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Tetracyano Complexes Incorporated in Natural Zeolitic Materials

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Abstract. New compounds, possibly of the host–guest type, were prepared by the combination of a natural zeolitic material of the clinoptilolite type and $Ni(NH_3)_2Ni(CN)_4 \cdot 2.75\, H_2O$. The new compounds showed an increase of crystallinity in the diffractographic measurements. The measured IR spectra, thermal analysis and GC experiments were used to identify the products.

Key words. Tetracyanonickelate, zeolitic material, clinoptilolite, host–guest complex.

1. Introduction

The inclusion compounds of tetracyano complexes of the type $M(B)_m M'(CN)_4 \cdot nG$ are known for their characteristic selective enclosure of the guest G (organic compounds or water molecules) in the layers forming the host H. It represents the type: H·G. Their stability is increased or decreased by the dependence on the interactions between at least two kinds of compounds. It is natural that each component – the host and guest – is formed by a system of molecules. They are capable of substituting G by one other, at least partially, and then they are of the form: $H \cdot G_1 \cdot G_2$. They may therefore be used in an effective way in sorption and separation processes [1] or electrochemistry [2].

The tetracyano complexes of the Hofmann and Hofmann-derived types, although usually named as clathrates, are not clathrates in the strict sense of Powell's definition [3]. According to Iwamoto [4] they form a pillared intercalation compound with G represented by an aromatic or aliphatic compound [5]. This term 'pillared' is the same as Burch [5] used in 1988 in his monograph *Pillared Clays*. Further proof of the analogy of synthetic and natural materials comes from the use of the terms organic clays [6], organic zeolites [7] etc.

This fact led us to make attempts to prepare host–guest-type complexes, formed by the combination of two such types of material. We have used the combination of the natural zeolitic material with cyclodextrin [8], and the combination of zeolitic materials with fertilisers and also with $Ni(NH_3)_2Ni(CN)_4 \cdot 2.75\, H_2O$. The last combination is the theme of this paper. Kijima [9] has already described the combination of montmorillonite with cyclodextrins.

Until now the tetracyano complexes are known as compounds forming only the *host* component in inclusion compounds. We succeeded in the combination of two

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compounds – usually forming the host in inclusion compounds – and, together with the guest, they represent a product of the following type: $H_1 \cdot H_2 \cdot G$. The zeolite structure [10] is possibly enclosing the tetracyano complex thus stabilising the latter to higher temperatures. In processes at higher temperatures the product may be capable of sorbing further guest components – at least to partially substitute the original one – and in such applications it is in the form: $H_1 \cdot H_2 \cdot G_1 \cdot G_2$ or $H_1 \cdot G_1 \cdot G_2$.

2. Experimental

2.1. MATERIALS

The natural zeolitic material of the clinoptilolite (CT) type from the East Slovak deposit at Nižný Hrabovec (content of pure clinoptilolite mineral 57.2%) was prepared by grinding to a grain size < 0.1 mm. In our work it was treated before the synthesis with Ca(II) and Cu(II) ions, using 1M solutions of $Ca(NO_3)_2 \cdot 4\,H_2O$ and $CuCl_2 \cdot 2H_2O$.

For the preparation of the clathrate KCN, $NiSO_4 \cdot 7\,H_2O$, and concentrated solutions of ammonia and acetic acid were used. For the chromatographic experiments three types of mixtures of compounds were used:

(a) C_9-C_{12} alkanes
(b) aromatics: benzene, toluene and *o*-, *m*-, *p*-xylene
(c) oxygen-containing compounds: C_1-C_4 alcohols and C_1-C_4 acetate esters.

All chemicals were from Lachema Brno.

The choice of mixtures was determined by the striking ability of the tetracyanonickelate clathrates to separate one oxygen-containing compound from the others.

