CLATHRATE COMPOUNDS OF TETRACYANO COMPLEXES OF NICKEL AND PLATINUM WITH PHENOL

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The double cyanides of nickel and platinum form structures capable of enclosing also phenol, for example, as guest molecule. Such clathrates are $Ni(NH_3)_2Pt(CN)_4$ $2\ C_6H_5OH$ and $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$. In the case of the tetracyano complexes, different thermal stabilities of their clathrate compounds could be achieved by alteration of the constituents of the cage structure and also of the guest molecules. According to the thermal behaviour, the clathrates may be divided into two groups: those which release the guest molecules in the first step of thermal decomposition $(Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH)$, and those which lose the guest component only after partial destruction of the host cage $(Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH)$. The temperature ranges of loss of the guest component may determine the interval for their use in sorptive experiments. The temperature range for release of phenol from $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ is $55-244°$, and from $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$ is $139-284°$. The model host molecules $NiPt(CN)_4 \cdot 6\ H_2O$ and $Ni(en)_3Pt(CN)_4 \cdot 3\ H_2O$ were also studied by thermal analysis.

The clathrate compounds of tetracyano complexes have been found [1] to exhibit higher thermal stabilities that other clathrate compounds described in the literature. This holds not only for the clathrate compounds themselves, generally written as

$M(NH_3)_2M'(CN)_4 \cdot 2\ G$ and
$M(en)_mM'(CN)_4 \cdot nG$, but
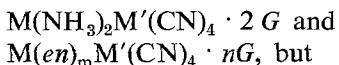
also for their host molecules the tetracyano complexes [2]. The host molecules have been prepared for a better understanding of the relations between the clathrate compounds, their properties described in the literature and also their behaviour in several sorptive processes [3].

The double cyanides form structures capable of enclosing guest components present in the reaction medium during the synthesis of the double cyanide. By altering the constituents of the cage structures of the host molecules, we could achieve different thermal stabilities of the resulting clathrate compounds. We used M in the form of Ni^{II}, Cu^{II}, Cd^{II} and Zn^{II}; M' in the form of Ni^{II}, Pt^{II} and Pd^{II}; and $m = 1$, 2 and 3.

Equally, the interaction of the cage with the individual types of guest molecules influences the thermal stabilities of the synthesized clathrate compounds. As guest

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molecules G we used benzene [4], aniline, thiophene, furan and pyrol [5], in amounts $n = 0.14-2$.

According to literature results, under normal conditions, the guest component is not resorbed after being lost on heating of the clathrate compounds. In contrast, by keeping our proposed conditions of heating, we observed the ability for resorption of the guest molecule originally present in the clathrates, and of other guest components [3].

The results of thermal analysis [6] permit one to predetermine the range of temperatures where the compounds persist as clathrates (till $n \longrightarrow 0$), and further the range of temperatures where resorption can be achieved. Thermal analysis was also carried out on model host molecules, in the form before clathrate synthesis and also during the synthesis. All our compounds may be divided into two groups according to their thermal behaviour [6, 7]:

1. Compounds losing the guest component G in the first step of thermal decomposition:

$$M(NH_3)_2 M'(CN)_4 \cdot 2\ G$$
$$M(en)\ M'(CN)_4 \cdot 2\ G$$
$$M(en)_3 M'(CN)_4 \cdot 0.28\ G.$$
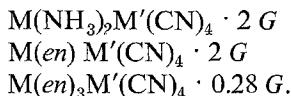
Within a given range of temperature they gradually lose their clathrate characteristics.

2. Compounds losing the guest component G only after partial thermal destruction of the host cage: $M(en)_2 M'(CN)_6 \cdot 0.14\ G$.

They remain as clathrate compounds, and may be utilized, up to a higher temperature range.

To widen the scale of prepared clathrates, we also attempted to enclose phenol as guest component in double cyanide of nickel and platinum. Here the phenol would be present with opposite function to that in the compound $6\ C_6H_5OH \cdot G$, described by Kazankin [8], where the phenol molecules formed the host cage enclosing other types of molecules.

