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THERMOCHEMICAL PROPERTIES OF NEUTRAL COMPLEXES IN LAYER SILICATES

I. [Ni(4-Etpy)$_4$(NCS)$_2$] complex in montmorillonite and pillared montmorillonites

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Abstract

The stoichiometry of thermal decomposition and enthalpy and structural changes were studied for the compounds formed by penetration of [Ni(4-Etpy)$_4$(NCS)$_2$] (**I**) into Ca-montmorillonite (**II**) or Cr-, Zr- and Al-pillared analogues (**III**, **IV** and **V**, respectively). The mass fractions of complex **I** in **II**, **III**, **IV** or **V** are different. It was found for all studied compounds that the release of L (L=4-Etpy) is a three-step process ($-2L$, $-1L$, $-1L$), and differences occurred in enthalpy changes (ΔH in kJ per mole of I) corresponding to the individual processes. These differences and the changes in diffraction and spectral properties of the species formed after intercalation are assumed to have their roots in different intramolecular guest-host interactions in the studied compounds.

Keywords: montmorillonite-Ni(II) neutral complex

Introduction

Montmorillonite (MMT) belongs to the groups of expanding layer-lattice silicate minerals known as smectite. The interlayer space can easily be occupied by water or organic molecules. In the prevailing part of previous works the interaction of the MMT with organic molecules entering the interlayer space of MMT is interpreted in terms of cation exchange reactions. Moreover, the thermal properties of the obtained compounds [1, 2] were studied. By introducing transition metal ions into the layer of MMT and then adding suitable ligands, complexes may be formed [3]. The behaviour of the complexes formed is as a rule significantly influenced by the unique environment on the silicate surface.

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Till now little attention has been paid to the possibility of combining MMT and its related layer analogues with neutral coordination compounds. In this work the thermal properties of the intercalation products of Ca MMT and Cr-, Zr- and Al-pillared derivatives (PIL) [4] with $[Ni(4\text{-}Etpy)_4(NCS)_2]$ complex (Ni-c) have been studied. The latter complex was used as a host phase for preparation of Werner clathrates of the type $[Ni(R\text{-}py)_4(NCS)_2]\cdot nG$ (R-py is alkylpyridine, G corresponds to the guest molecules) [5–7]. In this case, however, it plays the role of a guest.

Thermal analysis (TG, DTG, DSC), powder diffraction analysis and infrared absorption spectra were used to study:

(a) the stoichiometry of decomposition of the prepared products,
(b) the thermochemistry of the studied processes,
(c) the structural changes of the guest Ni(II) complex after intercalation.

Experimental

Syntheses of the samples

Less than 2 µm fraction of bentonite from Jelšovy Potok (bentonite deposit in the central part of Slovakia) was separated from the bulk sample and converted into the monoionic Ca-form using standard methods [8]. The crystallochemical formula of Ca-MMT is as follows:

$$Ca_{0.48}(Si_{7.59}Al_{0.41})(Al_{3.06}Fe_{0.34}Mg_{0.63})(OH)_4O_{20}$$

The syntheses of the chromium-, zirconium- and aluminium-pillared varieties have been described previously [9]. The method of preparation of $[Ni(4\text{-}Etpy)_4(NCS)_2]$ complex has also been published [6, 7]. Intercalation procedure: 0.50 g of the solids (MMT or PIL) were soaked in a saturated ethanol solution of the Ni(II) complex for 4 days at room temperature. Then the suspension was centrifuged, the solid phase was washed 3 times with 50% ethanol and finally dried at 50°C.

Analytical methods and equipment

The analytical methods used have been described earlier [6–8]. The stoichiometry of thermal decompositions was studied by a Derivatograph OD 102 (MOM Budapest). A sample mass of 100 mg and a rate of temperature increase of 10°C min^{-1} were used in particular thermal decompositions. The measurements were carried out in air using a platinum crucible.

For the determination of the heats of decomposition reactions a Perkin-Elmer Differential Scanning Calorimeter DSC-7 based on the null-balance power compensating principle was used (sample mass of 3.8–4.1 mg, pure N_2 gas, scanning rate $10^{\circ}C\ min^{-1}$). Pure indium (melting point at 156.6°C and enthalpy of fusion $\Delta_f H=28.47\ J\ g^{-1}$) was used to calibrate of the temperature and change of enthalpy axes.