2.2. INSTRUMENTATION

For the identification of products, starting materials and physical mixtures we used: Specord 80 IR Spectrophotometer (Carl Zeiss Jena) in the 4000–200 cm^{-1} range, KBr discs (4 mg: 400 mg KBr); Derivatograph (MOM 102 Budapest) – TG 100 mg, DTA 1/5, DTG 1/5, heating rate 10°C/min. Reference material Al_2O_3. The chromatographic experiments were performed on a Chromatograph CHROM-4 instrument.

A metallic column (0.5 m long and 3 mm diameter) was used. The injected volume of the tested mixtures was 1 mL, temperature: 150°C. Experiments were performed with nitrogen as the carrier gas (21 mL/minute). In preliminary experiments the column was heated to 80, 100 and 120°C. CHN analysis was carried out using a Perkin Elmer 2400 CHN Analyser.

2.3. METHODS

(a) The natural zeolitic material of the clinoptilolite type CT used in this work is described by Meier's formula enabling large substitution in the frame of the alumino-silicate [11]. Recently the used zeolite was described [10] by the crystallographic formula:

$$Ca_{(1.55-2.00)}Mg_{(0.1-0.4)}Na_{(0.6-0.8)}K_{(6.4-6.7)}Si_{29}O_{72}.$$

The ion exchanged zeolites were made [8] by contacting the zeolite with a solution of the Ca(II) and Cu(II) salts (1g of zeolite/6mL of 1M solution) at room temperature during a 10 day period. The treated zeolites are denoted as CT-Ca and CT-Cu.

(b) In the preparation of $Ni(NH_3)_2Ni(CN)_4 \cdot 2.75\ H_2O$ [12] the published procedure using a solution of KCN (3 g in 25 mL H_2O) and of Ni(II) ions (6g $NiSo_4 \cdot 7\ H_2O$) was used. After dissolving the precipitate in ammonia the pH was modified by 60% acetic acid to a value of 6. After filtering, washing with alcohol and ether and drying, the product analysed as $Ni(NH_3)_2\ Ni(CN)_4 \cdot 2.75\ H_2O$. The quantity n agreed with that in [13]. In the preparation we used either the dried clathrate, and then wetted it or the freshly prepared clathrate. The latter is used only in X-ray measurements.

(c) The preparation of the new product was attempted in three ways. Zeolite modified by Ca(II) or Cu(II) ions was left in contact with the solution of $Ni(NH_3)_m Ni(CN)_4$ or with the prepared and isolated microcrystalline $Ni(NH_3)_2Ni(CN)_4 \cdot 2.75\ H_2O$ compound. In both cases the contact was made during a 10 day period. In the first case no new product (according to IR spectra and TA measurement) could be detected. After 1–2 days standing it formed only a mixture of both starting materials. In the third case the presence of water as the guest in the tetracyano complex was used and the zeolite with sorbed Ca(II) and Cu(II) ions was left in contact with the wetted clathrate (3 mL of water to 1 g of the powdered clathrate). The washed and dried products obtained showed the characteristics of the new host–guest type product. They retained the characteristic features of both starting compounds. The product obtained from the Ca(II) form of the zeolite is referred to as (**1**) and the product from the Cu(II) form as product (**2**).

Both products were obtained by the reaction of two starting compounds used in their mass proportion 1 : 1.

(d) The physical mixtures of starting materials were prepared by simple co-grinding in a mortar.

3. Results and Discussion

3.1. PREPARATION

$Ni(NH_3)_2Ni(CN)_4 \cdot 2.75\ H_2O$ has unit cell dimensions [12] of: $a = 0.724$ nm, $b = 1.432$ nm, $c = 0.874$ nm. The clinoptilolite used in this work, according to Perchár [15], has parameters of $a = 0.746$ nm, $b = 1.7908$ nm, $c = 1.1613$ nm, $\beta = 90.58°$.

