

The Solvent Dependence of the Sorptive Abilities of Tetracyanocomplexes

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(Received: 12 May 1983; revised 19 September 1983)

Abstract. The two different types of tetracyanocomplexes $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ and $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ have been examined as sorptive materials in a simple contact with benzene, after their modification with auxiliary solvents and their use in gas chromatographic experiments. All forms of sorption experiments show identical characteristics from the view of the sorption of aromatic compounds as exemplified by benzene. The tetracyanocomplexes exhibit a permanent capability of sorption, even when heated to a temperature of 260°C and show a separation ability towards sorbed materials depending on the solvent used and on the degree of thermal degradation of the tetracyanocomplex. The products of the modification and sorption (in static and dynamic) experiments have been characterized by IR spectroscopy, X-ray patterns and by thermal analysis.

Key words: metal tetracyanocomplex hydrate, clathrate sorption, identification, properties and use of metal cyano complex.

1. Introduction

In our previous work [1–4] we have checked experimentally on the possibility of using the tetracyanocomplex clathrates $[\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}]$ and $[\text{M}(\text{en})_m\text{M}'(\text{CN})_4 \cdot n\text{G}]$ as sorbents. The model compounds $[\text{MM}'(\text{CN})_4 \cdot n\text{H}_2\text{O}]$, $[\text{M}(\text{NH}_3)_m\text{M}'(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ and $[\text{M}(\text{en})_m\text{M}'(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ were also found to be effective as sorptive materials in modelling experiments, using both static and dynamic contact with some organic compounds applied as potential sorbates. These properties of all the tetracyanocomplexes tested were present even above 200°C.

The behaviour of these compounds is different from that of other types of clathrates, e.g., Werner type clathrates [5–9], because of their greater thermal stability.

The presence of the organic guest in the clathrates and the water in the model compounds gives rise to their layered structure. It is thus possible to substitute the organic guest component in the clathrate compounds (or the H₂O component in the model compounds) by other

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appropriate organic compounds. The presence of the organic guest component or of the water, designated as n in the above formulae and differing from zero determines the sorption behaviour [3].

The sorptive abilities of water containing tetracyanocomplexes such as $[\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ [1], $[\text{NiPt}(\text{CN})_4 \cdot 6\text{H}_2\text{O}]$ [2] and $[\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ [10] are similar to that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and other compounds described in the work of Altenau [11]. $[\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ [12] and $[\text{NiPt}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ [13] are known to have layered structures and the interlayer space has been shown to be available for the sorption [2] of organic compounds. The structures of $[\text{Zn}(\text{en})_2][\text{Ni}(\text{CN})_4]$, and $[\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ [10] have also been correlated with their sorptive abilities.

The best method of depositing the tetracyanocomplex on the inert support when used as a stationary phases was found to be in the form of a suspension in a chosen auxiliary medium. Several types of polar or nonpolar solvents have been studied with $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ and $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$. The enclosing of polar and nonpolar compounds in the structure of these tetracyanocomplexes was also followed in this study.

2. Experimental

2.1. MATERIALS AND METHODS

The tetracyanocomplexes $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ were prepared [3, 14] in two forms, differing only in the method of drying: $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ (I) and $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ (II). The compound $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ was prepared according to the method given in [15].

The following mixtures were tested for sorption or separation: (A) n -paraffins C_5 – C_9 , (B) aromatic compounds (benzene, toluene, *o*-, *m*-, *p*-xylene), (C) n -alcohols C_1 – C_4 . Distilled water, benzene, hexane, cyclohexane, methanol, and 3-methylpyridine (β -picoline) were used as auxiliary solvents. All the materials used were of analytical reagent quality (Lachema, Brno, ČSSR).

The *identification* of the tetracyanocomplexes and of the products produced after sorption or their recovery from auxiliary solvents was carried out using thermal analysis, IR spectroscopy and X-ray diffraction.

IR spectra were measured in KBr discs using Perkin Elmer 557, and Specord 75 spectrometers.

The *thermal decomposition* was studied using a Derivatograph instrument (MOM 102, Budapest, Hungary).

X-ray photographs were measured using the powder technique (Micrometa 2, Chirana, Praha, ČSSR).

The *sorption experiments* were performed in three ways:

(a) *A simple contact* of the tetracyanocomplex with benzene or methanol in a glass vessel at 25°C for a period of 72 hours.

(b) *A dynamic contact* of the tetracyanocomplex with refluxing benzene in a Soxhlet apparatus for a period of 10 hours.

(c) The form of a *suspension* in an *auxiliary medium* was found to be the optimal mode for the use of tetracyanocomplexes as stationary phases in GC. The following preparative method was used: to a volume of the solvent 10% of the tetracyanocomplex and 90% by weight of the inert support (Chromosorb W/NAW, 80/100 mesh, Supelco, Inc. Bellefonte, U.S.A.) was added. The solvent was evaporated off on a water bath (100°C). In this way a dry, loose filling material for the chromatographic column was obtained.

The same preparation was used for the comparison of the structural changes of the tetracyanocomplex. The clathrate $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ or the tetracyanocomplex $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ was heated in the auxiliary solvents which were then removed by evaporation. The products were then examined by thermal analysis (TA), IR spectroscopy and X-ray diffraction.

