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Tetracyanonickelate Compounds as Sorptive Materials and the Substitution of their H_2O Content by D_2O

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Abstract. The compounds $NiNi(CN)_4 \cdot 3{,}5H_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$ have been studied to examine the possibility of substituting their H_2O or NH_3 content by D_2O. Contact with D_2O was performed after heating the compounds to several temperatures. Depending on the degree of decomposition of the original compounds different ranges of substitution were possible. In such manner the compounds $NiNi(CN)_4 \cdot 3{,}5D_2O$, $NiNi(CN)_4 \cdot 5D_2O$, $Ni(NH_3)_2Ni(CN)_4 \cdot D_2O$, and $Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$ were prepared and thermally they were less stable than the original ones. The substitution by D_2O is in agreement with the sorptive properties of the original tetracyanonickelate against different organic compounds using GC, since these could substitute the guest component and sometimes also the ligands during their decomposition.

Key words: Tetracyanocomplexes, substitution of H_2O by D_2O, thermal decomposition, temperatures for the substitution sorptive properties, $NiNi(CN)_4 \cdot nD_2O$, $Ni(NH_3)_2Ni(CN)_4 \cdot 1D_2O$, $Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$.

1. Introduction

The compounds $NiNi(CN)_4 \cdot nH_2O$ and $Ni(NH_3)_2Ni(CN)_4$ belong to the group of tetracyanocomplexes prepared and used in our department [1]. They are of the general formula $M(B)_mM'(CN)_4 \cdot nG$ (M = Ni,Cu,Cd,Zn, M' = Ni,Pt,Pd, $m = 0,1,2,3,4\ldots$, $n \neq 0$, B is an oxygen or nitrogen containing base, including H_2O. They represent possible sorptive materials under static or dynamic conditions [2]. The values of m and the type of ligands determine the conditions of their utilisation. The value of n is equally determinative but does not depend on the type of guest component [2] as in other types of such compounds [3,4].

The preparation of both compounds was preceeded in our department by the study of the pH region [5] and by analysing the mode of the isolation [6] of the compounds, both factors influencing the value of m and n.

The possibility of differentiating the water molecules existing either as the guest component or as the ligands in the host is known from the literature [7,3,8]. Recently Akyüz [9] described the inclusion of the dioxane molecule in the tetracyanocomplex prepared with methylpyridine as ligand in the Hofmann's type complex and its substitution with water.

After the modification of $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ with dioxane [10,1] or pyridine the differentiation is not complete, therefore we found it advantageous to use the substitution of the water molecules by its deuterated compound in several steps of the thermal decomposition in the studied compounds [11].

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2. Experimental

2.1. MATERIALS

$NiSO_4$	: p.a.	(Lachema, Brno)
KCN	: p.a.	(Lachema, Brno)
NH_4OH	: p.a.	(Merck)
D_2O	: 99%	(Chemapol, Praha)

2.2. METHODS

The *identification* was made by CHN analysis (Hewlett Packard Model 185), the presence of individual functional groups and the intermediates were checked by IR Spectroscopy (Specord IR-75) in the range 4000–400 cm^{-1} using KBr discs (10 mg/300 mg KBr).

The thermal decomposition was followed on Derivatograph (MOM OD 102) under dynamic conditions (in air) by heating (9°/min) to about 900°C (Al_2O_3 as reference material). The parameters were: sample weight: 100 mg; sensitivities used in measuring the derivatographic curves: TG 100 mg, DTA 1/10, DTG 1/15.

As a continuation of previous work [12] the tetracyanonickelates were used as packing materials in *gas chromatographic experiments* (Chrom 4, Laboratorní prístroje, Prague).

The compound was used in a dry and loose form. This was obtained by mixing the compounds (10% of weight) with 1,4 dioxane and with the inert support (Chromosorb W/NAW, 80/100 mesh, Supelco Inc. Bellefonte, U.S.A.) and then by the evaporation of the dioxane on a water bath (100°C).

The glass column was of length 2.5 m and i.d. 3 mm. The flow rate of the carrier gas was 24 cm^3 min^{-1}.

The chromatographic experiments started at 80°C and continued at gradually higher temperature up to 240°C. Then we returned to the starting temperature. We used for the separation two mixtures of organic compounds containing alkylderivatives of cyclohexane (mixture A) or of ketones (mixture B).

