

Inclusion Compounds as Sources of Activated Mixed Oxides

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Abstract. The reactivity of products or intermediates produced by the total or partial thermal decomposition of Hofmann type and related cyanocomplexes with general formula $[M(B)_m]_p [M'(CN)_4]_q \cdot nG$ ($M = Ni, Cu, Zn, Co, Ag$; $M' = Ni, Pt$; $G = C_6H_6, C_6H_5OH, H_2O$; $n > 0$) are studied. The changes in GC sorptive properties against organic compounds, in the morphology and electrical conductivity and capacitance are correlated with the final products and different intermediates. Sharp changes of these properties occur at characteristic temperatures. The sorptive properties may be observed up to a temperature (t_{conv}) at which some changes of properties in the compounds start and where stronger changes in morphology and some electrical properties start. The latter became more significant at a temperature of about 500–600°C (t_{max}), where oxides (or metallic Ag form) are already forming. Up to t_{conv} the decomposition process can be regarded as reversible, between t_{conv} and t_{max} as irreversible. The oxides obtained at t_{max} exhibit different properties than oxides prepared by the normal dehydration of hydroxides.

Key words: Inclusion compounds, cyanocomplexes, thermal decomposition products, electron microscopic observation, electrical conductivity and capacitance, topotactic reactions.

1. Introduction

There has recently been increasing interest in the theme of inclusion compounds [1] due to this increasing number and types. The conditions of their preparation and modification are being systematically explored; but the naturally occurring materials have also recently been described as inclusion compounds. The distinction lies in the chemical composition, in the structural differences of the hosts and included guests, or of the whole inclusion compounds, as well as in the different shapes and localisation of the cavities and canals created during the preparation of the host components.

The thermal stability or instability of a compound often determines its other properties and uses. Thermal decomposition can lead to simpler compounds and after reaching some temperature they may assume an activated form. We are studying the course and extent of changes in the reactivity of products obtained by the partial thermal degradation of tetracyanocomplexes. The results of thermal analysis are correlated with the morphological changes of the intermediates and

TABLE I. The compounds studied.

Sample No	Compound	Ref.
I	Ni(NH ₃) ₂ Ni(CN) ₄ · 2C ₆ H ₆	[2]
II	Ni(NH ₃) ₂ Pt(CN) ₄ · 2C ₆ H ₆ OH	[3]
III	Ni(en) ₂ Ni(CN) ₄ · 2.4H ₂ O	[4]
IV	[Co(NH ₃) ₆] ₂ Ni(CN) ₄] ₃ · 2H ₂ O	[5]
V	[Co(NH ₃) ₆] ₂ [Ni(CN) ₄] ₃ · 2H ₂ O doped with Se	
VI	Cu(NH ₃) ₄ Ni(CN) ₄ · 2H ₂ O	[6]
VII	Zn(NH ₃) ₂ Ni(CN) ₄ · 0.8H ₂ O	[4]
VIII	[Ag(NH ₃)] ₂ Ni(CN) ₄ · 0.1C ₆ H ₆	[7]
IX	NiO	[8]
X	CoO	[8]

with changes of their properties. The sorptive and electrical properties of the final products obtained from thermal decomposition were compared with analogous products prepared by other methods.

In our study the host-guest complexes used are described by the general formula: $[M(B)_m]_p[M'(CN)_4]_q \cdot nG$ without consideration of their different structures. The metal ions M and M' may be different or the same, and B represents a nitrogen- or oxygen-containing base.

2. Experimental

2.1. MATERIAL AND METHODS

The compounds used are listed in Table I. Other compounds used (dioxan, benzene, C₅–C₉ alkanes) were products of Lachema Brno, p.a. grade purity.

For the preparation of the intermediate products, thermal decomposition was performed with a Derivatograph OD 102 MOM (Paulik-Paulik-Erdey Budapest) with heating rates of 3°C and 6°C/min (α -Al₂O₃ as reference material). The parameters were: TG 100 or 200 mg, sensitivities used in measuring: DTA 1/5, DTG 1/5. For preparation of greater quantities heating in muffle furnace LM 212.11 (10°C/min) was used.

For combustion analysis a CHN Microanalyser (Hewlett Packard Model 185) was used, the presence of individual functional groups in all compounds was checked by IR spectroscopy (Specord M-80) in the range 4000–200 cm⁻¹ using KBr discs (2.5 mg/500 mg KBr).

Powder X-Ray photographs were obtained on a Micrometa-2 Diffractometer (Chirana, Prague).

For the study of the morphology a JEOL scanning electron microscope Model JSM-35 CF was used. Depending on the thermal and mechanical stability of the sample a voltage of 1–25 kV could be used, achieving a maximum magnification

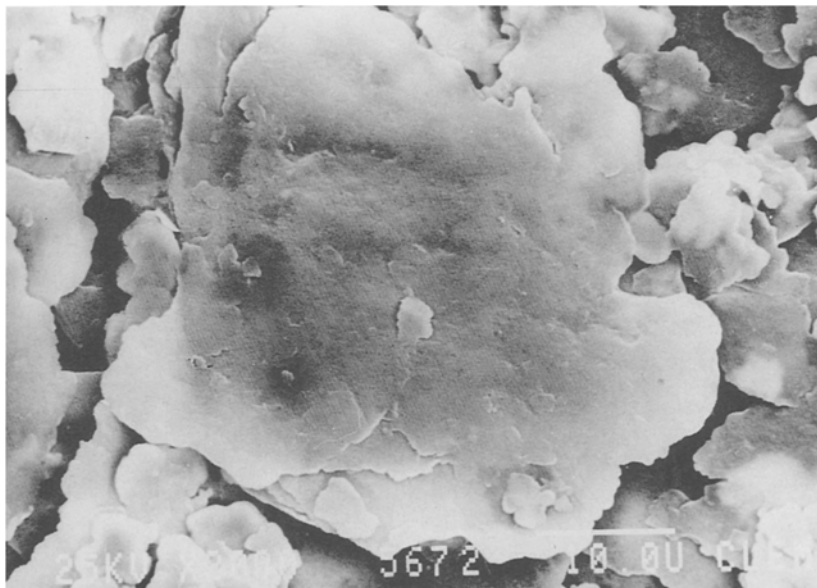


Fig. 1. Electron microscopic (SEM) picture showing $\text{Ni}(\text{NH}_3)_2\text{Pt}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{OH}$ partly decomposed on standing.

