

Influence of auxiliary solvents on tetracyano complex compounds

^aA. SOPKOVÁ, ^aF. KALAVSKÝ, ^bM. ŠINGLIAR, ^aJ. BUBANEC,
and ^aP. KRÁLIK

^aDepartment of Inorganic Chemistry, Faculty of Natural Sciences,
P. J. Šafárik University, CS-041 54 Košice

^bResearch Institute for Petrochemistry,
CS-971 04 Prievidza

Received 1 August 1984

Accepted for publication 19 April 1985

The interaction of the tetracyano complexes $\text{Cu}(\text{NH}_3)_m\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ and $\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ with water, methanol, hexane, cyclohexane, benzene, 3-methylpyridine, and pyridine was investigated. All these compounds influence the ability of sorption of tetracyano complexes and the last two solvents also bring about changes in their structure. The interaction of all these solvents with tetracyano complexes gives rise to a stationary phase which makes it possible to perform a better chromatographic separation of different organic mixtures at increased temperatures.

Исследованы взаимодействия тетрациано-комплексов $\text{Cu}(\text{NH}_3)_m\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ и $\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ с водой, метанолом, гексаном, циклогексаном, бензолом, 3-метилпиридином и пиридином. Все эти соединения влияют на степень сорбируемости тетрациано-комплексов, а два последних растворителя также вызывают изменения в их строении. При взаимодействии всех этих растворителей с тетрациано-комплексами возникает стационарная фаза, позволяющая лучше проводить хроматографическое разделение различных органических смесей при повышенных температурах.

Tetracyano complexes are known for their ability to form inclusion compounds of the clathrate type. The compounds investigated by us are of general formula $\text{M}(\text{B})_m\text{M}'(\text{CN})_4 \cdot n\text{G}$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$; $\text{M}' = \text{Ni}, \text{Pt}, \text{Pd}$; B is a base containing N or O; $m \geq 0$; G is an aromatic compound or H_2O ; $n > 0$). If the compound does not contain any guest component, it is not a clathrate in the sense of the proposed terminology [1] but a clathrand. As these compounds are nonstoichiometric species [2], there are no sharp transitions between these two forms [3—5].

A great number of inorganic substances usable as stationary phases in gas or liquid chromatography has been described in literature [6—9]. Different forms of tetracyano complexes have been used in studies [3—5] carried out in our

laboratory. The applicability of tetracyano complexes to this purpose is also mentioned in paper [10].

In order to elucidate deeper the hitherto known property consisting in possible substitution of other aromatic compounds for the original guest component G, we subjected tetracyano complexes of the type $M(\text{NH}_3)_m\text{M}'(\text{CN})_4 \cdot n\text{H}_2\text{O}$ and $\text{MM}'(\text{CN})_4 \cdot n\text{H}_2\text{O}$ to modification by using auxiliary solvents.

Experimental

Materials and methods

Tetracyano complexes of the type $\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ (*I*) were synthesized according to [11—13] and the complexes of the type $\text{ZnNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ (*II*) were prepared according to [2, 14]. The compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ (*III*) which was also subjected to modification is the subject of papers [15, 16].

We used infrared spectroscopy (Specord IR 75, wavenumber region $\tilde{\nu} = 700\text{—}4000\text{ cm}^{-1}$), thermal analysis (Derivatograph Q 1500 and MOM 101), and the methods of analytical determination of individual metal components for identification of the investigated compounds.

In contrast to preceding investigations [14], we extended the number of auxiliary solvents. Thus we used water, methanol, hexane, cyclohexane, benzene, and 3-methylpyridine. Moreover, we employed pyridine for compounds *II* and *III*.

The complexes $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ (obtained by six-month standing of complex *I*) and $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ were modified by direct contact with solvents and subsequent evaporation of the solvent. We used varying mass fractions of tetracyano complex (most frequently 10 mass %) and auxiliary solvent. For modification by methanol, 20 mass % of complex were used.

The sorptive ability of the modified forms of tetracyano complexes was investigated with a gas chromatograph Chrom IV (Laboratorní přístroje, Prague) equipped with a flame ionization detector. The initial temperature of column was 80 °C for measurements with compounds *I* and *II* or 60 °C for measurements with compound *III*. Subsequently, the temperature was raised by 20 °C at all times. The temperature at which the packing stopped to exhibit separative power was regarded as upper limit of measurement.

