

## *Review Article:*

# Inclusion Compounds – Possibility of Their Combination and Use in Different Branches of Chemistry

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**Abstract.** Hofmann-type and related compounds, a natural zeolitic material of the clinoptilolite type, and cyclodextrins have been studied. Different products, useful in the separation of organic mixtures, used with fertilizers and insecticides in agrochemistry, perfumes, and in the detoxication of raw materials, have been prepared by combinations of the inclusion compounds studied. In the Hofmann-type compounds and cyclodextrins the original guest is substituted; in the zeolite the original sorbate, as well as some part of the zeolitic host is substituted. The physical mixtures of the starting materials differed from the products in their thermal, spectral and diffractographic characteristics. Field test results and other supporting evidence are added.

**Key words.** Zeolitic material, clinoptilolite, Czechoslovak deposit, tetracyano complexes, cyclodextrins, perfumery, industrial fertilizer.

## 1. Introduction

Three kinds of inclusion compounds are the theme of this paper. All are formed by host (H) and guest (G) components and they may be simply described as compounds with the formula  $H \cdot G$ . The guest is usually an organic compound or water. The inclusion compounds considered are formed by tetracyano complexes, zeolites and cyclodextrins.

## 2. Compounds Studied

### 2.1. THE HOFMANN TYPE AND RELATED COMPOUNDS

Compounds of the  $M(B)_m M'(CN)_4 \cdot nG$  type have been studied in our department since 1970 [1]. They cannot be described as clathrates in the strict sense of Powell's definition [2]. The original  $NH_3$  (B in the above formula) has been replaced by other nitrogen- or oxygen-containing bases and the range of guests has been enlarged from the original benzene, even to include water. The existence of such inclusion compounds is only possible when the guest content, expressed by  $n$ , differs from zero. They may be more precisely designated as layered compounds, but the layers are more or less strongly intersected, depending on the size of B. The compounds are formed by at least two subsystems of molecules forming the H and G components.

In 1976 Kihara [3] prepared models for multipolar molecules forming different simple compounds, but not inclusion compounds. One potential host component,

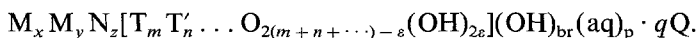
hydroquinone, is treated in his work. This displays different arrangements of the individual hydroquinone molecules in the system with different voids, not always offering the most convenient host lattice. In 1990 Iwamoto [4] illustrated two large subsystems forming the true Hofmann clathrate  $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ .

Inclusion compounds may also be formed by three or more components. The original guest may be resorbed or even substituted by another sterically compatible compound. Since 1974 we have tested and documented this property [5] of all of our compounds. They were useful as stationary phases [6] and they were capable of separating different mixtures of organic compounds. The original guest was partially substituted by a new one and the compounds could be described as  $\text{H} \cdot \text{G}_1 \cdot \text{G}_2 \dots$ .

In 1988 Iwamoto and his group [8] replaced the simple ammine by a rather longer one and used an aliphatic compound, hexanol, as the guest. The macromolecular layered areas are protruded strongly due to the ammine, and the authors designated the compounds as 'pillared intercalation compounds'.

## 2.2. THE NATURAL ZEOLITIC MATERIALS

These are inclusion compounds, water being the guest. The host in natural forms are not just simple  $(\text{Al}, \text{Si})\text{O}_4$  tetrahedra, but a broad substitution is possible and Meier's formula [9] is the best way of expressing their composition:



The zeolitic material used here is of the clinoptilolite (CT) type from the Czechoslovakian deposit at Nižný Hrabovec. Its chemical and morphological analysis [10] shows it to be similar to material from Hector or Castle Creek, U.S.A.

The zeolites exhibit different properties in comparison to other inclusion compounds. After release of their guest (always  $\text{H}_2\text{O}$ ) the solid retains its porosity, while with other compounds the porous, usually  $\beta$  form is changed into a compact (usually  $\alpha$ ) form. During the preparation of other inclusion compounds, different compounds may be used as possible guests, while with the zeolites only water induces the stabilization of the lattice. The sorption isotherms of the zeolites and other inclusion compounds have one analogous part, but they differ in the part near to zero [11].

Zeolites offer the possibility to exchange the sorbate, but in the case of some toxic cations or cations of fertilizers, some part of the host, can be exchanged as well.

## 2.3. THE CYCLODEXTRINS (CD)

These are well defined and well known [12–14] inclusion compounds. Besides the original water as guest, different drugs, aromas and alimentation specialities may be encapsulated, conferring increased stability, with a shift to higher temperatures. Their use in the form of stationary phases [15, 16] has also been studied.

**3. Results**

**3.1. COMBINATIONS OF THE INCLUSION COMPOUNDS**

**3.1.1. Entering of Further Guest:  $H \cdot G_1 \cdot G_2 \dots$**

(a) Different guests,  $G$ , may be exchanged in the tetracyano complexes  $M(B)_m M'(CN)_M \cdot nG$ . The experiments were performed using gas chromatography [5]. Figure 1 shows the elution curves (the dependence of the elution volumes ( $\log$