In the literature [15] Alberti has determined the parameters of clinoptilolite (heulandite type) samples from two different foreign deposits. The pore sizes were determined as 0.76 × 0.3 nm and 0.46 × 0.33 nm. Until the structure of the Czechoslovak clinoptilolite sample can be solved more precicely, we may only suppose that these facts enable some kind of incorporation of the tetracyanonickelate guest.

The CHN analysis data are:

(**1**): C 4.42; H 1.53; N 5.51;

(**2**): C 4.82; H 1.62; N 6.7;

which give the content of G in the products as 19.1% in product (**1**) and 23.2% in product (**2**).

The stoichiometry of the new products can then be formulated schematically as: CTCa·0.23 G and CTCu·0.3 G.

3.2. IR SPECTRA

On the basis of the IR spectra the new products (**1**) and (**2**) can be described as new host–guest-type complexes having conserved mostly all the characteristics of the zeolitic material [15–17] and of the Hofmann type clathrate $Ni(NH_3)_2$-

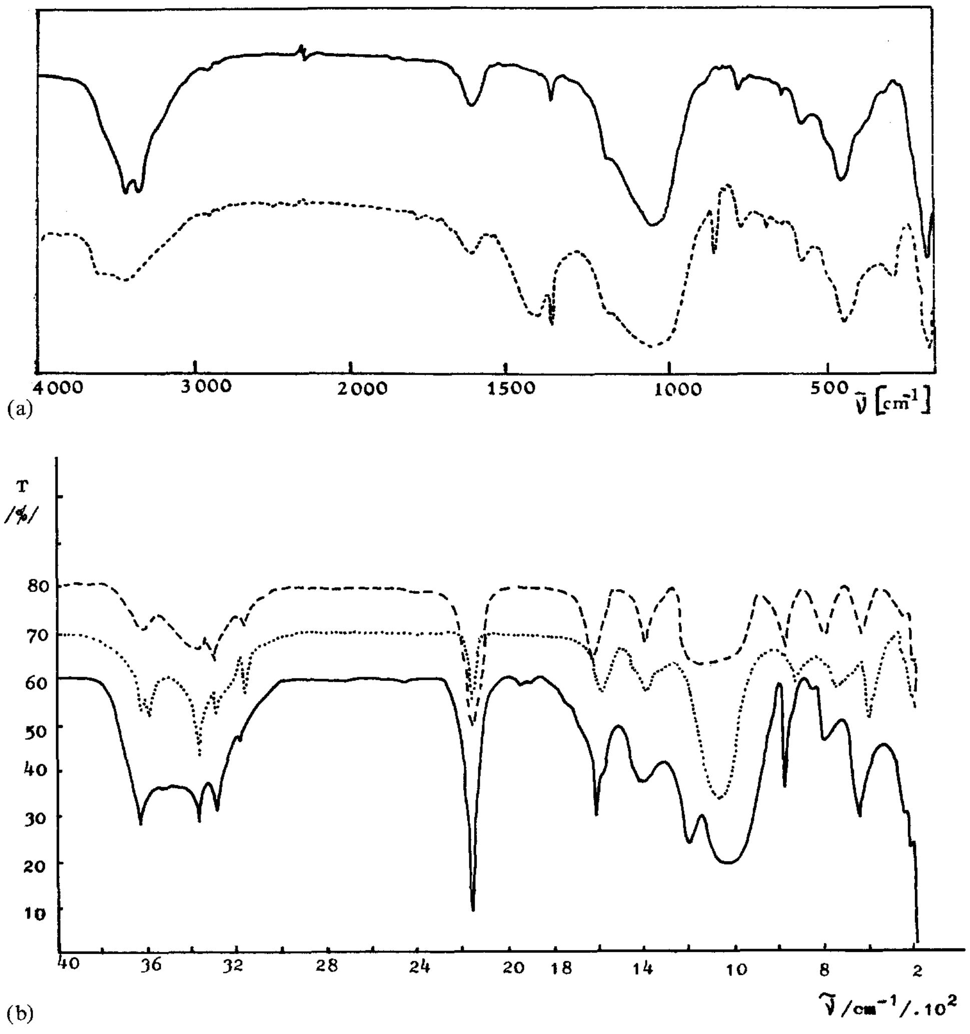

Fig. 1. IR spectra of the starting materials, of the new products and of a physical mixture. (a) The zeolite treated with Ca(II) ions (CTCa) ——— and with Cu(II) ions (CTCu) - - - (b) The new products (**1**) ———, (**2**) - - - and the physical mixture: (CTCa + clathrate) ···· .