After modification the tetracyano complexes were homogenized with the carrier (Chromosorb W NAW/"100 mesh") in necessary proportion under sufficient stirring and afterwards they were dried on a water bath. These mixtures were used for packing chromatographic columns (metallic columns, $l = 2.5\text{ m}$, $\varnothing = 3\text{ mm}$) *in vacuo*.

We applied the following model mixtures to chromatographic separation:

- a) pentane, hexane, heptane, nonane; also octane for compound *III*;
- b) cyclohexane, methylhexane, ethylhexane; also propylcyclohexane for compound *III*;
- c) benzene, toluene, xylenes;
- d) C-1—C-4 alcohols;
- e) methyl, ethyl, butyl, and amyl ester of acetic acid;
- f) acetone, ethyl methyl ketone, methyl propyl ketone (this mixture only for compound *III*).

Results

Infrared spectra

Original substances *I* and *II* exhibited even after standing for six months the following characteristic wavenumbers.

$\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$: $\rho(\text{NH})$ 690 cm^{-1} , $\delta(\text{M}-\text{OH})$ 800 cm^{-1} , $\delta(\text{N}-\text{H})$ 1620 cm^{-1} , $\delta(\text{HOH})$ 1625 cm^{-1} , $\nu(\text{CN})$ 2130 cm^{-1} , $\nu_s(\text{OH})$ 3190 cm^{-1} , $\nu_s(\text{NH})$ 3362 cm^{-1} , $\nu(\text{HOH})$ 3580 cm^{-1} (Fig. 1).

$\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$: $\nu(\text{OH})$ 3600 cm^{-1} and 3400 cm^{-1} , $\nu(\text{CN})$ 2160 cm^{-1} , $\delta(\text{HOH})$ 1640 cm^{-1} , $\nu(\text{MC})$ 575 cm^{-1} and 450 cm^{-1} (Fig. 2).

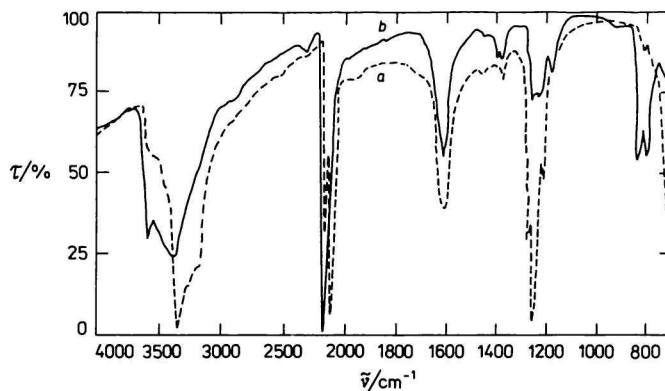


Fig. 1. Infrared spectrum of $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$.
a) Original spectrum ; b) spectrum after modification with water.

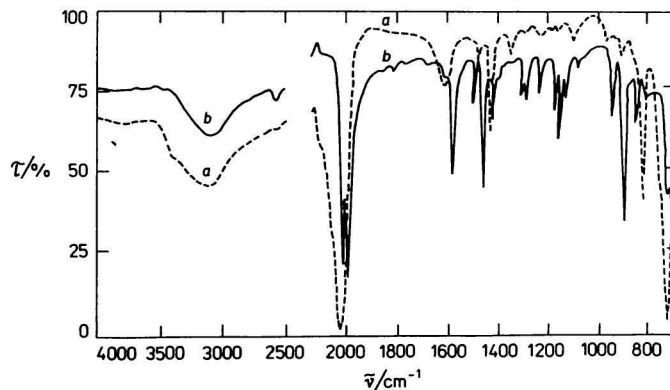


Fig. 2. Infrared spectrum of $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$.
a) Original spectrum ; b) spectrum after modification with pyridine.

Thermal analysis

The results of thermal analysis performed after standing for six months show that $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ is stable up to 152°C (Fig. 3). At this temperature a series of mass losses sets in and all processes are endothermic up to 320°C . The total relative mass loss at 320°C corresponding to the liberation of H_2O and a portion of the NH_3 ligands is 21.07 mass %. The substance $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ is stable to 60°C . The relative mass loss (0.5 mol of H_2O) at 430°C represents 3 mass % (Fig. 4).

