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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

INFRARED STUDY OF THE EFFECTS OF THERMAL TREATMENT ON MONTMORILLONITE-BENZIDINE COMPLEXES
IV. Mn-, Co-, Ni-, Zn-, Cd- and Hg-montmorillonite

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Abstract

Transition metal montmorillonites were saturated with benzidine (BEN) and heated gradually to 200°C, in a vacuum cell supported by KBr windows. IR spectra were recorded before and after the thermal treatment and at various temperatures during this treatment. X-ray diffractions were recorded before and after the thermal treatment. Hg clay shows properties similar to those of Mg and Ca clays. In the interlayer BEN is bound to Hg through a water molecule bridge, either by proton accepting (type *A*) or by proton donation (type *B*). Some BEN is also protonated (type *D*). Initially type *A* predominates, but after the thermal treatment, when the film is rehydrated, the amounts of types *B* and *D* increase. With Mn-, Co-, Ni-, Zn- and Cd-montmorillonite a direct coordination of the benzidine by the dehydrated metallic cation is obtained (type *C*), in addition to small amounts of types *A*, *B* and *D*. During the thermal treatment water is evolved and associations *A* and *B* are completely transformed to *C*. At elevated temperatures the following associations were identified in trace amounts, ammonium-amine, BEN bound to non-structured water, hydrophobic adsorbed BEN and BEN bound to the oxygen plane (types *E*, *F*, *H* and *J*, respectively). During the thermal treatment of Co and Cd clays some of the benzidine was oxidized, probably to semiquinone and quinoidal cation.

Keywords: montmorillonite-benzidine complexes, transition metal montmorillonites

Introduction

The surface acidity of clay minerals is a crucial problem, encountered in various areas where clays are to be found, such as agriculture, environment, different industrial technologies, water, beverages and oil clarification, organic geochemical diagenesis, etc. Surface acidity is responsible for many of the clay colloidal properties, i.e. its ability to be dispersed in various media or to adsorb

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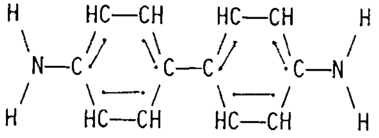
different molecules and ions. The catalytic activity of clay mineral, a very important property for many natural and industrial processes, is controlled by their surface acidity. Acidic and basic sites of different natures and with different strengths, appear simultaneously on the clay surface, and determine the bulk acidity of the mineral. In montmorillonite (MONT), where the interlayer space is the principal active site of the mineral, surface acidity is determined primarily by the exchangeable metallic cations and their hydration spheres [1–4]. The surface acidity of the oxygen plane of clay mineral and its contribution to the total surface acidity of montmorillonite was recently demonstrated [5].

In most studies on clay surface acidity, attention has been focused on the behaviour of major element exchangeable cations. In the interlayer space, these cations with their hydration spheres, are Bronsted acids. The adsorption of aniline and its derivatives ($ArNH_2$) was previously used for the study of surface acidity of montmorillonites saturated with several transition metal [6,7]. In addition to the association of anilines to water molecules of the hydration spheres of the exchangeable cations, anilines, although being weak bases, may be directly coordinated to the transition metal cations. In this type of association the NH_2- nitrogen donates its lone pair electrons to the cation, which serves as a Lewis acid. The extent to which anilines are directly coordinated to the cations or through water bridges, or are protonated, depends on one hand on the basic strength of the aniline and on the other, on the acidity of the transition cation. Other types of interaction in which anilines and transition metals can be involved are π interactions and polymerization. This has been observed with Fe(III)- and Cu(II)-$ArNH_2$ -MONT [8–10].