The materials mentioned above were tested in a gas chromatograph (Chrom 4, Laboratorní přístroje, Praha, ČSSR). Glass columns of length 1.5 m, ID 3 mm were used. The flow rate of the carrier gas (nitrogen) was $24 \text{ cm}^3 \text{ min}^{-1}$.

3. The Tetracyanocomplexes $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$

Two forms of $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ (**I** and **II**) differing in the guest content, n , were obtained depending on the method of drying.

3.1. IR SPECTRA

The IR spectra of compounds (**I**) and (**II**) are shown in Figures 1a and 4a and they show the characteristic absorptions of CN, OH (H_2O) groups and of other groups.

3.2. THERMAL ANALYSIS

$[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ (**I**) on heating (heating rate 5° min^{-1}) begins to decompose at 34° due to the loss of its water content in an endothermic process with a maximum in the DTA and DTG curves at 63°C (Figure 1, curve a). The weight loss up to 150°C is 6% and this is followed by a very slow gradual loss of 1% up to 308°C in a very slightly endothermic process. This total of 7% is equivalent to one water mole content (7.3% theor.). The exothermic process between $321\text{--}500^\circ\text{C}$ is linked with the decomposition of the residual lattice.

$[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ (**II**) is thermally less stable than (**I**); between $25\text{--}175^\circ\text{C}$ the whole water content is lost, a 17% weight loss (theor. 16.5%) with a maximum (Figure 2) at 115°C on the DTA curve.

The water content of both $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ (**I**) and (**II**) is approaching zero at temperatures between $150\text{--}170^\circ\text{C}$, with the loss being complete at 310°C . Thus as $n \rightarrow 0$, these compounds should show a sorptive ability towards organic compounds even at temperatures higher than 100°C .

4. Modelling Sorption Experiments

We performed the study of the behaviour of $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ in three ways. As shown in Sections 4.1 and 4.2 $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ was used with benzene and methanol. As shown in Section 4.3 $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ and $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ were used after their recovery from auxiliary solvents in order to prepare them as stationary phases.

