

## INTERACTIONS OF DIFFERENT HETEROCYCLIC COMPOUNDS WITH MONOIONIC FORMS OF MONTMORILLONITE

### Thermal, IR-spectral and X-ray studies of Ni(II)-montmorillonite with 3-R- and 2-R pyridines ( $R=CH_3, Cl, NH_2$ )

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Interactions of 3-R- and 2-R pyridine ( $R=CH_3, Cl, NH_2$ ) with Ni(II)-exchanged montmorillonite have been studied. Thermal and X-ray analyses indicate that pyridine derivatives are intercalated into the interlayer spaces of montmorillonite. Infrared spectral data shown that the Lewis and/or Brønsted type of interactions of pyridine derivatives is connected with different steric and inductive effects of the substituents (R) on the pyridine ring. The alkylpyridines increase the electron density on the donor nitrogen atom and support the coordination to the central atom. The halogen substituents have a negative inductive effect (-I), so that those ligands show a lower basicity and weaker  $\sigma$ -bonding properties than pyridine and also the lower possibility of the coordination.

**Keywords:** analysis, infrared spectroscopy, Ni(II)-montmorillonite, R pyridine derivatives, thermal, X-ray

## Introduction

It is known [1] that the clay minerals act as efficient catalysts for a variety of organic reactions. It has been accepted that the Brønsted acidity which gives rise to the catalytic activity of clays is derived from the polarization of solvent water molecules by the small highly charged interlayer cations. Environmental chemistry is another region where clay minerals play an important role and information on the adsorption of hazardous organic pollutants is essential for forecasting the migration of these molecules through soils and sediments and in the running water [2, 3]. This information is also important for industrial problems since clay minerals are used as filters in some industrial processes.

Much interest was devoted to the interactions between clays and organic compounds with the purpose of determining the thermal stability and structure of the organo-clay complexes and the types of bonds between clay component and the adsorbed organic species [4, 5]. Since the clay surface and its interlayer space are populated by Brønsted and Lewis acidic and basic sites, the principal interactions between the clay and the adsorbed organic compounds are of the acid-base type [6]. Many authors investigated organometallic compounds due to their chemical, bio-

logical and environmental importance and examined their various properties [7–32]. In our previous papers, we described the thermo-analytical properties of various organometallic compounds [33–57]. In order to examine the type of acid sites in clays, spectral (IR spectra) and thermal (TG, DTG) analysis were applied for the study of desorption of bases, as demonstrated for *n*-butylamine, cyclohexylamine and pyridine [4]. The differences in desorption characteristics were attributed to different electronic properties ( $pK_b$  values) of desorbed bases.

In this paper thermal, spectral and diffraction analysis have been used to study the thermal behaviour and the type of interactions of the pyridine derivatives with Ni(II)-exchanged montmorillonite in order to evaluate the importance not only electronic but also steric properties of studied bases. In this connection we have focused our attention on 3-R- and 2-R pyridine derivatives ( $R=CH_3, Cl, NH_2$ ).

## Experimental

### Materials

Less than 2  $\mu$ m-fraction of Jelšovský potok bentonite was separated from a bulk sample and converted into

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the monoionic Ca-form using standard methods [58]. The structural formula as calculated from the chemical analysis of the fine fraction is as follows:



The Ni(II)-exchanged montmorillonite was prepared from the Ca-form (3 g) by addition of a NiCl<sub>2</sub> solution (450 cm<sup>-3</sup>, *c*=1 mol dm<sup>-3</sup>) and the mixture was stirred shortly and left to stand for 24 h. After decantation, NiCl<sub>2</sub> solution was added again to the solid phase, stirred and left to stand as previously. This procedure was repeated four times. The solid product was then washed by water in order to remove the Cl<sup>-</sup> ions and finally dried at 60°C.