The purpose of the present investigation was to study the effects of temperature on surface acidity of montmorillonite and on the thermal acid base reactions taking place inside the interlayer space, applying IR thermo- spectrometry techniques. Benzidine (BEN, I) which is a derivative of aniline and is not evolved from the clay at 200°C, is suitable for this purpose. In part I of this study we described reactions occurring during the thermal treatment of montmorillonite saturated with benzidinium or benzidinium-benzidine (BENH-MONT or BEN·H·BEN-MONT, respectively) [11]. We followed after a proton transfer between the interlayer space and skeletal OH groups of alumino-silicate layers. In parts II and III of this study we described acid-base reactions occurring during the thermal treatment of montmorillonite saturated with major elements and benzidine [12, 13]. We showed that BEN initially associated with water molecules of the hydration spheres of the exchangeable cations with NH_2 group reacting as a proton acceptor (type *A*). To some extent the NH_2 group also reacted as a proton donor (type *B*) or was protonated (type *D*). During the thermal treatment the metallic cation was dehydrated and a direct coordination of the cation by BEN was obtained (type *C*). As well, the amount of $BENH^+$ increased. At the same time the thermal treatment gave rise to the development of BEN·H·BEN$^+$ (type *E*). In the case of Al-MONT, the principal species obtained in the interlayer space before any thermal treatment are BENH$^+$ and BEN·H·BEN$^+$.

When BEN is adsorbed by montmorillonite, a blue coloration is developed due to the oxidation of this molecule to the semiquinone cation [14-16]. In our previous studies we showed that in spite of the coloration of the clay, the spectrum was that of BEN and we concluded that only a small fraction of BEN was oxidized, and was not observed in the IR spectra.Only in the case of Cs-MONT and to a very small extent also in the case of Al-MONT, there were spectroscopic indications that the thermal treatment resulted in the oxidation of BEN to a semiquinone and a quinoidal cation (association type *Q*).

The direct coordination of major element cations by BEN gives a weak bonding. On the other hand, the direct coordination of transition element cations by BEN should give strong bondings. In the present paper we describe how this strong coordination affects the reactions which occur during the thermal treatment of BEN adsorbed by Mn-, Co-, Ni-, Zn- and Cd-MONT. Hg, although a transition element, does not form a stable coordination association with BEN. For comparison, the thermal reactions of BEN adsorbed by Hg-MONT are also described. The thermal reactions of BEN adsorbed by Cu- or Fe-MONT are more complicated and will be described at a later stage.



I, BEN

Experimental

The montmorillonite, the experimental procedures the thermal treatments and the instruments were previously described [12, 13].

Results and discussion

Adsorption of BEN by Mn-, Co-, Ni-, Zn-, and Cd-MONT

The IR spectra of these montmorillonites immersed in BEN solution, recorded before any thermal treatment, resemble one another, but differ from the appropriate spectra of montmorillonites saturated with the major elements by having additional absorption bands. Maxima of principal absorption bands are

Table 1 Frequencies of NH_2 stretching, NH···O combination and C–N stretching bands (cm^{-1}) and intensity ratios of bands I to II (R_1) bands III to II (R_2) and bands IV to II (R_3) of IR spectra of Na-, Ca-, Mn-, Co-, Ni-, Zn-, Cd- and Hg-MONT saturated with BEN, recorded at room temperature

	Benzidine				Assignments					Intensity ratios		
Cation	NH_2 stretching			N–H···O	NH_2 bend.		C–N stretching			R1	R_2	R_3
	I	II	III	IV	V	VI	VII	VIII	IX			
Na	3390m	3325	–	–	1613	–	–	1254	–	0.58	–	–
Ca	3390sh	3330	–	3200sh	1613	–	1328vw	1250	–	0.51	–	0.78
Mn	3390sh	3330	3270vw	3200sh	1613	1577	1312vw	1247	1235sh	0.39	0.67	0.67
Co	3400w	3335	3280	3200sh	1612	1576	1314w	1250	1228	0.58	1.20	1.05
Ni	3395sh	3335	3275	3200vwsh	1613	1580	1335vwsh	1250	1230	0.34	1.09	0.84
Zn	3390w	3310w	3235m		1610	1578	1328	1250	1215sh	0.53	1.84	–
Cd	3400sh	3335	3275	3200	1613	1575	1336sh	1254sh	1226	0.33	1.33	1.00
Hg	3395	3330m	–	3200	1615	–	–	1252	–	0.50	–	0.75