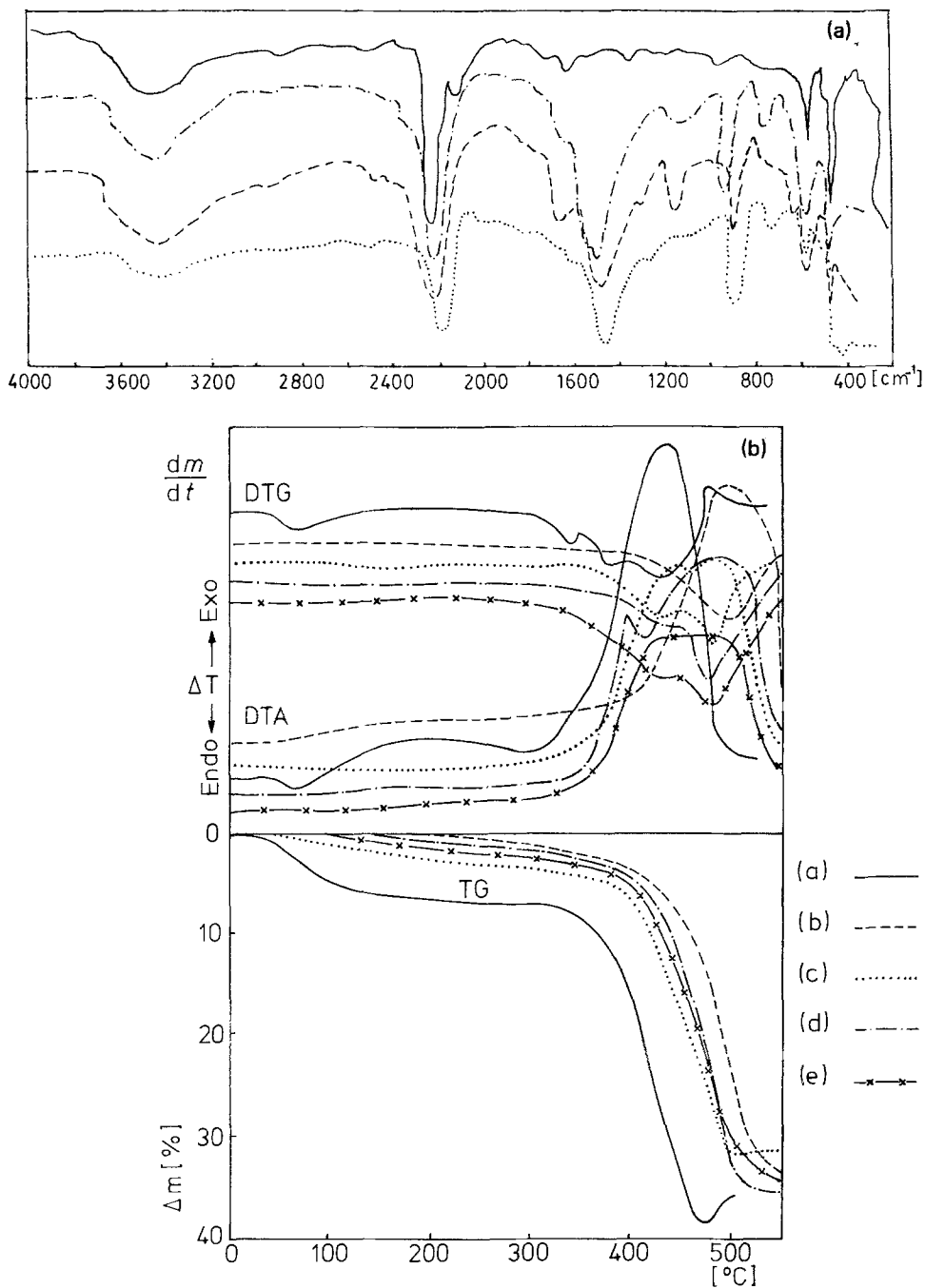


Fig. 1. The IR spectra and thermal analysis curves of $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ after the sorption experiments with benzene. (a) $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ original compound; (b) $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}] + \text{C}_6\text{H}_6$ (sorption at 25°C , measured immediately after experiment); (c) $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}] + \text{C}_6\text{H}_6$ (sorption at 25°C , measured two months after sorption experiments); (d) $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}] + \text{C}_6\text{H}_6$ (sorption at 80°C measured two months after sorption experiments); (e) $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}] + \text{CH}_3\text{OH}$ (sorption at b. pt. of CH_3OH – two months after sorption experiments).

4.1. THE SORPTION AT 25°C IN A SIMPLE CONTACT

The sorption of benzene and methanol at 25°C in a simple contact with $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ changed the compound but without any colour change.

4.1.1. *Spectra*

The IR spectra of the products obtained after treatment with benzene showed all the characteristics of benzene as well as the frequencies of the tetracyanocomplex (Figures 1b–1d).

We made the measurement of IR spectra immediately after finishing the sorption experiments (Figure 1b) and two months after the experiments (Figure 1c). There are only small differences between these two spectra. This phenomenon, together with the fact that the products were isolated, washed and dried in a desiccator before their identification, plus the results of the TA experiments exclude the possibility of adsorption of benzene on the surface of the tetracyanocomplex. The product is designated as $[\text{ZnNi}(\text{CN})_4 \cdot a\text{C}_6\text{H}_6 \cdot b\text{H}_2\text{O}]$, since the IR spectra indicate the presence of both C_6H_6 and H_2O .

4.1.2. *Thermal Analysis (TA)*

The thermal analysis curves of the products of sorption are shown in Figure 1 together with that of the original untreated compound. The thermogravimetric (TG) curve shows a gradual weight loss between 50–350°C (the original 1 mol H_2O content of 7%). A similar effect is seen in the curves recorded two months after the isolation of the product (Figures 1c–1e).

The greater thermal stability of the product resulting from the contact is due to the presence of the sorbed benzene and the compound releases its first component very slowly in a more prolonged interval (50–350°C) as compared with $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ (Figure 1a) and $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ Figure 2 (34–150 resp. up to 308°C).

4.2. MODELLING SORPTION EXPERIMENTS IN DYNAMIC CONDITIONS

The experiments performed in a Soxhlet apparatus at the boiling temperature of benzene and methanol gave products of the same quality immediately after preparation and also two months later.

4.2.1. *IR Spectra*

The situation after the sorption of benzene in the layered host compound $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ is shown in Figure 1d. The small change of the main νCN frequency at 2180 cm^{-1} is caused by a higher degree of degradation of the CN groups due to the partial exchange of water. The presence of H_2O is still indicated by the νOH (3450, 3640) and δHOH (1634 cm^{-1}) frequencies. The characteristic band of the included benzene, νCH , is seen at 700 cm^{-1} .

The product $[\text{ZnNi}(\text{CN})_4 \cdot a\text{C}_6\text{H}_6 \cdot b\text{H}_2\text{O}]$ obtained at 80°C and 25°C has two kinds of sorbed guest G_1 and G_2 , which are present in non-stoichiometric amounts and filling the volume available for sorption.

4.2.2. *Thermal Analysis*

The TA curves of the product are shown in Figures 1d and 1e. The product obtained after the sorption of benzene at about 80°C (when the lattice spacing is enlarged and more

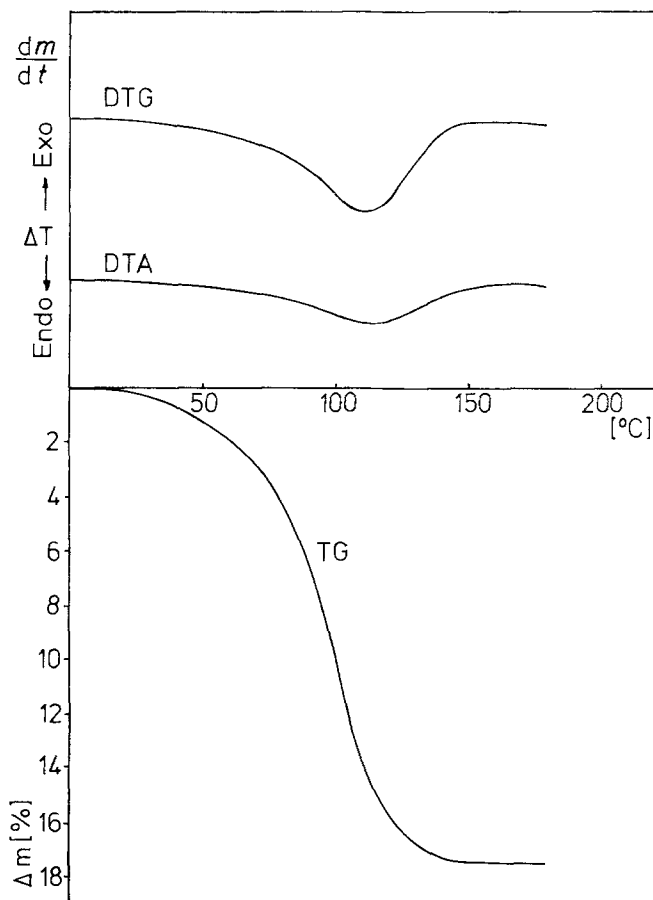


Fig. 2. Thermal analysis curves of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$.