Powder diffraction patterns were taken on an automated Brac-Brentano Dron UM-1 diffractometer with CuK_{α} radiation. The infrared absorption spectra were recorded with a Philips analytical UP 9800 FTIR spectrometer in the range of 4000–200 cm^{-1}.

Results and discussion

Stoichiometry of thermal decomposition and enthalpy changes

The analysis results obtained for the intercalation products show (Table 1) that the total amounts of the Ni(**II**) complex (Ni-c) inserted in the porous structure of the studied silicate species are relatively high and are decreasing in the following sequence: Ca-MMT≈Cr-PIL>Zr-PIL>Al-PIL. It is worth noting that the contents of the intercalated complex determined by different analytical methods, are well comparable.

Table 1 Elemental and thermal analysis results for Ni-c (**I**) and intercalated products **II**–**V** (*L*=4-Etpy)

Sample	Elemental analysis		TG Δm/%				DTG Peak temperature/°C		
	N/%	a/%[2]	$-2L$	$-L$	$-L$	a/%[2]	$-2L$	$-L$	$-L$
Ni-c (**I**)[1]	13.90	99.8	36	17	18	100	210	250	290
Ni-c/Ca-MMT (**II**)	9.12	65.6	22	12	11	66.2	220	260	300
Ni-cCr-PIL (**III**)	9.10	65.5	22	12	11	66.2	210	260	300
Ni-c/Zr-PIL (**IV**)	7.25	52.0	18	9	10	52.1	220	260	300
Ni-c/Al-PIL (**V**)	5.84	42.0	15	7	8	42.3	220	260	300

[1] Data from [6].

[2] a/% – mass ratios of Ni-c (in %) in the intercalation products.

The TG, DTG and DTA curves of non-treated compounds and those of intercalation products are shown in Figs 1 and 2. The thermal decomposition of Ni-c (**I**) under dynamic conditions proceeds in three distinct steps in the temperature range 70–300°C [6]. The first step corresponds to the release of 2 moles of *L* (*L*=4-Etpy) per mole of the starting complex while each of the other two reflects the release of 1 mol of *L*. The stepwise character of the ligand *L* escapes from the intercalation products, is under similar conditions identical and can be expressed by the following scheme (Table 1):

$$[NiL_4(NCS)_2]/R \xrightarrow{\Delta T} -2L_{(g)}, -L_{(g)}, -L_{(g)}$$

$$(R = \text{Ca-MMT, Cr-PIL, Zr-PIL or Al-PIL})$$

A pronounced double peak in the range of 30–230°C dominates the DTG curve of Ca-MMT (Fig. 1) and is assigned to the dehydration of the product. The dehydration related peaks are considerably lower in the case of pillared derivatives (Fig. 2). The absence of this dehydration phenomenon in the case of the Ni-c/Ca-MMT (**II**) and Ni-c/Zr-PIL (Figs 1 and 2, respectively) indicates that the water molecules in the MMT or PIL interlayer space were displaced by the inserted new guest molecules of Ni-c.

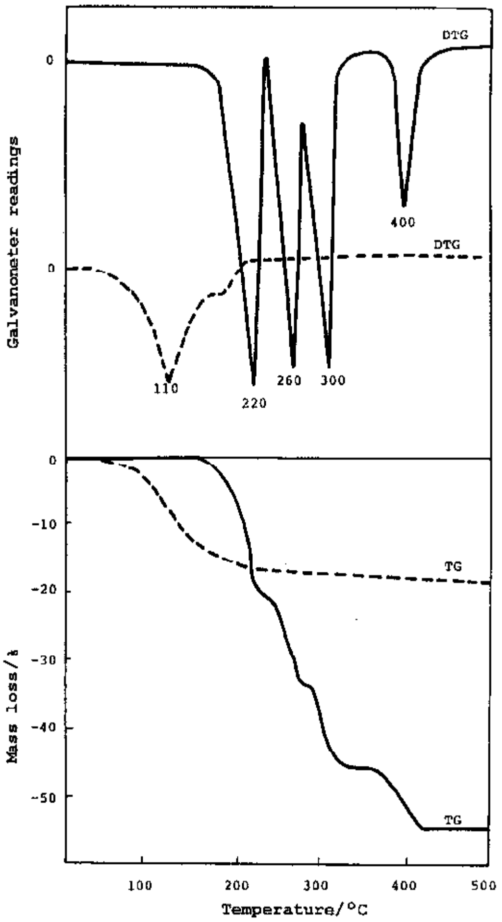

Fig. 1 TG and DTG curves of $[Ni(4\text{-}Etpy)_4(NCS)_2]$/Ca-MMT (**II**) (full line) and Ca-MMT (dashed line)