v – very, w – weak band, m – medium band, sh – shoulder, br – broad

given in Table 1. These spectra show three NH_2 stretching bands, one –NH···O combination band, two NH_2 deformation bands and three C–N stretching bands (bands I–IX in Table 1). For comparison, the frequencies of these absorptions in the spectra of Na- and Ca-BEN-MONT are also given in the table. The Na clay gives only one association with BEN, that is type *A* [12]. In the spectrum of Na-BEN-MONT there are only two NH_2 stretching bands, one NH_2 deformation band and one C–N stretching (bands I, II, V and VIII). The Ca clay gives two associations with BEN, type *A* and, to a small extent, also type *B* [13]. In the spectrum of Ca-BEN-MONT, in addition to the two NH_2 stretching bands and the single NH_2 deformation band, a combination band, attributed to –NH···O is also detected (band IV). As well, two C–N stretching bands are detected (bands VII and VIII). The C–N bond in type *B* has much more double bond character than that in type *A*. Consequently, the location of the C–N stretching of the latter is at a lower wavenumber than that of pure benzidine in a dilute CCl_4 solution (1280 cm^{-1}), whereas that of type *B* is similar or at a higher wavenumber. A band at 1250 or 1254 cm^{-1} in the spectra of Ca and Na clay, respectively, is attributable to association A and a band at 1320 cm^{-1}, not detected in the spectrum of the Na clay, is attributable to association *B*.

It has previously been shown [6,7] that a complex formation of anilines with transition metals displaces the NH_2 stretching and bending and C–N stretching vibrations to lower frequencies. It therefore seems probable that the additional bands observed in these spectra are due to complex formation in which the metallic cation is directly coordinated by BEN. Three types of associations are thus formed between BEN and interlayer transition metal cations: (i and ii) the NH_2 group of BEN is either bonded to the cations through water molecules, by H_2O proton donation to N or by NH_2 proton donation to water-O atom (association types *A* and *B*, respectively); (iii) the N atom is directly coordinated to the cation (type *C*). Bands I, II, V and VIII characterize association *A*, bands I, IV and VII characterize association *B* and bands II, III, VI and IX characterize association *C*.

The shift of the NH_2 stretching bands is related to the stability of the coordination bonds which are formed between the metallic cations and BEN. Table 1 shows that the stability of these associations increases in the order Co < Ni < Cd < Mn < Zn.

Ratios R_1, R_2 and R_3, between intensities of bands I, IIIand IV, respectively, and that of band II, were calculated from absorbance values measured from an extrapolated base-line in the range 3450–2620 cm^{-1} (Table 1). Comparison between these ratios may give information on the relative amounts of these three associations. Only general trends are significant because extinction coefficients are not known. The ratio R_2/R_1 and the tendency to form association *C* relative to *A* increases in the order Mn < Co < Ni < Zn < Cd. The ratio R_3/R_1 and the tendency to form association *B* relative to *A* increases in the order Ca < Mn < Co < Ni < Cd. This ratio could not be determined for Zn-MONT due to overlap of band III with band IV. The ratio R_2/R_3 and that between associations *C* and *B* increases in the order Mn < Co < Ni < Cd.

An additional adsorption is detected as a broad shoulder at 3130–3150 cm^{-1}. The assignment of this band is uncertain and it may be a combination band of NH_2 deformation vibrations. The intensity of this band is always related to the intensities of the bands which characterize association *C* and it may serve as a diagnostic band to identify this assemblage.

When the films are immersed in water for a few minutes, they adsorb additional amounts of water and association *C* disappears.

Thermal treatment of Mn- and Zn-BEN-MONT

Figure 1 shows IR spectra of Mn- and Zn-BEN-MONT, recorded before and after heating the films at different temperatures in a vacuum cell. When the films are heated, water is lost, association *A* and *B* gradually disappear and at 50–100°C association *C* becomes dominant. This is shown by the gradual disappearance of the characteristic absorption bands I and VIII for type *A* and bands IV and VII for type *B* (Table 2). It should be noted that when small amounts of association *A* are still present, band I is not observed and only band VIII is detected.