accessible) is stabilised by the presence of benzene. But the same weight loss (5%) exists as in case (b). It begins 20°C higher than in the product of sorption made at 25°C , the TG curve shows the same loss between $70\text{--}310^\circ\text{C}$.

4.3. THE MODIFICATION OF TETRACYANOCOMPLEXES WITH AUXILIARY SOLVENTS

Many types of clathrates [3, 5–9] and tetracyanocomplexes [1, 14] have been used successfully as stationary phases. In previous experiments, tetracyanocomplexes were modified with auxiliary solvents before their use as stationary phases. The solvents H_2O , methanol, and cyclohexane had similar effects on tetracyanocomplexes (i.e. no change of the structure) but β -picoline gave a different result.

Therefore, all measurements were made after the recovery of the tetracyanocomplexes from the solvents.

4.3.1. The Effects of Auxiliary Solvents on $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$

Figure 3 shows the IR spectra of $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ recorded after its recovery from the various auxiliary solvents. The structure of the clathrate $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$

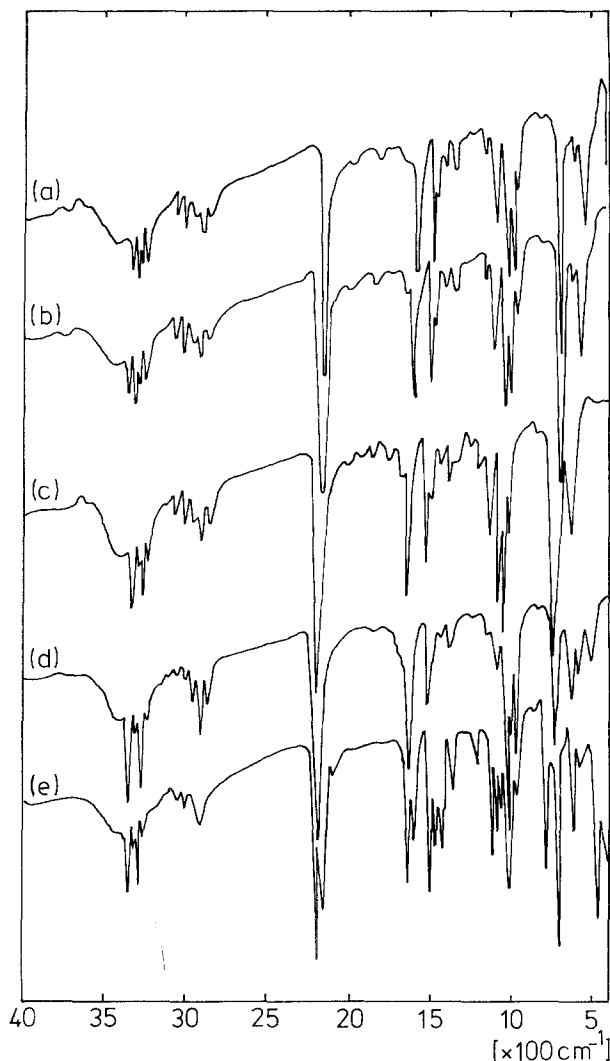


Fig. 3. IR spectra of $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$. (a) original compound, (b) after recovery from water; (c) after recovery from cyclohexane; (d) after recovery from methanol; (e) after recovery from β -picoline.

remains unchanged until 170°C and after its recovery from water (Figure 3b) or cyclohexane (Figure 3c) it remain unchanged.

In the case of methanol (Figure 3d), a small change of the absorption intensity was found in the region of 1000 and 700 cm^{-1} . The presence of two guests (methanol and benzene in non-stoichiometric amounts) can be deduced from Figure 3d where both benzene and methanol bands can be seen.

The IR spectra (Figures 3b-d) have the same main characteristics as those of the original compound (Figure 3a). After recovery from β -picoline (Figure 3e) the spectrum of the product differs strongly from that of the original (see Section 4.3.3.).

4.3.2. The Effects of Auxiliary Solvents on $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$

X-ray diffraction measurements have shown that clathrates of the $[\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{G}]$ and $[\text{M}(\text{en})_m\text{M}'(\text{CN})_4 \cdot n\text{G}]$ types have the $[\text{MM}'(\text{CN})_4]$ unit as the basic building block. Thus, the study of the simple tetracyanocomplex simultaneously with the clathrate is of importance.

The IR spectra of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ recovered from water (curve b), cyclohexane (curve c), methanol (d) and β -picoline (e) are shown in Figure 4.

