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ABOUT THE THERMAL DECOMPOSITION OF TETRACYANOCOMPLEXES

J. Bubanec and A. Sopková

Department of Inorganic Chemistry, Faculty of Sciences, P. J. Safarik's University
04154 Kosice, Slovak Republic

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Abstract

Tetracyanocomplex clathrates and their changes caused by heating were studied. The intermediates formed were characterized by IR and UV-VIS spectroscopy. Elemental analysis and XRD patterns were also used. For the visualisation of changes occurring on the surface and the distribution of metallic elements therein were studied by electron microscopy and EDX. The extent of the non-stoichiometric changes introduced by the topochemical course of the degradation reactions was correlated with the measured electrical values.

Keywords: electron microscopy, inclusion compounds, thermal decomposition products, topochemical reactions

Introduction

Inclusion compounds of the tetracyano-complex type may be represented by the simile form: H.G (Host and Guest component). In a more precise form their general formula is comprising a whole series with a broad energetical variety of bonds existing between the elements, ligands and components forming the whole compound. The general formula is:

$$[M(B)_m]_p[M'(CN)_4]_q \cdot nG$$

where: M=Ni(II), Cu(II), Cd(II), Zn(II), Mn(II), Fe(II), Co(II), Co(III), Ag(I),...[1–5], M'=Ni(II), Pt(II), Pd(II), Zn(II), Cd(II), Hg(II), Ag(I),...[1, 2, 6], B= NH_3, ethylenediamine, toluidine (*o*-, *m*-, *p*,), pyridine, dimethylamine, ammoniumalkalamine, 1,2-diaminopropane, dioxane,...[1, 2, 7–11], G=H_2O, C_6H_6, C_6H_5OH, $C_4H_8O_2$, C_4H_4S, C_5H_5N, $C_6H_5NH_2$, C_4H_4NH, C_4H_4O, $C_{12}H_{10}$, C_6D_6, C_4D_4NH, $C_6D_5NH_2$,, tetrachloroetane, C_6H_5F,, 1,2-dichlorethane...[1, 2, 9, 10, 12], n>0, m, p, q=stoichiometric coefficients.

The compounds has a heterodesmic structure. Very little energetic quanta-supplied in the form of heat – may, change the original compounds into products

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exhibiting different morphologies, thermal stabilities and properties. Little thermal effects may influence the formation of at least a part of weathered products. They differ in morphology and properties from the products obtained by a regulated heating in shorter time intervals [13]. In the former case the spontaneous reaction course exhibits an irreversible character from the beginning, in the latter the topochemical reactions, show reversible character up to their 'temperature of conversion $-t_{conv}$' [13], where the destruction of the host unit begins.

The compounds $Ni(NH_3)_2Pt(CN)_4 \cdot 2C_6H_5OH$, $[Co(NH_3)_6]_2[Ni(CN)_4]_3 \cdot 2H_2O$ and $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ may serve as examples. After storing for one year in the laboratory in a reaction bottle, the electron micrographs of the samples showed the presence of a portion of leaflets different from the original crystalline products. By a regulated heating of the same compounds (changing the heating rate from 3 to 6°C min^{-1}), products were obtained with a compact form, with different proportions of 'scarred' areas on the surface [13, 14]. The same or similar course could be observed also for the compounds $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and $Cd(en)_3Ni(CN)_4 \cdot 2C_6H_6$ [15]: the first step of the topochemical destruction reactions was accompanied by the diffusion of the included species.

The potential use of the compounds in selective separations of different guests G (organic compounds) is determined by the height and range of temperatures were the liberation, diffusion and decomposition of the ligand $B(t_{\Delta B}=t_{B(start)}-t_{B(end)})$ occur.