2.3. SYNTHESIS

The prepared and isolated compounds were:

$NiNi(CN)_4 \cdot 3,5H_2O$	**(1)**
$NiNi(CN)_4 \cdot 3,5D_2O$	**(1a)**
$NiNi(CN)_4 \cdot 5D_2O$	**(1b)**
$Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$	**(2)**
$Ni(NH_3)_2Ni(CN)_4 \cdot D_2O$	**(2a)**
$Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$	**(2b)**

The substitution reactions with D_2O in compound (**1**) and (**2**) were carried out after heating the appropriate compound to different temperatures, chosen according to the desired appropriate decomposition of the compound.

The simple tetracyanocomplex $NiNi(CN)_4 \cdot 3,5H_2O$ (**1**) was prepared in accordance with the literature method [3] in 99% yield.

$Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ ($n \geq 0$) was prepared by adding concentrated ammonia solution to the aqueous suspension of $NiNi(CN)_4$ at pH values of about 5.5 and 9.

With the former pH value the compound $Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$ (**2**) was obtained and with the latter pH value anhydrous $Ni(NH_3)_2Ni(CN)_4$ was obtained. The preparation at pH = 9 showed again [5,6] that this pH region is not the most favourable for the isolation of compounds with properties utilisable in the sorptive experiments ($n \neq 0$).

The deuterated compounds (**1a**) and (**1b**) were prepared by adding D_2O to the tetracyanocomplex (**1**) after heating it to 200 or alternatively to 260 °C. Both compounds remained in contact with D_2O for three months. After this time new products were isolated $NiNi(CN)_4 \cdot 3{,}5D_2O$ (**1a**) and $NiNi(CN)_4 \cdot 5D_2O$ (**1b**), respectively.

$Ni(NH_3)_2Ni(CN)_4 \cdot D_2O$ (**2a**) was obtained after heating compound (**2**) to 130 °C (when it loses the mole of H_2O). D_2O was contacted with anhydrous (**2**) for two weeks.

$Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$ (**2b**) was prepared by heating the compound (**2**) to 300 °C and then suspending in D_2O for three months.

For comparison we left compounds (**1b**) and (**2b**) in further contact with D_2O for a period of 12 months. The IR spectra of the products ($\mathbf{1b}_{12}$ and $\mathbf{2b}_{12}$) are reported in Table II.

3. Results and Discussions

3.1. THERMAL DECOMPOSITION

We were looking for the most efficient simulations of the sorptive experiments [1] with the tetracyanocomplexes (**1**) and (**2**) as stationary phase sorptive materials utilisable in different temperatures ranges by searching for the most useful temperatures for the deuteration reactions.

In the thermal decomposition of $NiNi(CN)_4 \cdot 3{,}5H_2O$ (**1**) it experiences the loss of all the water content during an endothermic process (with DTA maxima at 150 and 220 °C). The next step of its thermal decomposition is the destruction of the host in an exothermic process, the final product being NiO (2NiO 148.24 mg/mol; exper. 147.83 mg/mol).

$NiNi(CN)_4 \cdot 3{,}5D_2O$ (**1a**) loses its D_2O content at lower temperatures than compound (**1**) and it exhibits two endothermic processes (with DTA maxima at 135 and 200 °C).

Compound (**1b**) $NiNi(CN)_4 \cdot 5D_2O$ is evidently less stable (in comparison of the starting temperatures for the evolution of the D_2O) and on the DTA curve three maxima at 95, 135 and 200 °C can be seen. It loses its D_2O content in three ($1.5 + 1.5 + 2D_2O$) aliquots, thus differing from compounds (**1**) and (**1a**), where the evolution of D_2O exists only in two steps.

In all three compounds (**1**), (**1a**) and (**1b**) after the loss of D_2O at temperatures of 335, 300, and 280 °C respective an exothermic decomposition of the cyanide occurred to give nickel (at 540, 500, and 480 °C, respectively), which was then oxidised exothermally to give NiO.

The thermal decomposition of the normal clathrate compound (**2**) $Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$ starts as in a true Hofmann compound with the loss of water in an endothermic process with a DTA maximum at 130 °C. Above this temperature at 210 and 300 °C the endothermic release of ammonia occurs ($1NH_3 + 1NH_3$).