Above 100°C the bands which characterize association *C* (III, VI and IX) decrease. Very weak adsorptions appear at 3500–3430 and 1280 cm^{-1}. The location of these bands is similar to bands found in a CCl_4 solution of BEN representing NH_2 and CN stretching vibrations of free BEN molecules (type *H*) which are not hydrogen bonded to water molecules nor coordinated to the metallic cations. Very weak absorptions appear at 3375, 2580–2500 and 1250 cm^{-1} which characterise ammonium-amine (type *E*). Absorptions at 3375 and 1260 cm^{-1} are characteristic for BEN held in the interlayer by weak hydrogen bonds, probably to hydrophobic water molecules (type *F*), similar to the principal association found in Cs-BEN-MONT [12]. Thus, the reappearance of band I at temperatures above 100°C is significant for the formation of associations *E* and *F*.

The weak absorption at 1310–1330 cm^{-1} in the spectrum of Mn-BEN-MONT is remarkable. Band VII which is attributed to association *B*, and which appears before the thermal treatment, gradually disappears during the thermal treatment. However, above 150°C a new broad absorption appears at the same location and becomes stronger with the rise in temperature. Together with this band a very weak and broad absorption is developed at 3250–3180 cm^{-1}. These bands can be attributed to $NH\cdots O$ combination band and C–N stretching vibration of BEN molecules hydrogen bonded to the oxygen plane of the alumino-

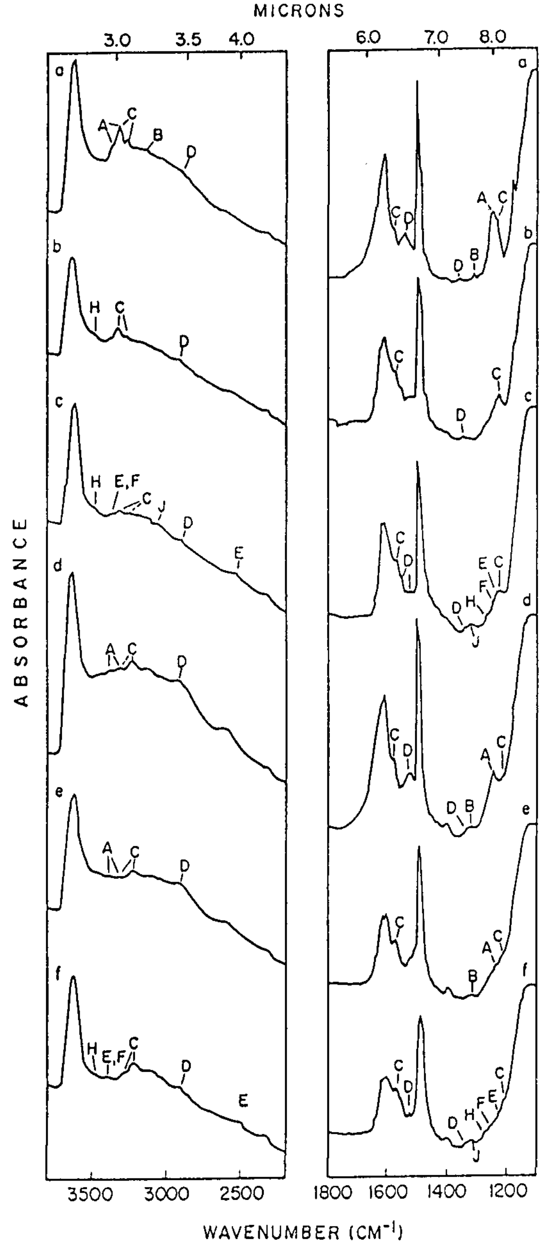


Fig. 1 IR spectra of (a) an air-dried film of Mn-MONT saturated with BEN; (b) sample a heated at 100°C under vacuum; (c) sample a heated at 220°C under vacuum IR spectra of (d) an air-dried film of Zn-MONT saturated with BEN: (e) sample d heated at 50°C under vacuum; (f) sample d heated at 200°C under vacuum. When spectra b, c, e and f were recorded, samples were kept in the vacuum cell

