

CLATHRATES OF TETRACYANONICKELATES CONTAINING 1,4-DIOXANE

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It was found after study of modifications of tetracyano complexes with 1,4-dioxane that a similar product is formed also by direct addition of 1,4-dioxane to a solution of $[\text{Ni}(\text{NH}_3)_m][\text{Ni}(\text{CN})_4]$ or to solid $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$; and 1,4-dioxane is initially bonded as a guest molecule and then as a ligand. The amount of guest component or ligand in the compounds $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a \cdot \text{Ni}(\text{CN})_4 \cdot (y - a)\text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$ and $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)_a \text{Ni}(\text{CN})_4 \cdot (n - a)\text{C}_4\text{H}_8\text{O}_2$ depends on the preparation conditions and on the conditions of storage of the solid product after isolation. The results of TA, IR, and GC analysis confirmed the presence of 1,4-dioxane bonded as a guest component and also 1,4-dioxane entering the host structure as a ligand.

The clathrates of tetracyano complexes with the general formula $\text{M}(\text{B})_m \text{Ni}(\text{CN})_4 \cdot n\text{G}$ (where B is a nitrogen- or oxygen-containing base, $m = 1, 2, \dots$, $n \neq 0$, and G is water or an aromatic compound) exhibit characteristic sorption capabilities for various organic compounds present in various mixtures¹⁻³. These properties improved after contact with auxiliary solvents (such as water, methanol, hexane, cyclohexane, pyridine, 1,4-dioxane and others). This modification could be carried out for compounds that are prepared and isolated from solution⁴. The clathrates of the compound $\text{Ni}(\text{NH}_3)_m \text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ after modification with 1,4-dioxane (after reaction with 1,4-dioxane and evaporation to dryness on a water bath)⁴ exhibited very interesting separation abilities in a rather broad temperature interval (80 to 240°C).

The amount of water n in the compound $\text{Ni}(\text{NH}_3)_m \text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ depends on the preparation conditions^{5,6}, primarily the pH. In strongly ammoniacal solution (above pH 9), the compound formed contains a low, nonstoichiometric amount of H_2O molecules. As the pH decreases, the amount of guest component increases.

Dempster and Uslu⁷ described clathrates with 1,4-dioxane enclosed as a guest component, prepared at pH 11 and 12, with the compositions $\text{Cd}(\text{NH}_3)_2 \text{Ni}(\text{CN})_4 \cdot .2 \text{C}_4\text{H}_8\text{O}_2$ and $\text{Ni}(\text{NH}_3)_2 \text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$. In spite of the fact the IR spectrum indicated that 1,4-dioxane is bonded with the NH_3 ligands of the host lattice through hydrogen bonds, the compounds were not stable. Decomposition began immediately after isolation, with loss of ammonia and 1,4-dioxane entered the host lattice struc-

ture as a ligand in place of the ammonia⁷. Decomposition of this compound also occurs during drying *in vacuo*.

Akyüz⁸ prepared the compound $\text{Cd}(4\text{-Me-py})\text{Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ (4-Me-py = 4-methylpyridine) which loses 1,4-dioxane on standing, which is replaced by water. All the characteristics of the host component remained intact in the IR spectrum after loss of the enclosed guest component. In agreement with the literature^{4,7,8}, when the compound contains 1,4-dioxane molecules, their function can change.

This work was carried out in order to study the direct synthesis of tetracyanonickel clathrates with 1,4-dioxane. The products formed should be similar to those obtained through modification of the clathrate compound $\text{Ni}(\text{NH}_3)_m\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ with 1,4-dioxane as an auxiliary solvent⁴. In this manner, an adsorption material should be simply obtained, with 1,4-dioxane incorporated into the molecule during the synthesis.