Some gas-chromatographic experiments [13, 16, 17] have revealed these properties of tetracyano-complex clathrates. In the case of pyridine or dioxane, some tendency to the substitution of the ligand B by the liberating G was observed – without the possibility to liberate them in a non-destructive way by heating the host. Above t_{conv} – after the diffusion of the whole G and about 1/3 of the ligands B a second step accompanied by a successive destruction of the compound occurs. The products resemble the original compounds only by their external shape. After forming the layered structure, the appearance of the intermediates is progressively changing to a more rectangularly fluted appearance in the outer and inner areas. The compounds $[Co(NH_3)_6]_2[Ni(CN)_4]_3 \cdot 2H_2O$, $Cd(NH_3)_2Ni(CN)_4 \cdot 1.5C_6H_6$ and $[Ag(NH_3)]_2Ni(CN)_4 \cdot 0.1C_6H_6$ (or $Ni(NH_3)_2[Ag(CN)_2]_2 \cdot 0.1C_6H_6$ [6]) have been dealt with in previous papers [13, 14, 18, 19]. We may find less often such destruction in $Cu(NH_3)_4Ni(CN)_4 \cdot H_2O$ or, in the case of $Ni(en)_2Ni(CN)_4 \cdot 2.4H_2O$ a total collapse into an amorphous mass follows. Mainly the temperature and time dependencies of the thermal degradation of tetracyano-complexes (near t_{conv}) affect the morphology of the products.

Experimental

Materials

A series of compounds $[M(B)_m]_p[M'(CN)_4]_q \cdot nG$ with M=Ni(II); M'=Cd(II), Co(III), Ag(I), Zn(II); $B=NH_3$, $NH_2(CH_2)_2NH_2$; and $G=H_2O$, C_6H_6, C_6H_{12},

Table 1 The clathrates of tetracyanocomplexes (TKK)

No.	TKK	No.	TKK	No.	TKK
1	$Ni(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$	15	$Zn(NH_3)_2Pd(CN)_4{\cdot}2C_6H_6$	29	$Cd(NH_3)_2Hg(CN)_4{\cdot}2C_4H_4S$
2	$Cu(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$	16	$Ni(NH_3)_2Pd(CN)_4{\cdot}2C_6H_5OH$	30	$Cd(NH_3)_2Hg(CN)_4{\cdot}2C_6H_5OH$
3	$Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$	17	$Ni(NH_3)_2Pd(CN)_4{\cdot}2C_4H_4S$	31	$Cd(en)Ni(CN)_4{\cdot}2C_6H_6$
4	$Zn(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$	18	$Cu(NH_3)_2Pd(CN)_4{\cdot}2C_4H_4S$	32	$Cd(en)Pt(CN)_4{\cdot}2C_6H_6$
5	$Ni(NH_3)_2Ni(CN)_4{\cdot}2C_6H_5NH_2$	19	$Cd(NH3)_2Pd(CN)_4{\cdot}2C_4H_4S$	33	$Cd(en)Pt(CN)_4{\cdot}2C_4H_5N$
6	$Cu(NH_3)_2Ni(CN)_4{\cdot}2C_6H_5NH_2$	20	$Zn(NH3)_2Pd(CN)_4{\cdot}2C_4H_4S$	34	$Cd(en)Pt(CN)_4{\cdot}2C_4H_4S$
7	$Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_5NH_2$	21	$Ni(NH3)_2Pd(CN)_4{\cdot}2C_4H_5N$	35	$Cd(en)Pt(CN)4{\cdot}2C_4H_4O$
8	$Zn(NH_3)_2Ni(CN)_4{\cdot}2C_6H_5NH_2$	22	$Cu(NH3)_2Pd(CN)_4{\cdot}2C_4H_5N$	36	$Cd(en)Pd(CN)_4{\cdot}2C_6H_6$
9	$Ni(NH_3)_2Pt(CN)_4{\cdot}2C_6H_6$	23	$Cd(NH_3)_2Pd(CN)_4{\cdot}2C_4H_5N$	37	$Cd(en)Pd(CN)_4{\cdot}2C_4H_5N$
10	$Cu(NH_3)_2Pt(CN)_4{\cdot}2C_6H_6$	24	$Zn(NH_3)_2Pd(CN)_4{\cdot}2C_4H_5N$	38	$Cd(en)Pd(CN)_4{\cdot}2C_4H_4S$
11	$Zn(NH_3)_2Pt(CN)_4{\cdot}2C_6H_6$	25	$Ni(NH_3)_2Pd(CN)_4{\cdot}C_{12}H_{10}$	39	$Cd(en)Pd(CN)_4{\cdot}2C_4H_4O$
12	$Ni(NH_3)_2Pd(CN)_4{\cdot}2C_6H_6$	26	$Cd(NH_3)_2Pd(CN)_4{\cdot}C_{12}H_{10}$	40	$Cd(en)Pd(CN)_4{\cdot}2C_6H_5OH$
13	$Cu(NH_3)_2Pd(CN)_4{\cdot}2C_6H_6$	27	$Cd(NH_3)_2Hg(CN)_4{\cdot}2C_6H_6$	41	$Cd(en)Cd(CN)_4{\cdot}2C_6H_6$
14	$Cd(NH_3)_2Pd(CN)_4{\cdot}2C_6H_6$	28	$Cd(NH_3)_2Hg(CN)_4{\cdot}2C_4H_5N$		

C_6H_{14}, $C_4H_8O_2$ were prepared [1]. For comparison, also other cyano-complexes [2] were used. Sotichiometric formulas are listed in Table 1 together with the numbering of the products used in this paper.