A thin layer (~250 mg) of monoionic forms of Ni(II)-montmorillonite was exposed to 3- or 2-CH<sub>3</sub> pyridine (Mepy) vapours for 72 h at room temperature. When the pyridine derivatives were in the solid state, monoionic form of Ni(II)-exchanged montmorillonite was added to 5% solution of 3- or 2-Cl pyridine and 3- or 2-NH<sub>2</sub> pyridine. The mixture was stirred 1 h and left to stand for 3 h. This procedure was repeated three times. On the second day the solid intercalation products were washed with ethanol and dried at 60°C.

### Methods

The thermal properties were studied with a TA Instrument SDT 2960. The measurement were carried out in nitrogen using a platinum crucible. A sample mass of 20–25 mg and heating rate 10°C min<sup>-1</sup> were used.

The infrared absorption spectra were recorded with Nicolet Magna 750 Fourier Transform IR spectrometer in the range of 400–4000 cm<sup>-1</sup>. The analytical methods used have been described elsewhere [58].

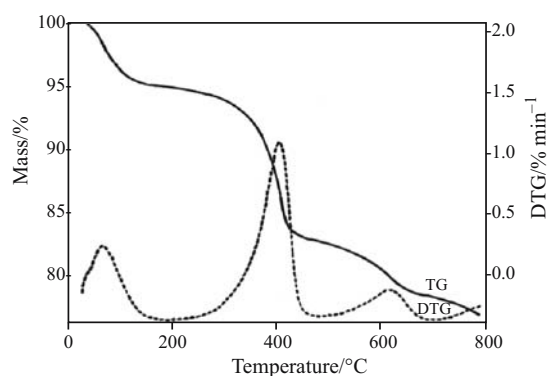
The X-ray diffraction profiles of pressed powder samples were recorded on a Philips PW 1050 diffractometer 2° (2θ) min<sup>-1</sup> using CuK<sub>α</sub> radiation.

## Results and discussion

As reported previously [4, 5] thermal analysis (TG and DTG) combined with measurement of IR spectra and diffraction properties can provide a precious information about the character of bonds between the adsorbed pyridine derivatives and monionic montmorillonite containing a transition metal ions in its inter-layer spaces.

### Thermal properties

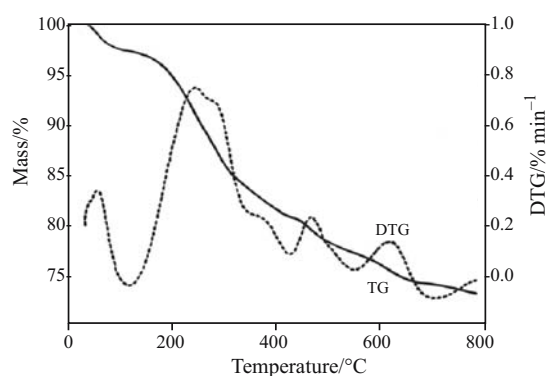
Thermal analysis results are summarized in Table 1 and the typical TG and DTG curves of 3-NH<sub>2</sub>/Ni–MMT and 2-NH<sub>2</sub>/Ni–MMT are shown in Ni–MMTs 1 and 2 as examples. The thermal decomposition of Ni-montmorillonite proceeds under dynamic conditions in the temperature interval 20–700°C in two distinct steps. The first step can be assigned to the release of adsorbed water molecules while the second one is connected with a release of water molecules from hydroxyl groups of Ni-montmorillonite. Three (3-R/Ni-montmorillonite) and/or four steps of decomposition of 2-R/Ni-montmorillonite (*R*=CH<sub>3</sub>, NH<sub>2</sub>) are observed in the temperature interval under study. The first step can be assigned to the physically adsorbed water molecules