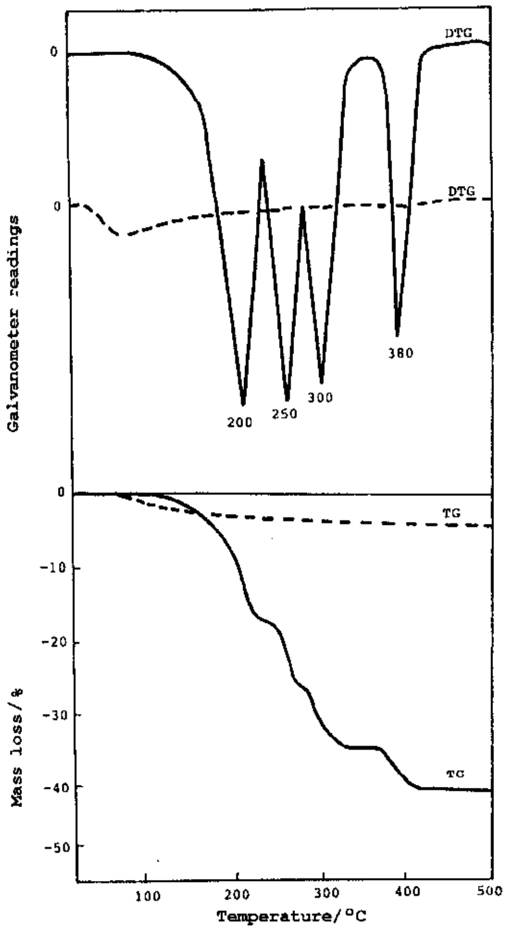

Fig. 2 TG and DTG curves of [Ni(4-Etpy)$_4$(NCS)$_2$]/Zr-PIL (**IV**) (full line) and Zr-PIL (dashed line)

The DSC curves of the Ni-c (**I**) and the studied intercalation products (**II–V**) are shown in Fig. 3. The curve of Ni-c (**I**) exhibits four maxima [6, 7] at ≈49, 197, 237 and 266°C of which the first one can be assigned to a phase transition, probably from non-clathrate α-phase to the 'empty' β_o-phase [7, 10], while the other ones correspond to a subsequent release of two, one and one moles of *L* per mole of **I**, respectively. The curves obtained for **II–V** indicate a similar course of the thermal decomposition of Ni-c contained in the intercalation products. The enthalpy changes (Δ*H*) corresponding to the particular processes are given in Table 2. Numbers (1)–(4) are assigned to the following effects:

(1): Phase transition of Ni-c. The values of $\Delta H_{(1)}$ for this effect are different and increasing in the sequence: **II**<**III**<**IV**<**I**. The effect was not observed for **V**, probably due to the decreased content of Ni-c in this product.

(2)–(4): Escape of *L*. Differences occur in the release of *L* from Ni-c in the individual host structures as illustrated by the $\Delta H_{(2)}$, $\Delta H_{(3)}$ and $\Delta H_{(4)}$ values for the thermal decomposition of the respective intercalation species at higher temperatures (Table 2). These differences may obviously be assigned to the different interactions between Ni-c and the individual host structures. It is worth mentioning, however, that the total values of enthalpy change $\Delta H(-4L) = \Delta H_{(2)}+\Delta H_{(3)}+\Delta H_{(4)}$ for **I**–**V** are approximately equal (155±4 kJ per mole of Ni-c).

Table 2 DSC data of the studied compounds

Compound	Process	T_{peak}/°C	$T_{interval}$/°C	ΔH/ kJ mol^{-1}(Ni-c)
$[NiL_4(NCS)_2]$	(1) PT	49	36– 59	3.2±0.3
(Ni-c)	(2) $-2L$	204	177–210	75±8
(**I**)	(3) $-L$	246	210–258	60±6
	(4) $-L$	276	258–295	46±5
Ni-c/Ca-MMT	(1) PT	42	36– 49	1.2±0.2
(**II**)	(2) $-2L$	201	177–209	50±5
	(3) $-L$	245	209–255	52±5
	(4) $-L$	280	255–301	53±5
Ni-c/Cr-PIL	(1) PT	42	36– 49	1.7±0.2
(**III**)	(2) $-2L$	183	144–200	60±6
	(3) $-L$	236	200–248	55±6
	(4) $-L$	265	248–288	41±4
Ni-c/Zr-PIL	(1) PT	42	35– 48	1.9±0.2
(**IV**)	(2) $-2L$	174	133–194	53±5
	(3) $-L$	234	194–248	57±6
	(4) $-L$	269	248–291	45±5
Ni-c/Al-PIL	(1) PT	–	–	–
(**V**)	(2) $-2L$	183	136–196	48±5
	(3) $-L$	236	196–249	54±5
	(4) $-L$	269	249–295	47±5