Methods

a.) The decomposition of a compound was studied in comparison with the original compound by: chemical analysis, IR spectra (Specord M-80 Zeiss Jena) in the range $\tilde{\nu}$=200–4000 cm^{-1} (2.5 mg/500 mg KBr) and electronic spectra (spectrophotometer M-40 Zeiss Jena) in the range $\tilde{\nu}$=11000–50000 cm^{-1} and using $BaSO_4$ as standard.

b.) Termogravimetric analysis was performed with an OD 102 (MOM, Hungary) derivatograph in ceramic crucibles, in dynamic conditions, in air, TG 100, DTA and DTG 1/5, w=100 mg, heating rate 3 and 6°C min^{-1} up to 600°C, using Al_2O_3 as standard.

c.) A Jeol, JSM-35 electron microscope was used for morphological studies. The adapter EDX Microanalyser Link 860 was used for determining the surface distribution of elements.

d.) X-ray diffraction measurements of some intermediates were performed by a Micrometa 2 instrument with goniometer (Chirana), CuK_α (λ=0.15418 nm).

Results and discussion

The most important part in the $[M(B)_m]_p[M'(CN)_4]_q \cdot nG$ compound is its host lattice – clathrand [20]. The CN^- group forms a bridge between the two metal ions M–M'. These ions are in their relatively most stable states d^5 (Mn(II)), d^6 (Fe(II), Co(III), d^7 (Co(II)), d^8 (Ni(II)), Pd(II), Pt(II)), d^9 (Cu(II)) a d^{10} (Zn(II), Cd(II), Hg(II), Ag(I)). The average Ni–C bond lengths are 0.184 –0.188 nm and the C≡N bond lengths 0.117–0.113 nm. The lengthening of heterobimetallic bonds of the tetracyanonickelates [21] depends on the increasing ionic radius of the metal M(Ni(II)<Cu(II)<Mn(II)<Cd(II).

In the majority of cases nitrogen containing bases represent the ligands B (preferring in complexes mostly $ns^o(n-1)d^{10}$ with n=4, 5, 6). In very rare cases [1, 11, 22] also oxygen containing compounds were used in the preparation, which were mostly linked only in non-stoichiometric amounts or in less stable forms. Different combinations of metal ions(II) form polymeric, layered, planar or differently undulated [3–5, 7, 8] structures, including structures very similar to aluminosilicates [9, 23].

Similarly as in other inorganic compounds also in $[Mn(CO)_3(\mu_3\text{–}OH)_4]$ – a neutral organometallic molecule – binding of a variety of large molecules (as a result of OH...X hydrogen bonding between the μ_3–OH groups and the H bond acceptor in the guest) may occur [24].