EXPERIMENTAL

Preparation

Compounds of the type $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (y - a)\text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$ (I). The synthesis of this type of clathrate compound is analogous to that for the clathrate compounds^{5,6} of the type $\text{Ni}(\text{NH}_3)_m\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$. Preparation was carried out in several ways:

(Ia). The light blue precipitate of $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ formed as an intermediate after the reaction of a solution of NiSO_4 with KCN was dissolved⁵ in 25% NH_4OH (the KCN solution was prepared by dissolving 3g of KCN in 25 ml H_2O and the NiSO_4 solution by dissolving 6g $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in 25 ml H_2O). 1,4-dioxane (20 ml) was added to the solution of $[\text{Ni}(\text{NH}_3)_m]\text{Ni}(\text{CN})_4$ obtained, which had a pH of 12. The solution was left to crystallize for 6–7 days. The purple crystals formed were dried in a dessicator (over silica gel).

(Ib). The preparation procedure was analogous to that for the previous compound, but the pH of the medium was decreased from 12 to 11 by addition of acetic acid (60%). During decreasing of the pH, a small amount of precipitate of the compound $\text{Ni}(\text{NH}_3)_m\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ was formed in the solution and was filtered off. Then 1,4-dioxane (20 ml) was added to the solution. The crystallization and drying procedure were the same as for Ia.

The synthesis procedure was varied for different concentrations of the ammonia solution, of 1,4-dioxane, pH, temperature, etc. The amount of 1,4-dioxane in the compounds obtained depended on the conditions.

Compounds of the type $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (n - a)\text{C}_4\text{H}_8\text{O}_2$ (II). This type of compound was prepared by direct action of 1,4-dioxane on the $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ precipitate in solid form, again employing several procedures:

(IIa). The freshly prepared precipitate was washed with 1,4-dioxane directly on the filter paper and dried similarly as in Ia, b.

(IIb). 1,4-dioxane was added to the freshly prepared precipitate. This synthesis procedure is not suitable as the $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ precipitate immediately swelled after addition of 1,4-dioxane, but did not dissolve. A light blue gel was formed that was very difficult to dry and partly decomposed.

(*Iic*). We found that it is preferable to dry the nickel (II) tetracyanonickel with composition $\text{NiNi}(\text{CN})_4 \cdot 5 \text{H}_2\text{O}$ (200 mg) and heat it to a temperature of 150°C , followed by addition of 1,4-dioxane to the hot precipitate (c. 1 ml) until the formation of an emulsion. The product is again dried.

All the chemicals employed were of *p.a.* purity.

Instruments and Methods

An OP 208 pH meter (Radelkis, Budapest) was employed to measure the pH, using a combined electrode.

Identification of substances. The elemental analysis of the synthesized substances and the thermal decomposition intermediates was carried out on a CHN analyzer (Hewlett-Packard, CHN Model 185). The nickel content was found complexometrically. IR spectra were measured (Specord IR 75, C. Zeiss, Jena) using KBr pellets (300 mg KBr/6 mg sample). For comparison, the IR spectrum of pure KBr and the IR spectrum of the sample using the Nujol technique were also measured.

Thermal analysis. The TG, DTG, and DTA analyses were carried out using a MOM derivatograph (Paulik-Paulik-Erdey) under constant conditions. The measuring parameters were as follows: sample weight 100 mg, sensitivity employed in the measurement of the derivatograph curves: TG 100 mg, DTA 1/5, DTG 1/5, maximum temperature 600°C , heating rate 6°C min^{-1} , atmosphere: air, comparison substance: solid Al_2O_3 , ceramic crucible. To emphasize the individual processes in the thermal decomposition, some of the samples were studied under changed conditions (200 mg sample, sensitivity of the derivatograph curves: TG 50 mg, DTA, DTG 1/3).

Gas chromatography. The gaseous products evolved from the partially decomposed products during thermal decomposition ($\text{C}_4\text{H}_8\text{O}_2$, H_2O , and NH_3) were analyzed qualitatively. The first two were analyzed by gas chromatography.