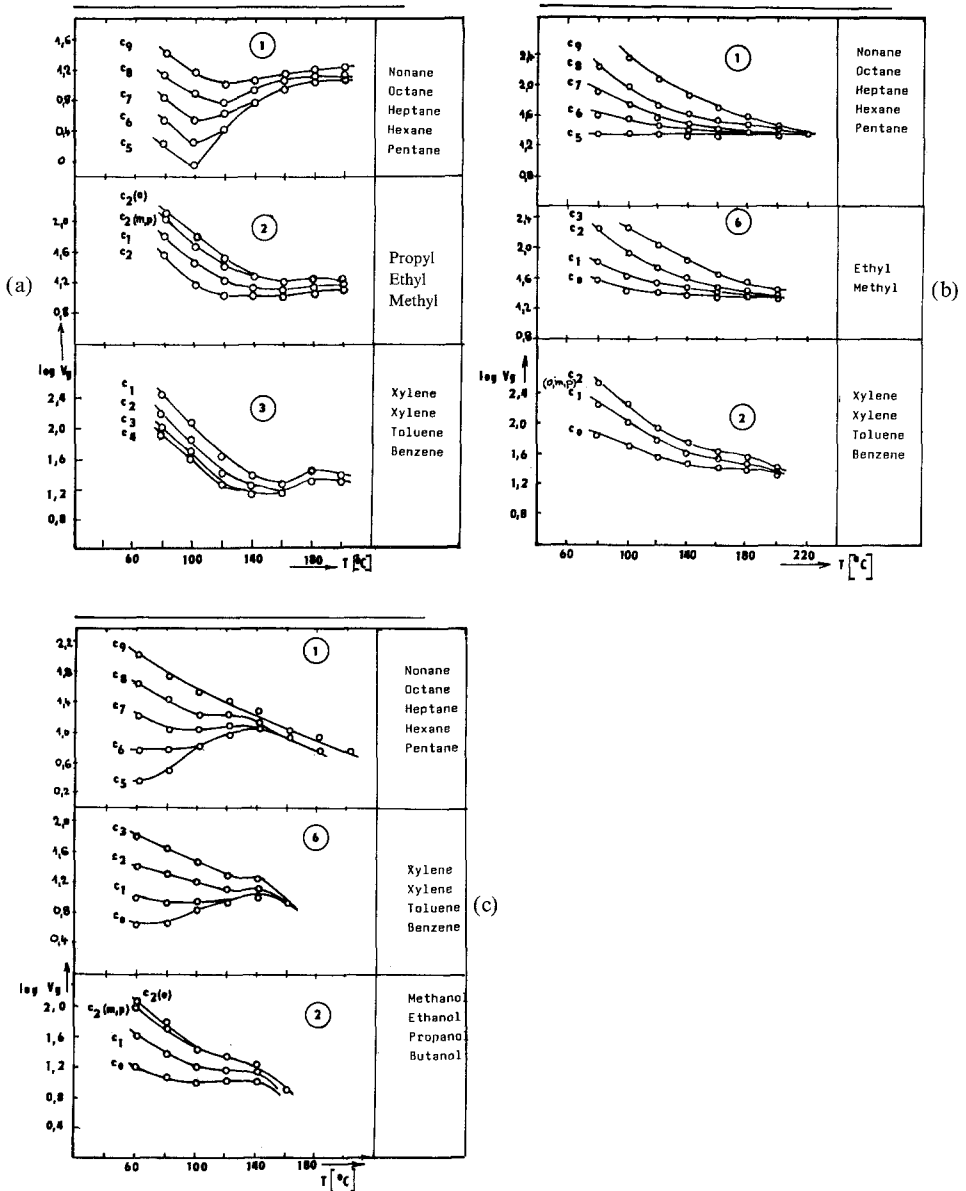


Fig. 1. The dependence of  $\log V_g$  on the temperature. Stationary phase:  $Ni(NH_3)_2Ni(CN)_4 \cdot 2H_2O$  (10%) modified by: (a) dioxane (b) pyridine (c) pentane.

$V_g$ ) on the temperature) for the same compounds, but always specific for different organic compounds used as the modifying solvent. The specificity is due to the spaces formed in the host and to their accessibility. The spaces and their shape and size also depend on the temperature and the extent of the decomposition.

