Some Less Usual Properties of Tetracyano Complexes[★]

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Abstract. The structure and reactivity of one unique molecule may be understood only in relation to its molecular surroundings. The non-stoichiometric forms of the tetracyano complexes $M(B)_m M'(CN)_4 \cdot nG$ (B = nitrogen or oxygen containing base; G = aromatic compound or H_2O, $m \geqslant 0$, $n > 0$) are understood in this respect. Their stoichiometric or non-stoichiometric forms, with voids either completely or more often partially occupied, are responsible for their observed sorptive and resorptive abilities. The effects of the surroundings are correlated with the results of thermal analysis, magnetic measurements and their sorptive abilities.

Key words: clathrate, molecular system, metal, tetracyano complex, hydrate clathrate, sorption, magnetic susceptibility.

1. Introduction

The structure and reactivity of one unique molecule may be understood only in relation to its molecular surroundings. This is valid for all compounds as well as in germanium and other solid metals [1]. It is particularly valid in a clathrate compound, where the guest molecule [2] is surrounded by the host. In this manner they form a system comprised of a number of components, each with its own properties and interrelated to those of the other components. Each part of the system is connected with the other parts.

A clathrate in the true sense shows us the simplest example – if we limit it only to a single molecule forming the host and to a single molecule forming the guest. But we know very well that there exists many molecules of the host component together with a number of molecules of the guest component in the inclusion compound. It is a real system, often with a layered host lattice structure (Fig. 1). The interactions represent the expected non-homogeneity of the structural patterns. Each change calls for further changes in all systems of the host and guest molecules (Fig. 2). The vacancies formed contribute to the properties of the macrocrystal.

In accordance with the preceding and with other ideas [2, 3–6] we may modify the definition of clathrates in the following way: clathrates are crystalline inclusion compounds which contain an ordered host lattice structure with voids, where the guest molecule can be incorporated, usually with a compositional disorder in that not all voids are filled with the guest, creating the stoichiometric or non-stoichiometric forms of clathrates. A significant guest – guest interaction can be present [7, 8].

The tetracyanocomplex $Ni(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_6$ and others have been described in the literature since 1897 with their structures becoming known fifty years later [5, 9–10]. Some of them, on standing in air or on heating, lose their ammonia content, sometimes partially. They also accept water from the air or on crystallisation from saturated aqueous ammonia

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[★] Dedicated to Professor H. M. Powell.
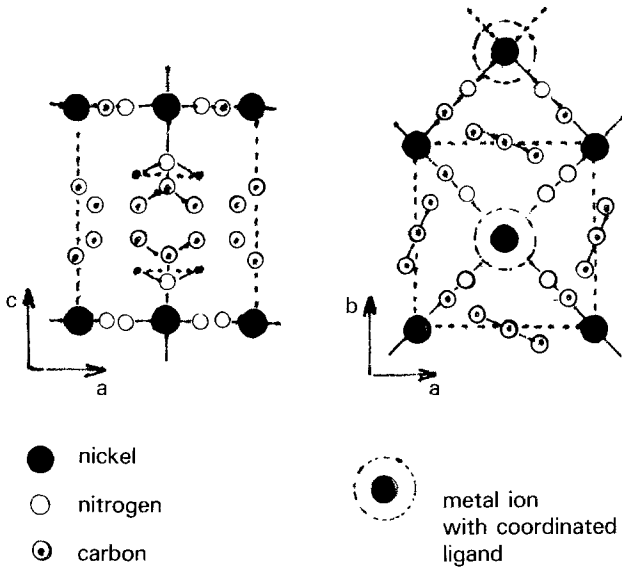[★★] Institute of Petrochemistry, 972 71 Nováky, Czechoslovakia.

Fig. 1.   Schematic representation of the inclusion of the guest molecule in the host in $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$.

solutions [5,8,11]. Model host compounds with variable water content are $Ni(CN)_2 \cdot NH_3 \cdot nH_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ [12–15]. These and other tetracyano complexes may be used [16] as sorptive material (when $n \to 0$ and where the loss of NH_3 does not significantly affect the structure). It is also possible to have two guests present: $M(NH_3)_2M'(CN)_4 \cdot aG_1 \cdot bG_2$.

Recently Iwamoto and coauthors [11] studied the reverse reaction in Hofmann-type clathrates during the substitution of their benzene content with water. They also found non-stoichiometric products.

The tetracyano complexes, being dependent on the surroundings of the host and guest molecules, exhibit a characteristic behaviour in sorption experiments and also after modification [17] with auxiliary solvents. The effects of several types of surroundings are studied.
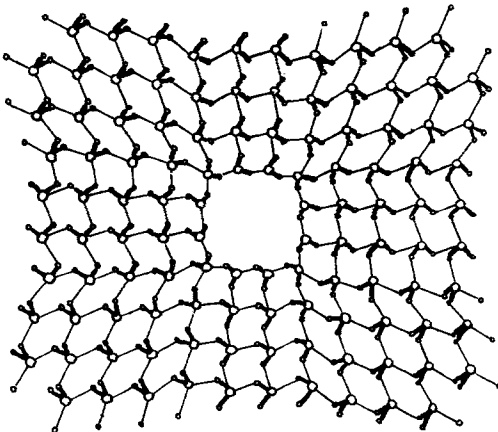

Fig. 2.   Water molecules structure surrounding the cavity in the clathrate [1].

2. Experimental

2.1. MATERIALS

The tetracyano complexes $NiNi(CN)_4 \cdot 7H_2O$, $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ ($n = 0.5; 2; 4$), $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and $Ni(NH_3)_2Ni(CN)_4 \cdot nC_6H_5OH$ ($n = 0.24$) were prepared according to the literature methods [13, 18]. The compounds were identified analytically and studied in the following ways:

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

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

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

The magnetic susceptibilities were measured on a magnetic balance (Präcizions and Analysenwaagen Sartorius GmbH, Germany), combined with an electromagnet (Carl Zeiss, Jena, Germany). $Fe(NH_4)_2 \cdot SO_4 \cdot 6H_2O$ was used as a standard.

2.2. METHODS

The following methods were used to alter the stoichiometry of the compounds and to control the influence of the surroundings on the parent tetracyano complex, $NiNi(CN)_4$.

(a) The sorption and resorption of the water as the guest in $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ was controlled by the TG curve during heating and cooling of the sample in an appropriate temperature interval. The products after heating and cooling were characterised by IR spectra and X-ray photographs.

(b) $NiNi(CN)_4 \cdot 7H_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ were compared in magnetic measurements, together with the products of the sorption experiments performed with the latter compound at 25°C and 80°C with benzene, as well as using TA, IR spectra and X-ray photographs. We tried to partially decompose $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ on heating to 240°C (245°C is the end of the loss of phenol in TA) and with the product of the thermal degradation we carried out the sorption experiments and studied them also in this way.