Table I. The infrared characteristics (cm^{-1}).

	Zeolite	Product **1**	Product **2**	Clathrate
ν_{as} OH	3630 s.	3620 m.	3620 w.	3620 m.
ν_{as} NH_3		3385 m.	3375 w.	3380 m.
ν_s NH_3		3305 m.	3315 w.	3300 s.
ν_s OH	3180 v.w.	3180 v.w.	3170 v.w.	
$\nu_s C{\equiv}N$		2175 v.s.	2175 v.s.	2173 v.s.
δ_{as} NH_3				1605 s.
δ_{HOH}	1630 m.	1610 m.[o]	1620 m.[o]	1605 s.
$\delta_s H_2O$		1400 m.	1400 m.	1400 m.
ov.TO_4[a]	1230 s.			
δ_s NH_3		1230 s.[o]	1220 s.[o]	1225 s.
TO_4ext.[b]	1150 v.w.			
ν T—O[c]	1100–950			
ν_{as} T—O[b]	1060–1030 s.	1090–1010 br.	1220–1020 br.	
H_2O liber.[a]	795 w.	795 s.	795 m.	
ν_s T—O[a]	725 w.			
H_2O liber.[a]	605 m.			
ν Ni—C		600 m.[o]	605 m.[o]	580 m.
δ OTO[a]	470 s.			
δ NiCN		445 s.	440 s.	440 s.
ν MOH[b]	270—90	230 v.w.	230 v.w.	
TO_4[c]	240—130	220 v.w.	215 v.w.	

[a] Taken from Ref. [15].
[b] Taken from Ref. [16].
[c] Taken from Ref. [17].
[o] Overlapped.

$Ni(CN)_4{\cdot}2.75\ H_2O$ [18]. The intensities of the bands of the tetracyano complexes are lower (Figure 1), due to its incorporation in the zeolitic host. The characteristics are in Table I.

Some characteristic bands of $Ni(NH_3)_2Ni(CN)_4{\cdot}2.75\ H_2O$ are shifted, naturally some bands characteristic of the zeolite and of the tetracyanonickelate are common and also overlapped in both products. Between compounds (**1**) and (**2**) there are some small differences, concerning the possible differing interactions of the copper and calcium ion, mainly with the OH group being present. They can be found in Figure 1.

The physical mixture (Figure 1b) differs from the zeolite alone mainly by strong $\nu C{\equiv}N$, $\nu N{-}H$ and H_2O librational bands. The ν_{as} (Al,Si—O) band is less broad in the physical mixture than in the analogous product, but similar to the zeolite alone.

3.3. THERMAL ANALYSIS

According to [15] the *zeolitic material* retains its structure up to 730°C. In the interval 75–1000°C the structure is changed with formation of a hydrated amorphous phase with local changes. The maximum loss of water (about 7.2%) occurs at 220°C, 2% in a further step (about 335°C), the rest of the water content escaping only at higher temperatures. During the dehydration at 530–730°C the rest of the water is split by the temperature and the positive charge of bivalent cations and it changes to the OH groups [15]. The total weight loss is about 13.3% (Figure 2a).