of $\times 4800$. The microscope was used without cooling accessories. The sample was fixed to the holder with electrically conductive paste (Dotite) and then treated by the ionic vaporisation of gold. Characteristic X-Ray radiation analysis was performed with a EDX Microanalyser Link 860.

The tetracyanocomplexes, after recovery [6, 9, 10] from auxiliary solvents, were used as stationary phases in gas chromatography to investigate their separation ability. The complexes were deposited (10% w/w) on silanized Chromosorb W/NAW, 100 mesh and packed into the column ($l = 2.5$ m, i.d.=3 mm). The chromatograph (GC) was a Chrom 4 (Lab.přístroje, Prague) with a flame ionization detector. The flow rate of the carrier gas (nitrogen) was $24 \text{ cm}^3 \text{ min}^{-1}$.

The conductivity and capacitance measurements were performed by an RCL automatic measuring equipment (BM 595 type Tesla, Brno, Czechoslovakia) using a 1V parallel connection of the cylindric conductivity cell (formed by electrodes i.d. 10 mm, distance 1 mm). It was filled with about 0.3 g of powdered sample, pressed to 5 Pa. Three frequencies (100, 1000 and 2000 Hz) were used at 20°C in the measurements.

The chemisorption measurements were performed with a Pulse Chemisorb 2700 system (SY-LAB, Purkersdorf, Austria) using ultrahigh purity N_2 , H_2 and O_2 at STP with a flow of 20 mL/min at 25°C .

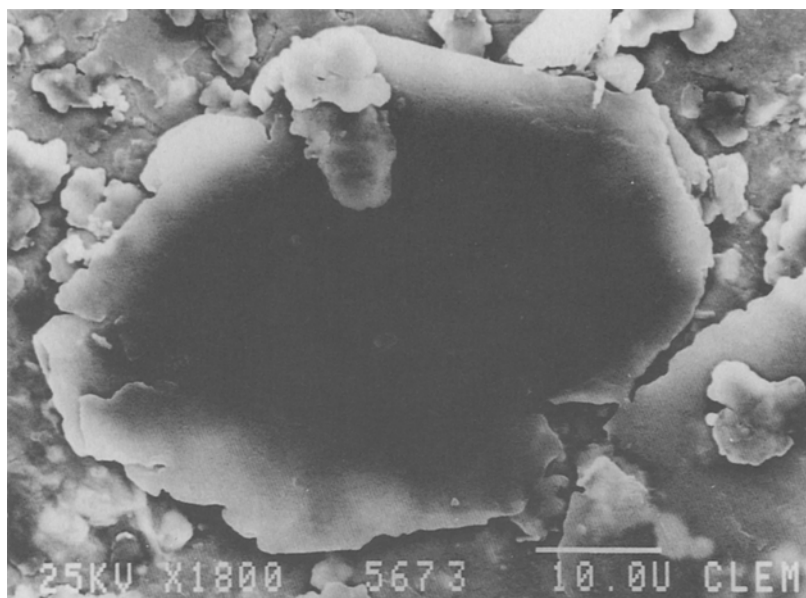


Fig. 2. SEM picture showing $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ partly decomposed on standing.

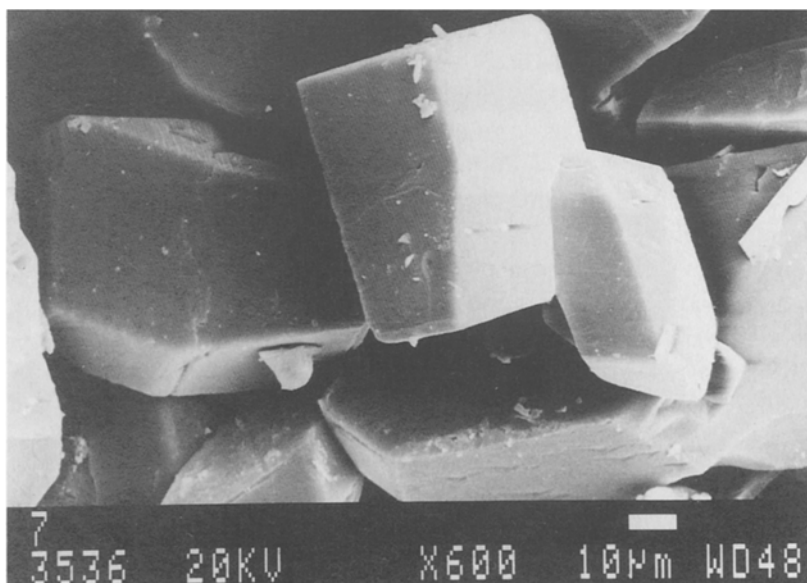


Fig. 3. Electron microscopic picture of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ in original freshly prepared form.

