

# The Thermal Degradation of Clathrate Tetracyanocomplexes and the Morphological Properties of Their Intermediates

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**Abstract.** The changes in the morphology of clathrates of tetracyanocomplexes and of the intermediate products obtained after thermal degradation of the original compounds have been studied by scanning electron microscopy. The accompanying topotactic changes were correlated with data obtained from IR and thermal analysis studies to about 600°C and evaluated. The results indicate new possibilities in the utilisation of the technique for clathrates.

**Key words.** Clathrate tetracyanonickelates, electron microscopic observation, thermal degradation, topotactic reactions.

## 1. Introduction

The character of the inclusion in the studied compounds depends on the steric arrangement of both components. The nature of the steric barrier of the host component determines its selectivity [1] against compounds capable of acting as possible guest components.

In the case of the clathrates of tetracyanocomplexes of general formula  $[M(B)_m]_p[M'(CN)_4]_q \cdot nG$  (where M and M' are not always divalent ions [2]; B is an oxygen- or nitrogen-containing base, including H<sub>2</sub>O; G is the guest component such as benzene, phenol, aniline, water; m, n, p, q are molar aliquots) the total volume and the shape of the voids in the host may depend mainly on the stoichiometry and localisation of the complex anion present in the structural unit of the clathrand. They then form different structural types of clathrates with different modes of localisation of the layers of the host.

We thought that the use of electron microscopy (with magnification of  $\times 1000$  and higher) could help in the comparison of the compactness of the porosity of the surface of the original clathrates in the crystalline form, similar to the way in which it has provided useful data on zeolites [3, 4].

We therefore used this method for the morphological study of the tetracyanocomplexes not only in the original form but also after their partial thermal degradation. A limiting criterion in the morphological study of all materials is the thermal and mechanical stability of the individual particles of the evacuated sample ( $10^{-7}$  Pa) against irradiation by the stream of electrons. The particles have to be neither destroyed nor damaged during this interaction. The inclusion compounds are in general less stable compounds and, apart from the zeolites [3, 4], they have not been reported in the literature.

We minimised these unfavourable effects by the use of a scanning electron microscope, where the acceleration voltage of the primary electrons could be gradually changed.

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We prepared five series of tetracyanonickelates ( a total of 24 compounds) [2] with different metals in the cationic part of the host ( $M = Ni^{2+}$ ,  $Co^{3+}$ ,  $Ag^+$ ,  $Zn^{2+}$ ), with ammonia or ethylenediammine as the base, B, in the general formula and with different guest molecules.

Here we report the morphological results of our study of two compounds:  $Cd(NH_3)_2Ni(CN)_4 \cdot 1.5C_6H_6$  – (I),  $[Co(NH_3)_6]_2[Ni(CN)_4]_3 \cdot 2H_2O$  – (II).

## 2. Experimental

### 2.1. MATERIALS

Details of the preparation of clathrates of tetracyanonickelates with  $M = Ni^{2+}$ ,  $Co^{3+}$ ,  $Ag^+$ ,  $Zn^{2+}$  are described in a recent publication [2]. For the the present study we used the compounds  $Cd(NH_3)_2Ni(CN)_4 \cdot 1.5C_6H_6$  [5] and  $[Co(NH_3)_6]_2[Ni(CN)_4]_3 \cdot 2H_2O$ . The chemical composition of (I) and (II) is shown in Table I.

The inclusion of  $H_2O$  in compound (II) is analogous to the  $C_6H_6$  in (I) i.e. it is present as a guest molecule. We checked the presence of all guests (being present also in non-stoichiometric quantities) by elemental and thermogravimetric analysis and by the comparison of their IR spectra. Their structures have not been reported to date.

### 2.2. METHODS AND INSTRUMENTATION

The identification of compounds (I) and (II) and their intermediates was made by CHN analysis (Hewlett Pakcard Model 185), the presence of individual functional groups in all compounds was checked by IR spectroscopy (Specord M-80) in the range  $4000-200\text{ cm}^{-1}$  using KBr discs (2.5 mg/500 mg KBr).

The thermal decomposition was studied on a Derivatograph, MOM OD 102, under dynamic conditions (in air) by heating ( $6^\circ/\text{min}$ ) to about  $600^\circ\text{C}$  ( $Al_2O_3$  as reference material). The parameters were: TG 100 mg; sensitivities used in measuring: DTA 1/5; DTG 1/5.

We also obtained some intermediates (after heating to  $350^\circ\text{C}$ ) using a microheating arrangement with an optical microscope (Boetius PH/MK 05), where we could better differentiate the changes in the colour during the thermal degradation of the clathrates (II) (after 100-fold magnification).

Table I. The chemical composition of the compounds  $Cd(NH_3)_2Ni(CN)_4 \cdot 1.5C_6H_6$  – (I) and  $[Co(NH_3)_6]_2[Ni(CN)_4]_3 \cdot 2H_2O$  – (II).

Clathrate compound	Elemental analysis					
	experimental (%) (calculated (%))					
	Co	Cd	Ni	C	H	N
(I)	—	26.27 (26.36)	13.75 (13.76)	36.65 (36.62)	3.63 (3.55)	19.78 (19.71)
(II)	13.84 (13.92)	—	20.75 (20.86)	16.81 (17.02)	4.67 (4.76)	39.70 (39.71)

For the study of the morphology [2, 4], we used a JEOL scanning electron microscope Model JSM-35 CF. Depending on the thermal and mechanical stability of the sample voltages of 1–39 kV could be used, achieving a maximum magnification of  $\times 180\,000$ . The microscope was used without cooling accessories.