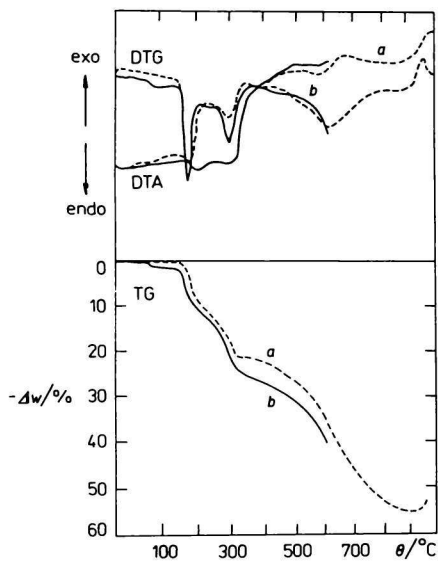


Fig. 3. Thermal decomposition of $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$.

a) Original substance; b) after modification with 3-methylpyridine.

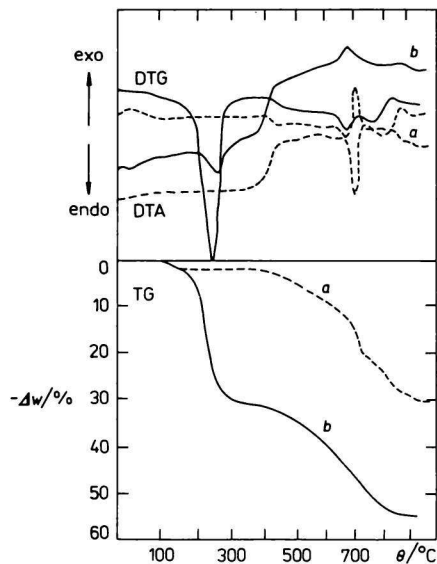


Fig. 4. Thermal decomposition of $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$.

a) Original substance; b) after modification with pyridine.

Tetracyano complex compounds after treating with auxiliary solvents

The infrared spectrum of the tetracyano complex $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ modified by treating with H_2O contained all characteristic bands observed in the spectrum of original substance. However, some changes appeared in the band intensity and some bands shifted. The bands corresponding to $\nu(\text{OH})$ and $\nu(\text{NH})$ changed in appearance (Fig. 1b) and the band $\nu(\text{CN})$ which at the original $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.38\text{H}_2\text{O}$ formed a doublet with the maximum at $\tilde{\nu} = 2130\text{ cm}^{-1}$

manifested itself in the spectrum of the modified substance as a singlet and shifted to 2180 cm^{-1} . The intensities of the bands $\delta(\text{HOH})$ and $\delta(\text{NH})$ also decreased after modification with water. Simultaneously, the band $\delta(\text{M—OH})$ split into a doublet with the peaks at $\tilde{\nu} = 790\text{ cm}^{-1}$ and 820 cm^{-1} , which indicated gradual liberation of H_2O (librational mode ν_{R} at $\tilde{\nu} = 790\text{ cm}^{-1}$).

No significant changes in position and intensity of bands appeared in the infrared spectrum of $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ after treating with methanol, hexane, cyclohexane, and benzene as auxiliary solvents [14]. These solvents have no significant influence on original structure of the tetracyano complex and there is no indication of their sorption in this complex (evidently the steric relations are not satisfactory).

Quite different results were obtained by using 3-methylpyridine as an auxiliary solvent. The bands in infrared spectrum belonging to original tetracyano complex (Fig. 5) did not change, but new bands corresponding to 3-methylpyridine ($\nu(\text{C}=\text{C})$ and $\delta(\text{C—H})$) appeared in the region $\tilde{\nu} = 1500\text{—}700\text{ cm}^{-1}$. Owing to the ability of 3-methylpyridine to enter into rather strong interaction with tetracyano complex, an excess amount of this solvent may thus be bonded as guest component in the host component — like in the Werner complexes [8]. This assumption was also confirmed by thermal analysis. In contrast to original complex, a small mass loss appeared after contact with 3-methylpyridine on the TG curve already at $50\text{ }^\circ\text{C}$ (Fig. 3). The relative mass loss represented 2.21 % at $150\text{ }^\circ\text{C}$ and 26.25 % at $367\text{ }^\circ\text{C}$. The process of thermal decomposition is clearly facilitated by modification. 3-Methylpyridine extends the distances between the layers in the host component, which results in the possibility of its bonding. Of course, it may be replaced by other species in the course of sorption.

