TRANSITION METAL TETRACYANO COMPLEXES, THEIR THERMAL AND SORPTION PROPERTIES

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The possibility of resorption of a guest molecule (G) or its substitution by other compounds is not known for $M(NH_3)_2N(CN)_4.2\,G$ (G = C_6H_6) or $M(en)_mM'(CN)_4 . n$G clathrates, or even for the parent $M(NH_3)_mM'(CN)_4 . n\,H_2O$, $M(en)_mM'(CN)_4 . n\,H_2O$, $MM'(CN_4) . n\,H_2O$ tetracyano complexes. These, however, are capable of sorption, and their lattice space can be reversibly or irreversibly filled with a suitable organic compound if the clathrates or tetracyano complexes in the hydrated form are allowed to be in contact with organic substances whose size and polarity fit the tetracyano complex lattice. The space within the lattice, however, develops as early as their formation from solution or suspension in the presence of the compound G (presence of water is actually sufficient).

Clathrate compounds of the $M(NH_3)_2M'(CN)_4 . 2\,G$ and $M(en)_mM'(CN)_4 . n$G types with M = Ni(II), Cu(II), Cd(II), Zn(II); M' = Ni(II), Pt(II), Pd(II); en = $= NH_2(CH_2)_2NH_2$; G = C_6H_6, C_6H_5OH, $C_6H_5NH_2$, C_4H_4S, C_4H_4N, etc.; $m = 1, 2, 3$; $n = 0.14 - 2$, have been studied[1]; model compounds of the host components have also been prepared[2,3]. Selective sorption materials have been obtained[4,5] in nonstoichiometric forms, usable also at higher temperatures; these comprise, in addition to the above clathrates, compounds of $M(NH_3)_mM'(CN)_4 . n\,H_2O$, $M(en)_mM'(CN)_4 . n\,H_2O$, and $MM'(CN)_4 . n\,H_2O$ types.

In all types, different thermal stability is obtained for different metals, ammine ligands, and guest components (G). If the guest component content decreases to zero, the tetracyano complex ceases to exist in the clathrate form. Heating of the initially stoichiometric species results in nonstoichiometric forms of clathrates[4] and tetracyano complexes. These forms, as well as new compounds prepared at our Department, were studied from the points of view of their stability and ability to sorb various organic substances. Their behaviour as gas chromatographic (GC) stationary phases was first examined[3]; this approach has been applied by other authors to Werner-type clathrates[6-9] and other inclusion compounds[10-12]. The sorption properties were also followed by us in model experiments using normal contact with organic substances[13] or in vacuum, using a McBain furnace[14].

It has been found that after expelling the clathrated compound G from $M(NH_3)_2 \cdot M'(CN)_4 \cdot n$ G and $M(en)_m M'(CN)_4 \cdot n$ G clathrates, their lattices are altered and they are not capable of resorbing G in conditions of conventional synthesis, e.g., from solution[15]. The infrared and Raman spectra indicate parameter changes after the liberation of G or even after allowing the substances to stand for a period of time[16,17].

In the $NiNi(CN)_4 \cdot n$ H_2O tetracyano complex itself, part of the water is of zeolite nature, part is coordinated to the metal ion[18,19]; the formula $Ni(H_2O)_2Ni(CN)_4 \cdot y$ H_2O was assigned to the compound. No indication, however, can be found in the literature that all or part of the water can be substituted by some organic compound.

In the present paper, the possibility of desorption and resorption, or substitution, of the guest component G (which can also be water) from tetracyano complex clathrates is demonstrated; attention is paid to relationships between the structure and sorption properties of the complexes examined.

EXPERIMENTAL

The following substances were synthesized[1,2,5,20-22]: $Cu(NH_3)_4Ni(CN)_4 \cdot n$ H_2O, $Ni(NH_3)_4 \cdot Pt(CN)_4 \cdot n$ H_2O, $Ni(NH_3)_2Pt(CN)_4 \cdot 2$ C_6H_6, $Ni(NH_3)_2Pt(CN)_4 \cdot 2$ C_6H_5OH, $Ni(NH_3)_2Pt(CN)_4 \cdot C_6H_5OH \cdot 2$ H_2O, $Cd(en)Ni(CN)_4 \cdot 2$ $C_6H_5NH_2$, $Cd(en)Pd(CN)_4 \cdot 2$ C_6H_6, $Cu(en)_2Ni(CN)_4 \cdot 0 \cdot 14$ C_6H_6, $ZnNi(CN)_4 \cdot H_2O$, $Zn(NH_3)_3Ni(CN)_4 \cdot H_2O$, and $Zn(en)_3Ni(CN)_4 \cdot H_2O$. Their identity was confirmed by infrared spectroscopy using a Perkin–Elmer 577 spectrophotometer $(4\,000 - 200$ $cm^{-1})$ and by thermal[4,23] and X-ray diffraction analysis on OD 102 (MOM, Budapest) and Mikrometa 2 (Chirana) and GON 3 instruments.