For the preparation of the sample it was found most convenient to fix the sample to the holder with electrically conductive paste (Dotite) and then to treat the sample by the ionic vaporisation of gold.

All electron microscope pictures contain the following data: the acceleration voltage (kV), the magnification, the number of the record and the scale – representing the number of  $\mu\text{m}$  (reading from the left to the right) representing by the white horizontal line.

### 3. Results and Discussion

#### 3.1. THERMAL DEGRADATION OF THE CLATHRATES $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$ AND $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$

##### $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$ – (I)

This clathrate is well known and characterised in the literature [5], it may also exist in non-stoichiometric forms [1]. The sample used was prepared one year ago and it was stored in a desiccator (with silica gel). Its elemental analysis (Table I) and the IR spectrum agreed with the formula and with the literature values [5].

During its heating to  $520^\circ\text{C}$  in the thermal analysis we could observe three distinct changes. We found in the interval  $38$ – $138^\circ\text{C}$  the loss of ligands (with a maximum on the DTA curve at  $120^\circ\text{C}$ ) and on heating to  $268^\circ\text{C}$  a diffusion of the benzene (with a maximum at  $205^\circ\text{C}$ ). The decomposition of the cyanide groups with the simultaneous oxidation of the metals present was observed at  $520^\circ\text{C}$ .

##### $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$ – (II)

The stepwise thermal degradation of compound (II) according to the thermal analysis (TG, DTA and DTG curves) is shown in Table II. The decomposition is accompanied by the diffusion or decomposition of the guest component  $\text{H}_2\text{O}$  (in the range  $48$ – $190^\circ\text{C}$  with a maximum on the DTA curve at  $117^\circ\text{C}$ ), of the ligands  $\text{NH}_3$  (in an endothermic process in the range  $190$ – $348^\circ\text{C}$  with maximum on the DTA curve at  $243^\circ\text{C}$ ) and  $\text{CN}^-$  (in the range  $348$ – $590^\circ\text{C}$  in an exothermic process).

Figure 1 illustrates the IR spectra of the various samples.

#### 3.2. THE MORPHOLOGICAL CHANGES IN THE SURFACE OF THE ORIGINAL CLATHRATE AND OF THE INTERMEDIATE PRODUCTS

##### 3.2.1. $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$ and Its Intermediates

The light yellow clathrate is stable to  $38^\circ\text{C}$ . It is in the form of small crystals with a tetragonal design, resembling stepwise pyramids. Their surface is smooth (Figure 2) with sharp edges of particles, obtained in the places of the dislocations obtained after the mechanical destruction. The layered structure is visible on the lateral planes of the crystals (the left part in Figure 3), which were obtained after the diffusion of the  $\text{NH}_3$  ligands by

Table II. The individual steps in the thermal degradation of the clathrate  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$ .

Intermediate compound	Temperature of the decomposition (°C)	Diffused or released components	Color of the product	Notes (topotaxy)
A	48	} $2 \text{H}_2\text{O}$ ↗	Light orange (after cooling too)	
B	190		dark orange (after cooling light yellow)	In the ruptures light pink colour – the diffusion of $\text{NH}_3$ → reorganisation of the system giving:
C	348	} $12 \text{NH}_3$ ↗	dark green (after cooling seablu)	$\text{Ni}(\text{CN})_2$ and $\text{Co}(\text{CN})_2$ (green) (blue violet)
				after cooling $\text{Co}(\text{CN})_2 \cdot 2 \text{H}_2\text{O}$ (blue violet)
		} $12 \text{CN}^-$ ↗		
D	590		greyish green metallic, on the surface changing colour (blue-green-pink)	$\text{NiO}$ (greenish black) $\text{Co}_3\text{O}_4$ (black) $\text{CoO}$ (greenish brown 30%)

Note: the colour of the original clathrate was orange.