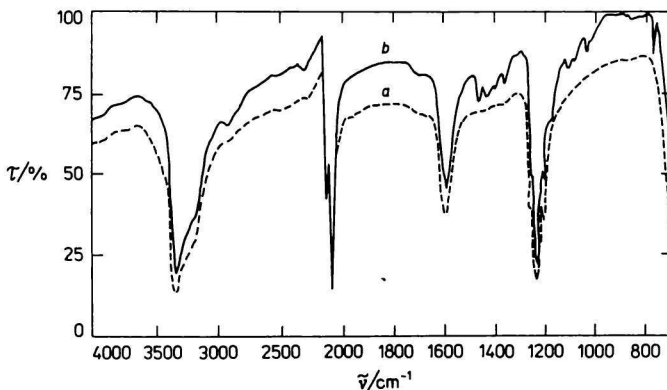


Fig. 5. Infrared spectrum of $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$.
a) Original spectrum; *b*) spectrum after modification with 3-methylpyridine.

The contact of the tetracyano complex $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ with water, methanol, hexane [14], cyclohexane, and benzene as modifying solvents did not bring about any change in the infrared spectrum. However, some changes appeared in the infrared spectrum of the modified compound after treating with 3-methylpyridine [14] and still more with pyridine (Fig. 2b). At present, we cannot exactly explain the pertinent changes in structure. Nevertheless, we may assume the sorption of pyridine and 3-methylpyridine into the structure of complex giving rise to $\text{Zn}(\text{B})_m\text{Ni}(\text{CN})_4 \cdot (n - m)\text{B}$ where B is pyridine or 3-methylpyridine. This view is also documented by confrontation of the TG curves of the original and modified substance (Fig. 4). An analogous effect of pyridine and still more of dioxan was also observed for modification of the compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ [15, 16].

Valuation of chromatographic measurements

Chromatographic measurements with the modified complex $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ were carried out by the use of four packings. The packing of compound I modified by methanol (10 mass % of complex) was suited to separation of hydrocarbons at 80 °C. However, the selectivity utterly decreased with increasing temperature. This packing also exhibited relatively good separative properties at 100 °C with respect to mixtures of alcohols and esters. The limiting temperature of usability of this packing is 160 °C (according to liberation of the guest component during thermal analysis the value of n approaches zero at 150 °C for this compound). The use of packing with 20 mass % of compound I confirmed the known fact [13] that a change in content of tetracyano complex had no essential influence on separative power of the packing.

By using benzene as an auxiliary solvent, the separative ability of the packing was considerably impaired. All the mixtures used were poorly separated even at the initial temperature of 80 °C. The temperature rise of 20 °C extinguished the selectivity with respect to hydrocarbon mixtures. The working interval was also shorter. The measurements were terminated at 140 °C.

The greatest change in separative properties was produced by the use of 3-methylpyridine as a solvent. This compound considerably improved the separative properties of the packing at all working temperatures (Fig. 6) and shifted its usability to higher temperatures. Thus it was unambiguously confirmed that the solvent is able to play the part of ligand as well as guest component. First of all, it is bonded as ligand and thus it extends the distance between layers, raises the thermal stability of the compound and improves its sorptive properties. The mixtures of hydrocarbons were fully separated even at lower temperatures. The temperature interval of usability of the packing increased and its separative properties vanished only at 180 °C.

The tetracyano complex $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ modified by methanol exhibited

separative properties especially at lower temperatures. The mixtures of aliphatic, cyclic and aromatic hydrocarbons were fully separated in individual components (Fig. 7). Alcohols and esters were sorbed in the column at lower temperatures and eluted at higher temperatures. The packing was usable up to the temperature of 220 °C.