The IR spectra compared with that of intact $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ (Figure 4a) are unchanged in the case of recovery from H_2O , cyclohexane and CH_3OH . The broad band

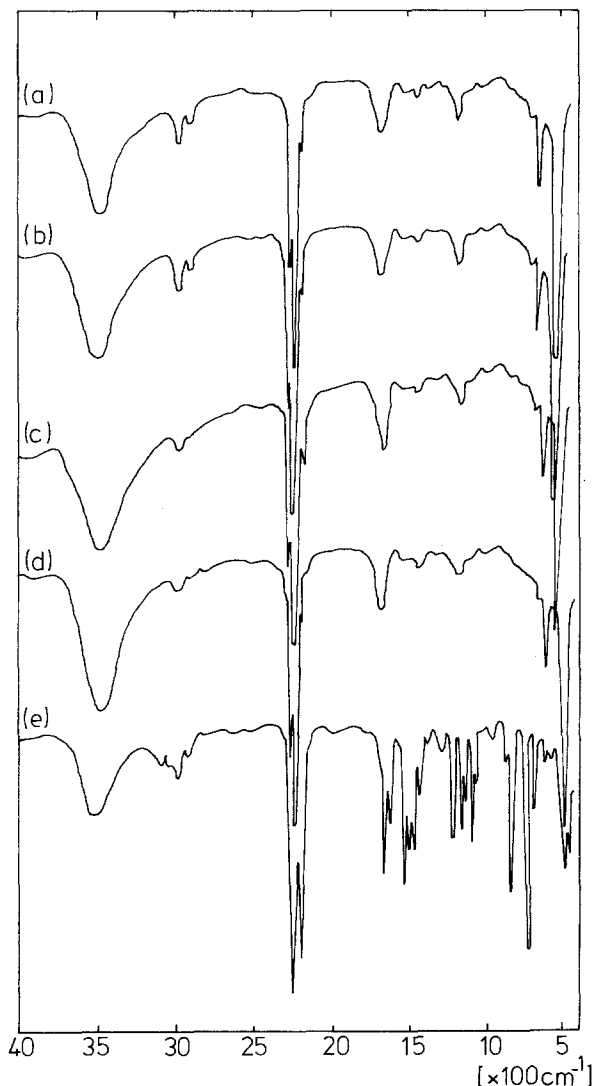


Fig. 4. The IR spectra of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$. (a) original compound; (b) after recovery from water; (c) after recovery from cyclohexane; (d) after recovery from methanol; (e) after recovery from β -picoline.

ascribed to the water molecule linked by hydrogen bonds is more intense in the case of recovery from water.

The X-ray patterns shown in Figure 5b–d confirm that the structural patterns of the tetracyanocomplex modified by auxiliary solvents do not differ appreciably from that of the original compound $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ (a).