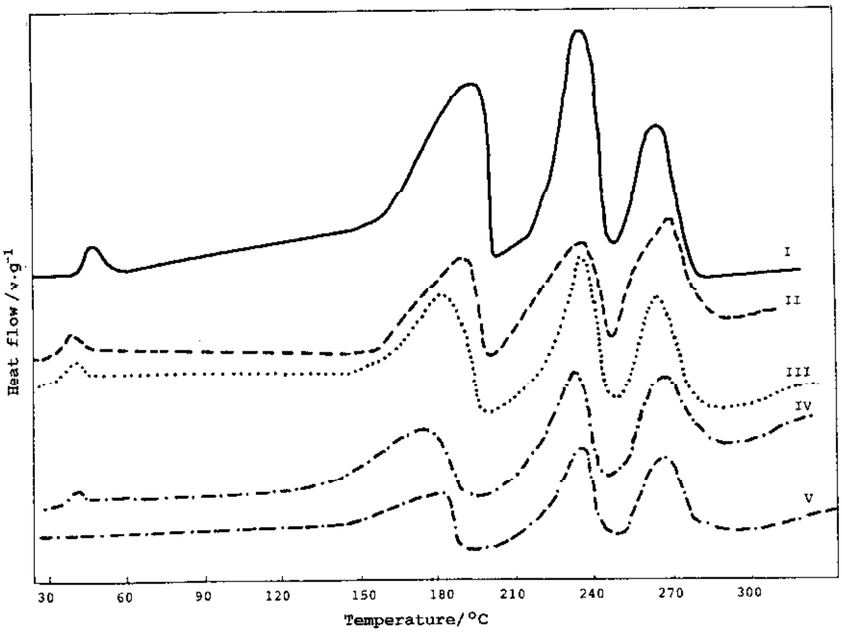

Fig. 3 DSC curves of the studied compounds (for assignment of curves see Table 1)

Structural changes

Selected diffraction patterns of the studied samples are shown in Fig. 4. The diffraction at 2Θ equal 9.14° dominates the X-ray powder pattern of the guest Ni-c complex (Fig. 4a). The occurrence of this diffraction in the powder pattern of the intercalation product Ni-c/Ca-MMT (Fig. 4c) as well as in those of pillared analogues (the powder pattern of Ni-c/Zr-PIL in Fig. 4e is shown as an example) proves the presence of the guest complex Ni-c in the samples under investigation. While an intense diffraction at 5.92° characterizes the intercalation product Ca-MMT (Fig. 4b) and occurs in the product Ni-c/Ca-MMT (Fig. 4c) as well, similar intense diffractions are missing in the pillared montmorillonite products (Zr-PIL is shown as an example in Fig. 4d). It is worth mentioning, however, that the powder patterns of the intercalation products of pillared species with [Ni(4-Etpy)$_4$(NCS)$_2$] show at 2Θ values higher that 8° a clear similarity with that of the intercalation product of Ca-MMT (cf. Figs 4e and 4c). Consequently, the diffraction measurements support the assumption that the guest complex may be inserted into the layer structures of MMT.

The results of IR spectroscopy are given in Table 3. The significant difference between pure Ni-c and the intercalated products **II–V** can be observed in the region of ν(C–N) stretching vibrations at 2075–2118 cm^{-1}. Whereas pure Ni-c produces one strong, sharp absorption band at 2075 cm^{-1}, the intercalated species