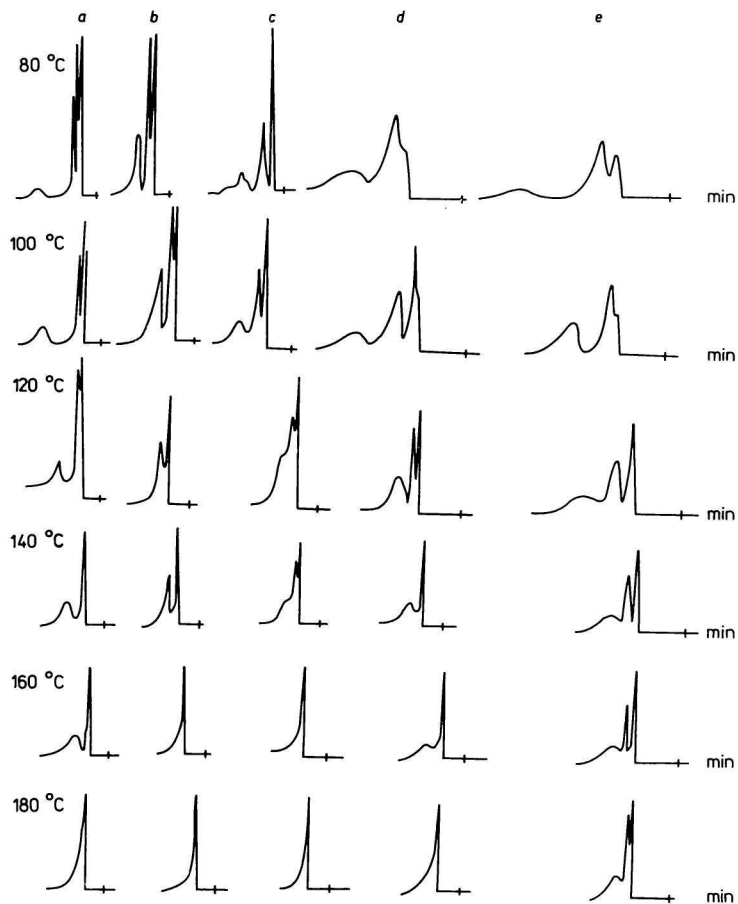


Fig. 6. Chromatographic curves of individual mixtures.

a) Pentane, hexane, heptane, nonane; b) cyclohexane, methylhexane, ethylhexane; c) benzene, toluene, xylenes; d) C-1—C-4 alcohols; e) methyl, ethyl, butyl, and amyl ester of acetic acid obtained at different temperatures by the use of 10 % $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2.4\text{H}_2\text{O}$ modified with 3-methylpyridine.

The packing containing $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ modified with pyridine showed good separative properties. However, its selectivity with respect to mixtures of aliphatic and aromatic hydrocarbons was poorer. On the other hand, a very high