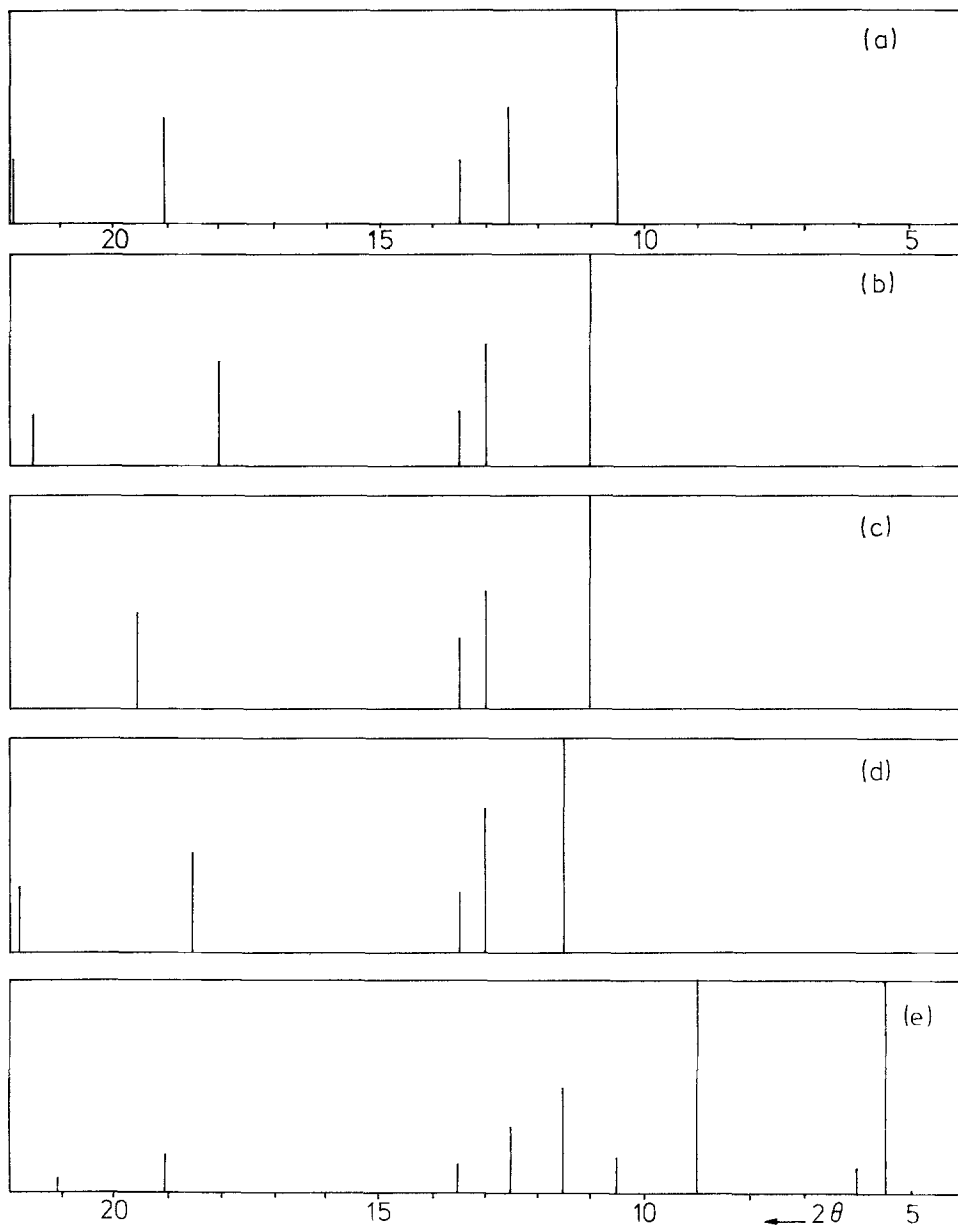


Fig. 5. X-ray powder patterns of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$. (a) original compound; (b) after recovery from water; (c) after recovery from cyclohexane; (d) after recovery from methanol; (e) after recovery from β -picoline.

4.3.3. The Effects of an Auxiliary Solvent Acting as a Strong Ligand

A different result has been obtained with $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ modified by β -picoline as an auxiliary solvent. This solvent can act as a strong ligand linking to the metal cations and thus producing a change in the structure of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ similar to the changes found in other clathrates of tetracyanocomplexes.

The IR spectra and TA curves show that our product differentiates its water content; it behaves similarly to $[\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot x\text{H}_2\text{O}]$ which has been documented in the literature [12]. We have really $[\text{Zn}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}]$ according to IR spectra and the β -picoline is substituting the H_2O in the inner coordination sphere first. Then this produces an increase in the spacing between the layers of the tetracyanocomplexes, as shown by diffraction measurements [16,17]. This fact then enables other compounds to enter the interlayer space and interact with the surrounding individual layers of the structure of tetracyanocomplexes. Therefore the presence of β -picoline influences strongly their sorptive abilities (Figures 7 and 8) for other organic compounds.

Thermal decomposition also confirms the modification made by β -picoline on $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$. The thermal stability of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ (really $[\text{Zn}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}]$) is greater by up to 64°C . On heating it loses up to 160°C the guest β -picoline – 18.2% (theor. 18.34%) in an endothermic way. In the next step two moles of picoline coordinated to Zn^{II} ion are released with a weight loss of 33.7% (theor. 36.9%) between 160 – 340°C . Then the lattice decomposes in a strong exothermic process with the weight loss being complete at 500°C . Thus, after recovery from β -picoline, the structure is changed with H_2O being substituted by picoline giving a compound similar to the Werner-type complex clathrates [7, 8, 16]. After identification by TA and IR spectra we propose the formula $[\text{Zn}(\text{pic})_2\text{Ni}(\text{CN})_4 \cdot \text{pic}]$.

The diffraction photographs also show the effects of the individual auxiliary solvents (Figures 5a-e). We may conclude that the compound $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ modified by water, cyclohexane and methanol have common features which differ markedly from the compound modified by β -picoline (Figure 5e).

4.4. THE USE OF $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ AS A STATIONARY PHASE AFTER ITS RECOVERY FROM AUXILIARY SOLVENTS

With different auxiliary solvents modified compounds are effective in different ways as stationary phases in GC when tested against the three mixtures of polar and nonpolar hydrocarbons. These differences arise because of the different separations of the layers in the structure [6] after the exchange of ligands (β -picoline \rightarrow H_2O) by the use of an auxiliary solvent.

The separations have been effected stepwise from 70°C in steps of 10°C until 160°C , and in the case of modification by β -picoline until 260°C .

4.4.1. Water, Cyclohexane, and Methanol as Auxiliary Solvents

The essential feature of $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ tested in the simple static sorption experiments – its capability (Figure 1) to sorb benzene (tested at 25 and 80°C) is also shown in GC experiments. Modification of the tetracyanocomplex, even with water, allows it to sorb benzene in an analogous temperature interval until 70°C (see its chromatograms in Figure 6).

If water is used as solvent (Figure 6a) then the mixture of aromatic compounds was separated, but *o*-, *m*-, and *p*-xylene isomers were not separated. In the case of cyclohexane

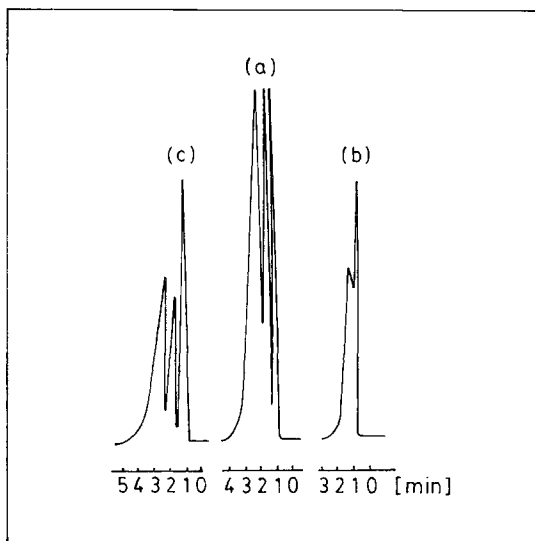


Fig. 6. $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ used as stationary phase in GC at 70°C (benzene, toluene [*o*-, *m*-, *p*-xylene] 1 : 1 : 1) after recovery from (a) water; (b) cyclohexane; (c) methanol.