Compound (**2**) after heating to 130 °C and reaction with D_2O gives the product $Ni(NH_3)_2Ni(CN)_4 \cdot 1D_2O$ (**2a**). It loses its D_2O content in an endothermic way at 108 °C and then the NH_3 content in two aliquots at 195 and 290 °C. By comparison with compound (**2**) all the DTA maxima are shifted to lower temperatures.

The compound $Ni(D_2O)_2Ni(CN)_4 \cdot 1D_2O$ (**2b**) loses its D_2O content at 130 and 200 °C in endothermic processes ($1D_2O + 2D_2O$). The course of the thermal decomposition is very similar to that of compound (**1a**) (with two maxima at 135 and 200 °C on the DTA).

The compounds (**2**), (**2a**) and (**2b**) after the loss of H_2O, NH_3 and D_2O undergo exothermic processes at about 520, 490, 475 °C when they decompose with release of the dicyanogen, the final product being nickel oxide.

By studying the thermal decomposition of all the compounds we can state in all cases that there is a lower thermal stability in the case of the compounds substituted with deuterated water in comparison with the analogous compounds containing H_2O. The differences in starting temperatures were 150 and 135 °C in the case of (**1**) and (**1a**) and 130 and 108 °C in

Table I. Characteristics of the thermal decomposition of $NiNi(CN)_4 \cdot 3.5H_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$ and of their deuterated forms

Compound	Temperature of the decomposition (°C)	*m* weight loss (g/mol)	*R* residual weight (g/mol)	Released components (mol/mol)	Notes about the course of DTA curve
$NiNi(CN)_4 \cdot 3.5H_2O$	150	64.45	$3.5H_2O$	(63)	*endo* w.
(**1**)	220				
	335	103.2	$2(CN)_2$	(104)	*exo* v.s.
	540	118	2Ni	(117.4)	
	590	147.89	2NiO	(148.24)	*exo* w.
$NiNi(CN)_4 \cdot 3.5D_2O$	135	72.86	$3.5D_2O$	(70)	*endo* sh., m.
(**1a**)	200				
200 °C[a]	300	101.5	$2(CN)_2$	(104)	*exo* v.s.
	500	115.6	2Ni	(117.4)	
	580	146.2	2NiO	(148.24)	*exo* m.
$NiNi(CN)_4 \cdot 5D_2O$	95	99.64	$5D_2O$	(100)	*endo* m., w., sh.
(**1b**)	135				
260 °C[a]	200				
	280	102.3	$2(CN)_2$	(104)	*exo* v.s.
	480	116.5	2Ni	(117.42)	
	530	145.3	2NiO	(148.24)	*exo* s.
$Ni(NH_3)_2Ni(CN)_4 \cdot 1H_2O$	130	21.87	$1H_2O$	(18)	*endo* l
(**2**)	210	35.54	$1NH_3$	(34)	*endo* br., w., l.
	300		$1NH_3$		
	320	98.44	$2(CN)_2$	(104)	*exo* v.s.
	520	117.58	2Ni	(117.42)	
$Ni(NH_3)_2Ni(CN)_4 \cdot 1D_2O$	108	19.28	$1D_2O$	(20)	*endo* m.
(**2a**)	195	35.81	$1NH_3$	(34)	*endo* m., sh.
130 °C[a]	290		$1NH_3$		
	300	102	$2(CN)_2$	(104)	*exo* v.s.
	490	118.2	2Ni	(117.4)	
	500	146	2NiO	(148.24)	*exo*
$Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$	130	59.09	$1D_2O$	(60)	*endo* w., m.
(**2b**)	200		$2D_2O$		
300 °C[a]	300	103.5	$2(CN)_2$	(104)	*exo* v.s.
	475	146.5	2Ni	(117.4)	
	500	140.3	2NiO	(148.24)	*exo*

[a] Temperature to which the original compound was heated before deuteration. The loss (theoretically) by heating in brackets. s = strong, m = medium, sh = sharp, v = very, l = little, br = broad, w = weak.

the case of compounds **(2)** and **(2a)**. Compound **(1b)** with the largest content of D_2O is the least stable one.

The absence of the NH_3 ligands affected the sorption of D_2O positively. The compounds containing NH_3 ligands sorbed D_2O (1 + 2) under the studied conditions; the first D_2O was intercalated in the layers of the host. On heating the compound loses this D_2O first and only then gradually loses the NH_3 ligands.