The *CTCa* and *CTCu* zeolites decompose (Figure 2a) in different ways. The former undergoes dehydration in less differentiated steps, being similar to the zeolite alone (the original zeolite contains 2.94% of Ca) and the modification increases the Ca content. Between 40–705°C a series of changes on the DTA curve (15% of weight loss) are observed. The strongest are at 510°C and 680°C. A further distinct step is between 705°C and 842°C (maximum on DTA at 760°C) with a loss of 4%. This partial step is caused by the decomposition of the OH groups attached to Ca(II) ions. Total weight loss up to 900°C is 19%.

The *CTCu* zeolite starts to decompose at 95–150°C, without a distinct maximum, the weight loss is 4.5%. The next step is at 158–295°C (with a maximum at 162°C), the weight loss is 5.5%. Further endothermic decompositions are at 295–342°C (maximum at 312°C) and at 342–580°C (maximum at 490°C), the weight losses being 3.5% and 3.5% respectively. Then 7% of the mass is lost in the interval

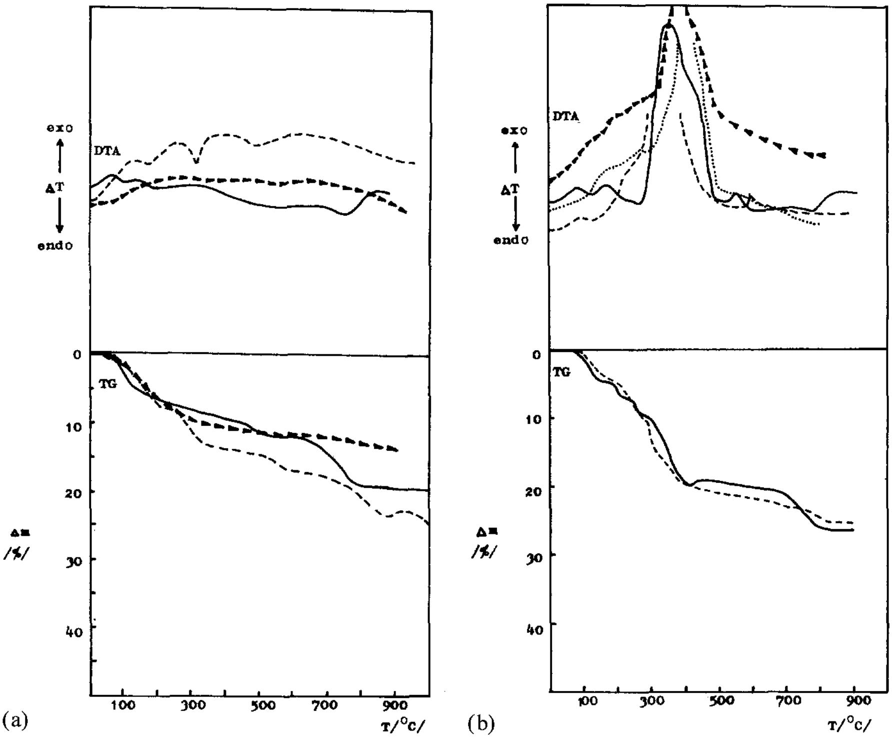

Fig. 2. Thermogravimetric analysis of the starting materials, of the new products and of physical mixtures. (a) The zeolitic material (CT) alone ▶ ▶ ▶ ▶ and treated with Ca(II) ions (CTCa) ——— and with Cu(II) ions (CTCu) - - - . (b) The new products (1) ———, (2) - - - and physical mixtures (CTCa + clathrate) ··· and (CTCu + clathrate) ▶ ▶ ▶ ▶.

580–895°C in agreement with the results of [15] in the mineral sample. Partial steps are in agreement with the general formula of the mineral, proposed by Meier [11]. The total weight loss (24%) is higher than in the CTCa sample.

The interaction of the metal ions with the zeolite has been explained [16] by their reaction with the structural water and with existing OH groups or with those formed during the decomposition. The change of the phase in the mineral alone at 560°C is not found in the CTCa and CTCu treated zeolites.