**Fig. 1** TG and DTG curves of 3-NH<sub>2</sub>/Ni–MMT (MMT-montmorillonite)

**Table 1** Thermal decomposition data of studied samples

| Sample                      | TG: Δ <i>m</i> /% |           | DTG: <i>T<sub>p</sub></i> /°C |    |          |
|-----------------------------|-------------------|-----------|-------------------------------|----|----------|
| Ni–MMT                      | 16.6              |           | 5.3                           | 82 | 656      |
| 3-Mepy/Ni–MMT               | 16.3              | 5.8       | 3.9                           | 84 | 433      |
| 3-Clpy/Ni–MMT               | 9.8               | 9.6       | 4.2                           | 80 | 345      |
| 3-NH <sub>2</sub> py/Ni–MMT | 4.2               | 10.0      | 3.5                           | 65 | 415      |
| 2-Mepy/Ni–MMT               | 6.0               | 10.0; 6.1 | 3.3                           | 67 | 136; 442 |
| 2-Clpy/Ni–MMT               | 9.9               | 10.4      | 4.9                           | 76 | 298      |
| 2-NH <sub>2</sub> py/Ni–MMT | 2.4               | 14.1; 3.1 | 2.7                           | 69 | 219; 464 |



**Fig. 2** TG and DTG curves of 2-NH<sub>2</sub>/Ni-MMT (MMT-montmorillonite)

and R-py derivatives while the last one corresponds to the lattice dehydroxylation. The second and third ones can be assigned to release of chemically bonded pyridine derivatives, as reported by Breen [4, 5].

### IR results

The results of infrared spectroscopy are given in the Table 2. Several peaks can be observed in the studied region (400–4000 cm<sup>-1</sup>) that were attributed to the stretching vibrations of O–H groups (3622–3629 cm<sup>-1</sup>), water molecules (3446–3448 cm<sup>-1</sup>), Si–O groups (1024–1043 cm<sup>-1</sup>), deformation vibrations of O–H groups (850–950 cm<sup>-1</sup>); AlAlOH at 916–918 cm<sup>-1</sup>, AlMgOH at 839–845 cm<sup>-1</sup>, deformation vibrations of Al–O–Si groups at 523 cm<sup>-1</sup> and Si–O–Si at 467–469 cm<sup>-1</sup>.

The significant difference between Ni-montmorillonite and the intercalation products can be observed first of all in the region 1450–1750 cm<sup>-1</sup>. Whereas Ni-montmorillonite shows only one peak at ~1634 cm<sup>-1</sup> assigned to the deformation vibration of H–O–H groups, the intercalated species exhibit in this region several peaks at 1638–1669, 1601–1632, 1580, 1540–1550, 1477–1488, 1444–1450, and 1384–1416 cm<sup>-1</sup> (Table 2). It is known that the peaks of pure ligands at ~1570–1594 cm<sup>-1</sup> (3-Mepy: 1594 cm<sup>-1</sup>, 3-Clpy: 1573 cm<sup>-1</sup>, 2-Mepy: 1590 cm<sup>-1</sup>,

2-Clpy: 1577 cm<sup>-1</sup>) shift to the higher frequencies upon complex formation [59–61]. The shift of these peaks to ~1606–1632 cm<sup>-1</sup> supports the conclusion about the formation of the coordination bond between Ni<sup>2+</sup> ions and nitrogen atoms of heterocyclic rings. This assertion was also supported by the presence of the Lewis peak at ~1447–1450 cm<sup>-1</sup> in 3-R pyridine derivatives. However, in 2-R pyridine/Ni-MMT samples the diagnostic Brønsted peak at ~1541–1543 cm<sup>-1</sup> can be observed.

### Diffraction properties and colour of studied samples

The interlayer distances together with colour of studied samples are summarized in Table 3. After interactions with pyridine bases, the basal spacing in montmorillonites increased and are close for all studied products. We assume that: (a) the arrangement of pyridine ring of the pyridine derivatives is similar and perpendicular to the layers of montmorillonite; (b) the observed changes in the basal spacing may be connected with the intercalation of pyridine derivatives into the interlayer spaces of montmorillonite [62, 63].