The sorption properties of the compounds were examined in conventional model experiments with a direct contact of the sorbate with the sorbent[13], in experiments performed in a vacuum in an apparatus including a McBain furnace[14], and in gas chromatographic experiments on a Chrom 4 apparatus (Laboratorní přístroje, Prague) using model sorbate mixtures.

The chromatographic packings were obtained by either of the two following procedures:

Procedure 1: The tetracyano complex under study was mixed with NaCl $0 \cdot 10 - 0 \cdot 25$ mm grain size, in a mass ratio of $1:9$ or $2:8$, on a rotary mixer until a visually homogeneous mixture emerged.

Procedure 2: The tetracyano complex was suspended in cyclohexane, Chromaton N AW HMDS support $0 \cdot 14 - 0 \cdot 20$ mm grain size was added (the complex-to-support mass ratio was typically $1:9$), and the solvent was removed by evaporation on a water bath.

The dry packing was delivered into the column by means of a pump.

RESULTS AND DISCUSSION

The tetracyano complex clathrates as well as the hydrated parent complexes behave as clathrates over the entire temperature region where they lose the component G or water. This clathrate nature, however, vanishes when $n = 0$ (refs[2-4]). The substances exhibit sorption properties with respect to additional organic compounds

just during the desorption of the guest component G or H_2O. The guest G can comprise molecules of two different kinds, G_1 and G_2, which fill in the space inside the host lattice; G_2 is often water[3-5,23]. The temperature regions of sorption of organic compounds agree with the desorption of the starting guest component (G or H_2O) in thermal analysis; the different ways of heating the stationary phase in GC and the compound in thermal analysis result in insignificant temperature shifts.

According to thermal analysis, $Zn(NH_3)_2Ni(CN)_4 . 2 C_6H_6$, $Zn(NH_3)_2Ni(CN)_4 .$ $. 0.2 C_6H_6$, $Cu(en)_2Ni(CN)_4 . 0.14 C_6H_6$, and $Cu(NH_3)_4Ni(CN)_4 . 3 H_2O$, for instance, are clathrates over the temperature ranges of $26-138$, $70-170$, $238-296$, and $80-150°C$, respectively. $Zn(en)_3Ni(CN)_4 . H_2O$, according to Fig. 1 loses water at $60-120°C$, with a DTA maximum at $90°C$, and the first ethylenedia-mine ligand at $155-215°C$, with a DTA maximum at $210°C$; this causes a slight motion in the 1st coordination sphere of the host complex, lattice disturbances, however, do not yet occur. The chromatogram shown in Fig. 2a demonstrates a selectivity with respect to an aromatics mixture (benzene, toluene, xylene) even after column heating to $200°C$ followed by cooling to $60°C$. Structure elucidation for this compound[22,24,26] has indicated significance of the presence of water in the compound, hydrogen-bonded to the nitrogen atoms in the CN^- groups in layers.

The use of $Cu(en)_2Ni(CN)_4 . 0.14 C_6H_6$ as a stationary phase is illustrated by the chromatogram in Fig. 2b, obtained at $220°C$. This behaviour agrees with the decomposition[4] (where $n \to 0$).

Clathrates can also be prepared so that they contain two different guest com-ponents, such as (in a general form) $M(NH_3)_2M'(CN)_4 . a G_1 . b G_2$. Their behav-iour is analogous. For instance, in addition to $Ni(NH_3)_2Pt(CN)_4 . 2 C_6H_5OH$, $Ni(NH_3)_2Pt(CN)_4 . C_6H_5OH . 2 H_2O$ was also synthesized.

$Ni(NH_3)_2Pt(CN)_4 . 2 C_6H_5OH$, subjected to thermal analysis, releases all phenol within the region of $55-244°C$. When the substance was heated in a vacuum[14], the phenol could be reversibly substituted by two molecules of benzene.

$Ni(NH_3)_2Pt(CN)_4 . C_6H_5OH . 2 H_2O$ was used as a stationary phase, prepared by Procedure 1, for a C_9-C_{13} alkane mixture. The substances eluted in different numbers of peaks of different shapes in dependence on temperature, even after heating of the column to $230°C$, cooling to $100°C$ and repeated heating. At $100°C$, the whole alkane mixture gives rise to two low peaks with rather long retention times (535 s, 1 000 s), indicating surface adsorption. At 120, 150, and $200°C$, the peak shape becomes more expressive, the retention time shortens, although the components do not separate completely; clathration, however, takes place (Fig. 3).