The new products (**1**) and (**2**) start their decomposition at 80°C and 78°C, respectively, a temperature higher than in the tetracyanonickelate alone (Figure 2b).

In product (**1**) the exothermic decomposition is between 270–475°C, with a weight loss of 9.5% (decomposition of cyanides and loss of water). The change in the phase at 540°C is accompanied by a weight loss of 1.8% between 475°C and 640°C. The total weight loss (without the aluminosilicates total decomposition) is 26.5%.

In product (**2**) the cyanide decomposition is an exothermic process (260–505°C) accompanied by the loss of one part of water. At 580°C a phase change is observed, together with a weight loss of 9% in the interval 505–900°C (without any other change on the DTA curve). The total weight loss is 25.6%.

The total weight loss in products (**1**) and (**2**), 26.5%, and 25.6%, respectively differ from those in CTCa and CTCu (19 and 24%) and even from the natural zeolite (13.3%). The exothermic process is the decomposition in air of the cyanide guest (distinctly seen in DTA). The values of Δm (13.2 and 12.3%), being $\Delta m_{\text{product}} - \Delta m_{\text{zeolite}}$, do not correspond to the content according to the CHN analysis.

The data on the thermal decomposition of both new products (**1**) and (**2**) do not support the hypothesis that the tetracyanonickelate is sorbed only on the surface.

The exothermic process in the physical mixtures display a shift to higher temperatures compared to (**1**): 205 vs 290, and (**2**): 205 vs 260°C. The mixture finishes the exo decomposition at higher temperatures than the products ((**1**): 475 vs 550°C, (**2**): 420 vs 505°C), indicating that one ingredient of the mixture is released during a longer time than the guest from the products.

3.4. GAS CHROMATOGRAPHIC EXPERIMENTS

The ability of the compound CTCu·$Ni(NH_3)_2Ni(CH)_4 \cdot y\, H_2O$ (**2**) to form the stationary phase in GC compared with the ability of the clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2.75H_2O$ and of the natural zeolitic material alone and with its Cu(II) exchanged form was studied together with a physical mixture of the starting materials. The new product (**2**) exhibited the ability to sorb organic compounds in a manner which may be considered as a combination of some spaces coming from the original compounds. The preliminary results are in Table II.

The spaces in the host are according to these results enlarged in the new product and they are accessible under convenient conditions to organic compounds of different types. The precise determination of the model of interaction between the new host and guest will be clarified only after finishing the measurements with all products prepared by the combination of the zeolites with other hosts.

Table II. Elution characteristics of the zeolitic material (A), its Cu form (B) and of the new product CTCu·Ni$(NH_3)_2$Ni$(CN)_4$·$y$$H_2O$(C).

Compounds		t_R[min]								
		80°C			100°C			120°C		
		A $t_M = 0.45$	B $t_M = 0.40$	C $t_M = 0.45$	A $t_M = 0.40$	B $t_M = 0.38$	C $t_M = 0.40$	A $t_M = 0.38$	B $t_M = 0.35$	C $t_M = 0.35$
Alkane	C_9	–	–	7.25	18.7	11.7	4.8	15.6	5.7	3.2
	C_{10}	–	–	13.0	36.2	19.4	8.5	28.8	11.8	5.00
	C_{11}	–	–	23.40	–	33.4	16.3	54.9	24.6	10.02
	C_{12}	–	–	43.0	–	56.0	27.9	–	52.1	16.6
Aromatics	B	12.8	14.6	4.23	10.2	5.8	3.60	8.8	2.81	2.8
	T	37.4	46.5	5.59	29.2	28.5	4.45	2.4	7.87	3.30
	o			7.4	44.1 el		5.1	39.7	16.84	3.9
	X_{m+p}	76	el	9.8	48.7 el	46.5	6.47	44.2	22.01	4.15
Alcohols	C_1	–	–	14.65	–	–	9.5		–	6.2
	C_2	–	–	18.65	–	–	11.90		–	11.65
	C_3	–	–	40.0	–	–	25.7	el	–	26.5
	C_4	–	–	88.0	–	–	56		–	60.4
Esters of acetic acid	C_1	–	–	12.85	–	–	8.20		–	5.8
	C_2	–	–	17.5	–	–	11.3		–	10.95
	C_3	–	–	23.9	–	–	15.6	el	–	20.98
	C_4	–	–	32.7	–	–	21.50		–	40.58

Note: el = elongated.