Table I

Tetracyano complexes as potential sorptive materials										
Thermal decomposition										
Type	Formula	Temperature /°C/								
		50	100	150	200	250	300	350	400	450
M(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·nH <sub>2</sub> O	C <sub>6</sub> H <sub>6</sub>	NI(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cd(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	NI(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
M(en) <sub>2</sub> NI(CN) <sub>4</sub> ·nH <sub>2</sub> O	C <sub>6</sub> H <sub>6</sub>	NI(en) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 2nC <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cu(en) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 1nC <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·3nC <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Zn(en) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 1nC <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	NI(en) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 2nC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·2nC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> NI(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
M(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2H <sub>2</sub> O	C <sub>6</sub> H <sub>6</sub>	NI(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cd(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		NI(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
	C <sub>6</sub> H <sub>5</sub> OH	NI(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·O, 2nC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·2nC <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
M(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·nH <sub>2</sub> O	C <sub>6</sub> H <sub>6</sub>	NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]							
		NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
	C <sub>6</sub> H <sub>5</sub> OH	NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cu(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
		Zn(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]							
C <sub>6</sub> H <sub>5</sub> N	NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> N	[Decomposition profile]								
	Cu(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> N	[Decomposition profile]								
	Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> N	[Decomposition profile]								
	Zn(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> N	[Decomposition profile]								
	Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> N	[Decomposition profile]								
C <sub>6</sub> H <sub>4</sub> O	NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>4</sub> O	[Decomposition profile]								
	NI(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·C <sub>12</sub> H <sub>10</sub>	[Decomposition profile]								
	Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·C <sub>12</sub> H <sub>10</sub>	[Decomposition profile]								
	Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·C <sub>12</sub> H <sub>10</sub>	[Decomposition profile]								
	Cd(NH <sub>3</sub> ) <sub>2</sub> Pd(CN) <sub>4</sub> ·C <sub>12</sub> H <sub>10</sub>	[Decomposition profile]								
M(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2H <sub>2</sub> O	Cd(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	[Decomposition profile]								
	Cd(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]								
	Cu(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]								
	Cd(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]								
	Pd(en) <sub>2</sub> Pd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	[Decomposition profile]								
M(NH <sub>3</sub> ) <sub>2</sub> M'(CN) <sub>4</sub> ·G <sub>1</sub> ·G <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> OH·H <sub>2</sub> O	Zn(NH <sub>3</sub> ) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 2C <sub>6</sub> H <sub>5</sub> OH·H <sub>2</sub> O	[Decomposition profile]							
		NI(NH <sub>3</sub> ) <sub>2</sub> Pt(CN) <sub>4</sub> ·O, 2C <sub>6</sub> H <sub>5</sub> OH·2H <sub>2</sub> O	[Decomposition profile]							
		Cu(en) <sub>2</sub> NI(CN) <sub>4</sub> ·O, 1nC <sub>6</sub> H <sub>5</sub> OH·H <sub>2</sub> O	[Decomposition profile]							
		NI(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·O, 1nC <sub>6</sub> H <sub>5</sub> OH·2H <sub>2</sub> O	[Decomposition profile]							
		NI(en) <sub>2</sub> Pt(CN) <sub>4</sub> ·O, 1nC <sub>6</sub> H <sub>5</sub> OH·2H <sub>2</sub> O	[Decomposition profile]							

Table I (contd.)

Type	Formula	Temperature /°C/
$M(en) Cd(CN)_4 \cdot 2O$	$Cd(en) Cd(CN)_4 \cdot 2C_6H_6$	[redacted]
$M(NH_3)_2 Ni(CN)_4 \cdot 2O$	$Zn(en) Cd(CN)_4 \cdot 2C_6H_6$	[redacted]
	$Cd(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_6$	[redacted]
$C_6H_5N$	$Cd(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_5N$	[redacted]
$C_6H_5S$	$Cd(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_5S$	[redacted]
$C_6H_5OH$	$Cd(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_5OH$	[redacted]
Modelling compounds of the host		
$M(NH_3)_2 M'(CN)_4 \cdot nH_2O$	$Zn(NH_3)_2 Ni(CN)_4 \cdot 3H_2O$	[redacted]
	$Zn(NH_3)_2 Ni(CN)_4 \cdot 0.5H_2O$	[redacted]
	$Ni(NH_3)_2 Pt(CN)_4 \cdot 0.5H_2O$	[redacted]
$M(en)_m M'(CN)_4 \cdot nH_2O$	$Ni(en)_m Ni(CN)_4 \cdot H_2O$	[redacted]
	$Zn(en)_m Ni(CN)_4 \cdot H_2O$	[redacted]
	$Ni(en)_m Pt(CN)_4 \cdot H_2O$	[redacted]
$M'(CN)_4 \cdot nH_2O$	$ZnNi(CN)_4 \cdot H_2O$	[redacted]
	$NiPt(CN)_4 \cdot 6H_2O$	[redacted]
	$NiNi(CN)_4 \cdot 0.24H_2O$	[redacted]
	$NiNi(CN)_4 \cdot 6H_2O$	[redacted]

Notes: [redacted] -temperatures of the guest desorption  
 [redacted] -temperatures of the host desorption  
new compound

Substitution is always possible in some appropriate interval of temperatures, where the original G is desorbed by thermal analysis. This enables the use of the tetracyano complexes at higher temperatures than is possible in other cases. The thermal decomposition of different tetracyano complexes prepared in our department is evident from Table I. The interval of temperatures, when the amount of the guest is decreasing ( $n \rightarrow 0$ ) shows the existence of the inclusion compound and its possibility of use for exchanging the original G for another one.

(b) The original water in  $Ni(NH_3)_2 Ni(CN)_4 \cdot nH_2O$  can be substituted by organic compounds and also by iodine and its ions [17, 26]. The product obtained has the general formula  $Ni(en)_m Ni(CN)_4 \cdot 0.5 KI_3 \cdot 0.4 I_2 \cdot 0.4 H_2O$  ( $2 < m < 3$ ) and exhibits an electrical conductivity  $\sigma = 10^{-6} S cm^{-1}$ .

(c) This kind of combination can be found in the product obtained from industrial fertilizers and zeolites of the CT type (potassium chloride entering as the ion pair guest [18]), but it is also possible to achieve substitutions of some parts of the zeolitic host (by  $NH_4^+$  cations, for instance). Five types of new slow releasing fertilizers have been prepared [19] from zeolites and potassium chloride (No. 1), liquid N-P fertilizer (No. 2), No. 2 enriched by potassium (Nos. 3 and 4) and from industrial N-P-K no finalised suspension (No. 5). According to IR and TA the useful nutrients are enclosed in the zeolites. They differ from the physical mixtures of the appropriate starting materials.