(Figure 6b), the benzene and toluene were eluted together from the column, with the xylene peak being just resolvable.

Methanol as an auxiliary solvent (Figure 6c) improved the separation of the components, the retention times increased, but the xylene isomers were still not separated.

In the separation of C_5 - C_6 alkanes on the stationary phase (Table I) modified by different solvents (water, cyclohexane or methanol), octane and nonane were separated, but the other

Table I. Elution characteristics of mixtures at 70°C using modified $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ as the stationary phase

Sorbed compound	Stationary phase								
	modified with H_2O			modified with cyclohexane			modified with methanol		
	t'_R (min)	$W_{1/2}$ (mm)	R	t'_R (min)	$W_{1/2}$ (mm)	R	t'_R (min)	$W_{1/2}$ (mm)	R
pentane	0.7	3	-	0.75	7	-	1.0	4	-
hexane	0.7	3	-	0.75	7	-	1.0	4	-
heptane	0.7	3	-	0.75	7	-	1.0	4	-
octane	0.95	2.5	0.9	0.9	8	0.2	1.25	3	0.71
nonane	1.5	6	1.69	1.15	7.5	0.32	1.9	6	1.44
benzene	0.8	3	-	0.65	3	-	1.0	4	-
toluene	1.15	3	1.16	0.85	6	0.44	1.3	3.5	1.71
<i>o</i> -, <i>m</i> -, <i>p</i> -xylenes	1.9	12	1.0	1.0	14	0.15	2.0	14	0.69
methanol	1.25	6.5	-	0.9	9	-	1.65	8	-
ethanol	1.25	16.5	-	0.9	9	-	1.65	8	-
propanol	1.65	14	0.29	0.9	9	-	1.65	8	-
butanol	2.05	28	0.19	1.5	11.5	0.54	1.95	12	0.3

alkanes were eluted together. The separation is relatively the best in the case of methanol. The mixture of alcohols (C_1-C_4) was only slightly separated (Table I).

In general, after the modification with H_2O , cyclohexane and methanol the chromatographic studies have shown some interesting and fine differences among the tested filling materials.

In the tables the adjusted retention times are given and these were calculated from:

$$t'_R = t_R - t_M$$

t_R = uncorrected retention time (in given chromatograms),

t_M = elution time of an unretained compound,

$W_{1/2}$ = the width of the peak at half height,

R shows the separation value:

$$R = \frac{2(t_{R2} - t_{R1})}{W_1 + W_2}$$

t_{R1} and t_{R2} refer to the two specified components in the chromatogram.

W_1 and W_2 are the widths at their bases of the chromatographic peaks.

From the results obtained (Table I) it is possible to conclude that the material modified with a polar organic solvent (methanol) has better separative properties for nonpolar compounds (*n*-paraffins) and vice-versa (cyclohexane-*n*-alcohols). This is probably due to two effects. The extraction of water from the clathrate and/or the blocking of active centres. The retention time for aromatic compounds is probably connected with the free space available for molecules with such relatively large volume. In the case of materials modified with cyclohexane this is blocked. On the other hand, some bipolar interaction may be present in the case of primary alcohols and materials prepared with water and methanol.

The higher interaction of aromatic compounds (longer retention times) is in relative agreement with our experiments described in Section 4.2 in the Soxhlet apparatus – mainly the interactions and also the diffusion of the mixture components at lower and higher temperatures. The polarity and the higher boiling points of the auxiliary solvents partly causes the increase of the retention time of the polar substances.

4.4.2. β -Picoline as an Auxiliary Solvent

Very interesting results were obtained from filling materials prepared after their recovery from β -picoline. The compounds had more selective sorptive properties. The separation has been improved stepwise (160°C – first relative optimum) with temperature and the optimal conditions (second optimum) were found (Figure 7) at 220°C (see Table II). This agrees with the results of the thermal decomposition of this modification (up to 160°C the guest β -picoline is released and, between 160 and 340°C, the β -picoline, acting as a ligand, is released).

In the case of alkanes (Figure 7a), a good separation of all the C_5-C_9 alkanes was achieved. The mixture of aromatic compounds (Figure 7b) was also well separated with the ortho isomer of xylene also being separated from the two other isomers. The separation of the mixture of alcohols was not very effective, with butanol (Figure 7c) only being separated from the other three components.

Figure 8 shows that 260°C is the optimal separation temperature for aromatic compounds with the meta and para isomers of xylene being well separated from the ortho isomer. Both alkanes and the alcohols were eluted together at this temperature.