The sorption experiments with all compounds made before magnetic measurements were performed in static (96 hours) contact at laboratory temperature and in dynamic contact with refluxing benzene (10 hours). The products after contact were dried and eluted with ether and alcohol. After drying in a dessicator the products were identified by IR spectra, TA, X-ray patterns and by chemical analysis:

$NiNi(CN)_4 \cdot 7H_2O$
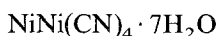
found:	Ni 35.15%	C 14.23%	H 2.2%	N 16.59%
calculated:	Ni 34.78%	C 13.37%	H 2.29%	N 15.8%

$Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$
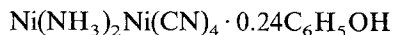
found:	Ni 42.21%	C 19.24%	H 2.18%	N 29.12%
calculated:	Ni 42.01%	C 23.4%	H 2.67%	N 30.12%

(c) $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ was modified by organic solvents (methanol, pentane,

dioxane and pyridine). The products were identified [21] by IR spectra, X-ray photographs, TA and also by their behaviour in gas chromatographic experiments (GC).

The form of a suspension of the compounds in an auxiliary medium was used as the stationary phase (Gas chromatograph Chrom 4, Laboratorní přístroje, Praha, ČSSR). The preparation of the stationary phase has been described previously [17] and the products were identified by IR spectra. The glass column used was of length 2.5 m and ID 3 mm. The flow rate of the carrier gas was 24 cm^3 min^{-1}.

Chromatographic experiments were started at 60°C or 80°C and then at gradually higher temperatures till the end of the sorptive ability of the compound [21]. After attaining the higher temperature we always returned to the starting temperature. In GC experiments the following mixtures were used:

No. 1: C_5–C_9 alkanes
No. 2: benzene(B), toluene(T), *ortho(o)*-, *meta(m)*- and *para(p)*-xylene
No. 3: C_1–C_4 alcohols
No. 4: dimethyl(1)-, methylethyl(2)- and methylpropyl(3)-ketone
No. 5: methyl(1)-, ethyl(2)-, butyl(3)- and amyl(4)-esters of acetic acid
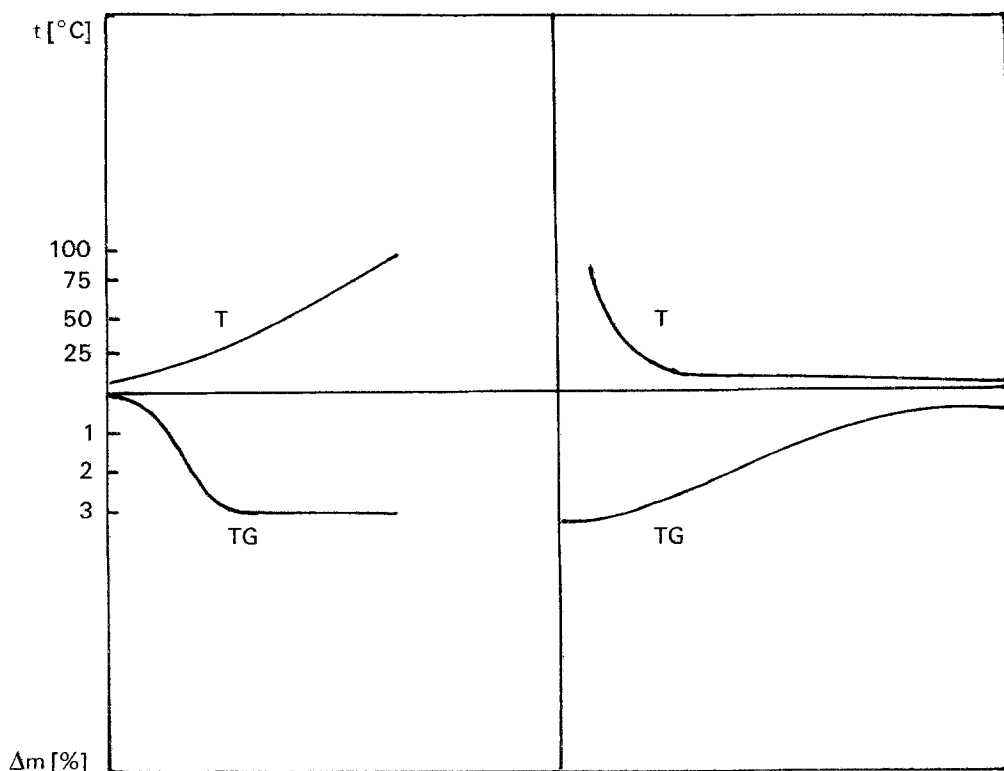No. 6: cyclo(a)-, methylcyclo(b)-, ethylcyclo(c)- and propyl(d)-cyclohexane.

Fig. 3.   Measured TG curves during heating and cooling of $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$.

3. Results and Discussions

3.1. THE ROLE OF WATER AND BENZENE IN $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ AND $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.

3.1.1. $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ during heating in TA loses its water content in the temperature interval 50–140°C and the ammonia ligands between 140–270°C. Figure 3 shows the loss of weight on heating to 100°C and the subsequent gain in weight as the sample cools. The product is identical with the original compound as shown by IR spectroscopy and by X-ray patterns. The role of the water situated in the layered [9] structure allows it to be fully resorbed and to be substituted by other compounds [16]. The same result was obtained with this compound by measuring its IR spectra [19] in the partially degraded samples.

The structure exists even after the loss of the water but also with the loss of some part of the amine ligands.