The gaseous products evolved during the first endothermic process (Figs 1a, b, 2) and after heating compounds *Ia* and *Ib* to 360°C and *Ila*, *Ilc* to 310°C were studied chromatographically (MCH-112, Laboratorní přístroje, Prague) using an SP 4 100 integrator (Spectra Physics). The carrier gas was nitrogen and, for water determination, hydrogen. 1,4-dioxane was determined using a column (2.5 m long) packed with Chromaton N-AW-DMCS with 10% OV-225 (grain size 0.20–0.25 mm) at a temperature of 130°C ; water was determined on a column packed with Porapak Q.

To obtain samples of the gaseous products, 200 mg of sample in a sealed ampoule (2.5–3 ml) was heated to 150°C for *Ia* and *b* and to 130°C for *Ila*–*Ilc*. The ampoule was terminated by a capillary, from which the gaseous product was removed using a syringe (1 μl) after cutting off the sealed end, and transferred to the gas chromatograph column. The gaseous products obtained at higher temperatures (310 , 360°C) were sampled for analysis in a similar manner, using a thick-walled ampoule. The gaseous samples of pure 1,4-dioxane and water were measured for comparison.

The presence of NH_3 in the sample was determined similarly by sampling. Tests using Nessler's reagent indicated the presence of ammonia in all the gaseous samples of products *Ia* and *b*, obtained after heating to 350°C .

RESULTS AND DISCUSSION

The results of TA, measured IR spectra, chromatographic tests and elemental analysis indicated that the action of 1,4-dioxane on $[\text{Ni}(\text{NH}_3)_m][\text{Ni}(\text{CN})_4]$ ($m > 2$)

in solution and on solid $\text{Ni}[\text{Ni}(\text{CN})_4]_n \cdot n\text{H}_2\text{O}$ ($n > 2$) led to enclosure of 1,4-dioxane as a guest molecule in the compounds formed, as well as partial substitution of the original NH_3 ligand (in *Ia* and *Ib*). According to the literature, $\text{Ni}[\text{Ni}(\text{CN})_4]_n \cdot n\text{H}_2\text{O}$ (where $n > 2$) exists⁹ as the layered compound $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot (n - 2)\text{H}_2\text{O}$ and 1,4-dioxane can substitute not only the water enclosed in the layers, but also that acting as a ligand.

The Thermal Stability of $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (y - a)\text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$
In contrast to the results given in the literature⁷, *Ia* obtained by the action of 1,4-dioxane on a solution of $[\text{Ni}(\text{NH}_3)_m][\text{Ni}(\text{CN})_4]$ ($m > 2$) at pH 12 is stable 12 days after isolation from solution. During thermal decomposition in the first endothermic process with a peak on the DTA curve at 105°C (Fig. 1a), 1,4-dioxane and water are released (Table I) with a mass loss on the TG curve of 23% (after a shorter drying time – for example 6 days – 25%).

Ammonia is released in a less marked endothermic process. The step in the thermal decomposition was also studied with changed parameters, with interruption at 400°C. The evolution of NH_3 occurred in two less marked endothermic processes with peaks on the DTA curve at 270 and 290°C (Fig. 1b).