An $Ni(NH_3)_2Pt(CN)_4 . n C_6H_5OH . n H_2O$ product where the phenol was only adsorbed was obtained by adjusting the synthesis conditions (temperature, phenol solidification) improperly. Unlike the genuine clathrate, this substance exhibited no sorption properties with respect to alkanes.
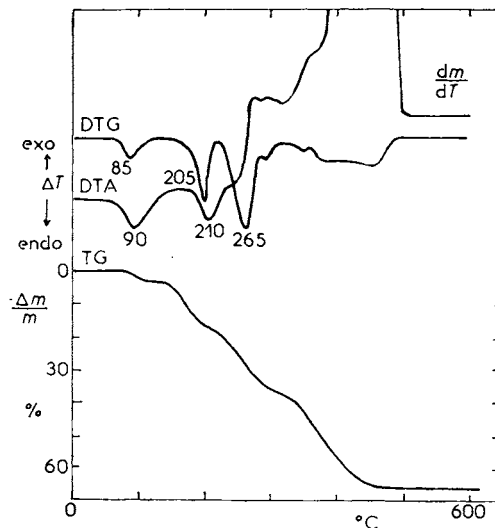
FIG. 1

Derivatograms of $Zn(en)_3 Ni(CN)_4 . H_2O$. Temperature program 6°C min^{-1}
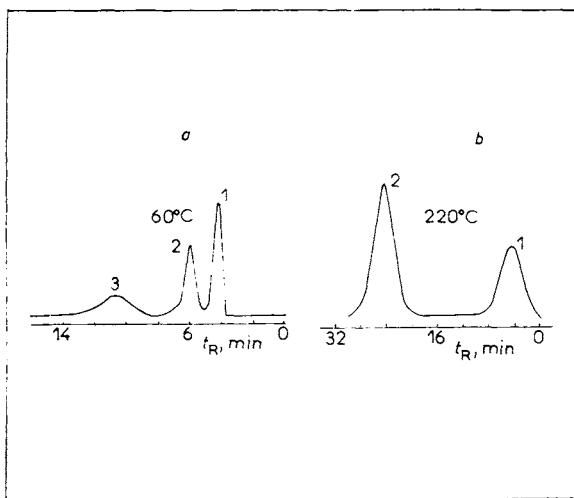
FIG. 2

a) Gas chromatogram of a benzene–toluene–o,m,p-xylene mixture (1 : 1 : 1) using $Zn(en)_3 Ni(CN)_4$. $. H_2O$ prepared by Procedure 2 as the stationary phase. $l = 0.5$ m, $d_c = 3$ mm, $F_m(N_2) = 25$ ml min^{-1}. TA behaviour of the stationary phase: $H_2O \uparrow 60-120°C$, en (1 molecule) $\uparrow$ 155—215°C. Peaks: 1 benzene, 2 toluene, 3 xylene; b) Gas chromatogram of a β-picoline–pyridine mixture (1 : 1) using $Cu(en)_2 Ni(CN)_4 . 0.14 C_6H_6$ prepared by Procedure 1 as the stationary phase. $l = 2.5$ m, $d_c = 3$ mm, $F_m(N_2) = 15$ ml min^{-1}. TA behaviour of the stationary phase: $0.14 C_6H_6 \uparrow 238-296°C$ (296°C: $n \rightarrow 0$). Peaks: 1 β-picoline, 2 pyridine

$Ni(NH_3)_2Pt(CN)_4 . 2 C_6H_6$ clathrate was allowed to be in contact with various solvents for 24 h at ambient or elevated temperatures. As follows from the IR spectra and TG curves (Fig. 4), products were ocassionally obtained where the component G had reacted with or had been substituted by the solvent used.

A part of the clathrate molecule changed on its contact with dimethylformamide, nitrobenzene or hydrochloric acid; with dimethylformamide, interaction with the organic part of the clathrate molecule was observed; nitrobenzene and hydrochloric acid liberated the organic part leaving the inorganic moiety intact.

Some solvents such as formamide or, particularly, formic acid in contact with the solid $Ni(NH_3)_2Pt(CN)_4 . 2 C_6H_6$ clathrate disturb both parts of the molecule even without heating, as demonstrated by Fig. 5.

$Cu(NH_3)_4Ni(CN)_4 . 3 H_2O$ was isolated[2,3] as a model for the host component of $Cu(NH_3)_2Ni(CN)_4 . 2 C_6H_6$ clathrate. Evolving two ammonia molecules in the first stage of heat treatment, this compound becomes similar to the clathrate, except that the water molecules are present instead of the organic compound. The derivatogram shows that two ammonia molecules are evolved at $20-80°C$, three water molecules, at $80-150°C$.