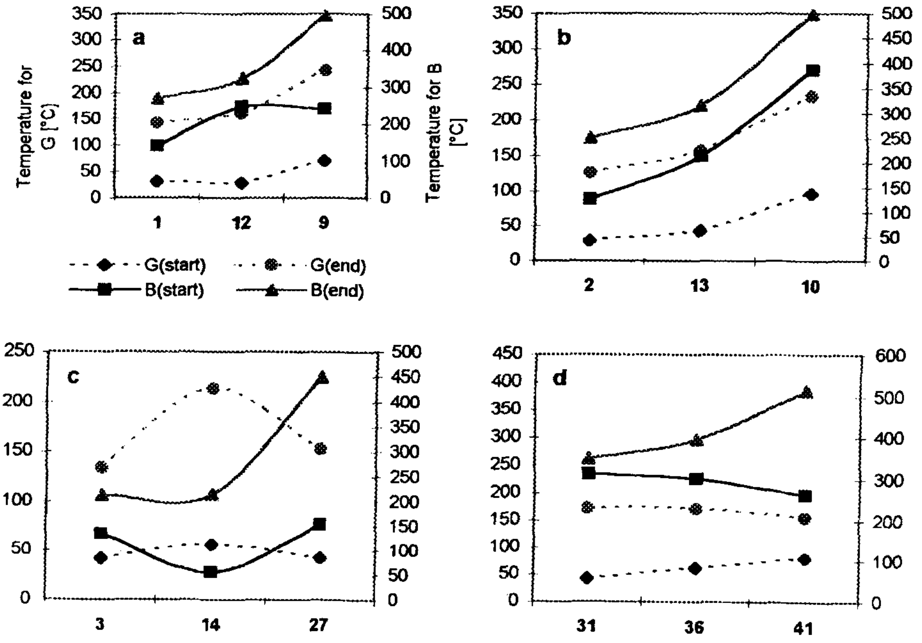

Fig. 1 Presence of *M'* affecting the thermal decomposition of tetracyanocomplexes. For the tetracyanocomplexes Nos. see Table 1

The undulation depth and frequency in the tetracyano-complexes depend on the size and structure of ligands *B*. These affect the cohesion of the layers in the compact crystal, but moreover they determine the area for the localization of the component *G*. The included components are held here by steric barriers, by van der Waals forces, but also by H bonds and by interaction of the d (in metallic ions) and p orbitals (of the guest components). From the point of view of the thermal stability, the interaction of the included species with the host lattice represents the weakest link. After heating the tetracyano-complex, the guest is emptying the area first (by diffusion or decomposition – rarely simultaneously with the liberation of the ligands *B*).

The presence of *G* normally contributes to the stability of the clathrand. In the crystals, the stabilizing influence decreases from the inner to the outer layers, which could be observed also in our experiments in the testing of the weathering of our products. If one of the metal ions is in another oxidation state, (Ag(I) or Co(III), then if used in the preparation together with the $[Ni(CN)_4]^{2-}$ they tend to form an ionic, hydrated compound [18, 25] and often the nickel and silver change positions. In both complexes some morphological changes have been observed [13, 14, 18] after heating to partial degradation, similarly to the intermediates of the clathrate.

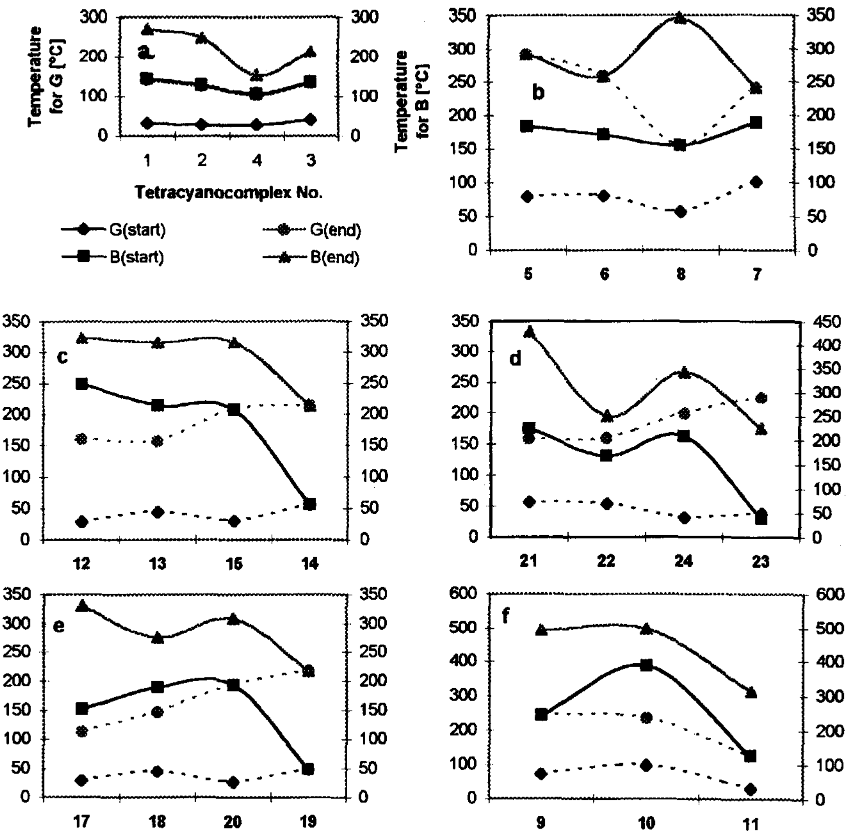

Fig. 2 Presence of *M* affecting the thermal decomposition of tetracyanocomplexes