The main proof of the inclusion comes from the results of two-year-long field tests. Figure 3 gives an overview of crops raised after the use of the new slow-release fertilizer (product No. 5) in the first and second year of trials. The figure shows a comparison with the crops raised in the same field tests, where only

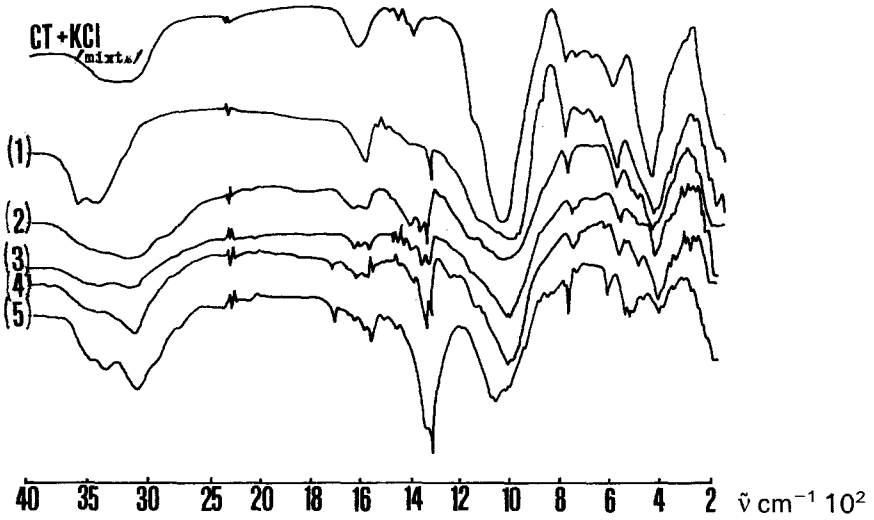
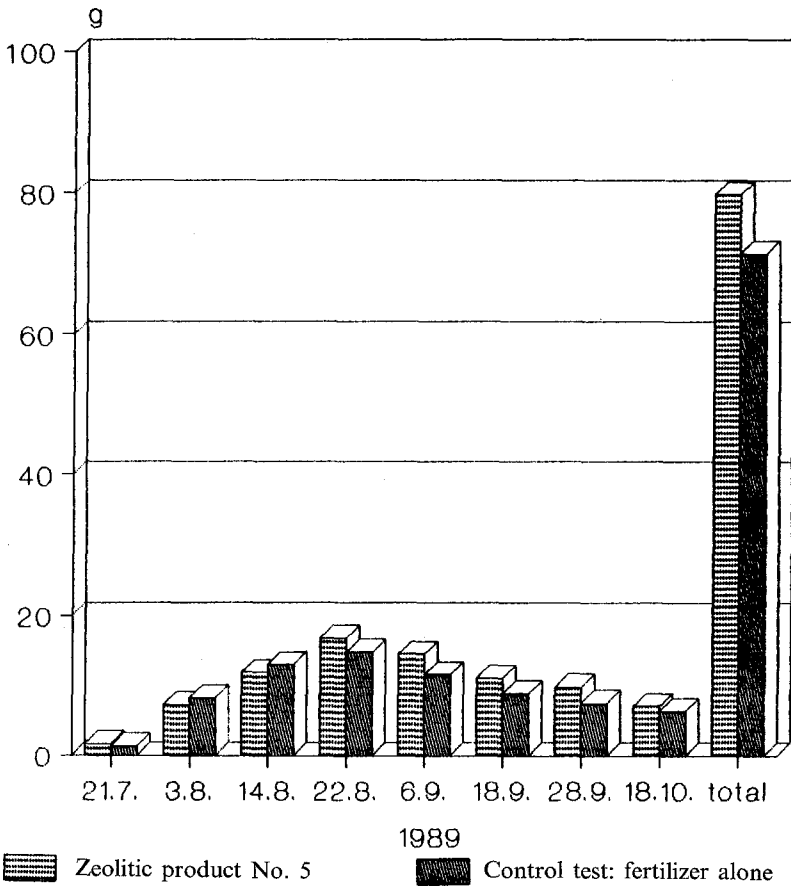


Fig. 2. IR spectra of: CT + KCl physical mixture (top trace) and: (1) new KCl containing fertilizer; (2) N - P suspension containing fertilizer; (3) N - P - K containing fertilizer; (4) N - P + K containing fertilizer; and (5) N - P - K suspension containing fertilizer. (1) - (5) are reproduced from [19].