The increase of basal spacing may be, however, partly due to hydration of montmorillonite. In order to exclude this possibility, the products were heated at 60°C. It was observed that basal spacing of all products did not change during the heat treatment. From these observation we concluded that the observed increase in the basal spacing was due to the intercalation of the pyridine derivatives into the interlayer spaces of montmorillonite [59]. The change in the colour of studied samples suggests the change in the coordination sphere of the interlayer Ni<sup>2+</sup> cations.

It could be concluded from the results that the presence of the substituents in the 2-position ( $\alpha$ -position) on the pyridine ring significantly influences the steric properties of ligands [64] and thereby also the complex formation in the silicate interlayers. When the position of the substituents are changed (from 3- to 2-position) the possibility of the coordination of the pyridine derivatives is decreased and formation of the Brønsted interactions is

**Table 2** Maxima of IR absorption bands in the region 1450–1750 cm<sup>-1</sup>

| Sample                    | Wavenumber/cm <sup>-1</sup> |      |      |      |      |
|---------------------------|-----------------------------|------|------|------|------|
| Ni-MMT                    | 1634                        | –    | –    | –    | –    |
| 3-Mepy/Ni-MMT             | 1645                        | 1609 | –    | 1488 | 1447 |
| 3-Clpy/Ni-MMT             | 1638                        | 1632 | 1540 | 1477 | 1448 |
| 3-NH <sub>2</sub> /Ni-MMT | 1634                        | –    | 1580 | 1498 | 1450 |
| 2-Mepy/Ni-MMT             | 1632                        | –    | 1543 | 1478 | 1384 |
| 2-Clpy/Ni-MMT             | 1629                        | –    | 1541 | 1491 | 1459 |
| 2-NH <sub>2</sub> Ni-MMT  | 1669                        | 1628 | 1542 | 1462 | 1416 |

**Table 3** Colour and representative diffraction data of Ni<sup>2+</sup>-montmorillonite and intercalation products

| Sample                    | Colour     | 2 $\theta$ /° | <i>d</i> <sub>001</sub> /nm |
|---------------------------|------------|---------------|-----------------------------|
| Ni-MMT                    | grey green | 6             | 1.47                        |
| 3-Mepy/Ni-MMT             | green      | 5.85          | 1.51                        |
| 3-Clpy/Ni-MMT             | green      | 5.89          | 1.5                         |
| 3-NH <sub>2</sub> /Ni-MMT | green      | 5.72          | 1.54                        |
| 2-Mepy/Ni-MMT             | green      | 5.88          | 1.5                         |
| 2-Clpy/Ni-MMT             | green      | 5.76          | 1.53                        |
| 2-NH <sub>2</sub> Ni-MMT  | green      | 5.88          | 1.5                         |

increased. However, the presence of the diagnostic Brønsted peak at  $\sim 1540\text{ cm}^{-1}$  in 3-Clpy/Ni–MMT show that the different inductive and mesomeric effects must be also consider. Alkylsubstituents have a positive inductive (+I) and a positive mesomeric (+M) effects, so that the basicity and  $\sigma$ -bonding ability of alkylpyridines should be greater and their  $\pi$ -acceptor capacity smaller than for pyridine itself [65]. Thus, the alkylpyridines increase the electron density on the donor nitrogen atom and support the coordination to the central atom. The halogen substituents have a negative inductive effect (-I), so that those ligands show a lower basicity and weaker  $\sigma$ -bonding properties than pyridine and also the lower possibility of the coordination. Therefore, alkyl-derivatives of pyridine give priority to Lewis bonding (first of all with substituents in 3-position), while the chloroderivatives show as well Brønsted interactions.

## Conclusions

Thermal and X-ray powder diffraction shown that 2-R- and 3-R pyridine derivatives were successfully intercalated into interlayer spaces of nickel(II)-montmorillonite. The formation of Lewis and/or Brønsted type of interaction of 2-R and 3-R pyridine ( $R=\text{CH}_3, \text{Cl}, \text{NH}_2$ ) to Ni(II) in the silicate interlayers is expressively influenced by the nature of the Ni–N bond which again is connected with the different steric and inductive effects of the substituents on the pyridine ring.

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