It can be seen from Table II that CTCu showed only a slightly higher selectivity than the zeolitic material alone. The zeolite complex incorporating the tetracyanonickelate separated the oxygen containing compounds – the C_1–C_4 alcohols and their acetate esters – at all tested temperatures. At all tested temperatures it separated also the tested aromatic mixture, with the xylenes into two fractions. This essential feature of the new product $CTCu{\cdot}Ni(NH_3)_2Ni(CN)_4{\cdot}\,y\,H_2O$ ($y \neq n$) of the host–guest type could possibly be used in other modes. It should be more emphasised at temperatures higher than 120°C, because in preliminary GC experiments we tested only its separative ability in the interval of temperatures, where only the first water part was deliberated. One may suppose that further steps of the decomposition [1] will allow the substitution of further different G in the compounds having enlarged spaces gained from both original inclusion compounds.

The tests with the physical mixtures performed under the same conditions and with the same modelling mixtures showed a quite different behaviour from the products.

The tested alkanes, aromatics and esters were blocked by the two strong adsorbing materials present in the physical mixture and they could not be eluted under 200°C. The alcohols could not be eluted even at 200°C. The H-bonding of alcohols is presumably responsible for their strong adsorption.

When compared with the data obtained at 80, 100 and 120°C with product (**2**) presented in Table II, a strong difference between the product and the physical mixture is apparent. Product (**2**) at 120°C eluted the C_9–C_{12} alkanes during the period 3.2–16.6 minutes, esters during 5.8–40.58 minutes, alcohols 6.2–60.4 and the aromatics, being more voluminous, eluted sooner (2.18–4.15 minutes).

The physical mixture of $CTCa + Ni(MH_3)_2Ni(CN)_4{\cdot}2.75\,H_2O$ showed the same behaviour as the $CTCu + Ni(NH_3)_2Ni(CN)_4{\cdot}2.75\,H_2O$ mixture.

The physical mixture is not suitable as a separation material.

3.5. DIFFRACTOGRAPHIC MEASUREMENTS

X-ray data of the new products (**1**) and (**2**) showed an increase in the crystallinity of both products as compared to the original zeolitic material. The patterns of samples prepared in different ways are shown in Figure 3. The physical mixtures have patterns different from products (**1**) and (**2**), (Figure 3c).

4. Conclusion

According to the identification of the new products arising from the combination of two inclusion compounds, the tetracyanonickelate clathrate is incorporated into the zeolitic host. The new products, schematically, $CTCa{\cdot}Ni(NH_3)_2Ni(CN)_4{\cdot}y\,H_2O$ and $CTCu{\cdot}Ni(NH_3)_2Ni(CN)_4{\cdot}yH_2O$ are all new individual compounds, differing from the starting materials and their physical mixtures as indicated by their IR spectra, thermal analysis, gas chromatographic measurements and diffractographic patterns.