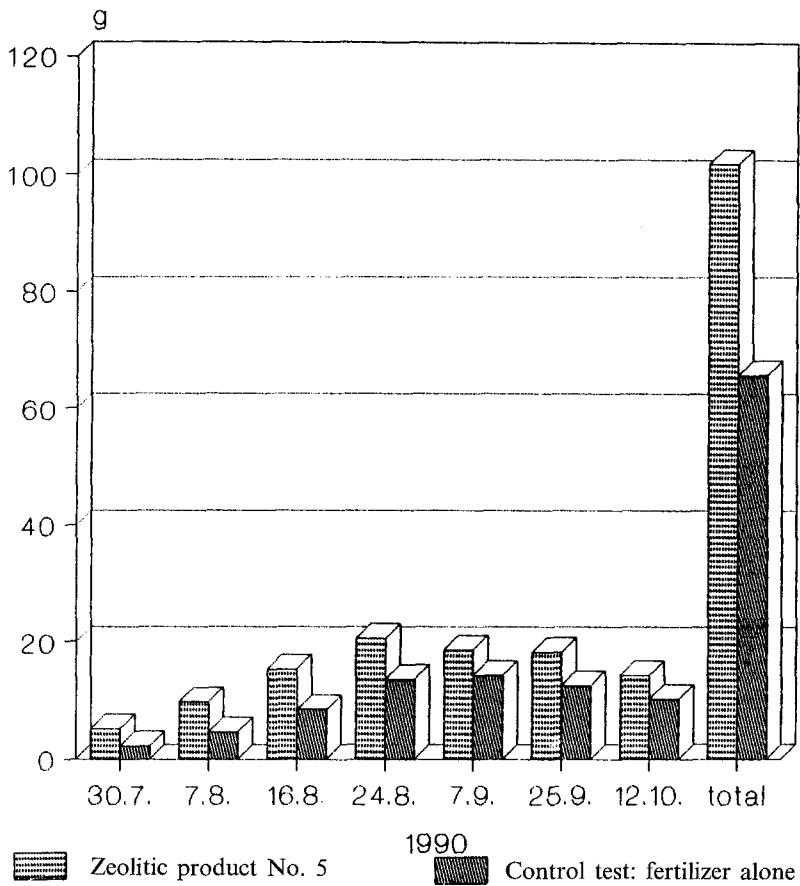


Fig. 3. Field test results using the No. 5. fertilizer on *Calendula officinalis*. The product used can be seen in Figure 7b<sub>3</sub>.

the fertilizers alone were used. The yield of flowers of the medical plant *Calendula officinalis* are compared during the first and second year of testing.

The first three partial crops are lower with the new zeolitic product, because the control fertilizer alone releases an important part of its nutrients. Then during August in the first year and during all of the second year the new zeolitic product slowly loses its included nutrients.

(d) Perfumery products and an insecticide were incorporated as guests, thus hindering their rapid evaporation. Supercypermethrine, methylbenzoate, acetophenone [20] and Citral [21] have been enclosed to date. The zeolite (CT), or its calcium(II) and copper(II) forms (CTCa and CTCu) were used as their carriers.

(e) Some toxic ions were also sorbed in the zeolitic material, exchanging some part of the host [22]. This was useful for the detoxication of fertilizers and their raw materials or wastes from cadmium, lead, mercury and chromium ions.

### 3.1.2. Combinations of Hosts: $H_1 \cdot H_2 \cdot G_1$

Using the zeolites host-guest complexes were prepared in which the voids of the zeolites facilitate the enclosure of further inclusion compounds, or their host. The parameters of the clinoptilolite used are:  $a = 0.7046$ ,  $b = 1.7908$ ,  $c = 1.163$  nm and  $\beta = 90.58^\circ$ . Besides the products obtained by a reaction of the zeolite and of the new guests in solution or at least in a slightly wetted state, the physical mixtures were simply prepared by cogrinding in a mortar. The combinations of the zeolite in the calcium (CTCa) or copper form (CTCu) with  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$  [23] or with different cyclodextrins [24] were studied.

The products differed from the physical mixtures in their spectroscopic behaviour, thermal decomposition and X-ray patterns. In the case of the combination with cyclodextrins, the guest (CD) modified by ethylenediamine (Cden) or hydroxyl-propyl (hpCD) was dispersed in the host, but the zeolite enclosing the tetracyanonickelate conserved its crystalline character. It also depended on the amount and physical form of the new guest enclosed. The compounds of both types

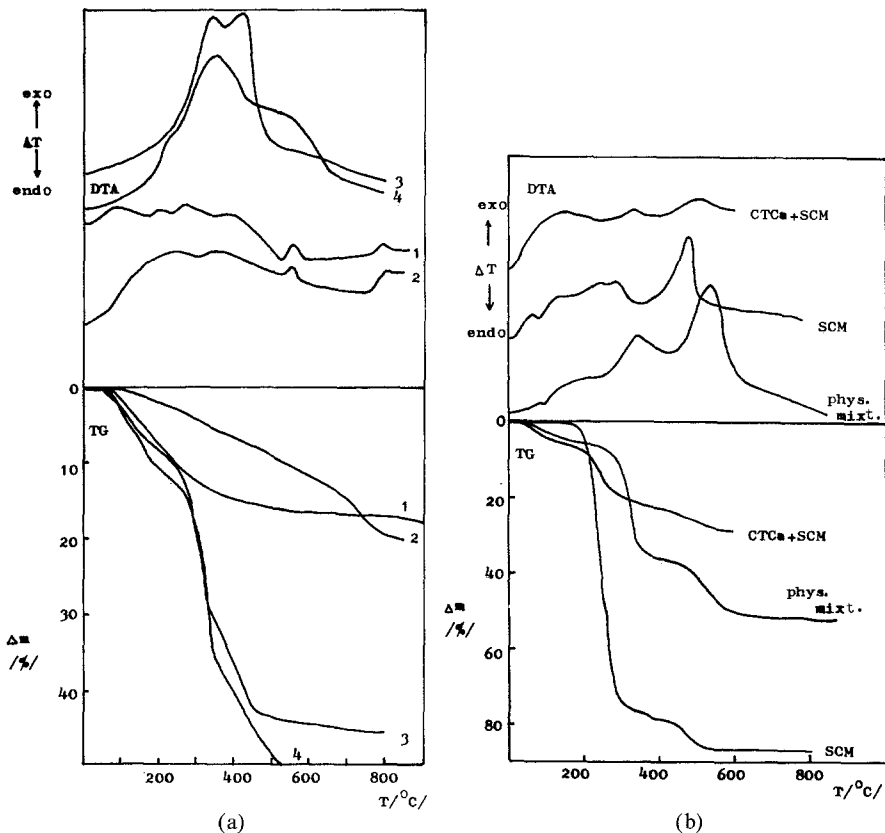


Fig. 4. Thermal decomposition of products and of the physical mixtures of the starting materials: (a) cyclodextrin Cden enclosed in CTCa (1) and CTCu (2), the physical mixture (3 and 4); and (b) the insecticide supercypermetrin (SCM) enclosed in CTCa and the physical mixture. (a) is partly reproduced from [24].



have higher thermal stability. The former combination may be used in slow-releasing pharmaceuticals or aromas, and the latter in separation processes.