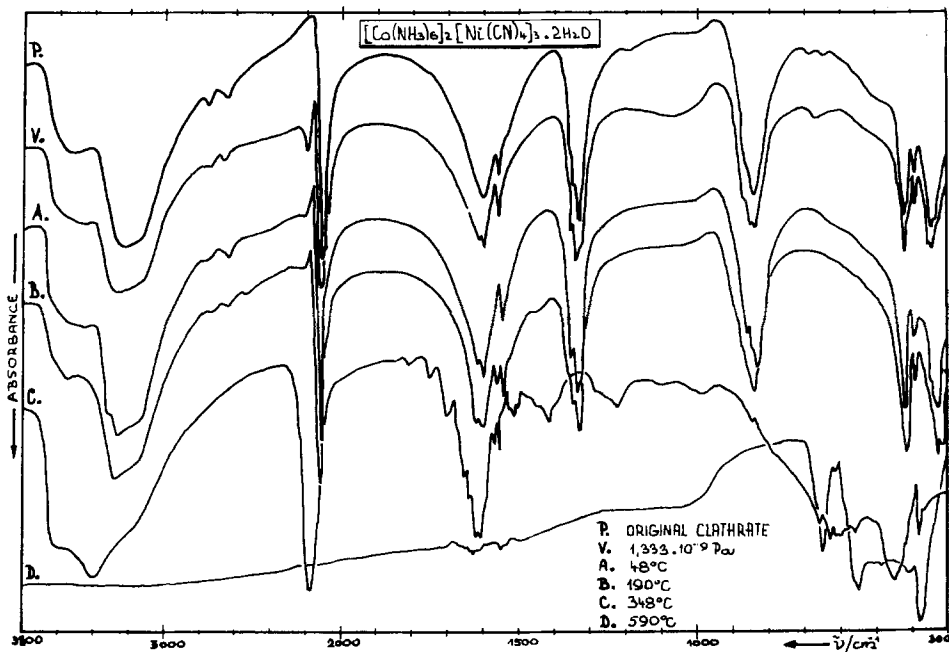


Fig. 1. The IR spectra of  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$  and of the intermediates (A, B, C, D) obtained at the temperatures indicated in Table II. P = original sample, V = sample after storing *in vacuo*.

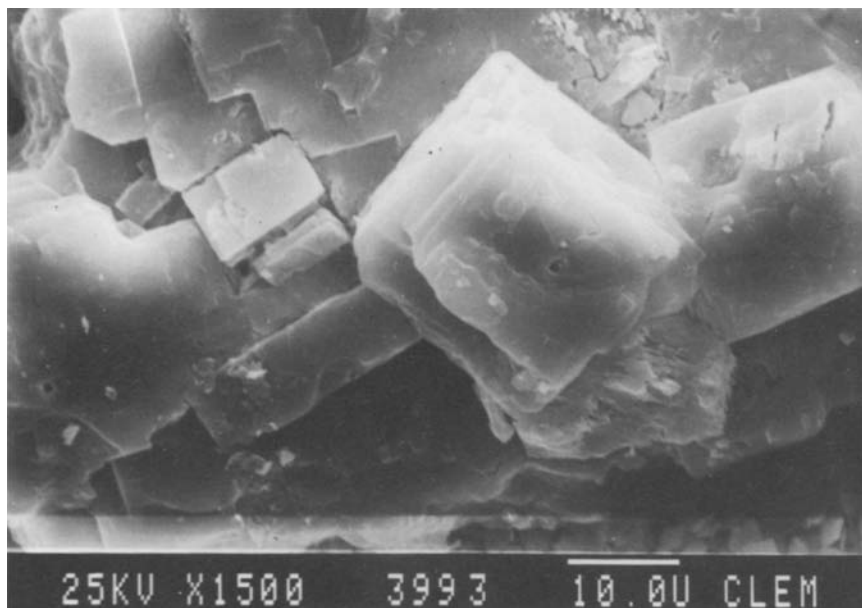


Fig. 2. SEM micrograph of the original clathrate  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$ , stable on heating to  $38^\circ\text{C}$ .

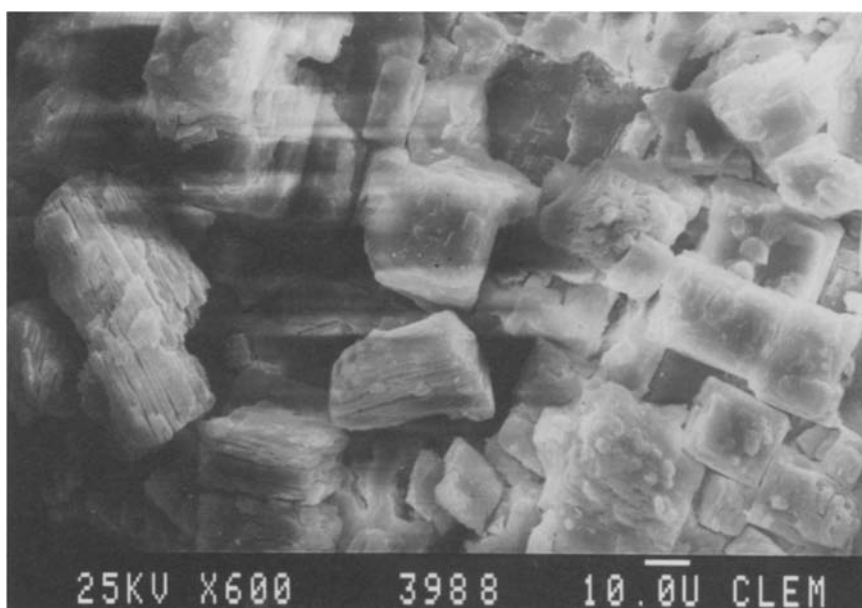


Fig. 3. SEM micrograph of the clathrate  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$  after heating to  $138^\circ\text{C}$ .

heating to  $138^\circ\text{C}$ . Because of the greater lability of the crystals against mechanical forces we could not obtain clearer pictures using a magnification higher than  $\times 600$ .

The intermediate isolated after heating to  $268^\circ\text{C}$  retains (see arrows in Figures 4a and 4b) the morphological characteristics of the sample obtained after heating to  $138^\circ\text{C}$ . We

can observe in the crystals a slightly undulated surface (with shallow voids) (Figure 4c), but we can see in some individual places an irregular destruction of the surface of the crystals (Figure 4a on the right).

The final product of the thermal decomposition obtained after heating to 520°C (Figure 5a) has a characteristic layered structure (arrows in Figure 5b) and also with a destroyed quasiundular surface (brown-black).