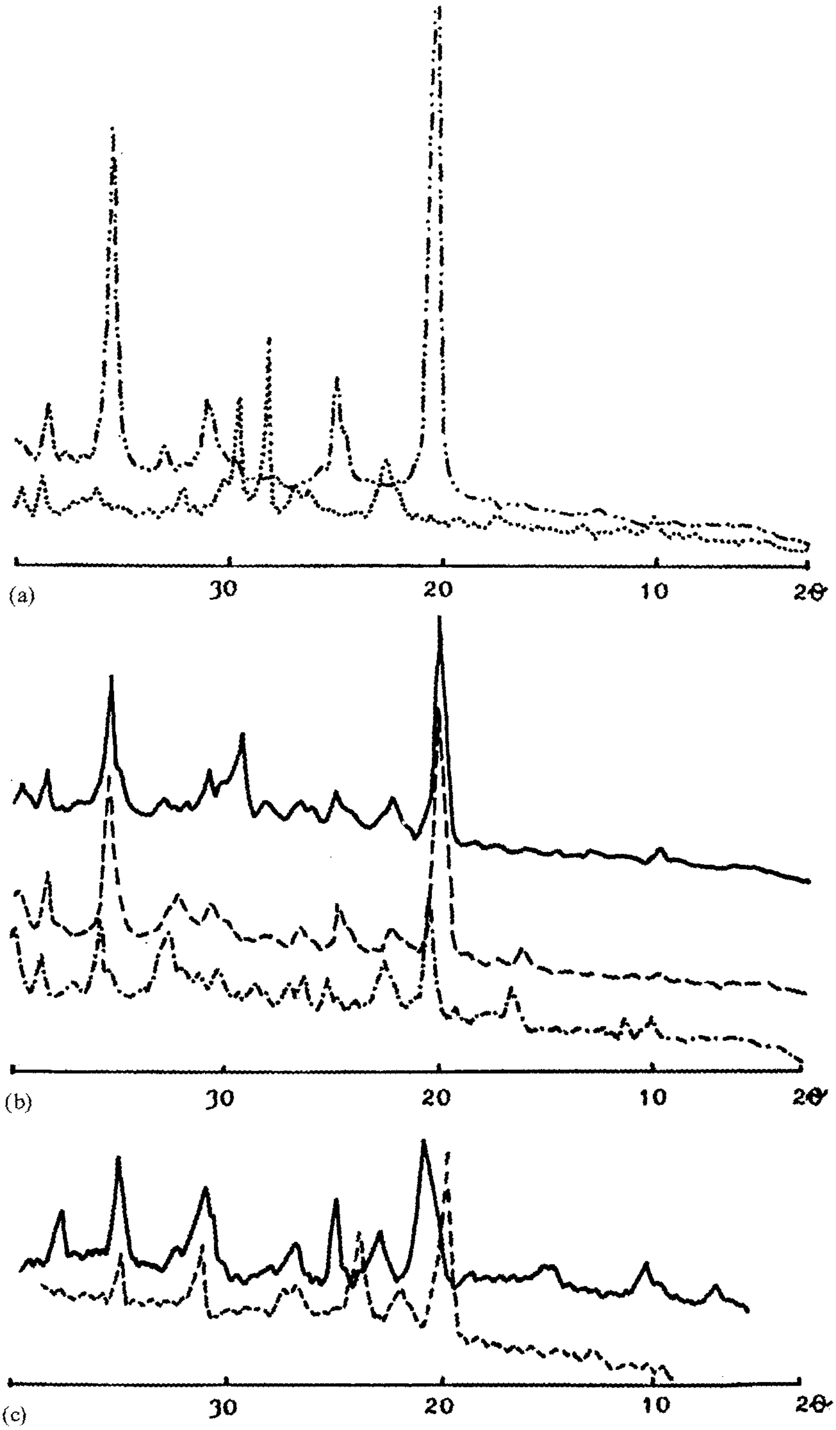

Fig. 3. Diffractographic patterns of (a) The zeolitic material (CT) ··· and clathrate - .. - .. - (b) products **(1)** ———, **(2)** - - - (with dried clathrate) and **(2)** - . - . - (with freshly prepared clathrate) (c) physical mixtures using product (1) ——— and (2) - - - .

New spaces created from the cages and channels of the zeolite and the layered tetracyanonickelate allows the partial substitution of the original water present as the guest by other organic compounds.

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