We succeeded with phenol, in spite of its physical properties being different from those of other guest molecules usually enclosed in tetracyano complexes. The compounds were identified and subjected to thermal analysis, and could be classified into two series: $M(NH_3)_2 M'(CN)_4 \cdot 2\ G$ and $M(en)_2 M'(CN)_4 \cdot 0.14\ G$.

The compounds examined were $Ni(NH_3)_2 Pt(CN)_4 \cdot 2\ C_6H_5OH$ [9] and $Ni(en)_2 Pt(CN)_4 \cdot 0.14\ C_6H_5OH$, together with the model host molecules.

Experimental

Synthesis

The conditions of synthesis of the clathrate compounds of tetracyano complexes with phenol are partly different; the synthesis is not made from solutions of the starting materials, $MM'(CN)_4$, ethylenediamine (*en*) and the guest molecule [4].

The reactions for their synthesis are as follows:

$$H_2PtCl_6 + 2\ NaCl \longrightarrow Na_2PtCl_6 + 2\ HCl$$
$$2\ Na_2PtCl_6 + N_2H_4 \longrightarrow 2\ Na_2PtCl_4 + 4\ HCl + N_2$$
$$Na_2PtCl_4 + 4\ NaCN \longrightarrow Na_2Pt(CN)_4 + 4\ NaCl$$
$$Na_2Pt(CN)_4 + NiSO_4 \longrightarrow NiPt(CN)_4 + Na_2SO_4$$
$$NiPt(CN)_4 + a(en) \longrightarrow Ni(en)_2Pt(CN)_4 + (a-2)en$$
$$Ni(en)_2Pt(CN)_4 + b\ C_6H_5OH \longrightarrow Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH +$$
$$+ (b-0.14)\ C_6H_5OH$$
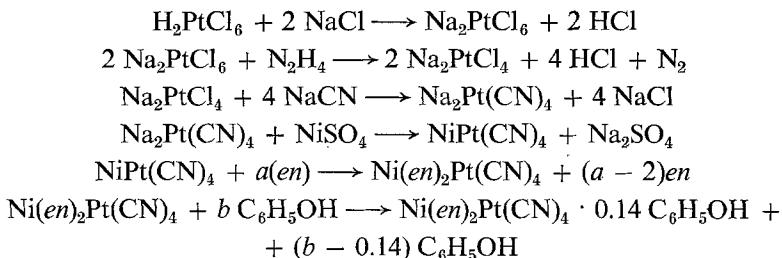
The precipitated $NiPt(CN)_4$, after having been filtered off and washed with water, was dried above conc. H_2SO_4 and served as starting material for two products differing in their water contents:

1. $NiPt(CN)_4$ was dissolved in ethylenediamine, the pH pas adjusted, and solid phenol was added with vigorous mixing; the resulting precipitate was washed with H_2O and ether.

2. A saturated aqueous solution of phenol was added to $NiPt(CN)_4$ dissolved in ethylenediamine. The synthesis was carried out in an atmosphere of nitrogene.

The compounds $NiPt(CN)_4$ and $Ni(en)_3Pt(CN)_4 \cdot 3\ H_2O$ were also prepared as models for host molecules.

All compounds were identified by chemical analysis and by IR spectra.

Thermal analysis

Thermal analysis was performed in air using a Paulik–Paulik–Erdey OD 102 derivatograph and platinum crucibles. Sample weights were 100 mg. The heating rates were 6° and 3°/min. Alumina was employed as reference material.

Results

$NiPt(CN)_4 \cdot 6\ H_2O$ (Fig. 1) released the H_2O in three distinct processes $(3+1+2)$ in the temperature range 30–200°, with endothermic maxima at 80, 102 and 165°. The exothermic decomposition began at 290° and ended at 385°.

$Ni(en)_3Pt(CN)_4 \cdot 3\ H_2O$ (Fig. 2) lost the water in an endothermic process with DTA maximum at 108°; a weak exothermic process was then to be seen, ending at 252°. The ethylenediamine was lost in exothermic processes at 252–320°, 320–348° and, together with decomposition of the cyanides, 348–400°.

$Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH)$ (1) started its decomposition at 40°. The loss of not the whole molar weight of *en* is as an edothermic process till 139° with a DTA maximum at 100°, and is followed by an endothermic process (139–284°) with a DTA maximum at 180° and immediately by an exothermic process (Fig. 3). The process at 139–284° shows a loss of weight equivalent to loss of the guest molecule. In a double exothermic process (284–336°) further ethylenediamine is
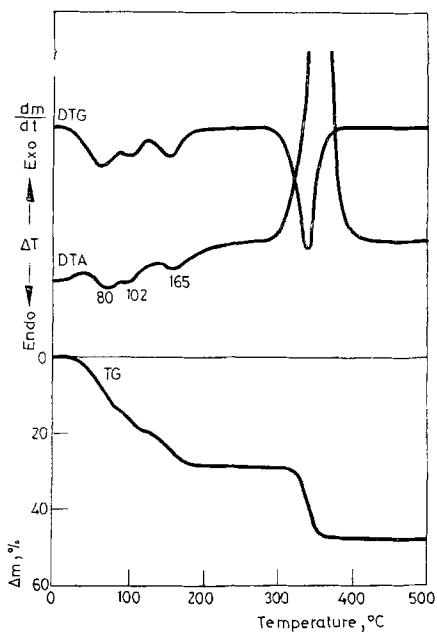
Fig. 1. Thermal curves for the decomposition of $NiPt(CN)_4 \cdot 6 H_2O$; heating rate: $6°/min$.
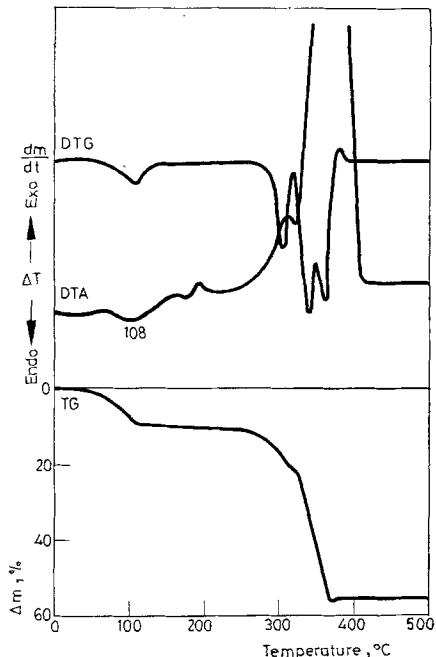
Fig. 2. Thermal curves for the decomposition of $Ni(en)_3Pt(CN)_4 \cdot 3 H_2O$; heating rate: $6°/min$.
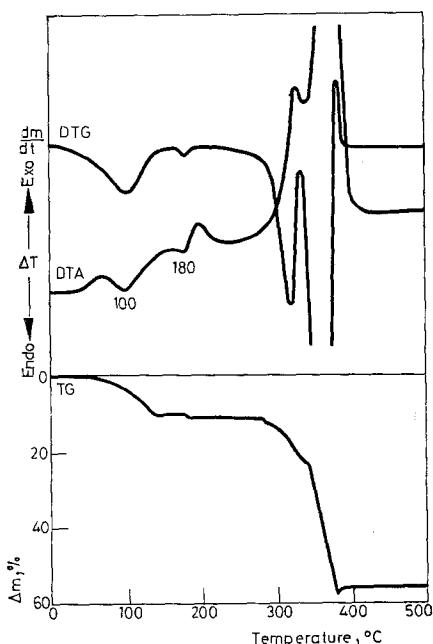
Fig. 3. Thermal curves for the decomposition of $Ni(en)_2Pt(CN)_4 \cdot 0.14\,C_6H_5OH$; heating rate: 6°/min.

lost. The decomposition continues in two distinct exothermic processes till 430°. The compound behaves as a clathrate till 284° ($n \rightarrow 0$).

Sample (2) was analytically identified as containing two molecules of H_2O. It preserved the characteristics of a compound of $M(en)_2M'(CN)_4 \cdot 0.14\,C_6H_5OH$ type. It lost the enclosed guest molecule in the range 148—282°, after a loss of weight equivalent to approximately 0.75 of the molar amount of ethylenediamine from the host cage.