### 3.1.3. Existence of Combinations

The thermal analysis of all our products reveals different TG and DTA curves from the starting materials or physical mixtures. The thermal decomposition of some combinations are shown in Figures 4 and 5. The weight loss ( $\Delta m$ ) in the products always depends on the enclosed new guest. Only the mineral fertilizer potassium chloride, product No. 1, is enclosed as an ion pair, substituting nearly all the water present in the zeolite (CT). Therefore its TG curve (Figure 5) is similar to that of the zeolite, despite the chemical analysis [19], where 19%  $K_2O$  was determined. The DTA curves are very interesting in all products. They always differ from the starting materials and also from their physical mixtures in all cases, whether the guest was represented by cyclodextrins (Figure 4a), insecticide (Figure 4b), one of the new fertilizer products (Figure 5), or odoriferous compounds [20, 21].

Some characteristics of the appropriate guest are to be found in the IR spectra (Figure 6) of all products prepared by the combination with the zeolite (CT, CTCa

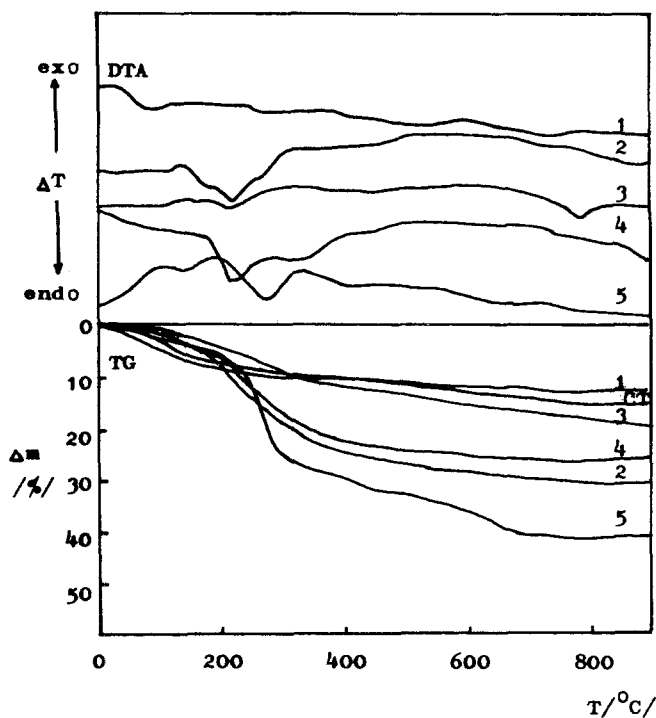


Fig. 5. Thermal decomposition of the five fertilizer containing products (1)–(5). The TG curves are compared with the original zeolite.