3.1.2. The compound $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ loses its benzene content between 55–185°C. We checked its loss using thermal analysis (Figure 4). In contrast to the former result the benzene inclusion compound does not show a gain in weight on cooling and the IR spectrum of the heated sample shows none of the bands of the benzene guest molecule. Thus, reversible sorption of guest does not occur under these experimental conditions. After the loss of the guest benzene we cannot expect its resorption because of its relatively low partial pressure in the surrounding of the decomposed sample in the furnace.
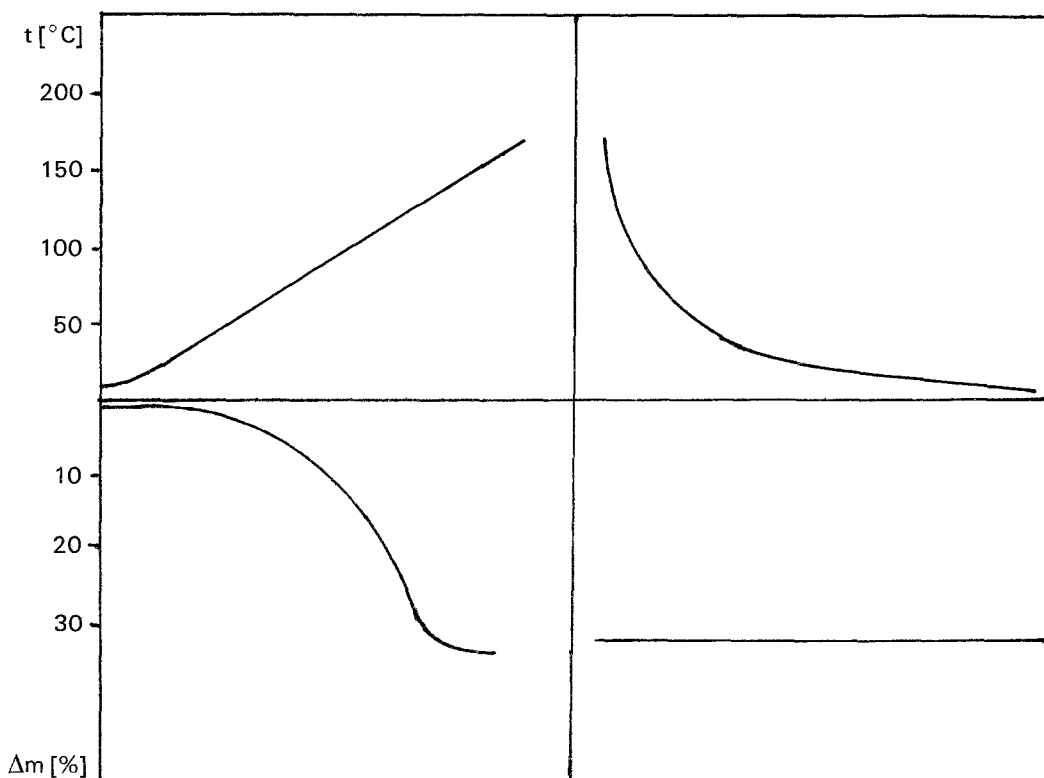

Fig. 4.   Measured TG curves during heating and cooling of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.

Table I. The values of interlayer distances and of the relative intensities for the original $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ clathrate

2θ	dp(pm)	dt(pm)	I/I_0 (%)
11.6	862.23	870.6	5.7
16.2	546.68	553.22	2.9
20	443.59	443.94	100
24.6	361.58	369.87	14.3
27.6	322.93	323.18	4.8
31.2	286.44	286.66	6.6
32.4	276.09	279.34	2.85
35.2	254.75	254.95	48.57
40.8	220.98	221.16	36.19
47	193.17	193.32	3.8
48.6	187.18	187.33	1.9
50.6	180.24	180.38	13.3
52.2	175.08	175.23	3.8

Table II. The values of interlayer distances for $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ after thermal degradation at $240°C$ and its contact at $80°C$ with benzene

2θ	dp(pm)	dt(pm)	I/I_0 (%)
15.4	574.89	575.35	9.3
17.2	515.12	515.52	9.3
18.2	487.03	487.42	11.6
18.9	471.62	471.99	6.9
20.2	439.24	439.59	100
25	355.88	356.17	20.9
24.2	367.47	367.76	11.6
24.6	361.58	361.87	13.9
27.6	322.92	323.18	60.5
29.4	303.54	303.79	5.8
30.8	290.06	290.29	13.9
32.2	277.77	277.98	4.6
35.6	251.97	252.18	4.6
37	242.76	242.95	44.19
41.2	218.92	219.10	27.90
42.7	211.58	211.75	6.9
46.8	193.95	194.10	16.3
48.4	187.90	188.05	9.3
51.2	178.27	178.41	13.9
53.2	172.03	172.16	9.3

3.2. $NiNi(CN)_4 \cdot 7H_2O$ AFTER CONTACT WITH OTHER COMPOUNDS: MAGNETIC MEASUREMENTS

X-ray photographs of $NiNi(CN)_4 \cdot 7H_2O$ are not influenced by the mode of elution. After contact with benzene at $80°C$ the product is isomorphous with the original. The clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ showed the strongest diffraction lines, identical with the model host compound $NiNi(CN)_4 \cdot 7H_2O$ (2, 20, 35, 40, 48°). This compound behaves up to

245°C (when $n \to 0$) as a clathrate [20]. In this work the structure of the clathrate, after static and dynamic contact with benzene, was not found to be changed. During the loss of the phenol guest by heating to 240°C, and consequently after its contact with benzene (Tables I and II) all fundamental lines were found and new strong ones equivalent to 27.6° and 37° appeared. The lattice was not destroyed, since sorptive ability persisted at 240°C; the original guest was retained, at least in traces, but all the space is conserved. The surroundings of the host by ligands, by the guest and further sorbates are shown in the measured (20°C) magnetic susceptibilities (Table III).

In the literature [12] NiNi(CN)$_4$ · nH$_2$O has a χ_m value which depends on the value of n: 11.42–11.9 × 10^{-6} cm^{-3} g^{-1}. The compounds with n higher than 4 always have χ_m a little changed from the value for the Ni(II) ion ($n = 6$: 11.75; $n = 5$: 11.52 against Ni(II) ion : 11.3). NiNi(CN)$_4$ · 7H$_2$O exhibited values (No. 2 and 3 in Table III) which agreed with the literature values, also the value for Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH (No. 4) agreed with other Hofmann type clathrates [12, 23, 22] and the calculated magnetic moment values agree with those observed [24] for Ni(II) ion (2.8–3.5). The values for the tetracyano complexes M(B)$_m$M'(CN)$_4$ · nG differ significantly from those of simple salts of Ni(II), such as NiX$_2$. They exhibit characteristic values of the magnetic susceptibilities appropriate for the polymeric forms of the tetracyano complex (No. 4, 5, 6 in Table III). The quantity of compounds present in the sample and the temperature of the sorptive experiments seem to influence the measured values (No. 4, 5, 6). The surroundings of the Ni(II) ion, starting with the simple tetracyano complex is gradually becoming complicated. Therefore the sample partially degraded on heating to 240°C (No. 7) exhibited a different observed value compared with the original (No. 4) compound and with the samples heated only to 25°C (No. 5) and to 80°C (No. 6).