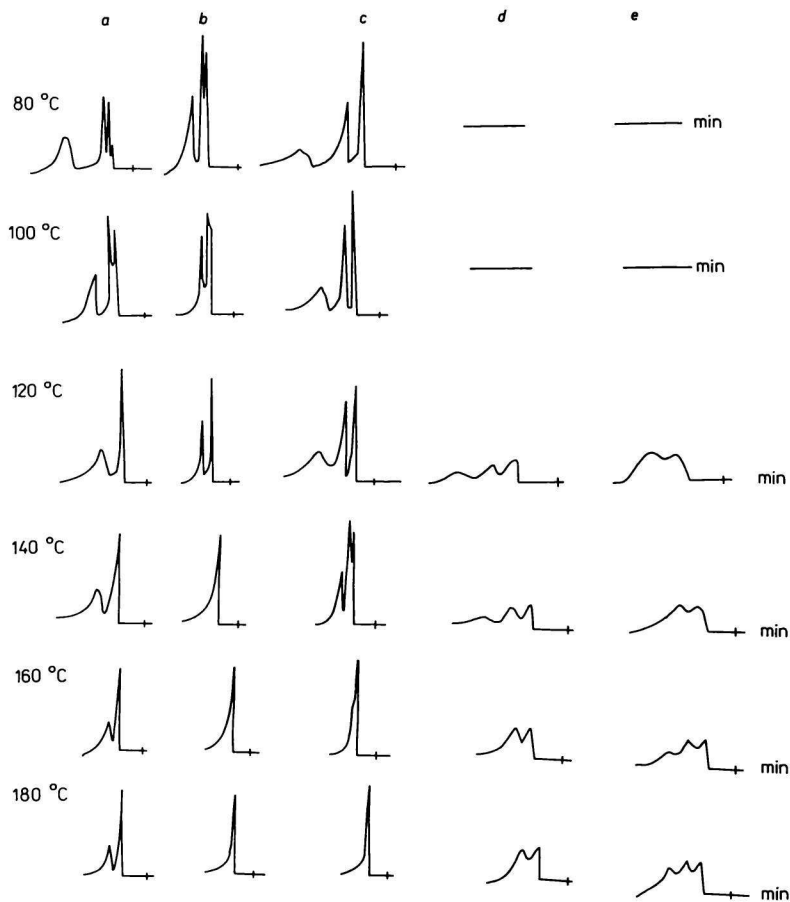


Fig. 7. Chromatographic curves of mixtures *a*, *b*, *c*, *d*, *e* (see Fig. 6) obtained at different temperatures by the use of $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ modified with methanol.

selectivity was observed for separation of a mixture of cyclic hydrocarbons. The separation of such mixture occurred as early as at 80 °C and still improved with further temperature increase. It is remarkable and a little surprising that the retention times decreased up to the temperature of 120 °C and started to increase with temperature at this point (Fig. 8). A further decrease was to be observed at 200 °C. This anomaly must be due to liberation of pyridine which functions not only as a ligand but also as a guest component in the tetracyano complex $\text{Zn}(\text{py})_a\text{Ni}(\text{CN})_4 \cdot (n - a)\text{py}$, owing to which new interlayer spaces become free for other substances. The increase in retention time is a consequence of longer detention of the components of mixture in freed spots.

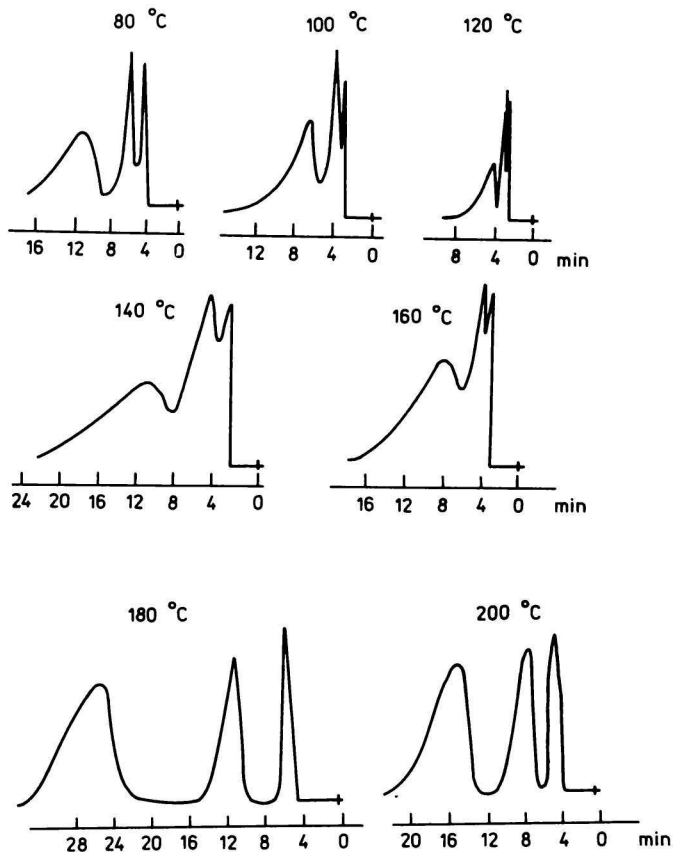


Fig. 8. Chromatographic curves of mixture *b* (see Fig. 6) obtained at different temperatures by the use of $\text{ZnNi}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ modified with pyridine.

Discussion

The tetracyano complex compounds show the character of inclusion compounds not only in the course of identification but also after modification with auxiliary solvents. Individual solvents differed from each other already by the character of the products of modification and still more by the properties of these products serving as stationary phases for chromatographic separation of six different mixtures of organic compounds. The limiting temperatures of usability of tetracyano complexes in separative processes are shifted to higher temperatures after modification when compared with nonmodified tetracyano complexes which can

be, in most cases, used [1] in the temperature interval where their guest components are liberated according to the thermal analysis.