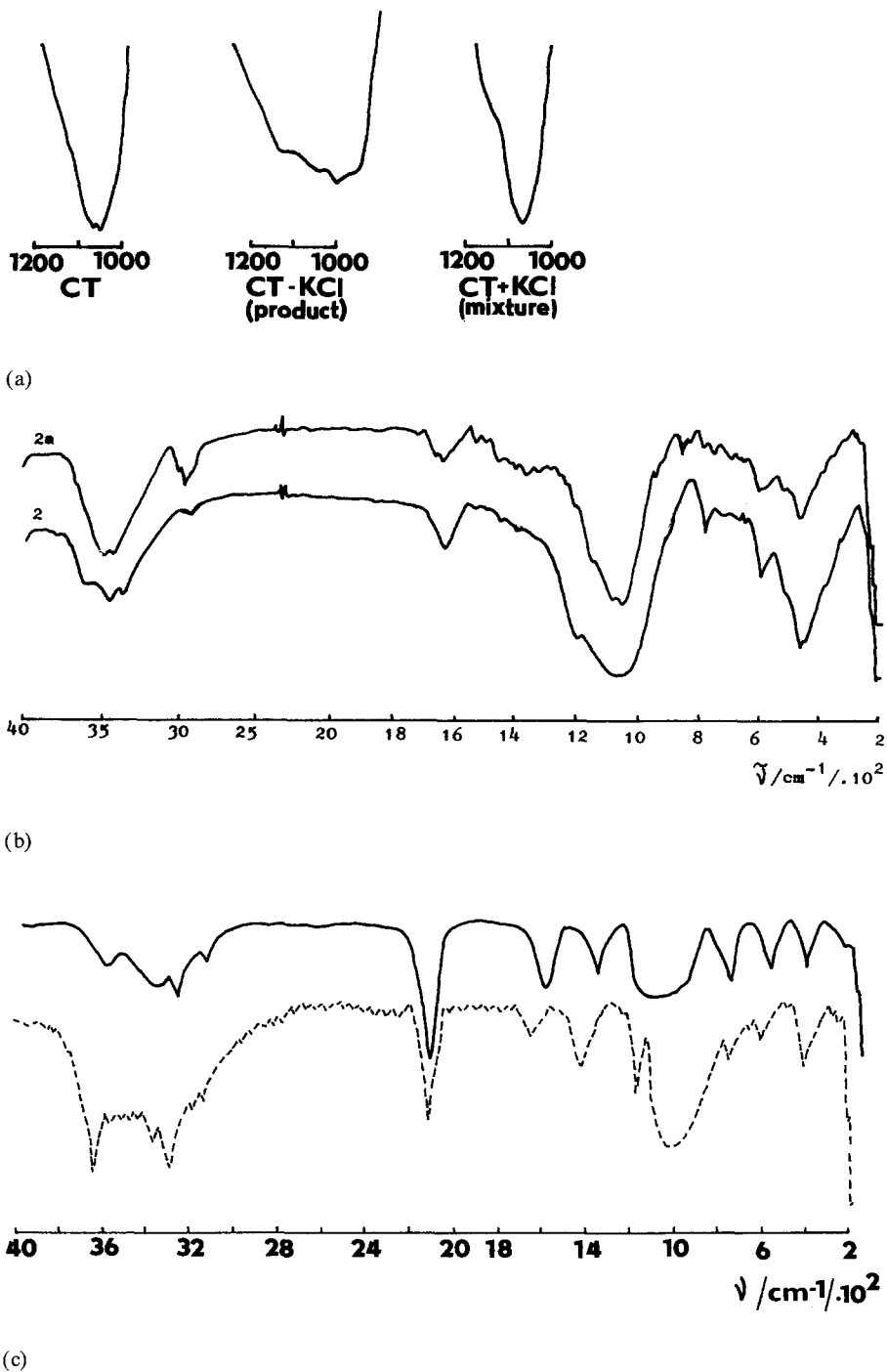
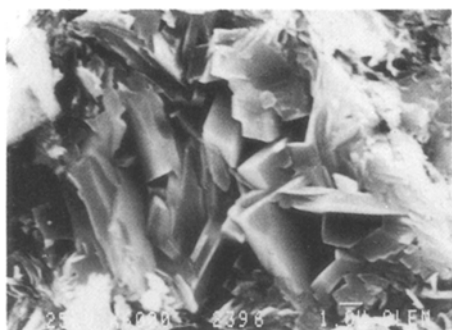
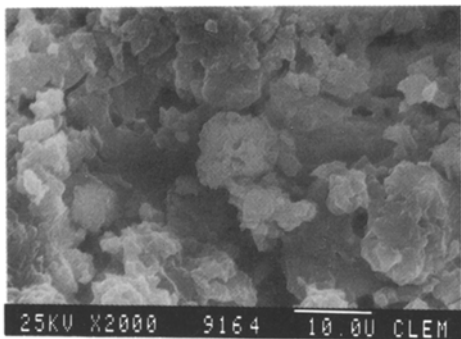


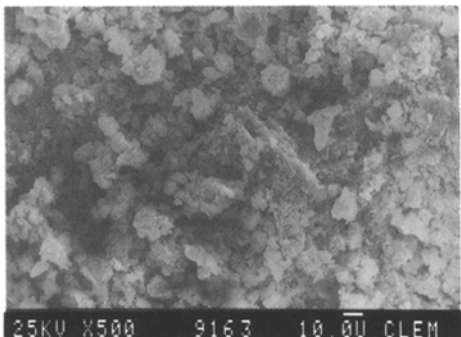
Fig. 6. IR spectra of some products and their physical mixtures: (a) the zeolite (CT), the new potassium chloride containing product (1) and the physical mixture: CT + KCl; (b) CTCu-hpCD (2); physical mixture (2a); (c) the tetracyanonickelate in the zeolite CTCu —; physical mixture - - -.



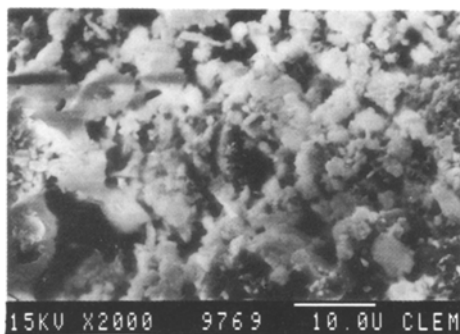
7a<sub>1</sub> CT



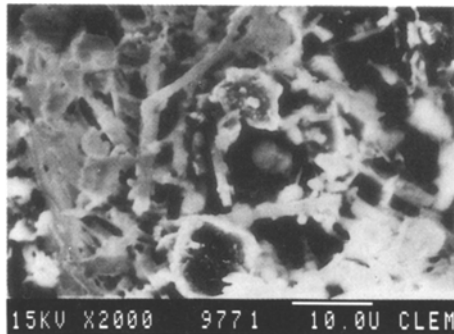
7a<sub>2</sub> CDen (2000x)



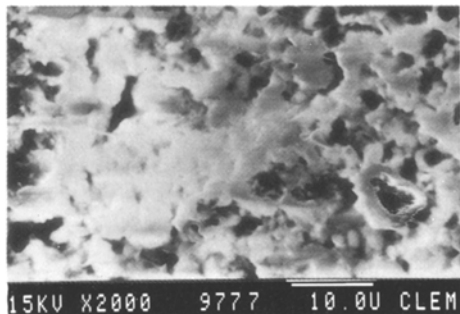
7a<sub>3</sub> CDen (500x)