In GC experiments with this compound, attempts were made to replace water by other organic compounds, e.g., picoline[3]. When the compound was heated
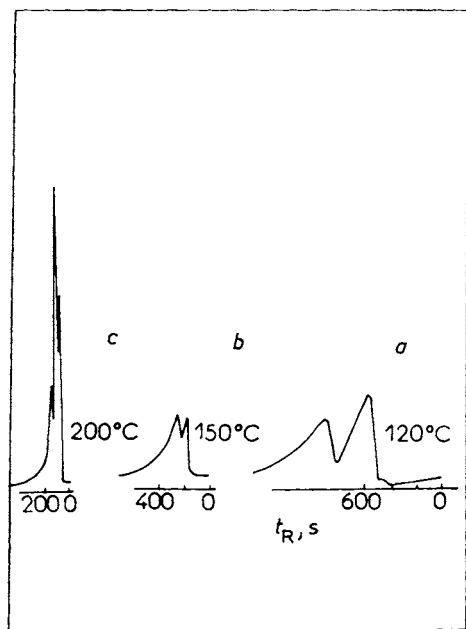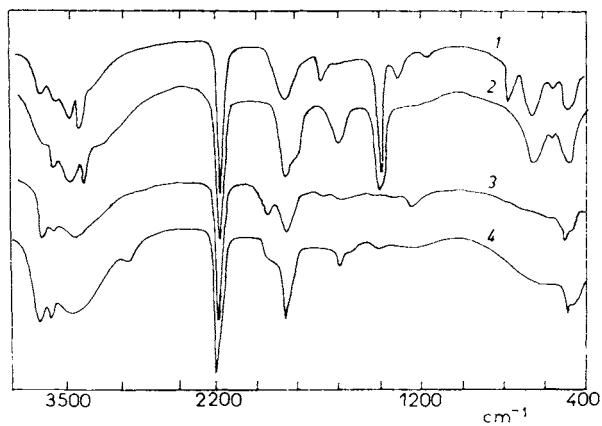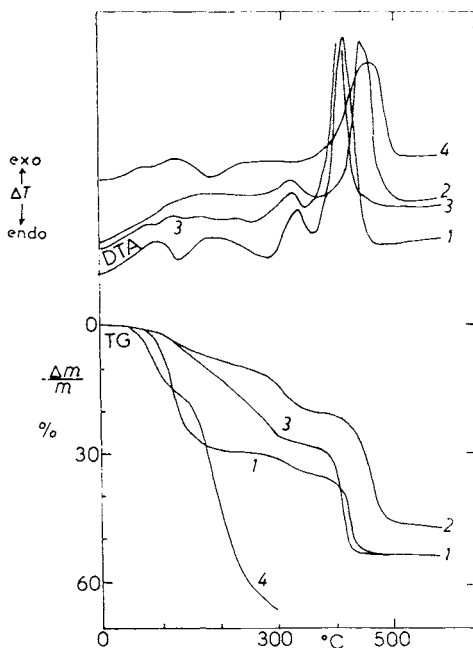

FIG. 3

Gas chromatograms of a C_9-C_{13} n-alkane mixture using $Ni(NH_3)_2Pt(CN)_4 . C_6H_5OH . . 2 H_2O$ as the stationary phase. Mixture composition (%(m/m)): C_9 0·6, C_{10} 16·4, C_{11} 42·6, C_{12} 35·6, C_{13} 4·7. $l = 0·72$ m, $d_c = 3$ mm, $F_m(N_2) = 30$ ml . min^{-1}, injected: 5 µl (a), 1 µl (b, c). TA behaviour of the stationary phase: $C_6H_5OH \uparrow 85-240°C$, 2 H_2O $\uparrow 240-330°C$

a

b

FIG. 4

a) Infrared spectra of $Ni(NH_3)_2Pt(CN)_4 \cdot 2\,C_6H_6$ clathrate untreated (1) and after the action of nitrobenzene (2), dimethylformamide (3), and HCl (4). *b*) Derivatograms of $Ni(NH_3)_2Pt(CN)_4 \cdot$ $\cdot\ 2\,C_6H_6$ clathrate untreated (1) and after the action of nitrobenzene (2), dimethylformamide (3), and HCl (4). Temperature program $6°C\ min^{-1}$
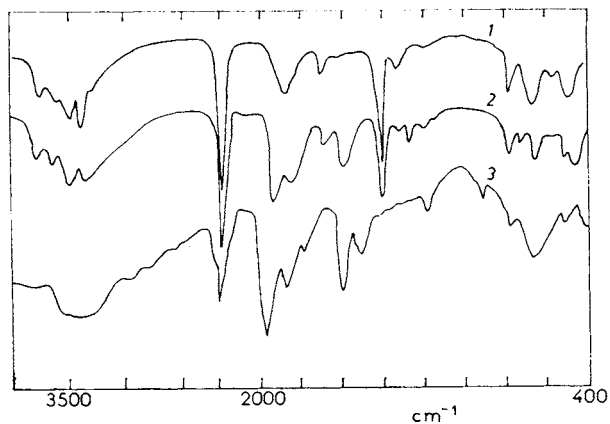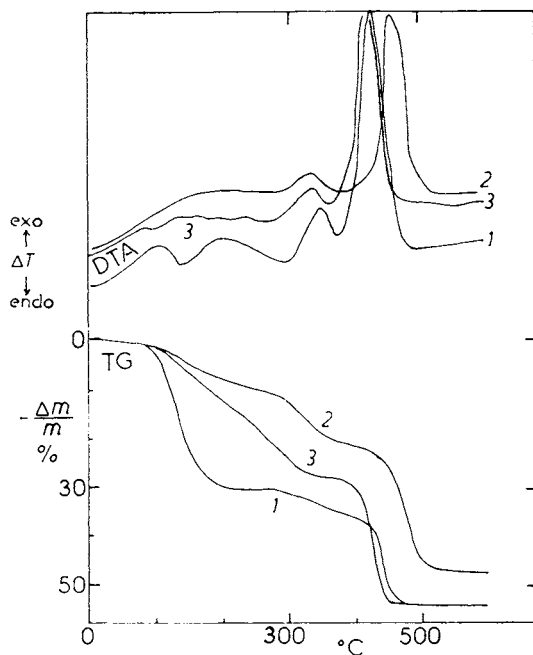
a) Infrared spectra of $Ni(NH_3)_2Pt(CN)_4 \cdot 2\,C_6H_6$ clathrate untreated (1) and after the action of formic acid (2) and formamide (3). *b*) Derivatograms of $Ni(NH_3)_2Pt(CN)_4 \cdot 2\,C_6H_6$ clathrate untreated (1) and after the action of formic acid (2) and formamide (3). Temperature program $6°C\ min^{-1}$