By heating compound **(2)** to 300 °C before contact with D_2O, we could study the sorption of three D_2O molecules. The last two were lost at analogous intervals of temperatures as were the NH_3 ligands lost from **(2)** and **(2a)**. In contrast compound **(1a)** containing D_2O only in the interlayer space does not lose the D_2O content in one step.

The thermal decompositions of the compounds are summarised in Table I.

3.2. IR SPECTRA

By comparison of the IR spectra of all compounds in Table II we may see different shifts depending [14–18] on the presence and amounts of D_2O and NH_3 present. Their ν_s, ν_{as} and θd frequencies are affected in such way.

The $\nu(C{\equiv}N)$ values are not affected by the substitution of H_2O by D_2O in the case of compounds **(1)**, **(1a)** and **(1b)** – in the absence of NH_3 ligands – but $\nu(C{\equiv}N)$ is changed (30 cm^{-1}) in the case of **(2)** after the substitution of H_2O or NH_3 by D_2O. The bond strength of $C{\equiv}N$ is increasing during the loss of NH_3 ligands, after the partial thermal degradation the interactions between ligands in the cationic and anionic part of the host and equally the linkage of D_2O instead of H_2O is affecting the bond strength of the $C{\equiv}N$ group.

The IR spectra show that D_2O is sorbed during its contact with both studied compounds. The in plane deformation is in the case of the enclathrated D_2O shifted to higher frequencies.

The role of the individual water molecules in **(2b)** may be differentiated only in further studies. The proposed form of **2b** is analogous to the compounds with linked pyridine or dioxane molecules [14], where the organic molecule is acting as a ligand rather than as a guest. Compound **(2)** in its reaction with D_2O after heating to 300 °C (when the H_2O and NH_3 content are lost) also gives these two forms.

In this connection we have to remember the situation, when compound **(2)** used as a stationary phase after modification with pyridine [12] or dioxane [13] and heated to 300 °C in GC experiments it could again sorb the organic compounds after cooling to 80 °C.

The D_2O sample will consist of an equilibrium mixture of D_2O, HDO and H_2O. Consequently the IR spectra contain the characteristic frequencies of all components of this system [17].

By comparison of the weight losses of H_2O, D_2O and HDO, respectively, their presence could be not differentiated in the thermal analysis or otherwise.

The frequencies of the degradation products obtained from D_2O containing samples could be assigned according to literature values. In the samples measured after a year long contact with D_2O, (**1b**$_{12}$ and **2b**$_{12}$) its band intensities were quite pronounced.

3.3. SORPTIVE EXPERIMENTS

The range of temperatures available for the sorption and elution of two different mixtures of organic compounds are shown on the chromatographic traces in Figure 1.

The experiments were performed with the original compound **(2)** to confirm in this method again the temperatures appropriate for the substitution of the guest component and ligands

Table II. The infrared characteristics (cm^{-1}) of the studied compounds

Assignment (cm^{-1})	(**1**)	(**1a**)	(**1b**)	(**1b**$_{12}$)	(**2**)	(**2a**)	(**2b**)	(**2b**$_{12}$)	References
δNiCN				425 m.		425 w.		435 m.	
πNiCN				450 m.	450 w.				
νNiC, ρNH^b				570 m.	550 m.	550 m.	560 v.w.	560 v.w.	
νMOH	1090 s.			1020 w.	1020 w.	1020 w.	1020 m.	1020 w.	
$\nu_s NH_3$, $\nu_d D_2O(s)^b$			1200 v.w.	1130 m.	1200 s.	1130 s.	1150 m.		1178 [17,13]
						1210 s.	1210 w.	1198 m.	
							1240 w.	1240 m.	1220 [18]
$\nu_d NH_3$, $\nu_d HDO(g)^b$		1390 m.	1390 m.	1395 w.	1400 s.	1410 m.	1402 m.		[15,16]
$\nu_d NH_3$, $\delta_{as} NH_3$, $\nu_d H_2O$	1590 s.	1585 m. br.	1590 m. br.	1595 w.	1585 s.	1595 m.	1605 m.	1605 w.	
νCN	2135 v.s., sh.	2140 v.s.	2140 v.s.	2140 v.s.	2135 v.s.	2150 v.s.	2165 v.s.	2165 v.s.	
$\nu_s OD(s)$, $\nu_{as} HOD(s)$		2420 v.w.	2420 w.	2420 m.		2450 m. br.	2450 m. br.	2450 m.	[16,18]
$\nu_s D_2O(g)$		2630 m.	2630 m.			2630 s.	2620 m.	2645 m.	2671 [16–18]
$\nu_s HDO(g)$						2720 m.	2730 w.	2730 w.	[16]
$\nu_s NH_3$, $\nu_{as} HDO(s)^b$		3300 br.	3300 br.	3300 br.	3270 w.	3270 w.	3270 w.	3300 br.	[16]
$\nu_{as} NH_3$, $\nu_{as} HDO(1)^b$		3400 br.	3400 br.	3400 br.	3350 m. br.			3400 br.	
$\nu_{as} OH$	3580 s.				3550 s. br.	3580 m. br.	3590 m.	3600 m.	
$\nu_{as} HDO(g)$							3707		[15,16,17]
				3850 m.		3850 w.		3850 w.	[18]