Table III. Experimental values of magnetic susceptibilities

No. of sample	α sample (mg)	$\Delta\alpha$ (mg)	m sample (mg)	$\chi_m \cdot 10^{-6}$ cm^3 g^{-1}
tube	− 0.780			
	− 0.7892			
1	7.1301	1.9564	5.9747	32.616
2	2.950	0.400	3.330	11.965
3	2.2798	0.3268	2.733	11.911
4	1.724	0.333	2.172	15.272
5	2.9992	0.519	3.2694	15.813
6	3.2164	0.5226	3.4738	14.985
7	1.8872	0.3214	2.3458	13.648
8	3.8962	0.44	4.2394	10.338
9	5.744	− 0.046	6.580	− 0.696

No. 1: Fe(NH$_4$)$_2$SO$_4$ · 6H$_2$O
No. 2: NiNi(CN)$_4$ · 7H$_2$O eluted with alcohol
No. 3: NiNi(CN)$_4$ · 7H$_2$O eluted with water
No. 4: Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH
No. 5: Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH after contact with benzene at 25°C
No. 6: Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH after contact with benzene at 80°C
No. 7: Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH after thermal degradation to 240°C
No. 8: Ni(NH$_3$)$_2$Ni(CN)$_4$ · 0.24C$_6$H$_5$OH after thermal degradation to 240°C and subsequent contact with benzene at 80°C
No. 9: CdenCd(CN)$_4$ · C$_{12}$H$_{10}$ after contact with benzene at 80°C.

The largest difference occurs with sample No. 8. The polymeric sheet is changed on thermal degradation but this changed product was also in contact with a further organic compound. The measured value of χ_m is less than those of the starting compound (No. 2 and 3).

As a control sample we show also sample No. 9 which contains diamagnetic Cd(II).

3.3. THE PROPERTIES OF $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ AFFECTED BY THE INTERACTION WITH SOLVENTS

The modification of tetracyano complexes was dealt with in a previous paper [17]. Recent results [21] reinforce the effects of the surroundings on the compound. The presence of some water in the original compound can be seen from the characteristic features in the IR spectra (Figure 5, a, b). The band (1220 cm^{-1}) in Figure 5 a, b, arising from $\delta_s(NH_3)$ in the undecomposed sample disappears on heating to 320°C (Figure 5 c). The total loss of the guest can also be seen. The IR spectra of the products obtained after the modification with four solvents (pyridine and dioxane not used previously) are shown in Figure 6. Solvents acting as strong ligands (Figure 6 d, e) enter into the host as possible ligands affecting the interlayer distance.

The identification of the tetracyano complex by TA, IR and chemical analysis after the modification [21] shows very interesting results concerning the stoichiometry and structure of the product. Pentane (Figure 6 b) did not affect the spectrum at all. Methanol (Figure 6 c) as a weak base lowered the H_2O content of the layers leading to the formula: $Ni(NH_3)_2Ni(CN)_4 \cdot 0.35H_2O$.

Dioxane as a strong electron donor changed (Figure 6 e) the surroundings concerning the ligands and the guest, giving the non-stoichiometric formula $Ni(NH_3)Ni(CN)_4 \cdot 0.45C_4H_8O_2 \cdot 1.5H_2O$ in analogy with the literature [25, 22]. Pyridine strongly affects (Figure 6 d) the surrounding of the framework, its stoichiometric formula is $Ni(NH_3)_{1.6}Ni(CN)_4 \cdot 0.45C_5H_5N \cdot 0.4H_2O$. The situation about its function as the guest needs to be clarified [26].

The properties of $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ modified by different solvents depend on the interaction possibility of the solvent. The chromatographic separation potential of the modified hosts are shown in Figures 7–10.

Each solvent modification gives rise to an appropriate temperatures range. The range of 60–200°C for sorptive abilities is displayed after the modification with pentane. The temperature range 80–240°C is effective after the modification with methanol [21], dioxane and pyridine, but the last two give more effective separations. Heating the column to 300°C and returning to the starting temperature did not change the abilities [21] to interact with further organic compounds. It means that the first coordination sphere may be partially disrupted and the layered structure stays intact. Figure 7 presents the situation after the modification with methanol, the influence of the preparative temperature on the separative ability in the case of pentane is shown in Figure 8. Solvents acting as strong ligands greatly affect the elution curves of the same tested mixtures of organic compounds (pyridine in Figure 9 and dioxane in Figure 10).

The use of $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ as a stationary phase after its modification with methanol is illustrated on Figure 7 where it is used at 140°C with mixtures No. 2–6 and at 160°C with Nos. 3, 4 and 6. The mixture of aromatics (No. 2) was completely separated, the last peak showing the *p*-isomer being separated from the *o*-, and *m*-isomers.

Mixture No. 3 is not well separated at either 140° or 160°C. We observe the common elution of the C_1, C_2 and C_3 alcohols, only butanol has been separated.

Mixture No. 4 was separated into its components at both 140° and 160°C, but with shorter