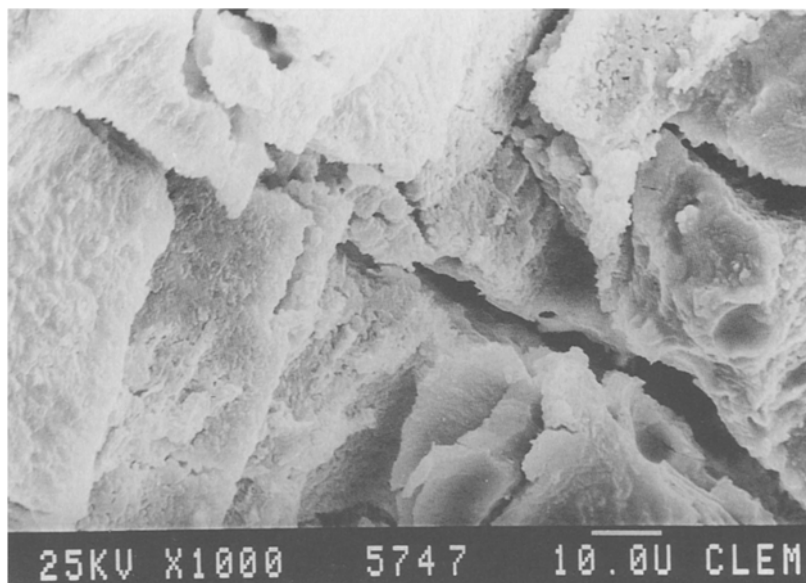


Fig. 4. SEM picture of $\text{Ni(en)}_2\text{Ni(CN)}_4 \cdot 2.4\text{H}_2\text{O}$ decomposed on standing – not forming leaflets.

3. Results and Discussion

3.1. PARTLY DECOMPOSED PRODUCTS AFTER LONG STANDING

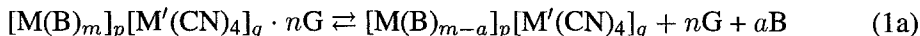
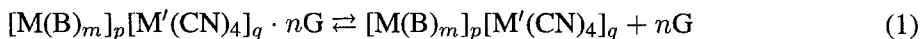
The morphology of products **II** and **IV** were studied after one year long standing in closed vials. The SEM pictures (Figures 1 and 2) were compared with their original form (Figure 3) in the case of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$. In all the products here shown the original microcrystalline shapes have changed to leaflets and they seem to some extent to have lost their three-dimensional character. It is interesting to note that a similar change was observed when the ammine groups in product **IV** were replaced by dioxane in the preparation.

Only in a few cases of standing in bottles did the decomposition exhibit a different morphological course (see Figure 4 in the case of $\text{Ni(en)}_2\text{Ni(CN)}_4 \cdot 2.4\text{H}_2\text{O}$) without the formation of leaflets.

3.2. PRODUCTS CAPABLE OF REVERSIBLY FORMING INCLUSION COMPLEXES

When microcrystalline compounds **I**, **III–VIII** were heated continuously (3°C or $6^\circ\text{C}/\text{min}$) no changes to leaflets were observed. According to the results of TA, IR spectra and X-ray measurements the first step in the decomposition was accompanied by loss of the guest component; sometimes a part of the base **B**

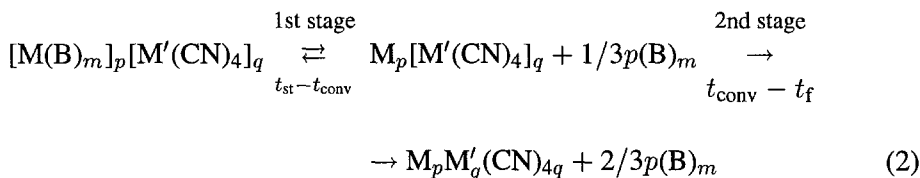
also accompanied the weight loss. The course of decomposition may be described generally in the form:



Some compounds were used in the separation of mixtures containing different organic compounds in gas chromatographic experiments [4, 6] and the cyanocomplex was often modified by solvents before its use as a stationary phase [11]. Evaluating the results gave the following observations:

(a) The course of the reaction according to Equation (1) may be regarded as reversible. The capacity to exchange the original guest for a new one was found under optimum conditions (temperature, pressure, carrier gas flow rate, the steric character of the newly included molecules) to be as high as 90% of the guest originally present.

(b) The reversibility rapidly diminishes with increasing quantity of the diffused base B (Equation (1a)). It occurs faster than gradual decomposition if the diffusion of the guest component G and of the base B is simultaneous. The efficiency of the cyanocomplex after the loss of one third of the original base contents ($a = 1/3m$) may decrease to less than 10% of its original value. The course of the decomposition of the host component occurring according to (1) may be expressed by Equation (2), in two steps:



In this case t_{conv} designates the temperature at which one third of the base B is lost, t_{st} the temperature at which the base B starts to be liberated and t_f the temperature at which loss of B is complete.