[a] Concerning the D_2O, HDO frequencies.

[b] In the appropriate case they may be overlapped.

(**1b**$_{12}$) Sample (**1b**) measured after a year long contact.

(**2b**$_{12}$) Sample (**2b**) measured after a year long contact.

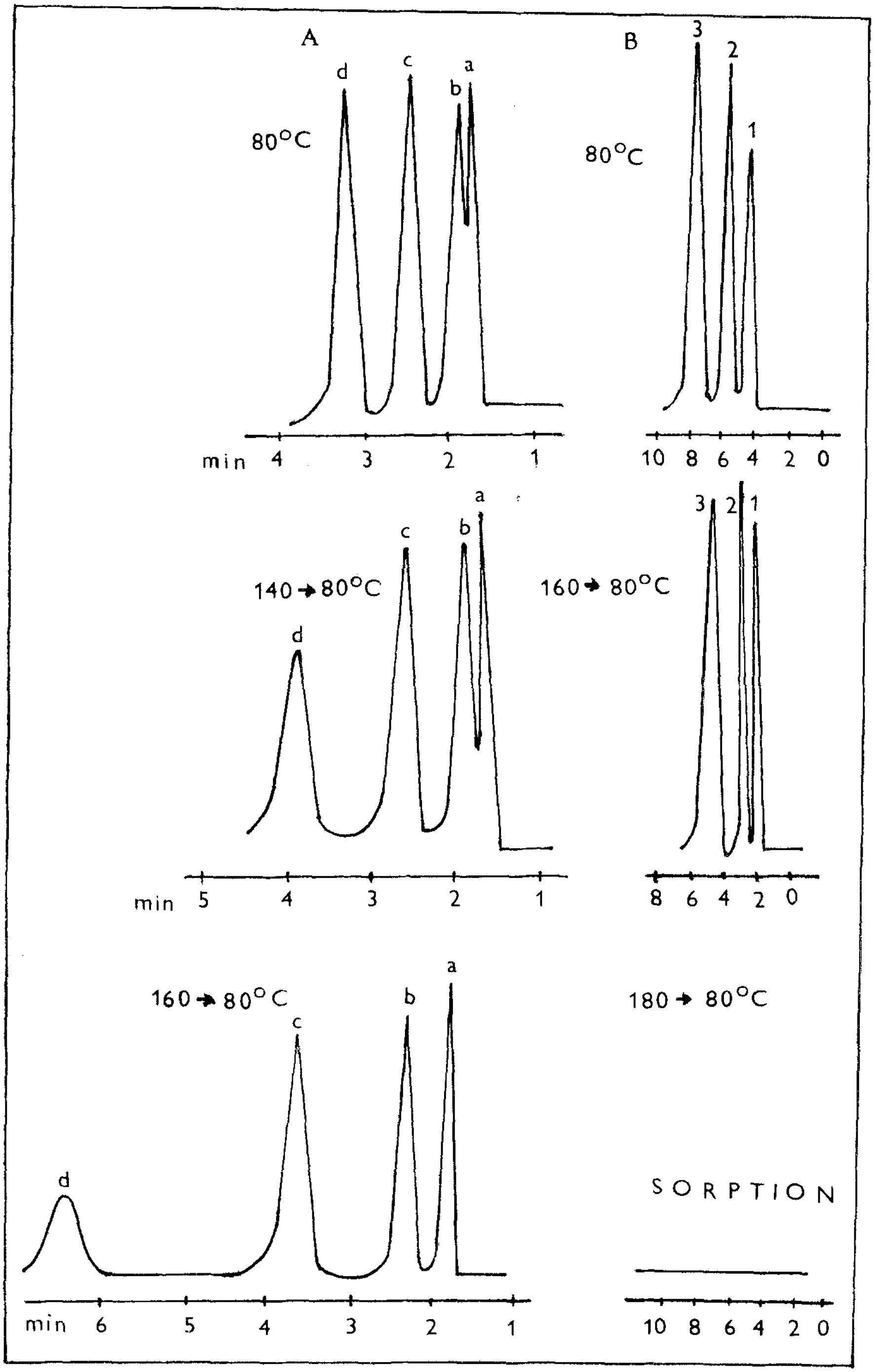

Fig. 1. $Ni(NH_3)_2Ni(CN)_4 \cdot H_2O$ as the stationary phase (10%) after modification with dioxane at different temperatures. Mixtures used: A: cyclohexane (a), methylcyclohexane (b), ethylcyclohexane (c), propylcyclohexane (d); B: dimethylketone (1), methylethylketone (2), methylpropylketone (3).

by D_2O. The temperature range for the chromatographic experiments agreed with the temperature used for heating compound (**2**) before its contact with D_2O.

The stationary phase was prepared in its best form [13] by its modification with dioxane, when it is effective in sorption between 80–240 °C. Thermal analysis shows that guest dioxane starts to be released between 80–160 °C and this temperature interval is the most convenient for the sorption of organic compounds. In our case using mixtures A and B the retention times at 80 °C are rather short, but they are gradually increased if after heating the column to 140–240 °C it is cooled to 80 °C (Figure 1). 1,4-Dioxane, which can also act as a ligand affects the structure of the host, mainly by enlarging the distance between the layers [3]. The second part of the dioxane content as a ligand is lost between 160–230 °C.

Mixture A is better separated (Figure 1) at higher temperatures, mainly during the escape of the dioxane from the broadened interlayer space (40–160 °C). This property was conserved after returning to the starting temperature of 80 °C.

Compounds of different size (mixture B) increase their retention times. After heating to 180 °C and returning to 80 °C the space was available for the sorption of the derivatives of ketones.