The geometrical coincidence of the voids and the diameters of the *G* component represents the main condition for the preparation of the clathrates. The included molecules may exert their stabilizing influence in different ways (dipole moments, disposition to hydrogen or donor bonds, dative mechanisms, etc). Very different amounts of included molecules may be achieved, resulting different thermal stabilities (in the case of hexane, cyclohexane, water, benzene, heterocyclic compounds, alkyl-aryls, amines, etc.). The stability of unsaturated components included is relatively high in the case of planar species (the delocalization is maximal). All five membered cycles are planar, their shape and volume are similar to C_6H_6, therefore they all stabilize the clathrates, in the sequence: benzene>pyrrole=thiophene >furan [26]. Pyridine as an extraordinarily stable cycle with non-polar and dipolar structure which is responsible for the observed substitution of the ligand *B*, when used [16] in GC experiments also at higher temperatures.

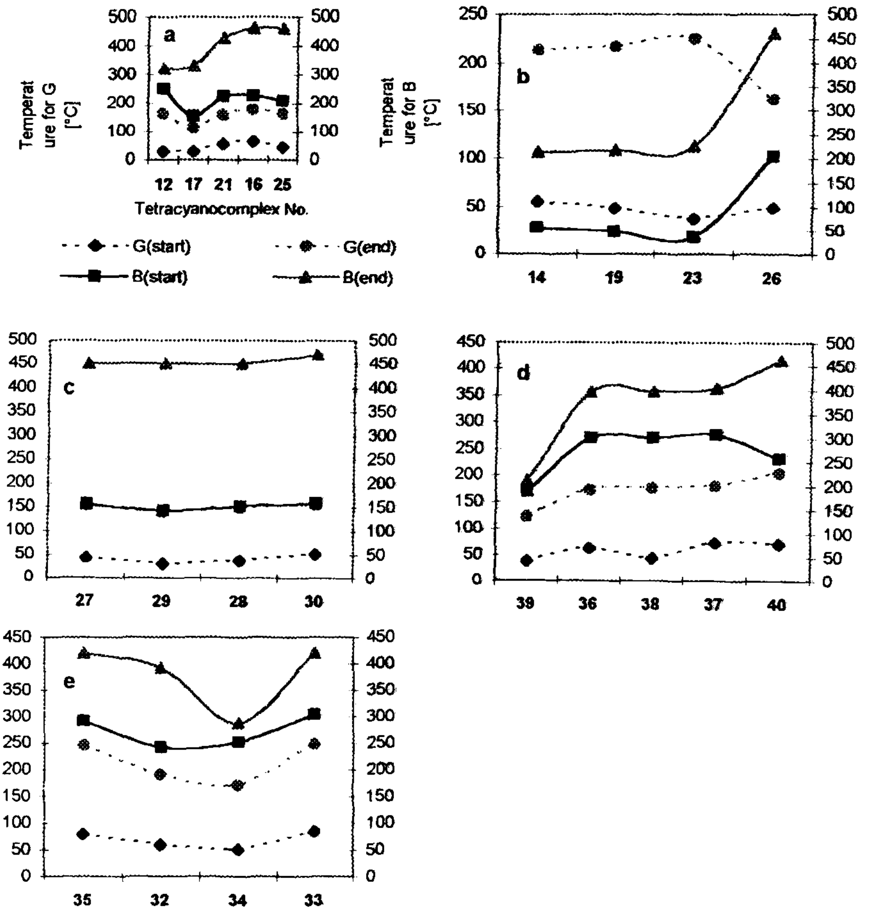

Fig. 3 Presence of the guest *G* affecting the thermal decomposition of tetracyanocomplexes

The graphical dependences shown in Figs 1–3 depict the expressed theoretical assumptions. There are differences in the measurement results of different authors owing to differences in the details of the preparation or evaluation methods. The compounds in Figs 1a, 3d and 3e are against the average values of clathrates in the other figures that are more compact even at the temperature where the ligand *B* decomposes. The temperature difference $t_{\Delta B}$ is very small. We may find the same course in the case of compounds No. 10, 12 and 13. Opposite signs – concerning the starting temperature for the decomposition of the ligand *B* – were found for compounds No. 3, 4, 14 and 22. Decreasing $t_{B(start)}$, and average values were found for $t_{\Delta B}$ compounds No. 11, 14, 19 and 23.