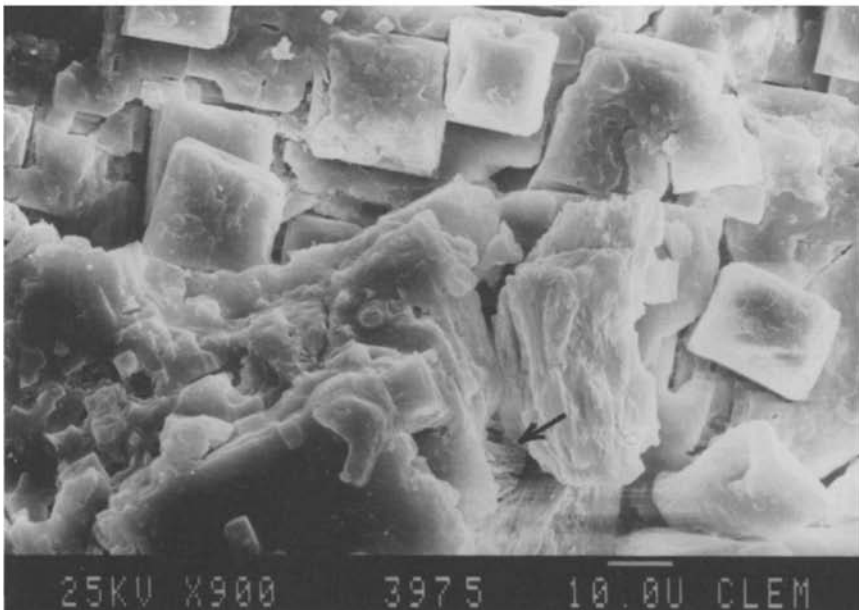
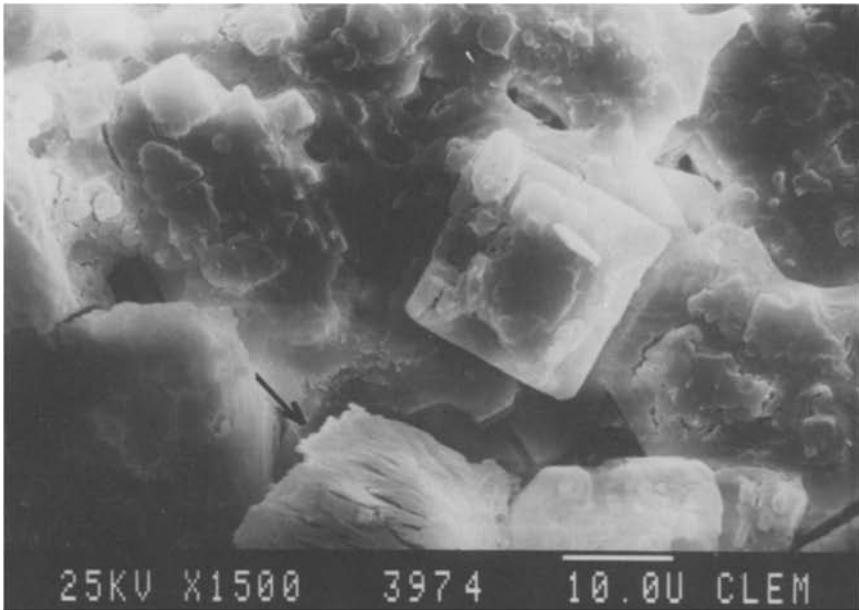


Fig. 4a,b.

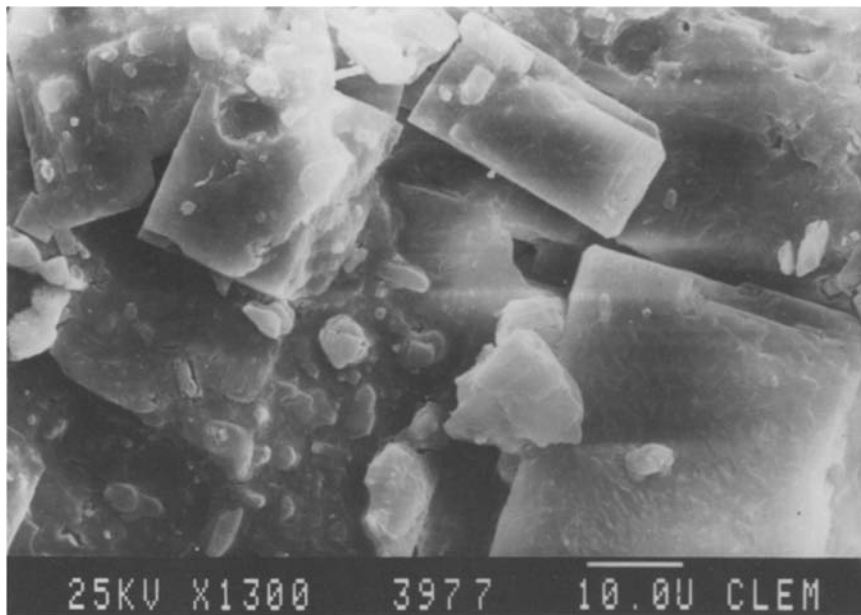


Fig. 4c.