Compound (**2**) used as a packing without modification loses the intercalated water between 40–140 °C and the remaining water is lost together with the NH_3 ligands between 150–350 °C. The favourable temperatures for the recent separation agreed with these and with the temperatures of the substitution of water by D_2O.

4. Conclusions

The compounds $NiNi(CN)_4 \cdot nH_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ after heating to appropriate temperatures and after reaction with D_2O may sorb it and after substitution of the H_2O the compounds formed are: $NiNi(CN)_4 \cdot 3{,}5D_2O$; $NiNi(CN)_4 \cdot 5D_2O$; $Ni(NH_3)_2Ni(CN)_4 \cdot D_2O$; and $Ni(D_2O)_2Ni(CN)_4 \cdot D_2O$.

The amount of D_2O linked in the compounds is also higher than the original amounts of H_2O (n) in the formula $M(B)_mM'(CN)_4 \cdot nG$ and the maximum value of n attained under these conditions was five. Regarding the higher mass of D_2O we can correlate it with the maximum amounts of H_2O in compound (**1**) by comparison with literature values [3, 17]. The molecules of D_2O are not only coordinated, but also blocked in interlayer spaces. Therefore they may interact also with those which are coordinated and the cohesion of layers may be higher and affecting the $\nu(C{\equiv}N)$ value. The presence of D_2O was still detectable after 12 months long contact with D_2O according to the IR spectra. But the characteristic frequencies of the samples show the presence of some aliquots of HDO or H_2O, respectively.

The possibility of substituting the water content by deuterated water in the compounds of the type $NiNi(CN)_4 \cdot nH_2O$ and $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ ($n \neq 0$) shows that the tetracyanocomplexes in sorption experiments are sorbing the organic compounds not just adsorbing them.

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