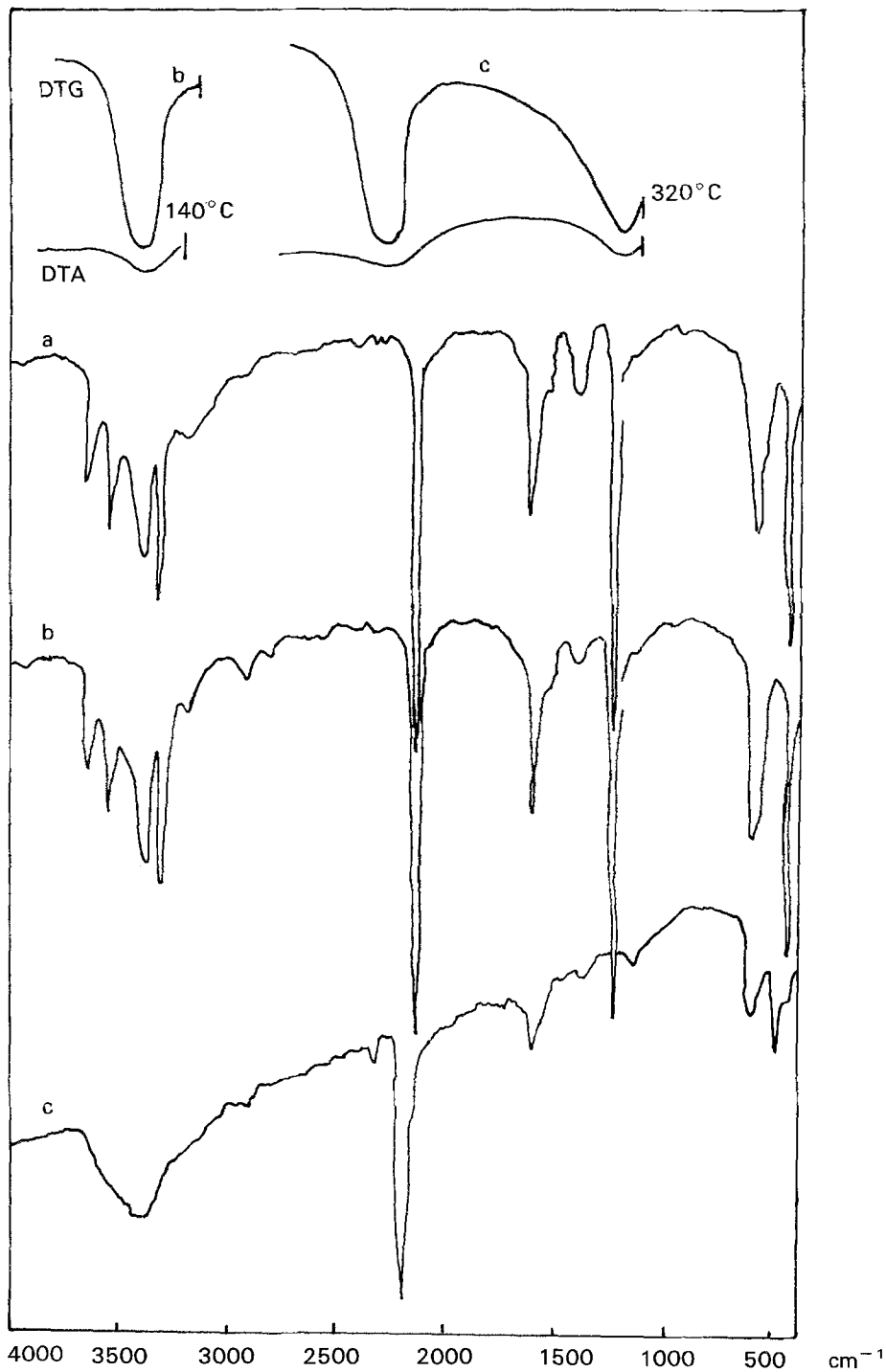Fig. 5. Thermal decomposition of $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ and the IR spectra of the original compound (a), and of the intermediate products obtained at $140°C$ (b) and $320°C$ (c).
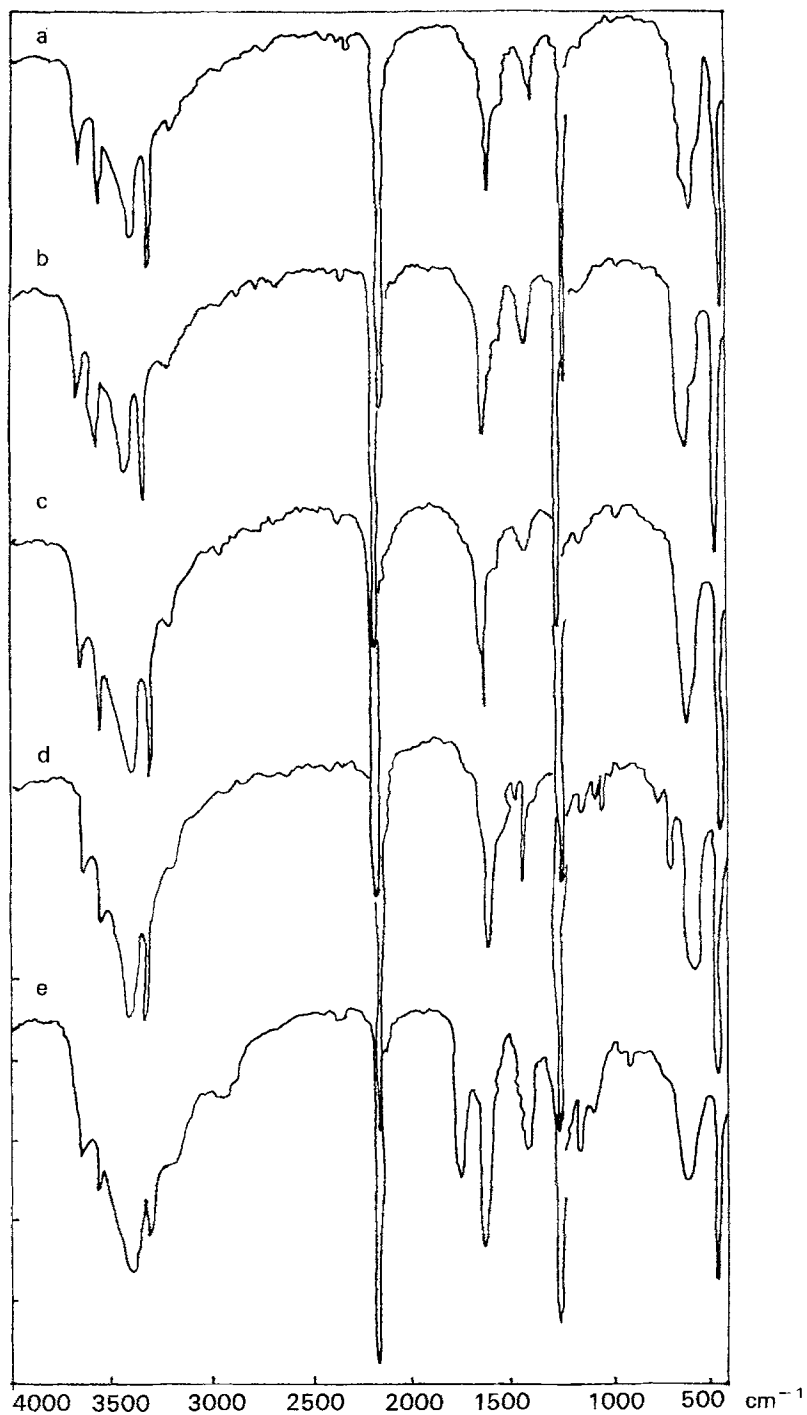
Fig. 6.   IR spectra for identification of Ni(NH$_3$)$_2$Ni(CN)$_4$ · 2H$_2$O (a), and after modification with pentane (b), methanol (c), pyridine (d) and dioxane (e).
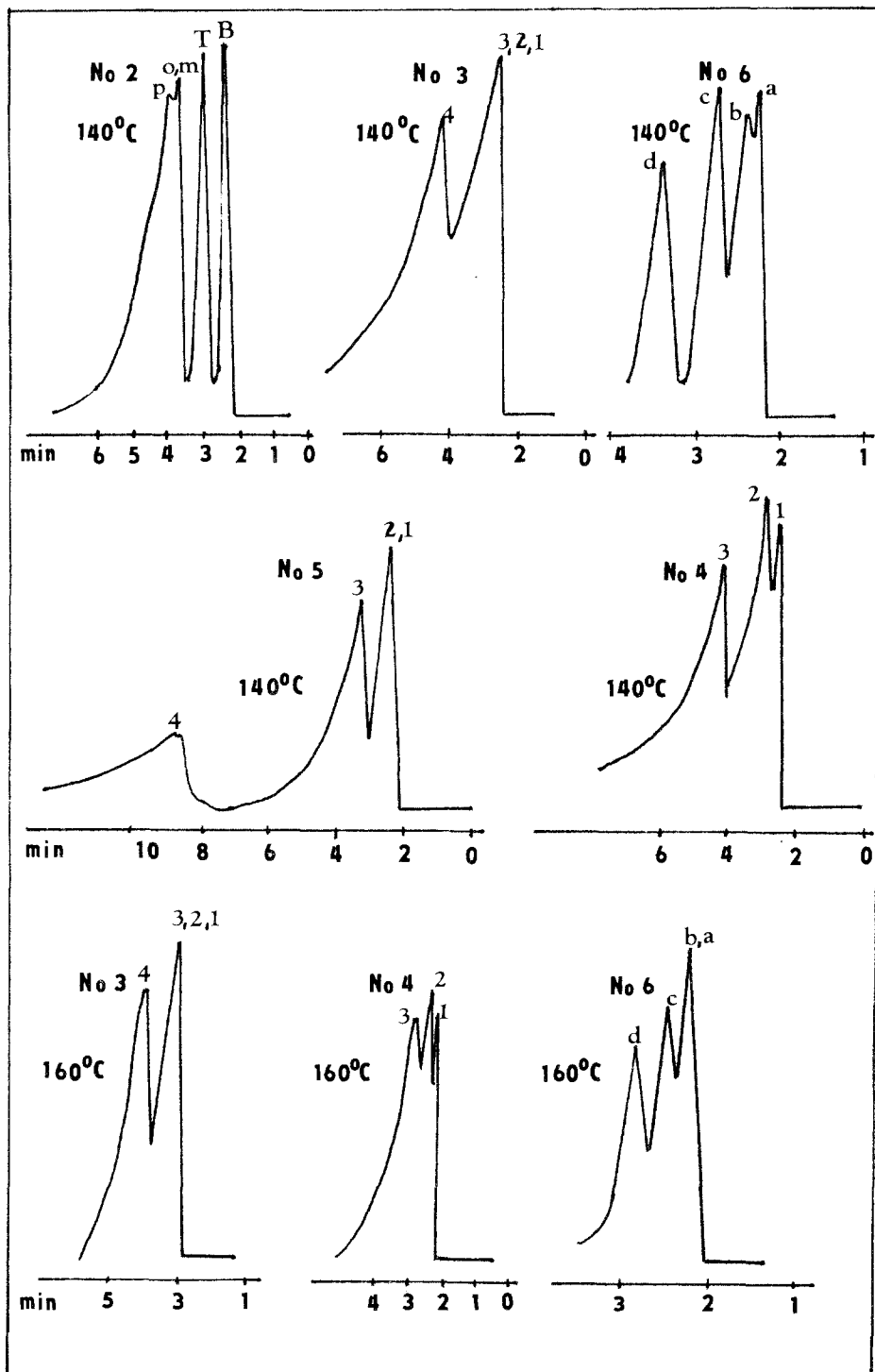
Fig. 7. Ni(NH$_3$)$_2$Ni(CN)$_4 \cdot$ 2H$_2$O as the stationary phase (10%) at 140°C and 160°C after modification with methanol using mixtures Nos. 2–6. See section 2.2 for the identification of the peaks.