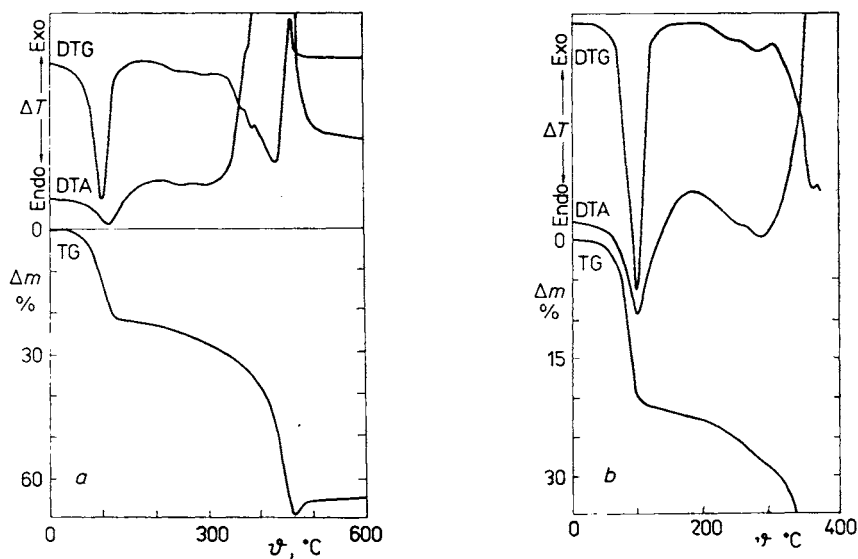


FIG. 1

The TG, DTG, and DTA curves of sample *Ia* at various sensitivities of the derivatograph curves: *a* TG 100 mg, DTA, DTG 1/5 (sample weight 100 mg); *b* TG 50 mg, DTA, DTG 1/3 (sample weight 200 mg)

A further amount of 1,4-dioxane — acting as a ligand, *i.e.* incorporated into the host structure — was released up to 360°C, where partial decomposition of cyanide occurs, accompanied by a sharp exothermal change on the DTA curve. The IR spectrum of the intermediates, obtained by heating the sample to 320°C, indicated that the cyanide begins to decompose in this region. The weak bands corresponding to NH₃ in the measured IR spectra indicated completion of evolution of NH₃ at 320°C. These weak bands are present together with the strong bands of the CH₂ and COC groups, indicating the presence of C₄H₈O₂. The final product of the thermal decomposition at 450°C is elemental nickel, which is oxidized to NiO in an exothermal process.

The clathrate compound *Ia* was also studied after storing for 36 and 120 days (in closed vessel in a dessicator over silica gel, as well as not stored in a dessicator). The shapes of the TG, DTG, and DTA curves are analogous to those obtained for the sample studied 12 days after isolation from solution. A small loss of 1,4-dioxane was found for samples stored in the open at laboratory temperature, under lower or higher pressure; this could be substituted by water.

Study of the thermal decomposition of samples isolated from solution at pH 12, prepared using half the amount of 1,4-dioxane, revealed differences in the mass loss in the individual processes and in the shape of the DTA curve. The mass loss in the first endothermal process is smaller, while that in the subsequent two endothermal processes (which are more marked) is greater. This sample has a lower content of 1,4-dioxane and higher content of NH₃ compared with *Ia*, confirmed by elemental analysis.

The thermal analysis of *Ib*, obtained from a solution with pH 11, yielded a curve with a similar shape as for sample *Ia* (Table I), obtained at pH 12. There was a slight

TABLE I

The contents of components in the clathrate compound with 1,4-dioxane Ni(NH₃)_m(C₄H₈O₂)_a-Ni(CN)₄·(y - a)C₄H₈O₂·n H₂O, samples *Ia* and *Ib*

Sample	pH	$\frac{m}{n}$	$\frac{a}{y-a}$	$(y-a)\text{C}_4\text{H}_8\text{O}_2 + \text{H}_2\text{O}, \%$	NH ₃ %	$a\text{C}_4\text{H}_8\text{O}_2 + (\text{CN})_2$ %
<i>Ia</i>	12	1.65	0.2	20.48 + 1.83 ^a	8.16 ^a	5.13 + 30.25 ^a
		0.35	0.8	23.0 ^b	7.5 ^b	36.0 ^b
<i>Ib</i>	11	1.40	0.3	21.88 + 3.55 ^a	6.72 ^a	29.37 + 5.74 ^a
		0.7	0.8	25.0 ^b	6.5 ^b	35.0 ^b

^a Calculated; ^b found.

difference in the results of the CHN analysis (Table II), indicating that sample *Ib* has a slightly higher water content, slightly higher 1,4-dioxane content and lower ammonia content, as a result of the decreased pH.