Table 2 Assignments and wavenumbers (cm^{-1}) of principal absorption bands in the spectra of Mn-, Zn- and Ni-MONT saturated with benzidine, recorded at room temperature, after thermal treatments under vacuum and after rehydration

	T /	Benzidine							Assignments				Associations
Cation	°C	NH$_2$ stretching				H$_2$O, NH$_2$ def.			Ring	CN stretching			Relative amounts expressed
			I	II	III		V	VI		VII	VIII	IX	by +; ( ) small amounts
Mn	r.t.	–	3390w	3330m	3270w	–	1613	1577	1503	1312vw	1247	1235sh	A+++,B+,C+++,D++
	50	>3440wbr	–	3330	3270	–	1612	1575	1500	1325vw	1247w	1235	A+,B+,C+++++,D++
	100	>3440wbr	3385, 3355, 3330		3270	1625sh	1613	1573	1500	–	–	1234	C+++++,D++,(E,F,H)
	150	>3440wbr	3380–3320		3270	1622	1612	1576	1497	–	1265sh	1233	C++++,D++,(E,F,H)
	200	>3440wbr	3380	3320	3270	1618	1608	1576	1495	1320w	1280sh	1235sh	C+++,D++,(E,F,H,J)
	rehy	–	3390w	3330m	3270w	–	1613	–	1503	1350sh	1248	1235sh	A++,B++,C+++,D++
Zn	r.t.	–	3390w	3310w	3235m	–	1610	1577	1500	1328w	1250	1220sh	A++,B+(?)C++++,D++
	50	–	3390w	3310vw	3235m	1617sh	1610	1577	1500	1328w	1248	1220sh	A+,B+(?)C+++++,D++
	75	–	–	3310vw	3235m	1617sh	1610	1577	1500	–	1248sh	1220sh	C++++++,D++
	100	3480wbr	3380vw	3305sh	3237	1620	1612	1575	1500	1325w	1245sh	1217sh	C+++,D++,(E,F,H,J)
	150	3450wbr	3390vw	3305sh	3245	1620–1608		1578	1497	1333w	1278sh	1217sh	C+++,D++,(E,F,H,J)
	200	3450wbr	3380vw	3305sh	3240	1620sh	1610	1576	1495	1333w	1278sh	1217sh	C+++,D++,(E,F,H,J)
	rehy	–	3390vw	3315vw	3235m	–	1612	1575	1503	1333br	1253	1223sh	A+,B+(?)C++++,D++

Table 2 Continued

	T/	Benzidine Assignments											Associations
Cation	°C	NH_2 stretching				H_2O, NH_2 def.			Ring	CN stretching			Relative amounts expressed
			I	II	III		V	VI		VII	VIII	IX	by +; ( ) small amounts
Ni	r.t.	3480vw	3395vw	3335	3275	–	1613	1580	1503	1335vwsh	1250	1230	A+,B+,C+++++,D+(H)
	50	–	–	3325	3270	–	1610	1580	1498	–	1250	1230	(A),C+++++,D+
	100	>3440wbr	–	3320	3270	1622sh	1610	1576	1495	1320vwsh	1280sh	1225sh	C+++++,D+,(H,J)
	150	>3440wbr	3375vw	3325vw	3265m	1618–1605		1576	1493	1320wsh	1280sh	1250sh	C+++,D++,(E,F,H,J)
	200	>3440wbr	3375wbr	3320wbr	3260vbr	1622	1606	1576	1496	1320w	1275vwsh	–	C++,D+++,(E,F,H,J)
	rehy	–	3390sh	3340	3280	1622	1613	–	1500	1320vbr	1260–1230		A+,B+,C+,D++++

r.t. – room temperature; rehy – rehydrated 72 h in ambient atmosphere;
v – very, w – weak band, m – medium band, sh – shoulder, br – broad

silicate layer (association *J*). A similar association was formed in Cs-BEN-MONT during the thermal treatment [12]. Associations *E*, *F*, *H* and *J* are obtained by the thermal dissociation of association *C*. It should be noted that they are present only in trace amounts, in Zn less than in Mn, because type *C* of the former is more stable than that of the latter and does not dissociate.