suitably during its contact with the organic substance in GC, water could be replaced by alcohols, alkanes, picolines, *etc.*, even by clathration. Fig. 6 shows that clathration was possible over the region of 80−150°C, hence, in the range where $Cu(NH_3)_4 \cdot Ni(CN)_4 \cdot 2\ H_2O$ loses water $(n \to 0)$.

Using a stationary phase prepared from 20% (m/m) $Cu(NH_3)_4Ni(CN)_4 \cdot 3\ H_2O$ by Procedure *1*, the GC retention times of $C_{11}-C_{14}$ alkanes were measured in dependence on temperature over the region of 80−150°C. The plot of logarithms of the net retention times *vs* inverse column temperature was not linear; instead, it exhibited a maximum (Fig. 7). A similar dependence was obtained for C_1-C_3 alcohols (Fig. 8), pyridine, 3-methylpyridine and for a mixture of dimethylpyridines, which eluted in a single peak.

The results indicate that over the temperature region where they only lose the two excess ammonia molecules, $Cu(NH_3)_4Ni(CN)_4 \cdot n\ H_2O$ complexes are adsorbents and the water in them does not take part in the separation process. Their surface activity is low, particularly with respect to aliphatic alcohols whose retention times at 80°C are very short. The sorption affinity for alkanes and nitrogen heterocycles is somewhat higher. The retention times decrease with increasing column temperature, as does the resolution, in agreement with the formula

$$\Delta t_R = L\Delta Q/RT$$

where Δt_R is the retention time difference for two successive substances, ΔQ is heat of adsorption, and T is column temperature.

At temperatures at which water starts to be released from the tetracyano complex, space inside the lattice becomes free for clathration of alkanes, alcohols and nitrogen heterocyclic compounds. In accordance with the retention times observed, their sorption at such temperatures is considerably stronger than at 80°C. According to

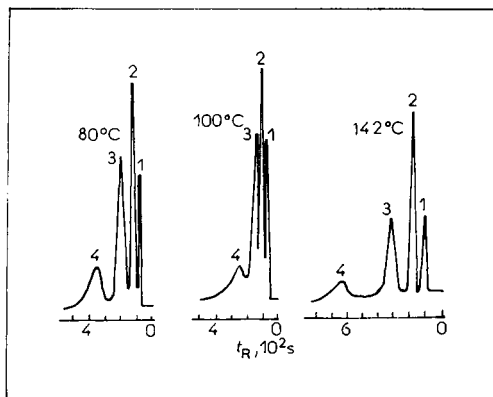FIG. 6

Gas chromatograms of a $C_{11}-C_{14}$ n-alkane mixture using $Cu(NH_3)_4\ Ni(CN)_4 \cdot 2\ H_2O$ as the stationary phase. $l = 2\cdot5$ m, $d_c = 3$ mm, $F_m(N_2) = 25$ ml min^{-1}. Peaks: 1 C_{11}, 2 C_{12}, 3 C_{13}, 4 C_{14}

the above relation, the differences between the retention times increase as well, and so the separation of mixtures of n-alkanes improves (Fig. 6). The maximum retention time is attained at temperatures at which water has not yet been liberated completely (its amount only approaches zero); the retention times then decrease with additional temperature rise, the complexes becoming mere adsorbents.

Pyridine and 3-methylpyridine were sorbed into the free space exceedingly strongly[3].

When the tetracyano complex is heated to 210°C, the third ammonia molecule is released, motion occurs in the lattice, the cavities, however, remain preserved and therefore the sorption properties are restored[3] on cooling to 80°C. The larger size of the space in the lattice after the loss of the ammonia which is a part of the host component of the genuine $M(NH_3)_2M'(CN)_4 \cdot n$ G clathrate, manifested itself in extended retention times (Table I). On additional temperature rise the retention times shortened; no changes in the space of the lattice occurred any more. When the tetracyano complex was heated at 230°C for 8 h, the lattice was disturbed and the sorption capability vanished.

For the analogous $Zn(NH_3)_4Ni(CN)_4 \cdot n \, H_2O$ complex, the same motion in the lattice was observed after the loss of the third ammonia molecule, and $Ni(CN)_2 \cdot Zn(CN)_2 \cdot NH_3$ was identified by X-ray measurements[4,21].