The Thermal Stability of $\text{NiNi}(\text{CN})_4 \cdot n\text{C}_4\text{H}_8\text{O}_2$ and $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (n - a)\text{C}_4\text{H}_8\text{O}_2$

Thermal decomposition of products *Ia* and *Ic*, obtained from solid $\text{NiNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, once again confirmed the presence of 1,4-dioxane, lost in two steps. Up to 130°C, the evolution of 1,4-dioxane is endothermal; the subsequent evolution is connected with a less strong exothermal process between 230 and 310°C (Fig. 2). Because of the long drying time, sample *Ib* was nonhomogeneous and was not further studied. Its thermal decomposition is analogous to that of samples *Ia* and *Ic*.

The Presence of 1,4-Dioxane and Water

The presence of 1,4-dioxane was confirmed for all the compounds obtained after contact with 1,4-dioxane, using gas chromatography. The retention time of gaseous 1,4-dioxane and of samples of the gaseous decomposition products from the clathrates was practically identical: $t_R = 5.30 \pm 0.05$ min. The presence of water was also confirmed by gas chromatography, with a retention time of $t_R = 2.55 \pm 0.05$ min.

TABLE II

Analysis of $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (y - a)\text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$, samples *Ia* and *Ib*

Sample	pH	m n	y a^a	Calculated/found			
				% C	% H	% N	% Ni
<i>Ia</i>	12	1.65	1	27.93	4.00	23.00	34.13
		0.35	0.2	27.68	4.00	23.16	34.23
<i>Ib</i>	1	1.40	1.1	28.43	4.09	21.31	33.09
		0.70	0.3	28.19	4.07	21.35	33.15
<i>b</i>	—	2	1	27.96	4.10	24.45	34.17
		0	0	—	—	—	—

^a Value calculated from the results of TG, DTA, and DTG curves; ^b values calculated for $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ are given for comparison.

IR Spectra

The IR spectra were measured both for samples stored at laboratory temperature and for samples obtained from interrupted thermal analysis at temperatures of 150, 200, 320, 360, and 400°C (Table III), to obtain more detailed information on the individual gaseous products and on the overall composition of the compound.

The IR spectra of *Ia* and *Ib* confirmed the presence of 1,4-dioxane, H₂O (in agreement with the gas chromatographic results) and NH₃. The valence vibrations of the CH₂ groups of 1,4-dioxane correspond to absorption bands^{7,10} in the region 2 990 to 2 850 cm⁻¹ and the valence vibrations of —C—O—C— to bands at 1 120 to 1 110 cm⁻¹ and 1 040 cm⁻¹ (Table III).

Samples *Ia* and *Ib* heated to 360°C also exhibited bands confirming the presence of 1,4-dioxane, as this temperature corresponds to the last stage in the evolution of this substance during thermal decomposition. At this temperature, the bands corresponding to the presence of NH₃ disappeared. At a temperature of 400°C, the IR spectrum of the sample contains only the strongest of the bands originally assigned to 1,4-dioxane, which are very weak.

The absorption bands assigned to water in the spectra of substances obtained after partial thermal decomposition indicate the presence of water intercalated in the interlayer space, replacing evolved 1,4-dioxane or 1,4-dioxane that occupies labile positions^{7,8}. The shift in the absorption bands of water is a result of the hydrogen bond between the water molecules and 1,4-dioxane¹¹.

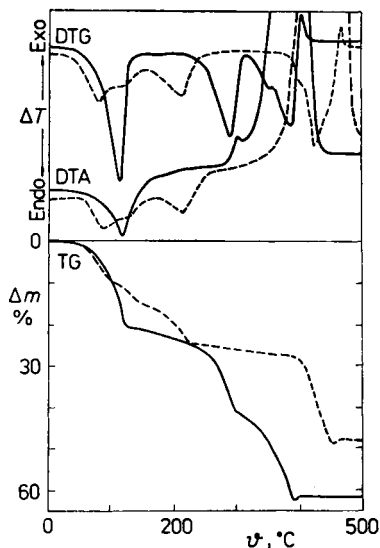


FIG. 2
The TG, DTG, and DTA curves of
Ni(C₄H₈O₂)Ni(CN)₄·C₄H₈O₂ (*IIC*) (—) and
NiNi(CN)₄·5 H₂O (-----)