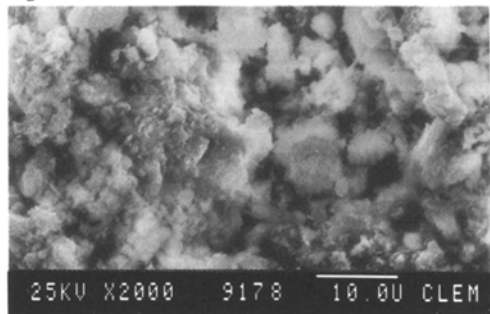
7b<sub>1</sub> - CT . KCl



7b<sub>2</sub> - CT . N-P (CT thermally activated)



7b<sub>3</sub> - CT . N-P-K



7b<sub>4</sub> - CT . SCM

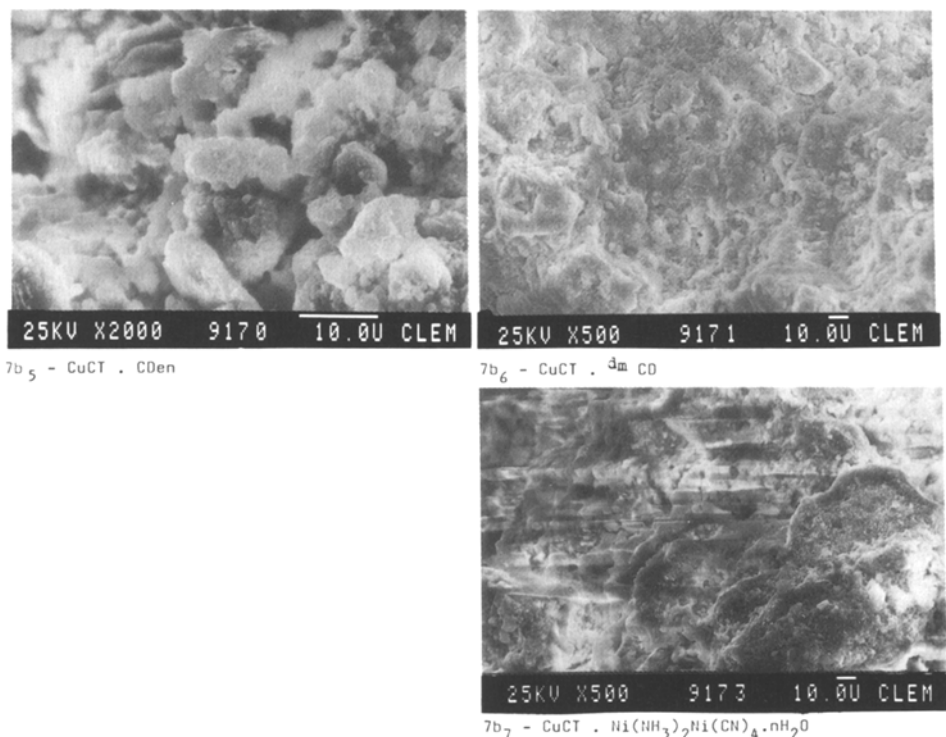


Fig. 7. Electron microscopic pictures showing: (a) some starting materials CT( $a_1$ ), CDen ( $2000\times$ ) ( $a_2$ ), CDen ( $500\times$ ) ( $a_3$ ); (b) product enclosing fertilizer KCl ( $b_1$ ), N–P (CT thermally activated) ( $b_2$ ), N–P–K ( $b_3$ ), insecticide ( $b_4$ ), CDen ( $b_5$ ), dmCD ( $b_6$ ), tetracyanonickelate ( $b_7$ ).  $a_1$  reproduced from [10],  $a_2$  and  $b_5$  from [24].

or CTCu). Besides them we may find as main feature the band  $\nu_{as}(\text{Si, Al—O})$ , showing the amorphous form of the aluminosilicate framework. This band exists otherwise [25] only in the zeolitic material CT after heating to higher temperatures – about  $900^\circ\text{C}$ . A broader band also exists in the thermally activated CT (used together with some fertilizer), iodine [26] or perfume [20]. The activation was performed by heating to  $220^\circ\text{C}$ . The band is sharp only in the zeolite alone, and in the physical mixture.

The broad band implies some change or some ‘preparation’ in the zeolite in all the products. Figure 6 shows the IR spectra of the new fertilizers (a), of the zeolites enclosing the hydroxylpropyl cyclodextrins (b), and tetracyanonickelate  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$  (c). The nature of the enclosure cannot yet be stated, because the products represent only the host–guest complexes.

The same preparation, or impregnation of the original host, can also be seen in the electron microscopic patterns (Jeol JSM–35 CF). Some kinds of little openings or ‘pits’ are formed in all products. One may also observe in all products the change of the previously very smooth surfaces present in the original zeolite CT.

Figure 7 compares the starting materials (the zeolite CT/a<sub>1</sub>), cyclodextrins CDen (a<sub>2</sub> and a<sub>3</sub>) and the products enclosing the fertilizers (b<sub>1</sub>–b<sub>3</sub>), insecticide (b<sub>4</sub>), cyclodextrins (b<sub>5</sub> and b<sub>6</sub>), and tetracyanonickelate (b<sub>7</sub>) in the zeolite (CT, CTCa or CTCu). Some change of the morphology is analogous to the changes of the  $\nu_{as}(Al, Si-O)$  band.

The parameters of the enclosing and enclosed compounds are here also visible (only two orders of magnification used) and they allow the enclosure and some interaction between the changed host and guest in all our products.

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