From the results of our morphological studies and from the above said we may conclude that the compounds changing to deformed or amorphous products

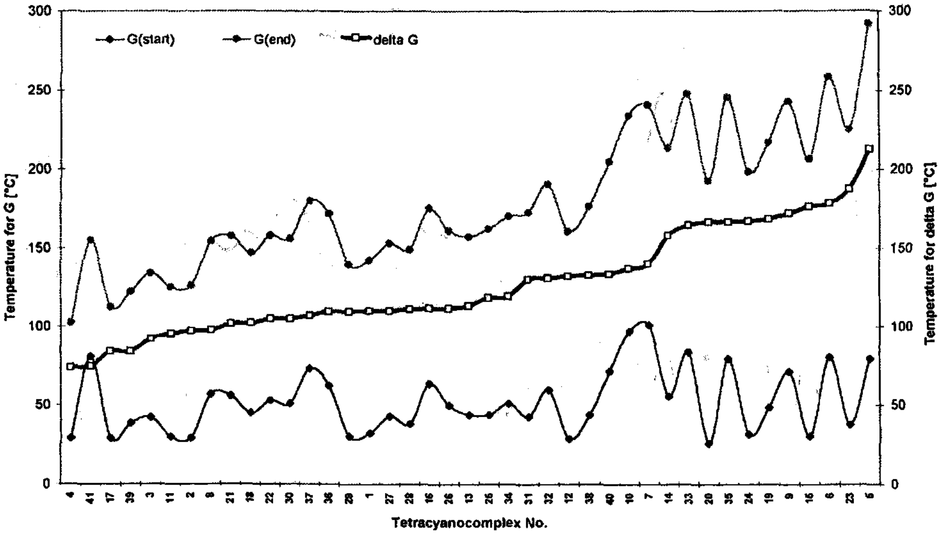

Fig. 4a The sequence of the increasing $t_{\Delta G}$ value

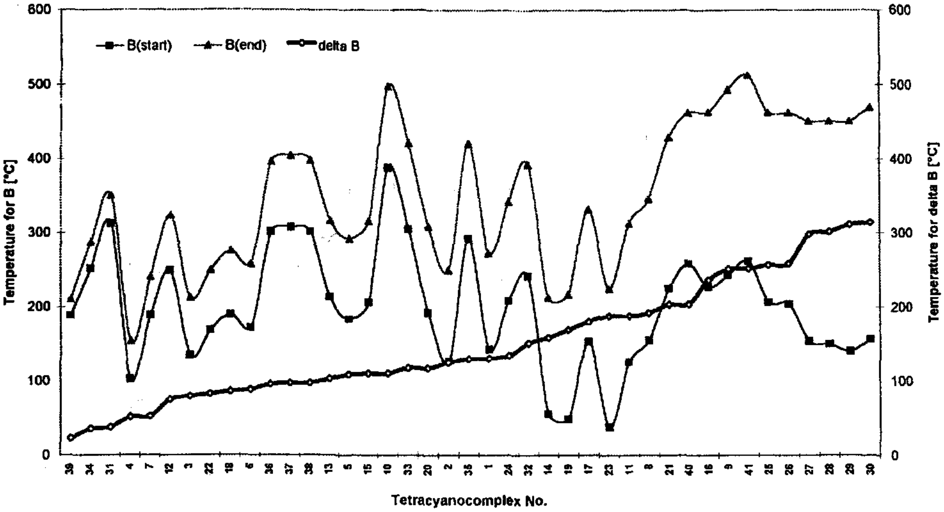

Fig. 4b The sequence of the increasing $t_{\Delta B}$ value

during their thermal degradation exhibited higher starting temperatures of the decomposition of the ligand $t_{B(\mathrm{start})}$. For the existence of deformed and amorphous forms may be explained by supposing a stronger bond between the ligand *B* and metal ion *M* (greater size of delocalization existing in the clathrand). Owing to the rapid liberation of ligands in a narrow temperature range at higher tem-

