le même composant de coordination et différents composants occlus. Indépendamment des conditions d'expériences, la libération du composant occlus *G* s'effectue toujours en une étape. L'étude thermique de la stoechiométrie de la décomposition effectuée dans les mêmes conditions d'expériences, a montré que les intervalles des températures dans lesquels les composants occlus sont libérés, se déplacent vers les températures plus faibles dans l'ordre suivant: $C_6H_5OH > C_6H_6 > C_4H_5N > C_4H_4S$. Les mesures de diffraction indiquent qu'après la libération thermique du composant occlus *G*, une variation considérable de la structure initiale des clathrates originaux apparaît.

Zusammenfassung — Die Stöchiometrie der thermischen Zersetzung einer bestimmten Gruppe von Klathratverbindungen vom Typ $Cd(en)Pd(CN)_4 \cdot 2G$ mit der gleichen Koordinationskomponente und verschiedenen Klathrat-Einschlußkomponenten wurde in dieser Studie untersucht. Ungeachtet der Versuchsbedingungen vollzieht sich die Freisetzung der eingeschlossenen Komponente *G* stets in einer Stufe. Die unter gleichen Versuchsbedingungen durchgeführte thermische Untersuchung der Zersetzungsstöchiometrie zeigte, daß die Temperaturbereiche, in denen die eingeschlossenen Komponenten freigesetzt werden in der Reihenfolge $C_6H_5OH > C_6H_6 > C_4H_5N > C_4H_4S$ in Richtung der niedrigeren Temperaturwerte verschoben werden. Die Diffraktionsmessungen weisen darauf hin, daß eine beträchtliche Änderung der Struktur der ursprünglichen Klathratverbindung nach thermischer Freisetzung der eingeschlossenen Komponente *G* sichtbar wird.

Резюме — Представлено исследование стехиометрии термического разложения особой группы клатратных соединений типа $Cd(en)Pd(CN)_4 \cdot 2G$ с одинаковой координационной компонентой и различной клатратной компонентой. Независимо от экспериментальных условий, выделение компоненты включения *G* всегда протекает в одну стадию. Термическое изучение стехиометрического разложения, выполненное при одинаковых экспериментальных условиях, показало, что температурный интервал выделения компоненты включения сдвигается к более низким температурам в ряду $C_6H_5OH > C_6H_6 > C_4H_5N > C_4H_4S$. Рентгено-диффракционные измерения показали, что значительное исменение структуры первоначальных клатратных соединений происходит после термического выделения компоненты включения *G*.