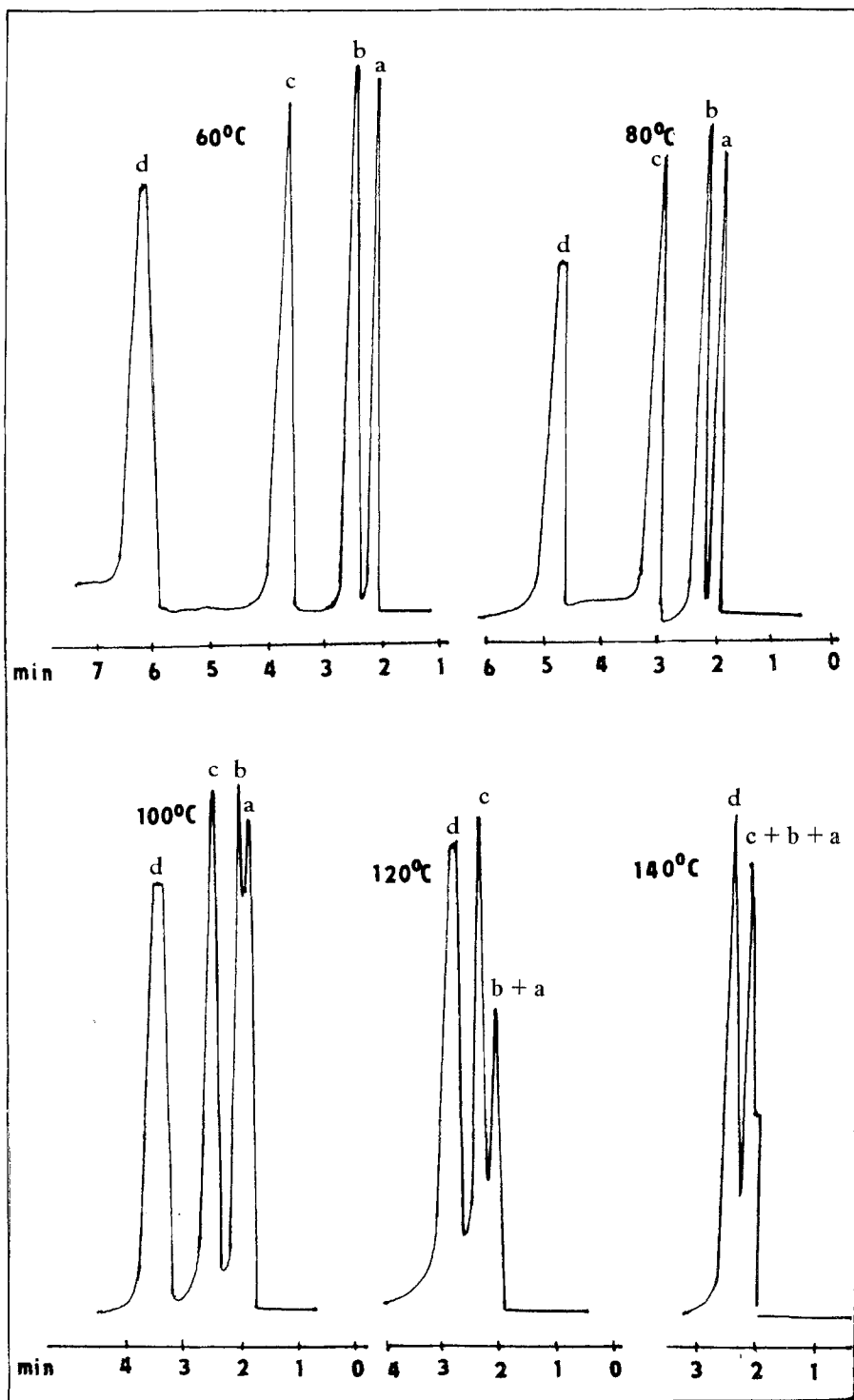Fig. 8.   Ni(NH$_3$)$_2$Ni(CN)$_4 \cdot$ 2H$_2$O as the stationary phase (10%) after modification with pentane at different temperatures using mixture No. 6: cyclo (a), methylcyclo (b), ethylcyclo (c), propylcyclohexane (d).