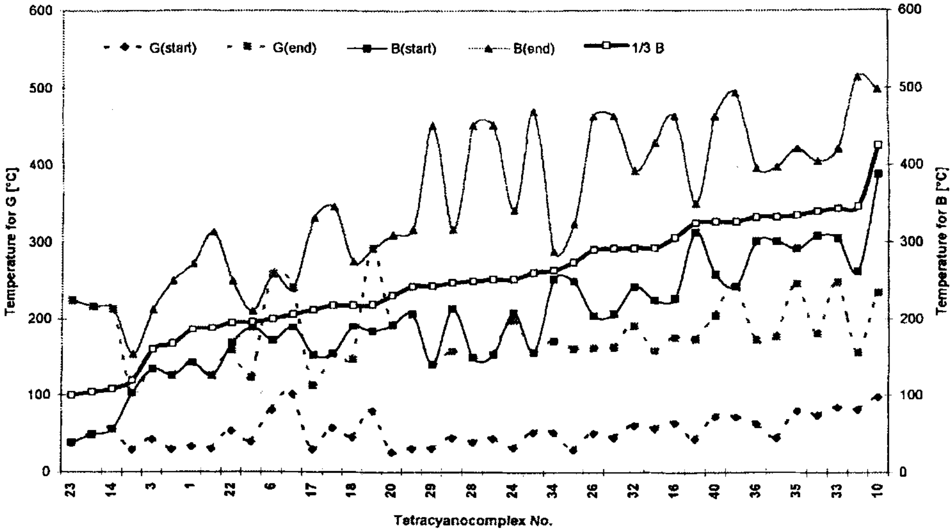

Fig 5 Approximate starting temperature for the Host component degradation

peratures and in a short time interval the topochemical reactions in the solid do not attain equilibrium. A higher pressure of the gaseous products inside the crystals and the rather rapid changes in volume (during the decomposition) may be [13, 19, 27] the cause of the crystals crumbling at the end in their amorphous forms and also of the formation of less active double oxides. The vaporization and diffusion of the component *G* during $t_{\Delta G}$ (between $t_{G(start)}$–$t_{G(end)}$) affect less strongly the resulting morphology and the properties of the final products.

It is known from the literature that inorganic polymers, silicates, borates, phosphates can be transformed relatively easily into amorphous solids by appropriate heating. Otherwise such processes are less known in the solid state. Sometimes transformation from the disordered amorphous structure to the ordered crystalline one is achieved by the formation of a new compound inside the amorphous matrix, which has changed its chemical composition too. L. Stoch and I. Waclawska [28] have tried to use their experience from the study of borates for the explanation of the amorphisation in cases of layered silicates, too.

In [2, 29–31] the thermal stabilities of new inclusion compound combinations are dealt with. Morphological studies showed a changed situation after the formation of the new products prepared from clinoptilolite (CT) zeolites. After the inclusion reaction the original CT plates with very smooth surface were visibly impregnated in the SEM pictures [2] with newly formed little pits. Some amorphisation with the change in chemical composition and behaviour occurred [2] similarly as in [28]. Similar kinds of impregnation or preparation were found on the surface of the products by A. K. Galwey [32] in the case of new inorganic products and he held it for some kind of foaming structure.

Some forms of mixed oxides with part of the cations in less usual oxidation states characterize the resulting product. In the case of silver compounds the silver is disperged in the oxide of the other metal. The values measured by specific conductivity and impendance methods [13, 33] for the products differed markedly from the same products prepared by other methods or from other starting compounds. This increased activity allows us to suppose the use of properties necessary in heterogeneous catalysis e.g., in substitution of the precious metals.

In Fig. 4 we show the sequence with the temperature range of the vaporization and diffusion of $t_{\Delta G}$, the diffusion and decomposition of ligand $t_{\Delta G}$. The first members have to be further – concerning the temperature and time – optimized for the potential utilization of their intermediates.

In Fig. 5 we show the series of tetracyano-complexes with their increasing t_{conv}. This temperature may be used for approximation of the end of the reversible topochemical reactions and simultaneously also for the start of the irreversible structural reorganization. It represents the limits for the use of clathrates of tetracyano-complexes in their original form (for separation and similar purposes) and for the use of the active forms of their thermal degradation products (in heterogeneous catalysis and in similar directions).

Conclusions

The clathrates of tetracyano-complexes as structurally heterodesmic compounds may be very lightly affected by the surrounding temperature changes. Based on experiments and testing we may improve their separation properties at elevated temperatures and the results with the use of inclusion compounds in the realization of the idea of the thermal pump [34, 35]. Morphological studies of our degraded products and measurement of their electrical values revealed [13, 33] that they have higher activity in comparison with the same compounds prepared in other modes. The comptactness of the starting compounds is conserved also after the chemical and structural changes (over 500°C) during the topochemical reactions occurring in the solid and the compact form is a pre-requisite of the increased activity.

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