Discussion

The compound containing the *en* ligands has different thermal behaviour from the analogous compound [9] with simple ammine ligands $Ni(NH_3)_2Pt(CN)_4 \cdot 2\,C_6H_5OH$.

The compound $Ni(NH_3)_2Pt(CN)_4 \cdot 2\,C_6H_5OH$ released the whole phenol content in the temperature range 55—244° in a process with DTA maximum at 184° and behaved as a clathrate compound up to 244° (Fig. 4).

Thermal analysis of the guest molecule alone (phenol) showed an analogous decomposition in the range 55—210° (Fig. 4).

Because of its two *en* ligands, $Ni(en)_2Pt(CN)_4 \cdot 0.14\,C_6H_5OH$ is not capable of enclosing the maximum amount of G; it releases its 0.14 moles of phenol at 139—

284°, a temperature range analogous to that for $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$, but only after the loss of a non-stoichiometric portion of not exactly one mole of *en* ligand.

The clathrate compounds $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ and $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$ show the physical properties of the phenol (Fig. 4) in shifting the
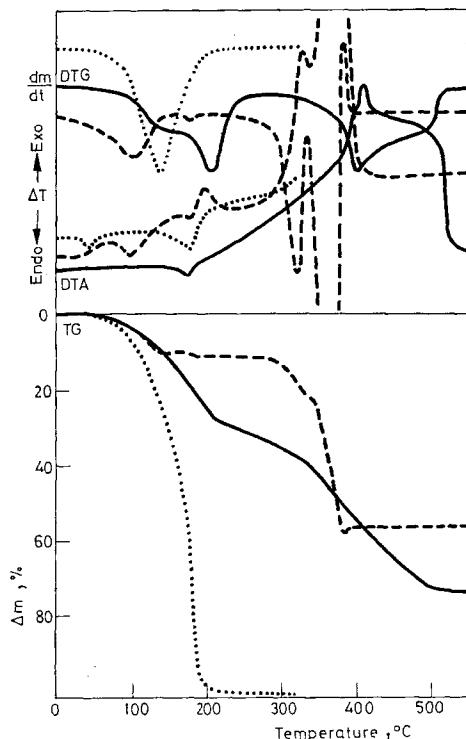
Fig. 4. Thermal curves for the decomposition of C_6H_5OH(. . .), $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$ (- - -) and $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ (———); heating rate: 6°/min.

temperature range of phenol to higher temperatures and equally in the thermal stabilities of the clathrates. They counterbalance asymmetric shape of the phenol molecule, which hinders its enclosure.

$Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ may be included in the group $M(NH_3)_2M'(CN)_4 \cdot 2\ G$; these have maximally filled cage spaces, and release the total enclosed guest component in the first step of thermal decomposition.

$Ni(en)_2Pt(CN)_4 \cdot 0.14C_6H_5OH$ behaves as a clathrate compound up to higher temperatures, and furthermore, in accordance with the behaviour of other compounds of this type, after partial destruction of the host cage it approaches the clathrate compound with maximum amount *n* of guest molecule. During synthesis

the *en* ligands do not permit enclosure of the maximum amount of guest molecule *G*. Therefore, it loses the phenol content, similarly as for the whole group of $M(en)_2M(CN)_4 \cdot 0.14G$ type, only in a higher thermal interval ($139-284°$), after partial destruction of the host cage. This type of thermal destruction, the incapability of the compound to enclose phenol in maximum amount during synthesis, together with the escape of phenol only in the second step of its thermal decomposition, are appropriate for the compound satisfying the stoichiometry of $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$. The non-stoichiometric amount is limited during the synthesis by the number of *en* ligands ($m = 2$). The compound belongs to the group $M(en)_2M'(CN)_4 \cdot 0.14G$ with higher thermal stability. It is assumed, it will follow the sorptive ability of such clathrate compounds.