3.3. THE PRODUCT OF CONVERSION GAINED BY HEATING

(a) In this part we analyzed the products of reactions obeying Equations (2) in its first step. The loss of the base B may be described by three temperatures ($t_{st} < t_{conv} < t_f$). These limit the temperature interval within which the inclusion compound may exist, and characterize its change to a still compact but in some sense activated form. Most of the intermediate products formed in this temperature interval (mainly $t_{st} - t_{conv}$) exhibited some anomalies in their GC elution curves. An experimental relation between elution volume and temperature is known ($\log V_g \doteq f(1/T)$). The intermediates formed in this temperature region, where the

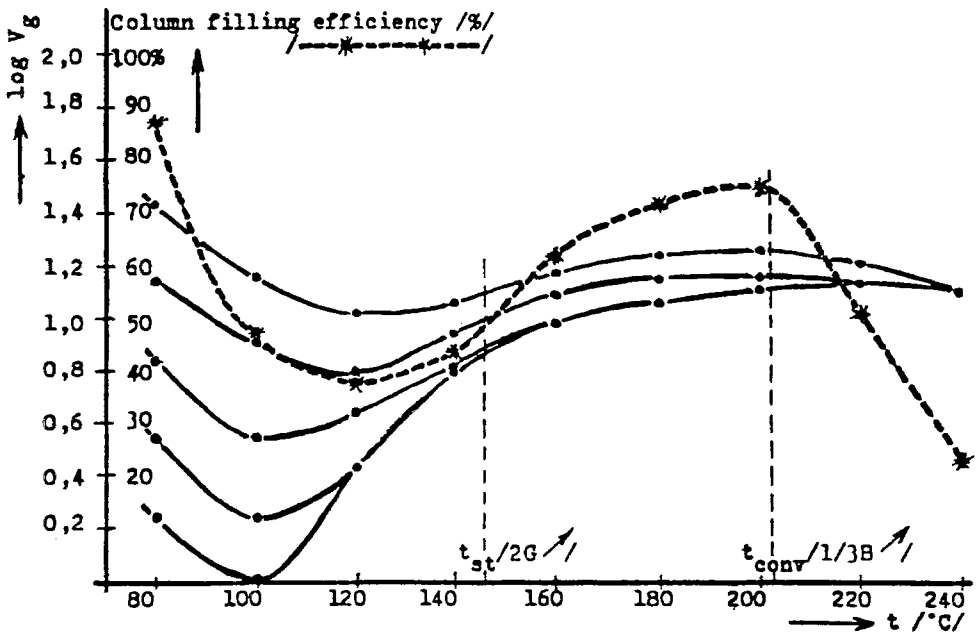


Fig. 5. $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ modified by dioxane used as a stationary phase for the separation of alkanes.

conversion occurred, showed an opposite dependence around t_{conv} . The irregularity in the volume changes with increasing temperature may be regarded partly in this connection.

Figure 5 shows the course of the separation of a mixture of C_5 – C_9 alkanes. Our product was used after its recovery from $\text{C}_4\text{H}_8\text{O}_2$ [6, 9, 10, 12]. According to the thermal analysis [4], the temperature of its conversion (t_{conv}) is 200°C . Some sorptive properties of the tetracyanonickellate are still conserved here, but its selectivity for alkanes ends near t_{st} .

The variations of the volume changes are shown in Table II.

The results of the specific surface measurements [4] of the decomposition products compared against the original inclusion compounds exhibited a large increase of the absorbed nitrogen (Table III). We assume here that the decomposition products are porous, as confirmed by the SEM photographs. But simultaneously the material persists in a compact form with the original crystal size (Figures 8–10). The specific volume increase may be explained by the formation of new cavities and canals.

The EDX spectra were used as an indirect method for the evaluation of the surface changes in the intermediates (Figure 6). If there are no changes in the proportion of the metal contents in the intermediates and if similar conditions were used then the variations of the metal concentrations in the intermediate may be

TABLE II. Retention time t'_r , for the mixture of alkanes $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ (10%) used after its modification by dioxane as a stationary phase in GC.

Mixture of alkanes $\text{C}_5\text{--C}_9$	Retention time t'_r (s)									
	80	100	120	140	160	180	200	220	240	
pentane	0.10	0.05								
hexane	0.20	0.10	0.15							
heptane	0.40	0.20	0.25	0.35	0.55	0.65	0.70			
octane	0.80	0.40	0.35	0.50	0.70	0.80	0.80	0.80		
nonane	1.50	0.80	0.60	0.65	0.85	1.00	1.05	0.95	0.80	

TABLE III. Surface area of the original compound in comparison with the intermediate products.

Compounds	Surface area (m^2/g)	
	Original $t_{\min} = 20^\circ\text{C}$	Product at $t_{\max}/(^\circ\text{C})$
$[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 0.5\text{C}_6\text{H}_6$	nonmeasurable	8.49 / (610)
$[\text{Ag}(\text{NH}_3)]_2\text{Ni}(\text{CN})_4 \cdot 0.1\text{C}_6\text{H}_6$	0.24	7.33 / (596)
$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$	2.87	16.24 / (424)
$\text{Zn}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.8\text{H}_2\text{O}$	4.79	22.81 / (483)

regarded as a consequence of some 'respiring' of the decomposing compound. Equally it may be ascribed to the changes in the internal cavities.

When we compare the surface areas of the $\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$ compound and its intermediates formed, an increase of 5% is observed at t_{conv} (268°C) and a decrease of 10% at t_f (373°C). At higher temperatures an increase of 14% is observed at t_{max} (600°C).

The volume changes, together with the starting thermal activation of the metallic ions, as a consequence of topochemical reactions, contribute to the selectivity and to the reported anomaly. In the GC experiments the intermediates formed mainly in the temperature interval $t_{\text{st}} - t_{\text{conv}}$ showed selectivity against oxygen- or nitrogen-containing compounds.