Because the relative free volume has been drastically changed at 220°C after the exchange

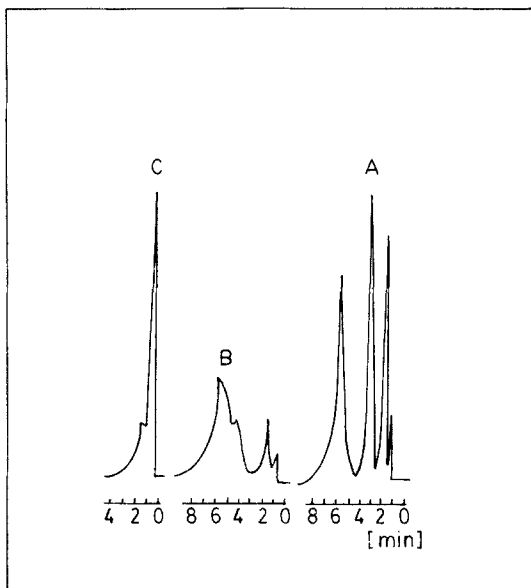


Fig. 7. $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ as the stationary phase in GC at 220 °C after modification with β -picoline using mixtures A, B and C.

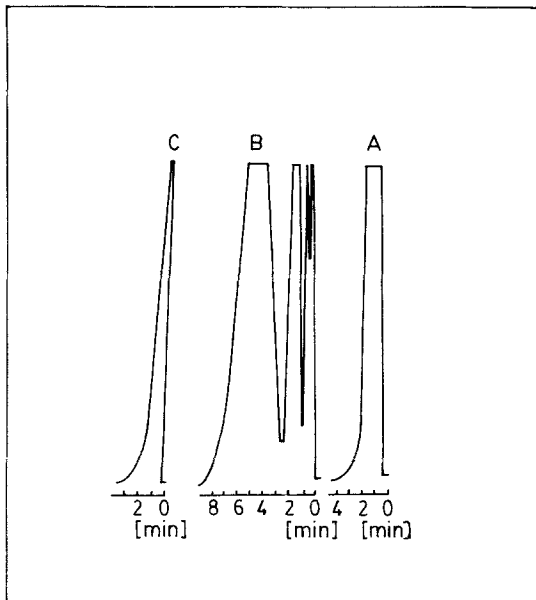


Fig. 8. $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ as stationary phase in GC at 260 °C after modification with β -picoline using mixtures A, B and C.

of ligand, it is possible to explain this phenomenon by the higher diffusion of the molecules which results in higher retention times (Table II) of the higher alkanes.

Table II. Elution characteristics of mixtures at 220°C using $[\text{ZnNi}(\text{CN})_4 \cdot 2.5\text{H}_2\text{O}]$ modified with β -picoline

Sorbed compound	t'_R (min)	$W_{1/2}$ (mm)	R
pentane	0.5	1.5	–
hexane	0.8	5	0.92
heptane	1.2	4.5	0.84
octane	2.3	10	1.51
nonane	5.95	21.5	1.68
benzene	0.6	9	–
toluene	0.9	6	0.4
<i>o</i> -xylene	4.6	30	1.94
<i>m</i> -xylene	6.0	42	0.44
<i>p</i> -xylene	6.0	30	–
methanol	0.55	0.65	–
ethanol	0.55	0.65	–
propanol	0.55	0.65	–
butanol	1.3	18	0.61

5. Conclusions

The products of the simple sorption experiments are proof of a very stable sorption of compounds.

The products of the sorption of benzene on the tetracyanocomplex $[\text{ZnNi}(\text{CN})_4 \cdot \text{H}_2\text{O}]$ under both static and dynamic conditions give very different IR spectra, X-ray powder patterns and TA curves from the original compound. All techniques showed the presence of the sorbed molecule. The measurements made after two months gave similar results, showing the absorption of the aromatic compound in the interlayer spacing. Neither temperature nor time affected the product of sorption which can be formulated as $[\text{ZnNi}(\text{CN})_4 \cdot a\text{C}_6\text{H}_6 \cdot b\text{H}_2\text{O}]$.

The tetracyanocomplexes $[\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}]$ and $[\text{Cd}(\text{en})\text{Pd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6]$ are very stable materials which retain their characteristics even after heating and recovery from auxiliary solvents.

The structure, as shown by IR spectroscopy, X-ray patterns and thermal analysis after their recovery from solvents is unchanged when using water, cyclohexane and methanol as auxiliary solvents, but the recovered material can separate aromatic compounds chromatographically (Figure 6).

β -Picoline has the strongest influence on the structure of the tetracyanocomplex, particularly at higher temperatures, resulting in the longer separation of the layers of the original tetracyanocomplex.

In general the choice of auxiliary solvent for the preparation of the suspension for the filling of GC columns determines the separation abilities of the tetracyanocomplex.

For the separation of polar compounds it is adequate to prepare the filling from the tetracyanocomplex with a nonpolar auxiliary solvent and for the separation of nonpolar compounds to use polar auxiliary solvents.

The filling prepared from methanol is able to separate hydrocarbons with longer chains.

Some affinity for organic compounds exists from the view of the compensation of the active sites (unblocked by polar compounds) which is different from the distance of fundamental layers, and influenced by the type of solvent. Using β -picoline, the structure is changed by

the presence of a new ligand and those layers are available for increasing sorption and separation of several organic compounds.

The proposed fillings are advantageous also at higher temperatures for preparative chromatography.

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