Fig. 4. (a) SEM micrograph of the clathrate  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$  after heating to  $268^\circ\text{C}$ . (b) Another view of the clathrate  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$  after heating to  $268^\circ\text{C}$ . (c) SEM micrograph of details on the surface (obtained at  $268^\circ\text{C}$ ).

### 3.2.2. $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$ and Its Intermediates

In Figure 6a we see the photograph of the original clathrate (stable to  $48^\circ\text{C}$  and light orange coloured), showing the size of the crystals: about  $40 \times 30 \mu\text{m}$ , the thickness being about  $30 \mu\text{m}$ . The planes show a smooth surface with fine elevated areas orientated in one direction which may arise during the growth of the crystals (because of the mixing).

Relatively big canals or shallow voids of different shape (Figure 6b) often exist on the surface of the same crystals, and may arise from a relatively low concentration gradient being present during the formation of the crystals. Neither the morphology of the crystals nor the chemical composition changes on heating up to  $48^\circ\text{C}$ . All IR characteristics are the same, as in the original clathrate.

By raising the temperature from  $48$  to  $190^\circ\text{C}$  (water release) some fine mainly elongated ruptures occur. The colour of the crystals is deeper and well observed until  $126^\circ\text{C}$ . On cooling the crystals absorb moisture (on IR spectra  $\nu_{\text{s(OH)}}$  at  $3540 \text{ cm}^{-1}$ ) and they became lighter coloured. During the heating from  $190$  and  $348^\circ\text{C}$  the colour changes (to dark green and after cooling to sea blue). In both cases in the place of the ruptures the reflected light shows a light pink colouring. We can suppose here that with increasing rate of diffusion of the  $\text{NH}_3$  ligands the system becomes reorganised. Green  $\text{Ni}(\text{CN})_2$  and gradually also the blue violet  $\text{Co}(\text{CN})_2$  is formed. The colour indicates the presence of  $\text{Co}(\text{CN})_2 \cdot 2 \text{H}_2\text{O}$  (whereas its trihydrate is reddish grey).

The surface of crystals obtained at  $190^\circ\text{C}$  is the same as at  $348^\circ\text{C}$  (Figure 7a), they differ only in the number of ruptures, which are lighter coloured.

In Figure 7b using a higher magnification, in the left (framed) part of the photograph we can observe a darker rupture about  $0.4 \mu\text{m}$  in length (which may signify the beginning of

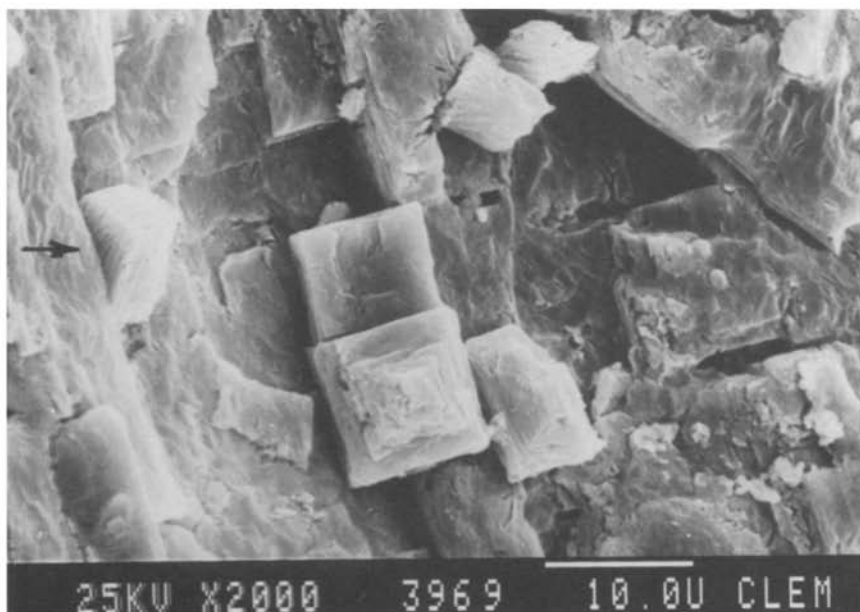
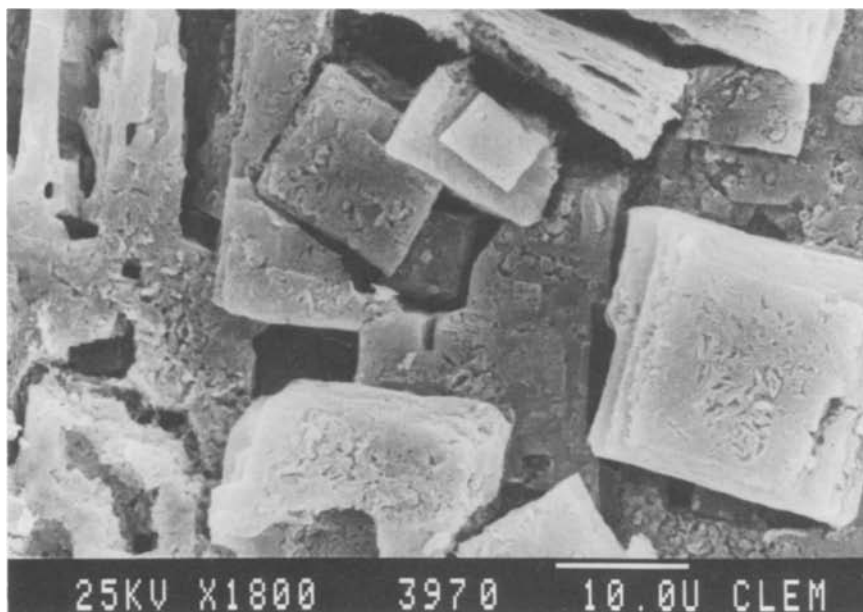


Fig. 5. (a) View of the surface of the final product obtained from  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$  obtained after heating to  $520^\circ\text{C}$ . (b) SEM micrograph of the clathrate  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5 \text{C}_6\text{H}_6$  after heating to  $520^\circ\text{C}$ .