The other compounds of the host components also exhibited a clathrate nature if prepared in the hydrated form. Fig. 9 shows the chromatogram of a $C_7 - C_9$ n-alkane mixture obtained by using the hydrated form of $Ni(NH_3)_4Pt(CN)_4 \cdot 0.5 \, H_2O$ (prepared by Procedure *1*) as the stationary phase.

The effect of column temperature on the separation of a $C_9 - C_{13}$ n-alkane mixture for a stationary phase of $Ni(NH_3)_4Pt(CN)_4 \cdot 2 \, H_2O$ (Procedure *1*) is shown in Fig.
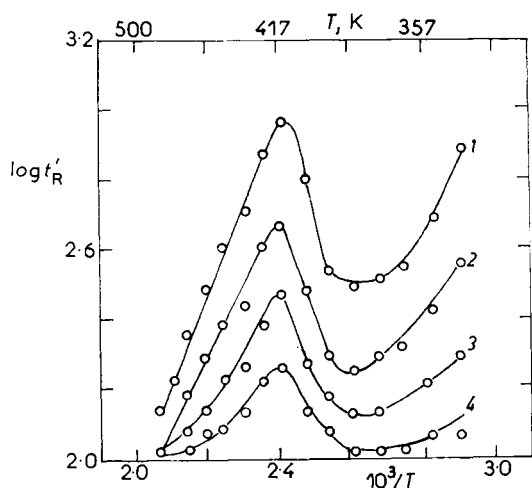

FIG. 7

Dependence of the net retention times on column temperature for $C_{11} - C_{14}$ n-alkanes using stationary phase of 20% (m/m) $Cu(NH_3)_4Ni(CN)_4 \cdot 3 \, H_2O$. *1* C_{14}, *2* C_{13}, *3* C_{12}, *4* C_{11}

10. The retention times shortened with increasing temperature so that at 200°C, a single peak was observed. After heating the column to 210°C the initial number of peaks was preserved, the retention times, however, were shorter.

TABLE I

Change in retention times of $C_{11}-C_{14}$ paraffins using $Cu(NH_3)_4Ni(CN)_4 . n H_2O$ as the stationary phase, after heating to 210°C

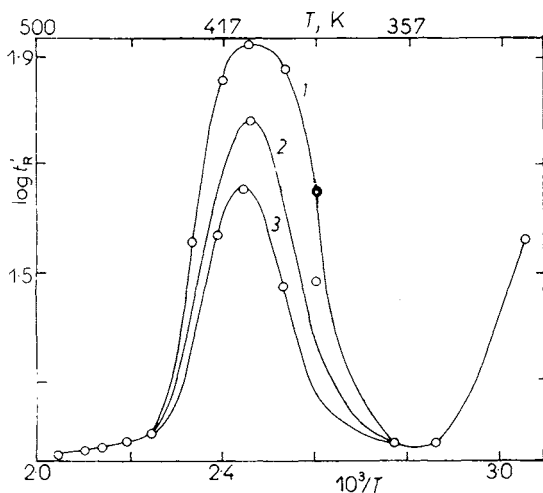| Paraffin	t'_R, s							
	before heating				after heating to 210°C			
C_{11}	120	135	180	135	185	165	150	105
C_{12}	150	130	255	130	330	240	225	135
C_{13}	195	300	465	270	675	465	405	195
C_{14}	345	630	930	510	3 195	1 035	855	345

FIG. 8

Dependence of the net retention times on column temperature for C_1-C_{13} alcohols using $Cu(NH_3)_4Ni(CN)_4 . 3 H_2O$ as the stationary phase. *1* C_3, *2* C_2, *3* C_1
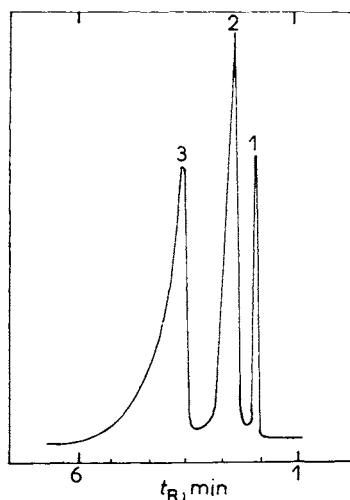

FIG. 9

Gas chromatogram of a C_7-C_9 n-alkane mixture (1 : 1 : 1) using $Ni(NH_3)_4Pt(CN)_4 .$ $. 0.5 H_2O$ as the stationary phase. $l = 1.5$ m, $d_c = 3$ mm, $t_c = 40$°C. Peaks: *1* C_7, *2* C_8, *3* C_9

$Zn(NH_3)_3Ni(CN)_4 . 0.5 H_2O$ used as a stationary phase for the GC of C_7-C_9 n-alkanes also exhibits sorption properties at temperatures of liberation of water (Fig. 11).