With the rise in temperature and the dehydration of the interlayer space, π interactions between the aromatic ring and the oxygen plane are developed and the C–C stretching vibration is shifted from 1503 to 1495 cm^{-1}. As well, band V, which has a contribution of the ring vibration, and which is initially located at 1613–1610 cm^{-1}, becomes broad and splits to several maxima and shoulders. At high temperatures some of the exchangeable cations may penetrate into the alumino-silicate layers through the di-trigonal holes of the oxygen plane. Consequently, all the bands which belong to the BEN molecules are broad.

When the thermally treated films are rehydrated for 24 h at ambient atmosphere the IR spectra become very similar to the original spectra, recorded before the thermal treatment. It shows that the dehydration process is reversible and the films contain associations *A*, *B* and *C*. However, if they are immersed in water for short periods, association *C* disappears being converted to associations *A* and *B*.

Protonation of BEN in transition metal montmorillonites

In addition to molecular amine, films of Mn-, Co-, Ni-, Zn-, Cd- and Hg-BEN-MONT contain protonated BEN (benzidinium ion, $BENH^+$, association *D*), identified from NH_3^+ stretching and deformation absorptions at 2920 and 1520–1575 cm^{-1} and the combination band at ≈2600 cm^{-1}. Water molecules coordinated to metallic cations dissociate under the polarizing effect of the cation. The cationic species $BENH^+$ is obtained from BEN by accepting protons from hydrated cations as follows:

$$\{[Me(HOH)_m]^{2+} + BEN\}\text{-MONT} \rightarrow \{[Me(HOH)_{m-1}(OH)]^{+} + BENH^{+}\}\text{-MONT}$$

Accurate amounts of the ionic species cannot be determined but significant information on the effect of temperature on relative amounts can be obtained from absorbance ratios of NH_3^+ absorptions in the range ≈1530–1550 cm^{-1} to a C–C band at ≈1500 cm^{-1}, the latter representing total BEN in the clay [13]. They were calculated from absorbance values, measured from and extrapolated base-line in the range 1760–1380 cm^{-1} and are given in Table 3. Comparison between these ratios may give information on the relative polarizing effect of the cations and on the effect of thermal treatment on the protonation of BEN.

With transition metal montmorillonites, protonated BEN is found in considerable amounts, less than has been found previously in Al-BEN-MONT, but