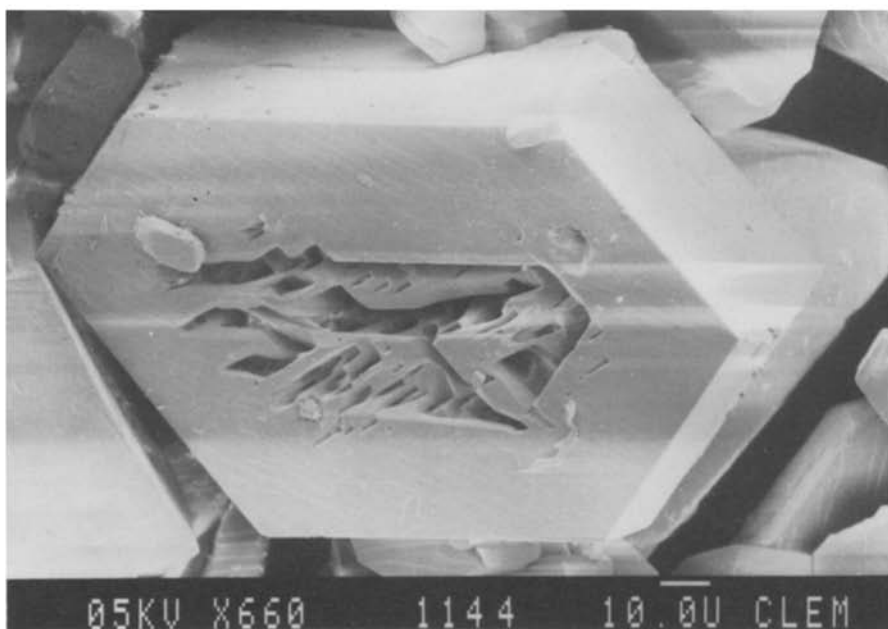
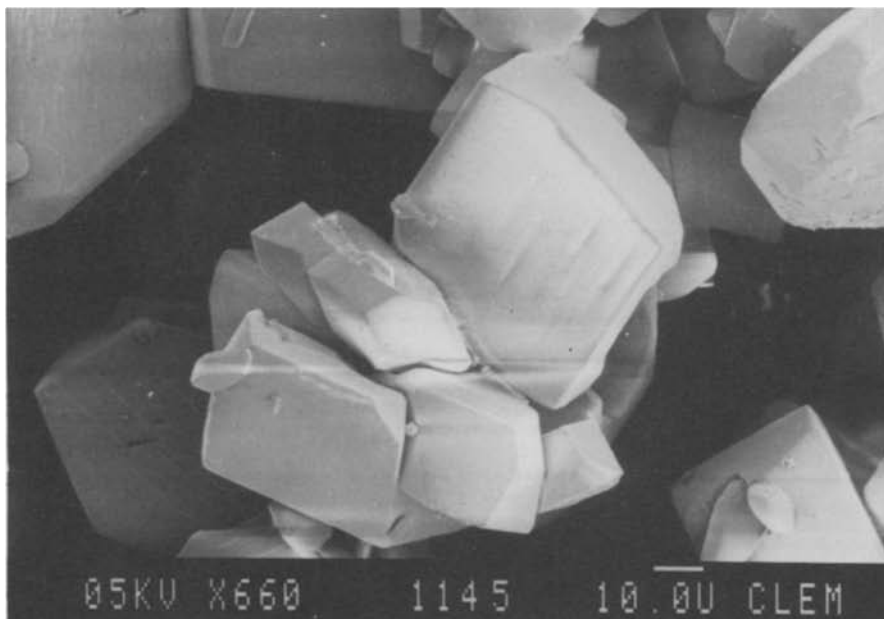


Fig. 6. (a) SEM micrograph of the clathrate  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$ . (b) Other view of the crystals of the original clathrate  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$ .