(b) In the following we study the products of reactions obeying Equation (2), second step, and Equation (3). The decomposition of the host lattice after reaching the temperature t_{conv} may be regarded as irreversible. Non-stoichiometric oxides are gradually formed by topochemical reactions by heating in air. The solid product from Equation (2) is decomposed by air oxidation to give dicyanogen and oxides. The oxides are double, or else a mixture of the non-stoichiometric forms of the same metal or with regularly mixed elemental metal (depending on the metals present). The process may be described in a simple way by the following equation:

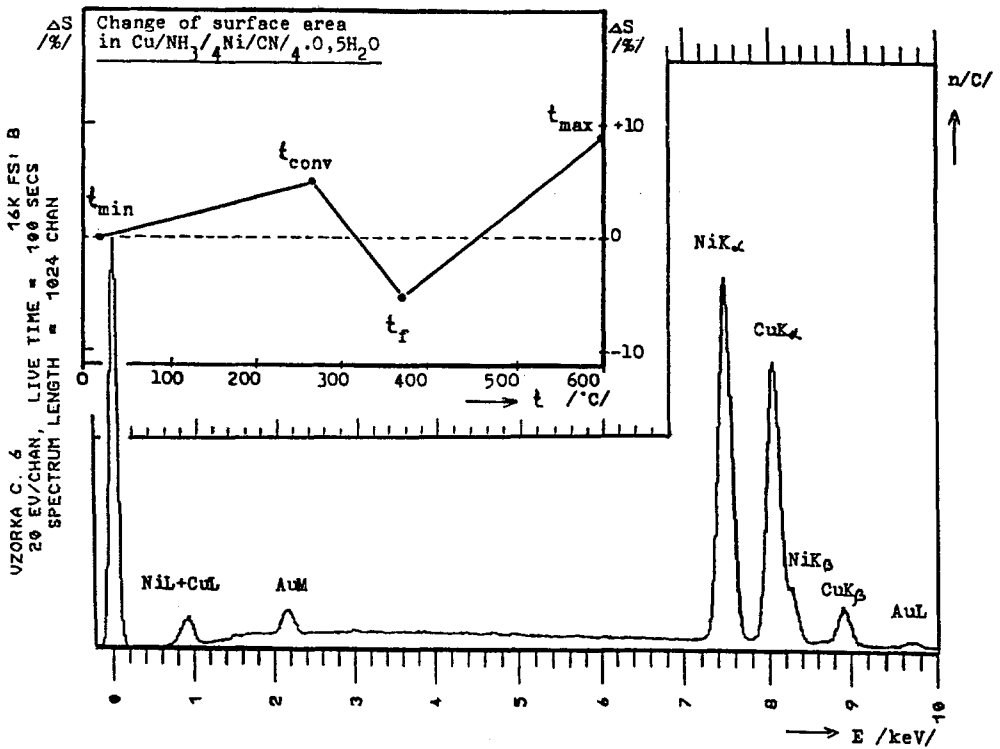
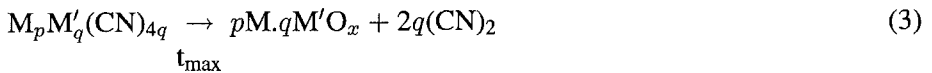


Fig. 6. The EDX spectra of the intermediate gained at 373°C from $\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot 0.5\text{H}_2\text{O}$.



A rather large homogeneity of the product has its origin in the crystalline character of the starting compounds. The homogeneity is found also in the constant characteristic copper and nickel signals at $t_{\min} - t_{\max}$ (Figure 6).

The nonstoichiometric oxides affect the electrical behaviour of the intermediates and of the final products obtained at about 500–600°C. The thermal degradation of the inclusion compounds of tetracyanocomplexes gives oxides with homodesmic structures from inclusion compounds representing a heterodesmic structure (also SEM picture). The topochemical reactions gave such nonstoichiometric oxides as products.

4. Changes in the Properties of the Intermediate Products

4.1. MORPHOLOGY

The very fine microcrystalline product $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (Figure 7) could not be very clearly evaluated in morphological terms. We prefer here to com-

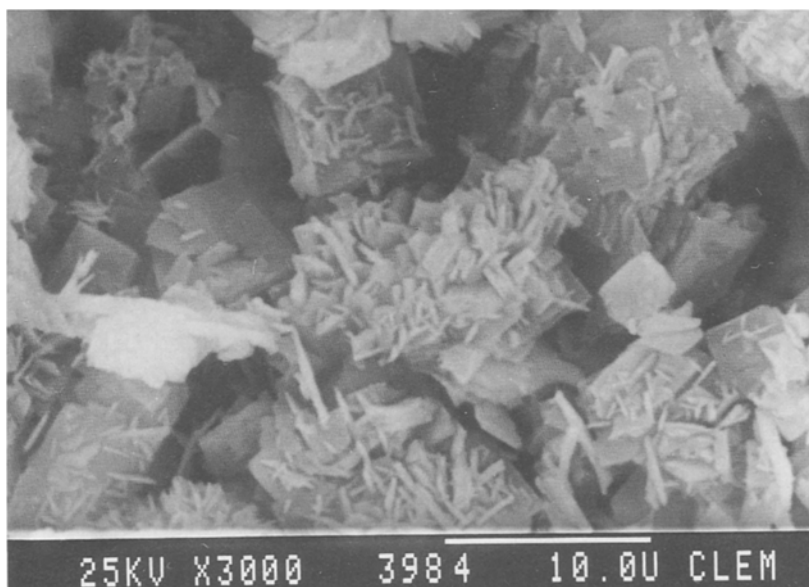


Fig. 7. SEM picture of the original $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ compound.

pare the morphology of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ (Figure 3). The structure of compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ is known [14], and the structure of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ was solved recently [15, 16]. The nonstoichiometric homogenous forms of the oxides formed have different properties from the pure oxides. The crystals of the oxides obtained are always compact, but more or less voluminous voids arise in the lattice. The structures are illustrated in Figures 3 and 8–11.