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RÉSUMÉ — Les cyanures doubles de nickel et de platine forment une structure capable de se comporter comme une « structure d'accueil » vis-à-vis de la molécule de phénol. Les composés $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ et $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$ entrent dans cette catégorie. Dans le cas des tétracyanocomplexes, on a pu atteindre une stabilité thermique différente de celle de leurs clathrates en changeant les constituants de la structure d'accueil ainsi que des molécules encagées. Leur comportement thermique se divise en deux groupes: dans le premier, les molécules encagées se dégagent lors de la première étape de la décomposition thermique [$Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$], tandis que le deuxième groupe ne perd le composant encagé qu'après destruction partielle de la molécule d'accueil [$Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$]. Les intervalles de température où s'effectue le départ du composant encagé permettent de prédire l'intervalle de leur utilisation dans les expériences de sorption. On a étudié, par analyse thermique, également les molécules d'accueil $NiPt(CN)_4 \cdot 6\ H_2O$ et $Ni(en)_3Pt(CN)_4 \cdot 3\ H_2O$.

Les intervalles de températures du dégagement du phénol sont $55-244°$ pour $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ et $139-284°$ pour $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$.

ZUSAMMENFASSUNG — Die Struktur der doppelten Cyanide von Nickel und Platin bietet die Möglichkeit auch Phenol als Gastmolekül einzuschließen. Hierzu zahlen Verbindungen wie $Ni(NH_3)_2Pt(CN)_4 \cdot 2\ C_6H_5OH$ und $Ni(en)_2Pt(CN)_4 \cdot 0.14\ C_6H_5OH$. Bei den Tetracyanokomplexen konnte eine verschiedene Wärmebeständigkeit ihrer Klathratverbindungen durch Änderung der Bestandteile der Käfigstruktur und auch der Gastmoleküle erreicht werden.

Ihr thermisches Verhalten kann in zwei Gruppen unterteilt werden: die erste Gruppe verliert das Gastmolekül in der ersten Stufe der thermischen Zersetzung [Ni(NH$_3$)$_2$Pt(CN)$_4$·2C$_6$H$_5$OH], die zweite nur nach teilweiser Zerstörung des Empfängerkäfigs [Ni(en)$_2$Pt(CN)$_4$·0.14C$_6$H$_5$OH]. Der Temperaturbereich der Abgabe der Gastkomponente gestattet Voraussagen bezüglich ihres Nutzungsbereichs in Sorptionsexperimenten. Die Modelle ihrer Gastmoleküle, NiPt(CN)$_4$·6 H$_2$O, Ni(en)$_3$Pt(CN)$_4$·3 H$_2$O wurden ebenfalls mittels Thermoanalyse untersucht.

Die Temperaturbereiche der Phenolabgabe sind 55 bis 244° bei Ni(NH$_3$)$_2$Pt(CN)$_4$· ·2 C$_6$H$_5$OH und 139 bis 284° bei Ni(en)$_2$Pt(CN)$_4$·0.14 C$_6$H$_5$OH.

Резюме — Двойные цианиды никеля и платины образуют структуры, способные включать фенол как гостевую молекулу. Такими соединениями являются Ni(NH$_3$)$_2$Pt(CN)$_4$·2C$_6$H$_5$OH и Ni(en)$_2$Pt(CN)$_4$·0,14C$_6$H$_5$OH. В случае тетрациановых комплексов различная термическая стабильность их клатратных соединений может быть достигнута варьированием составных частей структуры остова, а также гостевых молекул. Термическое поведение может быть разделено на две группы: первая с выделением гостевых молекул на первой стадии термического разложения — Ni(NH$_3$)$_2$Pt(CN)$_4$·2C$_6$H$_5$OH, а вторая с потерей гостевой компоненты только после частичной деструкции молекулы «гостителя» — Ni(en)$_2$Pt(CN)$_4$·0.14C$_6$H$_5$OH. Температурные области потери гостевой компоненты может определять интервал для их использования в сорбционных экспериментах. С помощью термического анализа изучены также модели молекулы-«гостители»—NiPt(CN)$_4$·6H$_2$O и Ni(en)$_3$Pt(CN)$_4$·3H$_2$O. Температурной областью выделения фенола для Ni(NH$_3$)$_2$Pt(CN)$_4$·2C$_6$H$_5$OH является 55—244°, а для Ni(en)$_2$Pt(CN)$_4$·0.14C$_6$H$_5$OH — 139—284°.