If we use for modification the solvents able to enter as a ligand into the first coordination sphere of the host component, we obtain more convenient interlayer spaces. For instance, that is valid for hydrocarbons, alcohols, and acetic acid esters in case of modification with 3-methylpyridine and for cyclic hydrocarbons in case of modification with pyridine. However, higher temperatures are to be recommended for material modified with pyridine because this, to a greater degree, stabilizes the cyano complexes.

The investigated compounds belong into the compound class expressed by the formula $M(B)_mM'(CN)_4 \cdot nG$ and are suited to the use as stationary phase for every form with $n \neq 0$ (m may exceed 2). The examined $Cu(NH_3)_2Ni(CN)_4 \cdot 2.4H_2O$ originated in six months' standing of $Cu(NH_3)_4Ni(CN)_4 \cdot nH_2O$ ($n > 2.4$). The first step of the thermal decomposition of this substance starts at 20 °C and involves the liberation of two excess NH_3 ligands. This information shows the virtue of tetracyano complexes. They are usable, even if they lose a part of H_2O or other ligands by standing. The sorptive properties remain preserved at different content of the guest component G as well as after partial loss of the ligands B containing N or O provided their layered structure is not impaired [16, 17]. The interlayered spaces in lattice [18] occupied by certain portions of the guest component (it may also be H_2O) and some sort of cutting of the layers by ligands (NH_3 , H_2O , 3-methylpyridine, pyridine) determined by the value of n and m are responsible for the sorptive ability of the investigated complex compounds.

References

1. Weber, H. and Josel, P., *J. Incl. Phen.* 1, 79 (1983).
2. Sopková, A., *J. Mol. Struct.* 75, 81 (1981).
3. Sopková, A., Šingliar, M., Chomič, J., Skoršepa, J., and Matejčíková, E., *Czechoslov.* 186492 (1978).
4. Šingliar, M., Sopková, A., Chomič, J., Skoršepa, J., and Matejčíková, E., *Czechoslov.* 185986 (1978).
5. Sopková, A., Šingliar, M., Bubanec, J., Görnerová, T., and Králík, P., *Czechoslov.* 222610 (1983).
6. Kemula, W. and Sybilska, D., *Nature* 185, 237 (1960).
7. Lipkowski, J., *J. Mol. Struct.* 75, 13 (1981).
8. Kemula, W., Sybilska, D., Lipkowski, J., and Duszczyk, J., *J. Chromatogr.* 204, 23 (1981).
9. Davies, J. E. D., Kemula, W., and Powell, H., *J. Incl. Phen.* 1, 3 (1983).
10. Iwamoto, T. and Nishikiori, S., in *Proc. 2nd Int. Symp. on Clathrate Compounds and Molecular Inclusion Phenomena*, p. 69. Parma, 1983.
11. Sopková, A., in *Proc. Int. Microsymp. on Clathrate and Molecular Inclusion Phenomena*, p. 30. Stará Lesná, 1981.

12. Sopková, A. and Šingliar, M., in *Inclusion Compounds*, Vol. III. (Atwood, J. L., Davies, J. E. D., and MacNicol, D. D., Editors.) P. 245. Academic Press, London, 1984.
13. Šingliar, M. and Sopková, A., *Petrochémia* 17, 18 (1977).
14. Sopková, A., Králik, P., and Šingliar, M., *J. Incl. Phen.* 1, 263 (1984).
15. Šingliar, M., Sopková, A., and Matanin, J., *Petrochémia* 24, 23 (1984).
16. Šingliar, M., Sopková, A., and Bubanec, J., *Czechoslov. Appl.* 7881 (1984).
17. Sopková, A., Šingliar, M., and Matanin, J., *Abstractbook 3rd Int. Symp. on Clathrate Compounds and Molecular Inclusion Phenomena*, p. 279. Tokyo, 1984.
18. Černák, J., Chomič, J., Dunaj-Jurčo, M., and Kappenstein, C., *Inorg. Chim. Acta* 85, 219 (1984).

Translated by R. Domanský