Figure 4 shows the crystals of the original $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ compound. The reaction described by Equation (1) gives an intermediate product at 190°C which has visible but not very regular surface localised fissures (Figures 8).

The course of the topochemical reactions is initiated by the diffusion of the ammine ligands in the $t_{\text{st}} - t_{\text{f}}$ ($190\text{--}348^\circ\text{C}$) interval. We show in Figure 9 the morphological view of the product obtained at t_{f} (348°C). At t_{max} (590°C) we obtain as final product the double oxides $\text{Co}_3\text{O}_4 \cdot \text{NiO}$, having a large number of rather large voids (Figure 10). Their number increased if during the preparation of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ we added a little quantity of selenious acid. The difference in the morphology of the original and selenium doped form is clear from Figures 10 and 11.

The final product after heating the Hofmann compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ to $t_{\text{max}} = 424^\circ\text{C}$ is NiO . In comparison with the preceding double oxides (Figures 11 and 12) it exhibits a rather large increase of the less voluminous voids.

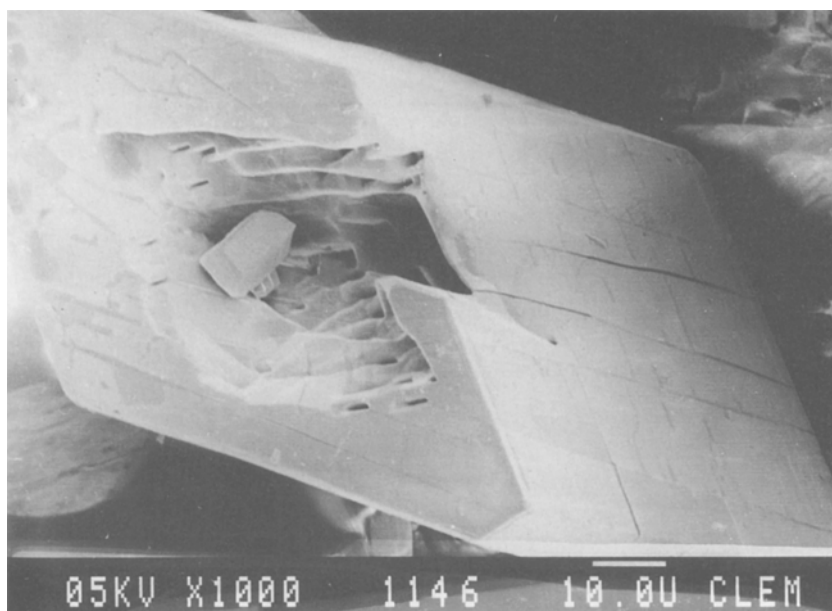


Fig. 8. SEM picture of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ after heating to 190°C .

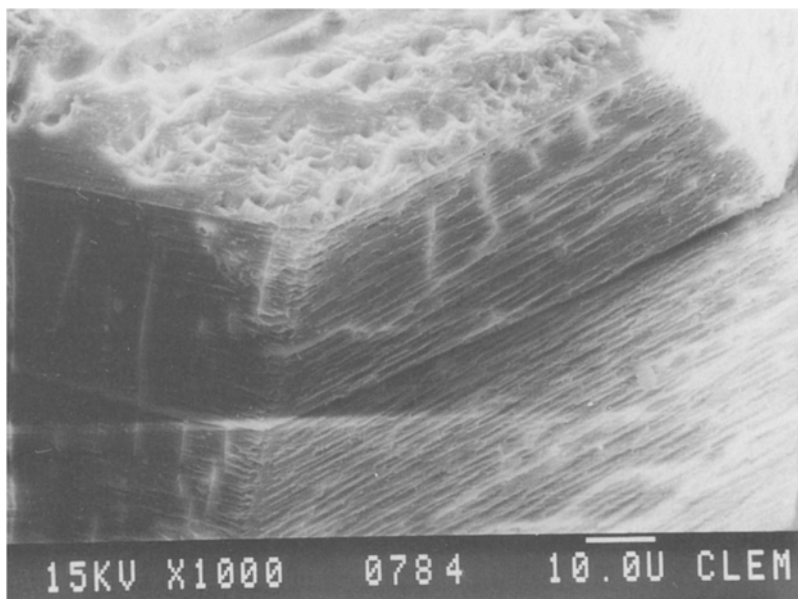


Fig. 9. SEM picture of $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 0.5\text{C}_6\text{H}_6$ after heating to 348°C .

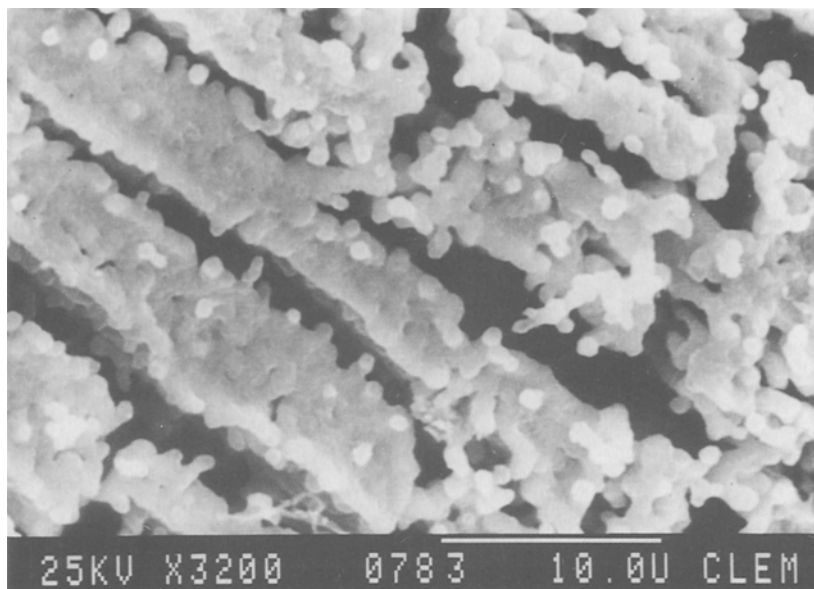


Fig. 10. SEM picture of the final product obtained from $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ heated to 590°C .