TABLE III

Some of the vibrations characterizing the compound $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a\text{Ni}(\text{CN})_4 \cdot (y - a) - \text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$ (samples *Ia, b*) heated to the given temperatures

Assignment ⁷	25°C	150°C	200°C	320°C	360°C	400°C
$\nu_{\text{as}}(\text{H}_2\text{O})^a$	3 620 m, b	3 625 m, b	3 625 m, b	3 630 m		
$\nu_s(\text{H}_2\text{O})^a$	3 550 w	3 555 m, b	3 560 m, b	3 565 vw		
$\nu_{\text{as}}(\text{NH}_3)^a$	3 360 m, b	3 380 m, b	3 375 m	3 375 w		
$\nu_s(\text{NH}_3)^a$	3 280 m	3 305 s	3 300 m	3 305 m		
ν_{11} stretch	2 960 w	2 990 m	2 990 m	2 990 m	2 990 w	
$(\nu_{13} + \nu_{22})$	2 920 m	2 940 m	2 940 m	2 940 m	2 940 m	2 940 w
$(\nu_{13} + \nu_{22})$	2 920 m	2 940 m	2 940 m	2 940 m	2 940 w	
		2 910 vw	2 910 vw	2 910 vw		
$(\nu_3 + \nu_{30})$	2 890 vw	2 890 vw	2 890 vw	2 890 vw		
ν_{12} CH ₂ stretch	2 860 s	2 870 m	2 870 m	2 870 w		
$\nu(\text{CN})$	2 150 vs	2 160 vs	2 155 vs	2 200 vs	2 205 vs	2 200 vs
		2 155 vs		2 170 vs	2 170 vs	
$\delta(\text{H}_2\text{O}), \delta(\text{NH}_3)^a$	1 605 s	1 605 s	1 605 vs	1 610 m	1 610 m	1 615 w
ν_{30} CH ₂ sciss	1 450 s	1 450 m	1 450 m	1 455 s	1 455 m	1 455 w
ν_{13} CH ₂ sciss	1 440 w	1 440 vw	1 440 vw	1 440 vw	1 440 vw	
ν_{31} CH ₂ wag	1 375 m	1 380 m	1 380 vw	1 380 vw	1 380 w	
ν_{14} CH ₂ wag	1 370 m	1 370 m	1 370 m	1 375 m	1 375 w	
ν_{32} CH ₂ twist		1 300 m	1 305 m	1 310 s	1 310 m	
ν_{15} CH ₂ twist	1 290 s	1 290 m	1 285 m			
	1 250 s	1 255 m	1 255 m	1 255 s	1 260 s	
$\delta_s(\text{NH}_3)$	1 220 vs	1 225 vs	1 225 vs	1 230 s		
ν_{16} r.stretch	1 120 vs	1 110 s	1 100 s	1 110 vs	1 110 s	1 110 w
ν_{17} CH ₂ rock	1 075 s	1 080 s	1 080 s	1 090 s	1 090 s	
		1 075 m	1 075 w	1 075 s	1 075 s	
ν_{33} r.stretch	1 045 s	1 045 s	1 045 s	1 050 s	1 050 s	
	1 040 s					
ν_{34} CH ₂ rock	885 m	890 w	890 w	890 w	890 w	
ν_{18}	860 vs	875 vs	870 vs	885 w	880 vs	875 m
				875 vs		
$\rho(\text{H}_2\text{O}), \rho(\text{NH}_3)^a$	775 m	775 w	780 w	790 vw		
ν_{35}	605 vs	600 s	600 s	610 s	610 s	610 m
$\rho(\text{NH}_3)$	565 s	570 s	570 s	570 vw		
$\nu(\text{Ni}-\text{C})$	540 w	545 w	545 w	510 m	505 s	500 s
$\delta(\text{Ni}-\text{CN})$				445 vs	445 vs	
	425 vs	435 vs	435 vs	425 m		430 b

^a The bands may overlap.