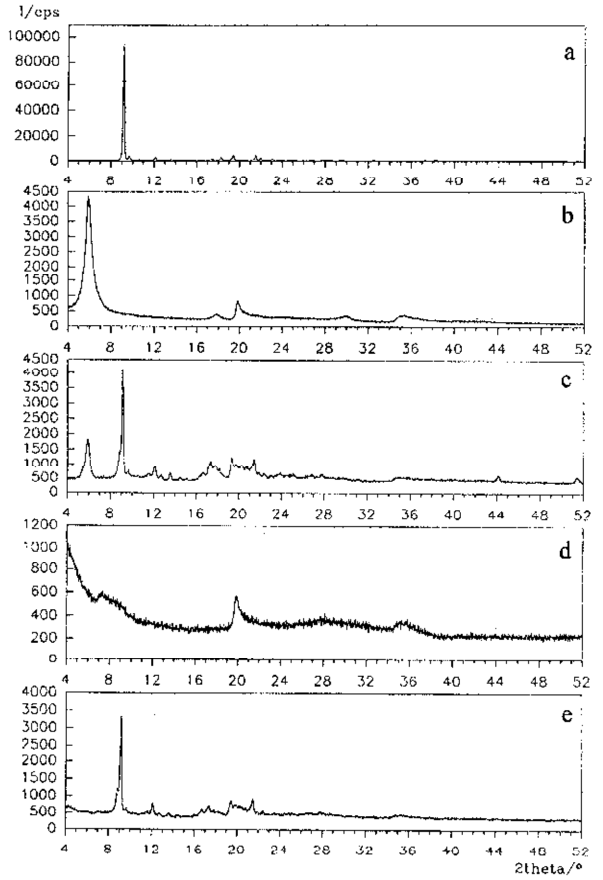

Fig. 4 Selected diffraction patterns of the studied samples: a – $[Ni(4\text{-}Etpy)_4(NCS)_2]$ (**I**); b – Ca-MMT; c – $[Ni(4\text{-}Etpy)_4(NCS)_2]$/Ca-MMT (**II**); d – Zr-PIL; e – $[Ni(4\text{-}Etpy)_4(NCS)_2]$/Zr-PIL (**IV**)

exhibit in this region a double peak at 2118 and 2075 cm^{-1}. Similar differences were observed for the non-clathrated and clathrated complex in Werner clathrates of the $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$ type and the authors explained it by the interaction of the host and guest molecules of the clathrate [10, 11]. Analogously, the above changes in IR spectra indicate the incorporation of Ni-c into the porous system of the host compounds and a changed arrangement of the NCS groups after their interactions with the host structure.

On the other hand, the complex in the intercalation products behaves as a monomeric Ni-c since two single bands (ν(Ni–NCS) and $\nu(Ni\text{–}N_{(4\text{–}Etpy)})$, respectively) are registered in the low frequency region (600–200 cm^{-1}) as predicted for monomeric $[NiL_4(NCS)_3]$ complexes (*L*=heterocyclic nitrogen ligand) [12]. The

Table 3 Some IR vibration frequencies of NCS and 4-ethylpyridine groups in the studied compounds

Compound	Vibration frequencies/cm^{-1}				
	ν(C–N)	ν(C–S)	γ(C–H)	ν(Ni–NCS)	ν(Ni–N(py))
Ni-c **(I)**	2075 (s)	804 (w)	790 (w)	285 (m)	237 (s)
Ni-c/Ca-MMt **(II)**	2076 (vs) 2118 (m)	804 (w)	791 (w)	285 (w)	237 (w)
Ni-c/Cr-PIL **(III)**	2083 (s) 2112 (s)	800 (w)	785 (w)	283 (m)	239 (m)
Ni-c/Zr-PIL **(IV)**	2076 (m) 2118 (s)	804 (w)	787 (w)	287 (m)	239 (m)
Ni-c/AL-PIL **(V)**	2074 () 2118 ()	804 (w)	791 (w)	285 (w)	237 (w)

vs – very strong; s – strong; m – medium; w – weak

values of vibration frequencies in Table 3 are in good agreement with this assumption.

Conclusions

The presented results revealed that mineral montmorillonite and its pillared analogues have provided suitable reaction media for the incorporation (in their porous structure) a neutral complex [Ni(Etpy)$_4$(NCS)$_2$] from its solution. A new type of intercalation samples containing two typical host components (Ni-c is frequently used for the preparation of Werner clathrates [5–7] have been studied.

It can be expected that these and similar intercalation compounds will exhibit specific properties from the point of view of adsorption and catalysis.

The thermal effects accompanying the escape of L (L=4-Etpy) from the pure Ni(**II**) complex and intercalation products indicate that the stoichiometry of thermal decomposition ($-2L$, $-L$, $-L$) is preserved for all studied compounds. The small differences in the enthalpy changes and ν(C–N) stretching vibrations are assumed to have their roots in different intermolecular guest-host interactions in the studied compounds.

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