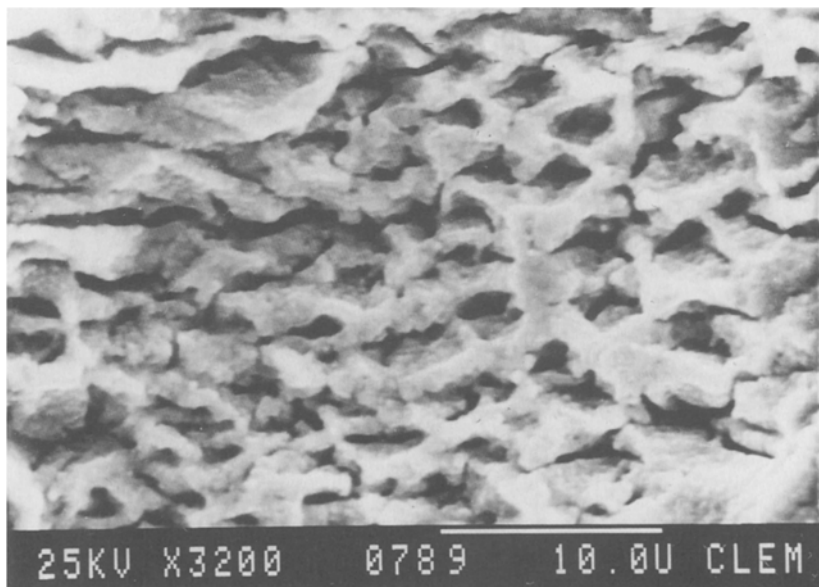


Fig. 11. SEM of final product from selenium doped $[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$.

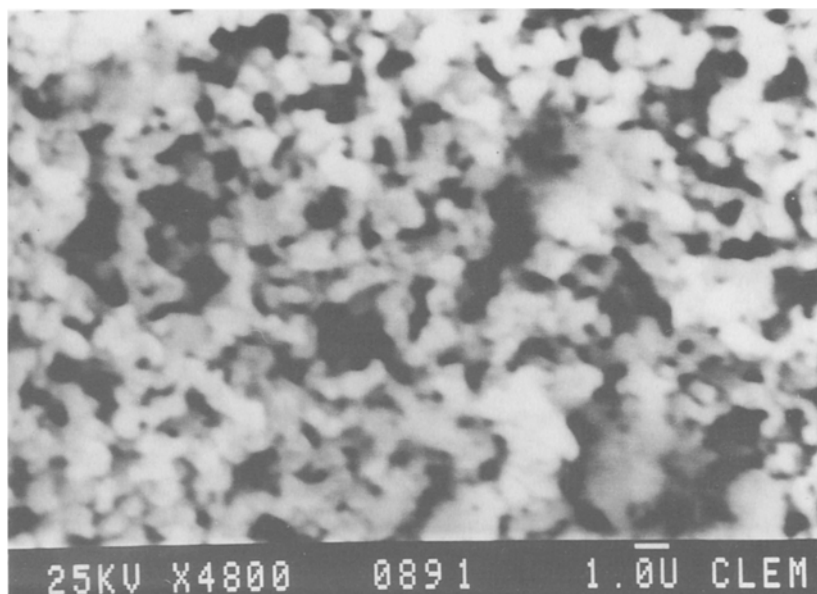


Fig. 12. The final product obtained at 422°C from $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$.

TABLE IV. Characterisation of the oxides studied.

Sample No.	Oxide	Decomposition Starting compounds	temperature (°C)
1	CoO	$\text{Co}(\text{OH})_2$	168 (partial vacuum)
2	NiO	$\text{Ni}(\text{OH})_2$	230 (partial vacuum)
3	NiO	$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$	424
4	$\text{Co}_3\text{O}_4 \cdot \text{NiO}$	$[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$	590
5	$\text{Co}_3\text{O}_4 \cdot \text{NiO}$	$[\text{Co}(\text{NH}_3)_6]_2[\text{Ni}(\text{CN})_4]_3 \cdot 2\text{H}_2\text{O}$ doped by Se	590

A different course of the thermal degradation was found in the case of $\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. In Figure 13 we see voids of different diameters instead of 'fissures'.

4.2. ELECTRICAL PROPERTIES OF ACTIVATED MIXED OXIDES

A rather strong differentiation between the individual intermediate products and final products was found (Tables IV and V). The σ -values of the starting compounds for samples 4 and 5, including their intermediate products, are no higher than $17.8 \times 10^{-3} \text{ nS cm}^{-1}$. The capacitance is always below 4 pF.