The simple models for the host components, *viz.* hydrated double cyanides $MM'(CN)_4 . n H_2O$, also exhibit sorption properties when used as a GC stationary phase at a suitable column temperature (Fig. 12); different amounts of water can be bonded in the complex.

The anhydrous compounds, on the other hand, do not display sorption properties even if used as stationary phases in the static mode. Their IR spectra and X-ray patterns remain unaltered (Fig. 13). The thermogravimetric curve in Fig. 13 indicates that a mere surface adsorption takes place even with so strong ligands as methyl-pyridine; there is no space in the lattice available for clathration.

Stationary phase of $Cd(en)Ni(CN)_4 . 2 C_6H_5NH_2$ clathrate, with a nitrogen in the functional group, separates organic nitrogen substances, but it does not separate C_1-C_3 alcohols or C_6-C_8 alkanes. These alkanes were partly separated at 90°C on $Cd(en)Pd(CN)_4 . 2 C_6H_6$ stationary phase prepared by Procedure *1*;
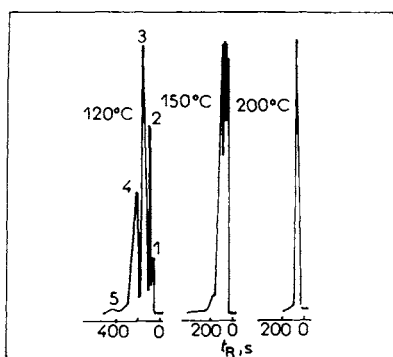
FIG. 10

Gas chromatogram of a C_9-C_{13} n-alkane mixture using $Ni(NH_3)_4Pt(CN)_4 . 2 H_2O$ as the stationary phase. Mixture composition as in Fig. 3. $l = 1.5$ m, $d_c = 3$ mm. TA behaviour of the stationary phase: $2 H_2O \uparrow$ $40-200°C$ ($n \rightarrow 0$). Peaks: **1** C_9, **2** C_{10}, **3** C_{11}, **4** C_{12}, **5** C_{13}
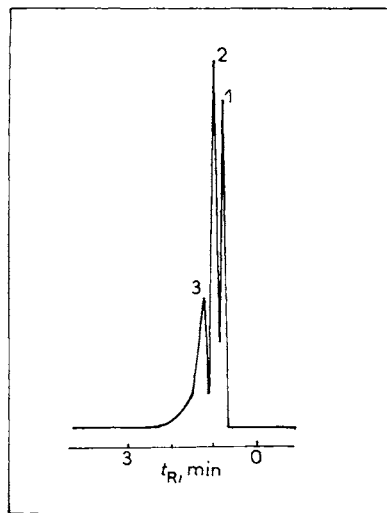
FIG. 11

Gas chromatogram of a C_7-C_9 n-alkane mixture (1 : 1 : 1) using $Zn(NH_3)_3Ni(CN)_4 .$ $. 0.5 H_2O$ prepared by Procedure 1 as the stationary phase. $l = 0.5$ m, $d_c = 3$ mm, $t_c = 60°C$. TA behaviour of the stationary phase: $0.5 H_2O \uparrow 37-87°C$ ($n \rightarrow 0$). Peaks: **1** C_7, **2** C_8, **3** C_9

benzene, methylpyridine, and pyridine were separated on this phase at 70, 170, and 190°C, in agreement with the decomposition[20] of this compound.

The results can be summarized as follows:

Only compounds in which a guest component G or water is present are capable of clathrating other organic compounds during the sorption process. The maximum space in the lattice forms as early as the synthesis stage, even if a nonstoichiometric quantity only is clathrated. In suitable circumstances, *e.g.*, if the compounds are used as gas-chromatographic stationary phases, the free space can be filled by sorbates. Sorption and resorption capability could not be observed if the substances had been heated to so high temperatures that the lattice constituting the space for clathration had been disturbed. A similarly changed structure was found[20] during the isothermal heating of clathrates of the type in question up to temperatures at which the guest component content had yet attained zero value $(n = 0)$.

The models for the host components were obtained in three forms, *viz.* $M(en)_m$ . . $M'(CN)_4$. $n\ H_2O$, $M(NH_3)_m M'(CN)_4$. $n\ H_2O$, and $MM'(CN)_4$. H_2O. The water