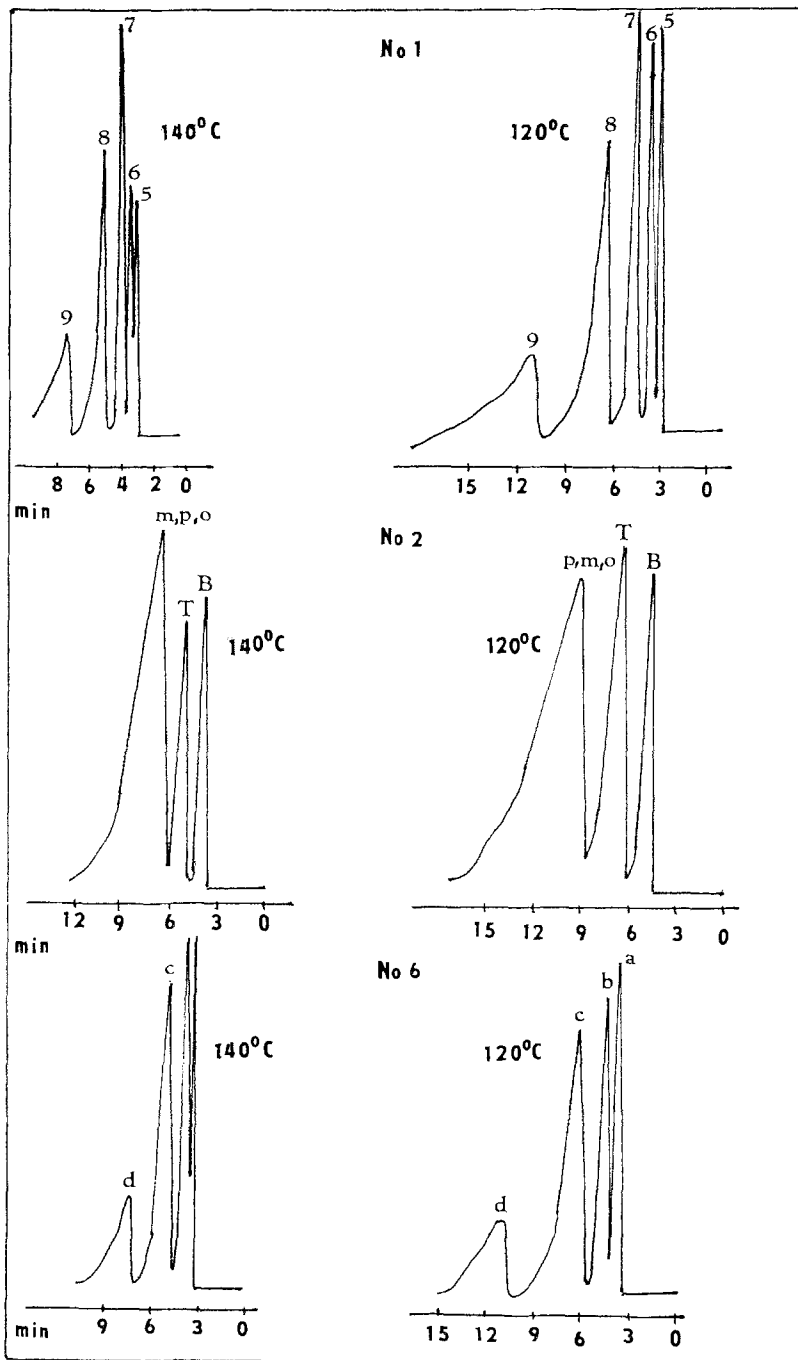Fig. 9. Ni(NH$_3$)$_2$Ni(CN)$_4$·2H$_2$O as the stationary phase (10%) after modification with pyridine at different temperatures, using mixtures Nos. 1, 2 and 6. See section 2.2 for he identification of the peaks.
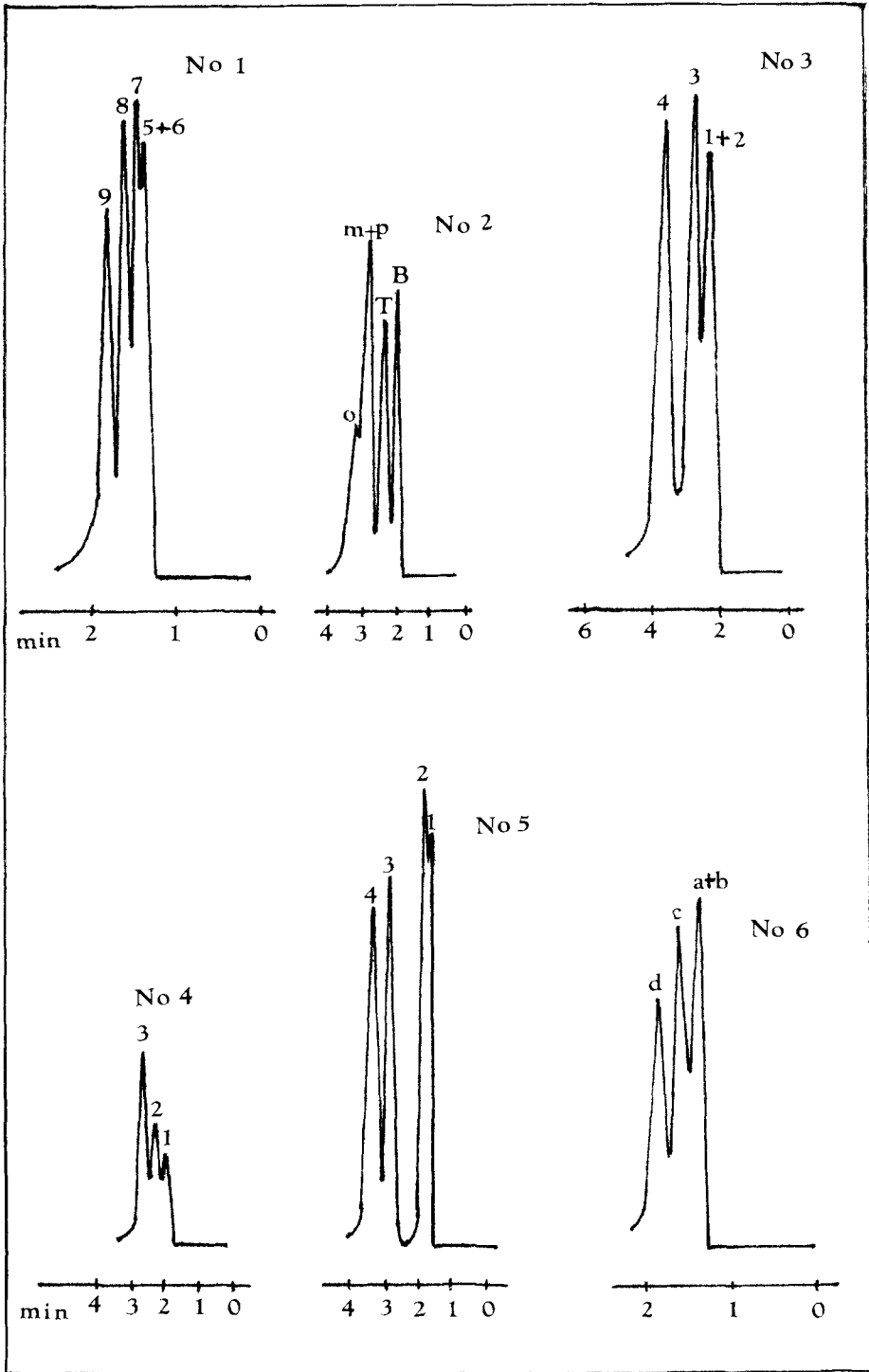
Fig. 10.   Ni(NH$_3$)$_2$Ni(CN)$_4 \cdot$ 2H$_2$O as the stationary phase (10%) after modification with dioxane at 120° using mixtures Nos. 1–6. See section 2.2 for the identification of the peaks.