The intensity of the absorption bands corresponding to the presence of 1,4-dioxane in the IR spectra of the intermediates obtained at 150–360°C is weaker than for the original samples (measured after storage at 25°C).

The IR spectra of samples *Iia*–*Iic* and their intermediates after partial thermal decomposition (in agreement with the shapes of the TG, DTA, and DTG curves) once again confirmed the presence of 1,4-dioxane.

The Chemical Composition of the Products

Comparison of the results of elemental analysis with the theoretical values indicated that samples *Ia* and *Ib*, obtained by the action of 1,4-dioxane on a solution of $[\text{Ni}(\text{NH}_3)_m][\text{Ni}(\text{CN})_4]$, have a composition very similar to the compound $\text{Ni}(\text{NH}_3)_2\text{-Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ (Table II).

However, a change in the synthesis conditions (various ammonia solution concentrations, 1,4-dioxane concentrations, pH, temperature during the crystallization, etc.) yields a compound whose composition has been indicated by elemental analysis, TA, IR, and GC as being generally expressed by the formula $\text{Ni}(\text{NH}_3)_m(\text{C}_4\text{H}_8\text{O}_2)_a\text{-Ni}(\text{CN})_4 \cdot (y - a)\text{C}_4\text{H}_8\text{O}_2 \cdot n\text{H}_2\text{O}$, where $m = 1.2\text{--}1.8$, $y = 0.5\text{--}1.1$, $a = 0.1\text{--}0.3$, and $n = 0.3\text{--}1$.

When the amount of 1,4-dioxane employed in the synthesis is decreased by half (compared to sample *Ia*), a minimal amount of NH_3 ligands is replaced by 1,4-dioxane.

It has been pointed out in the literature⁷ that the compound with the composition $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ is unstable and decomposes immediately after isolation from solution, with partial delocalisation of 1,4-dioxane into the first coordination sphere. Part of the NH_3 is lost from the host lattice and is replaced by 1,4-dioxane.

Changes occur in the composition of compounds *Ia* and *Ib* during the synthesis (6 days of crystallization in the air and 6 days drying in a dessicator), during which part of the 1,4-dioxane bonded as a guest component in the clathrate spaces replaces part of the NH_3 ligands, which are lost from the host lattice. During drying, water from the surrounding atmosphere enters the free space and is bonded through hydrogen bonds to the oxygen atoms of 1,4-dioxane, which is coordination bonded to the nickel ion. The measured IR spectra and thermal analysis curves indicated that dry samples *Ia* and *Ib* stored in closed bottles (or in a dessicator over silicagel) had analogous composition after several months or even after a year. It is possible that small changes occur during storage, connected with delocalisation of the 1,4-dioxane in the clathrate compound, (from the guest to the host components), but these small changes are difficult to observe on the IR spectra, as pointed out in the literature⁸. Partial decomposition occurs in samples stored in the air at laboratory temperature or *in vacuo*.

The reaction of 1,4-dioxane with solid $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ yields compounds *Ila* and *Ilb*, with composition $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)\text{Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$. A change in the synthesis conditions can yield a compound with the general composition $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)_a\text{-Ni}(\text{CN})_4 \cdot (n - a)\text{C}_4\text{H}_8\text{O}_2$, where 1,4-dioxane is again present as a guest component as well as acting as a ligand bonded to the host component. Dioxane replaces water in the original compound, $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$, in agreement with the results in ref.¹².

Compound $\text{NiNi}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ exhibits^{1,13} strong sorption capabilities for various organic compounds. Even partial replacement of the NH_3 or H_2O ligands by 1,4-dioxane results in better approachability of the interlayer spaces in tetracyanonickel clathrates¹³.

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