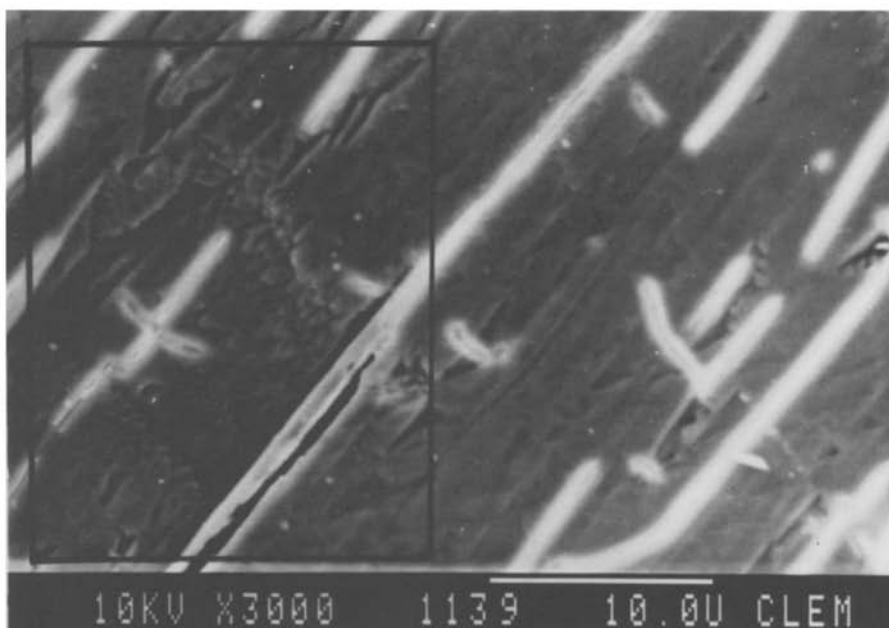
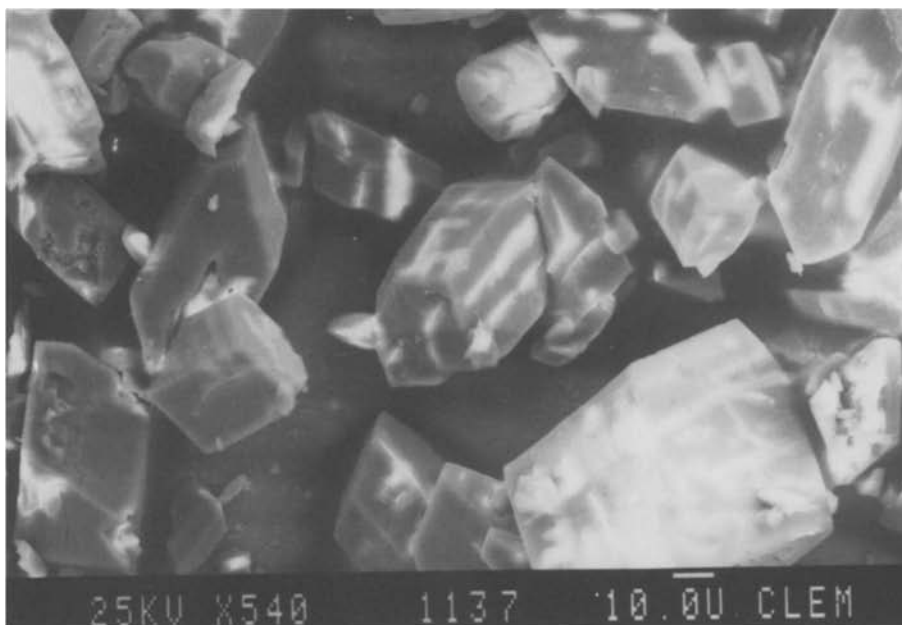


Fig. 7. SEM micrograph of  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  – after heating to  $348^\circ\text{C}$ . (b) SEM micrograph showing an area on the surface of the intermediate obtained after heating to  $348^\circ\text{C}$ .

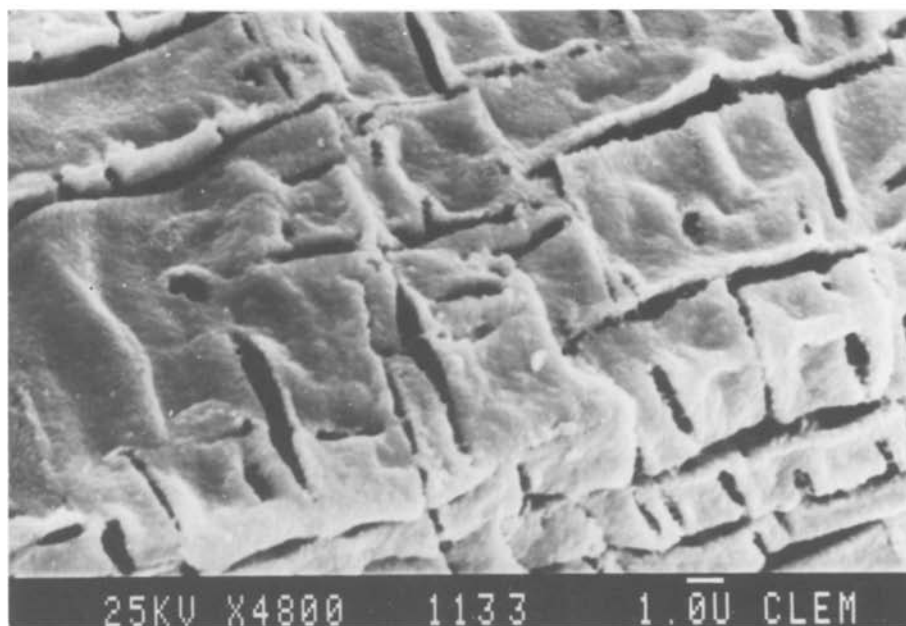
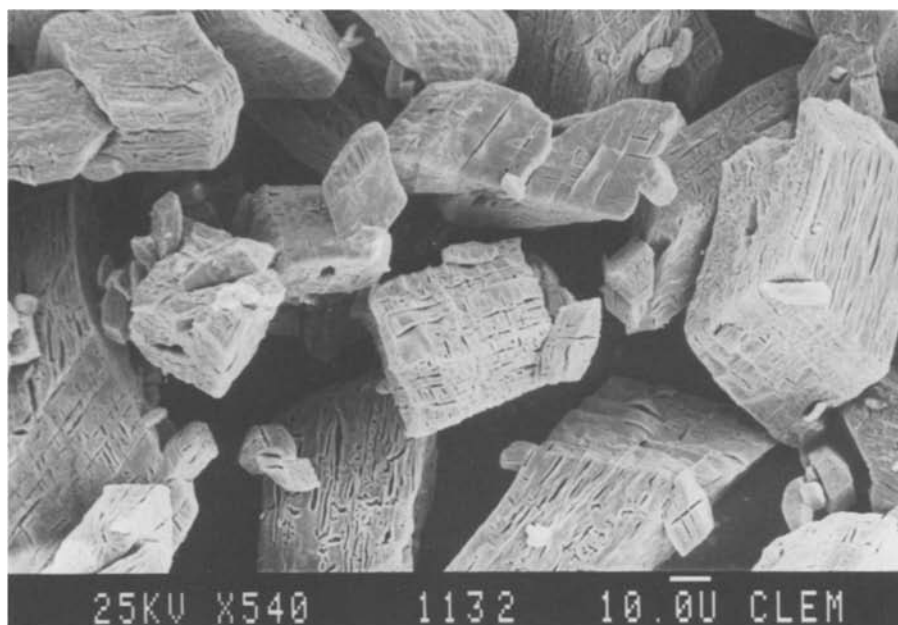