retention times at the higher temperature. From the mixture of esters (No. 5) the amyl- and butyl-ester were separated, but the methyl- and ethyl-esters are eluted together.

In the case of cyclic compounds (No. 6), the mixture is completely separated at the lower temperature, but not at the higher temperature.

The use of $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$ as a stationary phase after the modification with pentane is compared in Figure 8 at increasing temperatures for the separation of mixture No. 6. We observe the well known phenomenon viz. with increasing temperatures the retention times are reduced and the separation abilities of the fillings are less favourable. At 60° and 80°C a complete separation of the mixture into its 4 components is achieved. At 100°C we observe some overlapping of cyclohexane and methylcyclohexane. By increasing the temperature to 120°C the first two components are eluted together. At 140°C only the propylcyclohexane is separated from the mixture.

In Figure 9 we see the modification with pyridine and the separation abilities of the filling against mixtures 1, 2 and 6, at two temperatures (120° and 140°C). The lower temperature enables the complete separation of all the mixtures. By increasing the temperature a reduction of the retention times occurs, but the separation abilities are retained. Each component of all the mixtures is separately eluted. The filling is thus effective at this temperature, the increased thermal stability and efficiency [21] of the filling is a new property of the tetracyano complex, gained after the modification with pyridine.

In Figure 10 the different but satisfactory separation potentials of the filling, prepared by the modification with dioxane [21] are shown at 120°C against all six mixtures of organic compounds.

The components of mixture No. 1 C_9, C_8 and C_7 are separated, but pentane and hexane are eluted together.

The individual components of the aromatic mixture (No. 2) are separated and there is again an indication of the differentiation of the xylenes.

The components with lower boiling points from the mixture of alcohols (No. 3) and cyclic compounds (No. 6) are eluted together. We observe mixtures No. 4 and 5 being completely separated into their individual components.

After the modification with methanol (Figure 7) and pentane (Figure 8) we may see in all the GC curves its positive effect in all the temperature ranges, where the water as guest has been lost from the original tetracyano complex. Temperatures over 140° were not very effective.

By comparison of the modification of the same compound, $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$, with four solvents and its separation ability against the same mixture of compounds we find some differences. Mixture No. 6 shows, at the same temperature, different retention times after the modification. Methanol in Figure 7 at 140°C is more advantageous for the separation of mixture No. 6, the retention times are longer and the separation is more complete (four peaks). In the case of pentane in Figure 8, at the same temperature, only three peaks exist. This is in accordance with the modification effects, the pentane showed absolutely no change in the IR spectrum of the product of the modification, but methanol exhibited a change, although very fine. The retention times achieved with methanol and pentane are very much shorter than those in Figure 9, after the modification of the tetracyano complex with pyridine, which represents a more drastic contact with the tetracyano complex and thus offers a more spatious area in its lattice.

4. Conclusions

Several types of compounds, after being in contact with $NiNi(CN)_4 \cdot nH_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$, do not change the compounds and they retain their fundamental framework structure. They only affect the situation and surroundings of the metal ion in the compound and in such manner the originally sorbed guest may be resorbed or substituted in a partial or total way. After the partial loss of the guest, and the partial loss of ligand from the first coordination sphere, they may now further accept some other guest or substitute the ligands. The newly formed product thus has a different stoichiometry; it is richer in the number and quantity of its components, but the fundamental structure is maintained.

The values of the magnetic susceptibilities are also slightly affected by the contact with other compounds. The contributions of each individual diamagnetic guest component (and their different quantities) are shown only in very fine gradations. When $NiNi(CN)_4 \cdot 7H_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot 0.24C_6H_5OH$ were in contact with some compounds, they sorbed them and formed a more complicated compound and the new compound exhibited positive values of χ_m, being very close to the values of the paramagnetic Ni(II) ion. Only the destruction of the polymeric forms (only partial) affected the measured value.

The compound $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ after its modification with solvents still belongs to compounds of the $M(NH_3)_m M'(CN)_4 \cdot nG$ type. When acting as a sorptive material the quantity n must, after the modification, be different from zero during the preparation of the fundamental framework. The original value of m may be changed or may also be zero. This was shown mainly by the sorption after heating the column to $300°C$ and returning to the starting temperature [21] in sorptive experiments in GC. The retention times depend on the volumes of voids created in the lattice, on the shape of the organic compounds used for the separation and on their boiling points. In the structures modified by solvents, particularly by pyridine or dioxane, the components of individual mixtures may remain longer in the more spatious layers, compared to the compounds which have been modified only slightly (methanol) or remain unchanged (pentane).

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