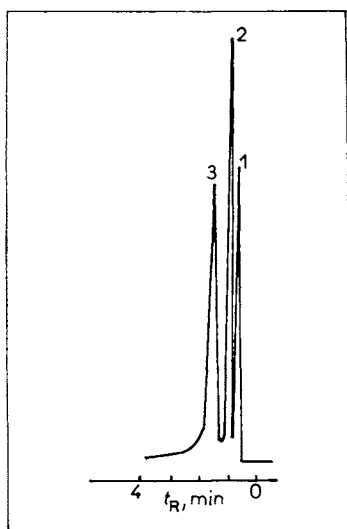
FIG. 12

Gas chromatogram of a C_7-C_9 n-alkane mixture $(1:1:1)$ using $ZnNi(CN)_4$. H_2O as the stationary phase. $l = 1\cdot5$ m, $d_c =$ $= 3$ mm, $t_c = 70°C$. TA behaviour of the stationary phase: $H_2O \uparrow 34-150°C$ $(n \to 0)$. Peaks: 1 C_7, 2 C_8, 3 C_9
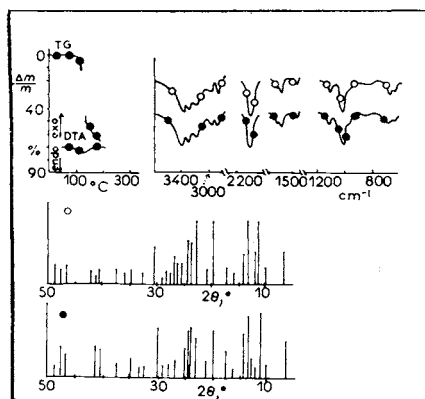

FIG. 13

Infrared spectra, derivatograms and X-ray diffraction patterns of $Cu(en)_2Ni(CN)_4$; attempted sorption of β-picoline at 25°C. Temperature program 6°C min^{-1}. ○ $Cu(en)_2Ni(CN)_4$, ● $Cu(en)\ Ni(CN)_4 +$ $+$ β-picoline

content was found to be the factor determining the behaviour of the host components of the tetracyano complex clathrates. Compounds that did not contain any organic component G or any amount of water did not exhibit clathration capability.

All of the clathrates studied can be employed at temperatures up to 150 or 220°C, hence, at higher temperatures than Werner complex clathrates. While losing G or water during the heating, the tetracyano complexes retain their individuality[25] and they remain clathrate compounds[4] as long as $n \rightarrow 0$, retaining also their sorption capability. If only surface-adsorbed, organic substances are not amenable to substitution or clathration.

REFERENCES

1. Sopková A.: *Thesis.* Komenský University, Bratislava 1970.
2. Sopková A., Jesenák V., Chomič J., Dzurillová M., Matejčíková E., in the book: *Thermal Analysis. Theory, Inorganic Chemistry* (G. Lipthay, Ed.), p. 863. Akademiai Kiadó, Budapest 1975.
3. Šingliar M., Sopková A.: Petrochémia *17*, 18 (1977).
4. Sopková A.: J. Mol. Struct. *75*, 81 (1981).
5. Sopková A., Bubanec J.: J. Mol. Struct. *75*, 73 (1981).
6. Gavalek G., Trautmann H., Koenecke K. G.: Chem. Techn. *16*, 409 (1964).
7. Bhattacharayya A. C., Bhattcharjee A.: Anal. Chem. *41*, 2053 (1969).
8. Bhattacharayya A. C., Bhattcharjee A.: J. Chromatogr. *41*, 446 (1969).
9. Kemula W.: Chem. Anal. (Warsaw) *13*, 1013 (1968).
10. Makin E. E.: Separ. Sci. *9*, 541 (1974).
11. Smolková E., Krýsl S.: J. Chromatogr. *184*, 1013 (1980).
12. Šingliar M.: *Proceedings of the Conference Pokroky a využitie analytickej chémie v praxi* (*Advances in the Use of Analytical Chemistry in Practice*), Piešťany 1982, p. 60.
13. Sopková A., Králik P.: *Proc. Intern. Microsymp. Clathrate and Molecular Inclusion Phenomena,* Vysoké Tatry — Stará Lesná 1981, p. 87.
14. Gérard N., Barret P.: Fr. 921010.
15. Bhatnagar W. H.: *Clathrate Compound*, p. 23. Chand, N. Delhi 1968.
16. Davies J. E., Dampster A. D., Suzuki S.: Spectrochim. Acta *A 30*, 1183 (1973).
17. Suzuki S., Orville-Thomas W. J., Sopková A., Skoršepa J.: J. Mol. Struct. *54*, 1 (1979).
18. Mathey Y., Mazieres C.: Can. J. Chem. *52*, 3637 (1974).
19. Ludi A., Hügi R.: Helv. Chim. Acta *50*, 1283 (1967).
20. Skoršepa J.: *Thesis.* Šafárik University, Košice 1980.
21. Sopková A., Bubanec J., Mišura D., Šingliar M., Görnerová T.: *Proc. IXth Intern. Conf. Coordination Chemistry.* Prague 1978, p. 114.
22. Sopková A., Černák J., Králik P., Bubanec J., Šingliar M.: Pol. J. Chem., in press.
23. Sopková A., Bubanec J.: J. Therm. Anal. *12*, 97 (1977).
24. Dunaj-Jurčo M., Černák J., Sopková A., Králik P.: *Proc. Intern. Microsymp. Clathrate and Molecular Inclusion Phenomena.* Vysoké Tatry — Stará Lesná 1981, p. 185.
25. Gutmann V., Resch G.: Z. Chem. *19*, 406 (1979).
26. Černák J., Kappenstein G.: Inorg. Chim. Acta *85*, 219 (1984).