Fig. 8. (a) View of the clathrate  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  after heating to  $590^\circ\text{C}$ . (b) SEM micrograph of details existing on the edges of the intermediate (obtained at  $590^\circ\text{C}$ ).

the destruction of the crystal), also further ruptures lying in both directions (in the places of minimal cohesion) and less visible ruptures in the layered structures.

On heating the compound from 348 to 590°C the cyanogroups decompose and the oxides of both metals present are formed (greyish green metallic surface). In Figure 8a we can see that the individual crystals conserve their rather compact form but they contain ruptures in their texture (in the places with minimal cohesion).

When a higher magnification (4800 against 540 on Figure 8a) was used (Figure 8b) we can observe also an undular surface, which represents a characteristic morphological sign of this intermediate.

The IR spectrum of the final product of the thermal degradation of  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$  exhibits bands at 660, 560 and 390  $\text{cm}^{-1}$ , which belong (besides the vibrations of the polyatomic groups and of the internal vibrations) to the presence of  $\text{Co}_3\text{O}_4$  (with 20–30% of  $\text{CoO}$ ) [6, 7]. The characteristic band of  $\text{Co}_3\text{O}_4$  ( $\text{CoO}$ ,  $\text{Co}_2\text{O}_3$ ) at 390  $\text{cm}^{-1}$  is overlapping with that of  $\text{NiO}$ .

#### 4. Conclusion

The present results show that the clathrates of tetracyanocomplexes – and also their intermediates – are sufficiently stable for observations using electron microscopy. The mode of the preparation of the sample was also satisfactory in the case of all clathrates and intermediates.

The results obtained show the differences in the morphology in the surfaces of the clathrate compounds studied containing different pairs of metals in the host: Cd and Ni, Co and Ni. All results agree with the chemical and structural changes observed in the intermediate products obtained after their partial or total thermal decomposition. The final products are porous, but a compactness of the sample persists. This shows that the reactions which occur in the solid-state system during the stepwise thermal degradation of the clathrates  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.5\text{C}_6\text{H}_6$  and  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2 \text{H}_2\text{O}$  have as in [8, 9] a topotactic character.

The final products obtained show a new property. The corners and edges are moderately changed, but the fundamental shape of the crystals is conserved. We can observe the layered structure on the peripheral planes of the crystals. The upper part of the surface seems to be porous. This property is clearly differentiated also in the morphological views of other tetracyanocomplexes (e.g.  $[\text{Ag}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{G}]$  studied in [2]. This property indicates also new areas for the utilisation of these compounds and of their decomposition products (e.g. for catalysis).

#### References

1. A Sopková and M. Šingliar in: J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.) *Inclusion Compounds* Vol. 3, p. 245 (1984), Academic Press, London.
2. J. Bubanec: Dissertation, Chemical Faculty, Slovak Technical University, Bratislava (1986).
3. F. A. Mumpton: *Clays and Clays Minerals* 24, 1 (1976), Pergamon Press, London.
4. A. Sopková and J. Bubanec: *Chem. průmysl* 38/63, 11 (1988).
5. Y Sasaki: *Bull. Chem. Soc. Jpn.* 42, 2412 (1969).
6. R. A. Nyquist and R. O. Kagel: *Infrared Spectra of Inorganic Compounds* (1971), Academic Press, London.
7. L. Lang: *Absorption Spectra in the Infrared Region* (1974), Akadémiai Kiadó, Budapest.
8. F. K. Lotgering: *J. Inorg. Nucl. Chem.* 9, 113 (1959).
9. H. R. Oswald: *Thermal Analysis*, ICTA 80 Bayreuth, Vol. 1, p. 1 (1980), Birkhäuser Verlag, Basel.