The stoichiometric form of nickel oxide (light green) has insulating properties [17], it becomes darker by heating in a pure oxygen atmosphere and it exhibits

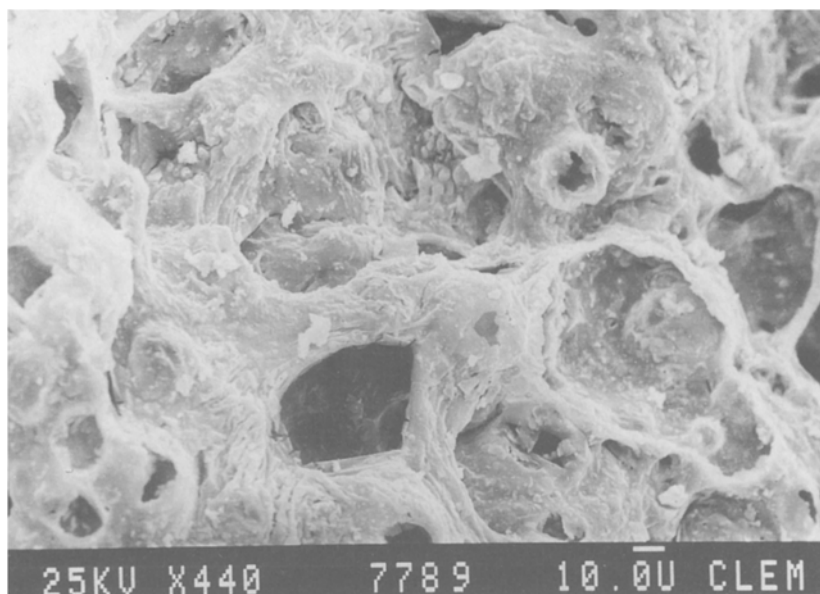


Fig. 13. Mixed oxides obtained from $\text{Cu}(\text{NH}_3)_4\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ heated to 600°C .

TABLE V. The final products of the thermal decomposition and the electrical properties: σ and C .

Samp. No.	Conductivity σ (nS cm^{-1})			Capacitance C (pF)		
	100 Hz	1000 Hz	2000 Hz	100 Hz	1000 Hz	2000 Hz
1	63.6×10^{-3}	63.7×10^{-3}	50.9×10^{-3}	28	11	10
2	229.1×10^{-3}	216.5×10^{-3}	178.2×10^{-3}	49	32	24
3	1.9×10^3	1.9×10^3	2.0×10^3	57	48	43
4	0.3×10^3	0.5×10^3	0.7×10^3	17	12	11
5	11.2×10^3	11.2×10^3	11.3×10^3	870	246	183

semiconducting properties (Ni(II), Ni(III)). By comparison of the values of samples 2 and 3, sample 3 showed increasing value, in spite of the fact that the original $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ was not heated in pure oxygen. In the case of the double oxides (No 4) cobalt(III) is also present (No 5). Two orders of higher values are in the starting compounds doped by selenium. Its highest capacity values in the case of the mixed oxides gained from sample (5) was found at 100 Hz.

4.3. SORPTION PROPERTIES

We assume that the higher values shown in Table V are not just caused by nonequivalent valencies existing in the final products. From the literature [18–20] it is known that oxygen positively affects the conductivity of semiconductors, such as NiO. The existence of some sites with a higher energy content is assumed and, equal-

TABLE VI. Data showing the chemisorption of O₂ and H₂ [21].

Original compound	Sorption on intermediates isolated at	
	110°C	410°C
	H ₂ (ccm/g)	O ₂ (ccm/g)
Ni(NH ₃) ₂ Ni(CN) ₄ · 2H ₂ O	0.023	0.655
[Co(NH ₃) ₆] ₂ [Ni(CN) ₄] ₃ · 0.5C ₆ H ₆	0.106	0.503

TABLE VII. Stoichiometry of the intermediate products used in sorption experiments.

Original compounds	Stoichiometry of intermediate isolated at temperature		Degree of conversion at t_{410} (%)
	110°C	410°C	
	Ni(NH ₃) ₂ Ni(CN) ₄ · 2H ₂ O	Ni(NH ₃) ₂ Ni(CN) ₄ · 0.3H ₂ O	
[Co(NH ₃) ₆] ₂ [Ni(CN) ₄] ₃ · 0.5C ₆ H ₆	[Co(NH ₃) ₆] ₂ [Ni(CN) ₄] ₃ · 0.1C ₆ H ₆	2/3(Co ₂ [Ni(CN) ₄] ₃) + 1/3Co ₃ O ₄ · 4.5NiO	33

ly, an increase in the sorptive properties. By testing the chemisorption of oxygen and hydrogen on the intermediate products (gained at 110°C and 410°C from Ni(NH₃)₂Ni(CN)₄ · 2H₂O and [Co(NH₃)₆]₂[Ni(CN)₄]₃ · 0.5C₆H₆) we could check the effects of the former on the conductivity. In the case of both gases we show in Table VI their chemisorbed quantities (on the intermediates of tetracyanocomplexes).

According to the thermal analysis the intermediate products used in these experiments showed the stoichiometries, shown in Table VII.

In Tables VI and VII the temperature of 110°C lies between the values of $t_{\min} - t_{st}$, and 410°C between $t_f - t_{\max}$. It is a technical disadvantage of the experiments in Table VI that the intermediates could not reach the temperature t_{\max} . The compounds Ni(NH₃)₂Ni(CN)₄ · 2H₂O and [Co(NH₃)₆]₂[Ni(CN)₄]₃ · 0.5C₆H₆ need heating to 522°C and 610°C.

5. Conclusion

The aim of this contribution is to look for further uses of the inclusion compounds of tetracyanocomplexes. In addition to the variability and accessibility of the voids enabling a selective inclusion of molecules (in liquid or gaseous form) in chromatography, the compounds are able, after reaching the temperature t_{conv} , to produce new forms of oxides with highly activated properties. This could be further extended by their combination with carriers, also represented by natural inclusion compounds. The properties of high homogeneity, porosity and energetical nonequivalency of their sites govern their use in the field of activated materials.

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