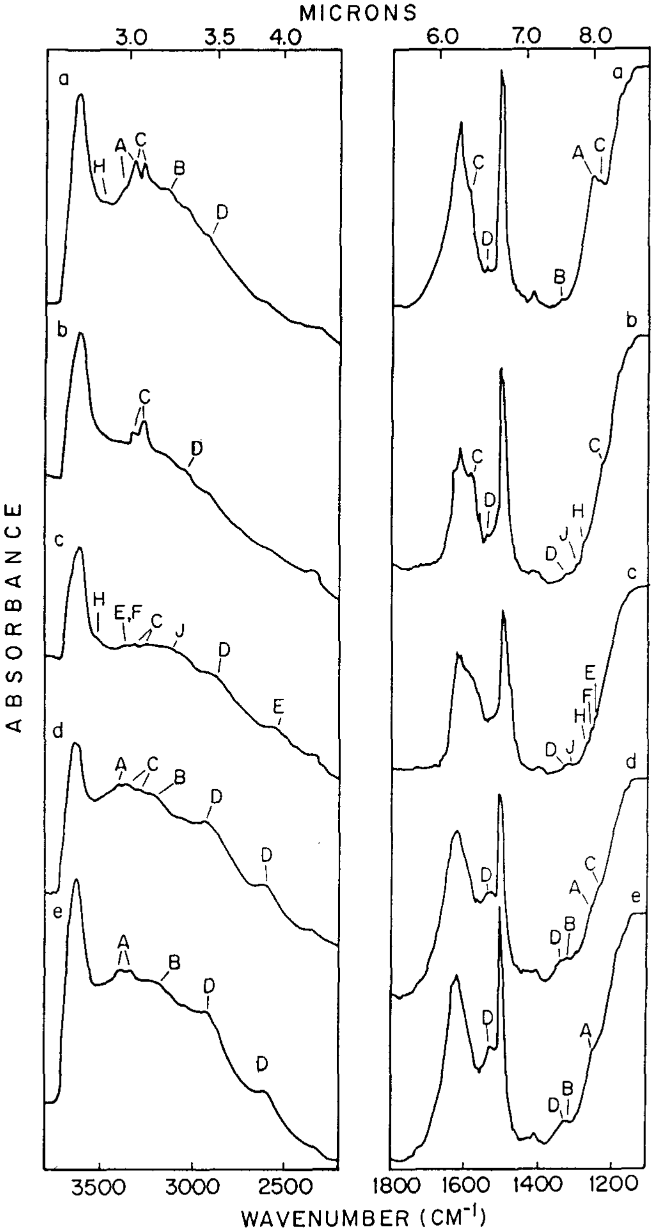


Fig. 2 IR spectra of a film of Ni-MONT saturated with BEN (a) air dried; (b) heated at 100°C under vacuum; (c) heated at 200°C under vacuum; (d) rehydrated (72 h – ambient conditions); (e) sample d immersed in water for a few minutes. When spectra b and c were recorded, the sample was kept in the vacuum cell

Table 3 Intensity ratio of NH_3^+ absorbance at 1530-1540 cm^{-1} to C-C absorbance at ≈1500 cm^{-1} of IR spectra of Li-, Ca-, Mn-, Co-, Ni-, Zn-, and Cd-MONT saturated with BEN, recorded at room temperature and after thermal treatment

Cation	r.t.	50°C	100°C	150°C	200°C	Cooled u.v.	Rehydrated a.a.
BENH*	0.41	0.28	0.26	0.20	0.17	0.20	0.41
Na	0.10	1.11	0.14	0.05	0.06	0.05	0.12
Ca	0.19	0.17	0.22	0.26	0.24	0.25	0.39
Mn	0.24	0.24	0.22	0.23	0.18	0.17	0.22
Co	0.29	0.28	0.28	0.30	0.27	0.29	0.53
Ni	0.17	0.14	0.19	0.24	0.33	0.33	0.60
Cu	0.72	0.45	0.50	0.56	0.60	0.59	0.70
Zn	0.27	0.24	0.17	0.22	0.18	0.21	0.31
Cd	0.29	0.23	0.45	0.51	0.57	0.55	0.64
Hg	0.28	0.28	0.28	0.29	0.28	0.30	0.37

u.v. - under vacuum; a.a. - ambient atmosphere.

* - contains trace amounts of ammonium-amine.

much more than in Na-BEN-MONT and similar to those found in Li-, Mg- or Ca-BEN-MONT, because these cations are stronger acids compared with Na^+ but weaker than Al^{3+}. According to this table the acid strength at room temperature increases in the order Ni < Mn < Zn < Hg < Cd < Co. As a result of the thermal treatment this order changes slightly and the acid strength increases in the following order Mn < Zn < Hg < Co < Ni < Cd.

The effect of temperature on the degree of protonation of BEN was discussed in part III of this series [13]. Except for Mn- and Zn-BEN-MONT, the amount of $BENH^+$ increases during the thermal treatment, shown by the increase of the absorbance ratio of rehydrated samples. It is not clear from the spectrum whether one or two NH_2 groups of a BEN molecule are simultaneously protonated.

Figure 2 brings IR spectra of Ni-BEN-MONT, recorded before and after heating the film at different temperatures in the vacuum cell. The first stages are similar to those occurring with Mn- or Zn-BEN-MONT, water is evolved and associations *A* and *B* are gradually converted into association *C*. At 100°C the bands which characterize $BENH^+$ (association *D*) are very weak but at higher temperatures these bands become strong and the bands which characterize association *C* become weak. At 200°C the spectrum shows a very broad absorption at 3150 cm^{-1}, attributed to non hydrogen bonded $BENH^+$. In spite of the thermal dehydration of the film, the spectrum shows a weak band at 2925 cm^{-1}, which represents hydrated $BENH^+$. When the sample is rehydrated at ambient

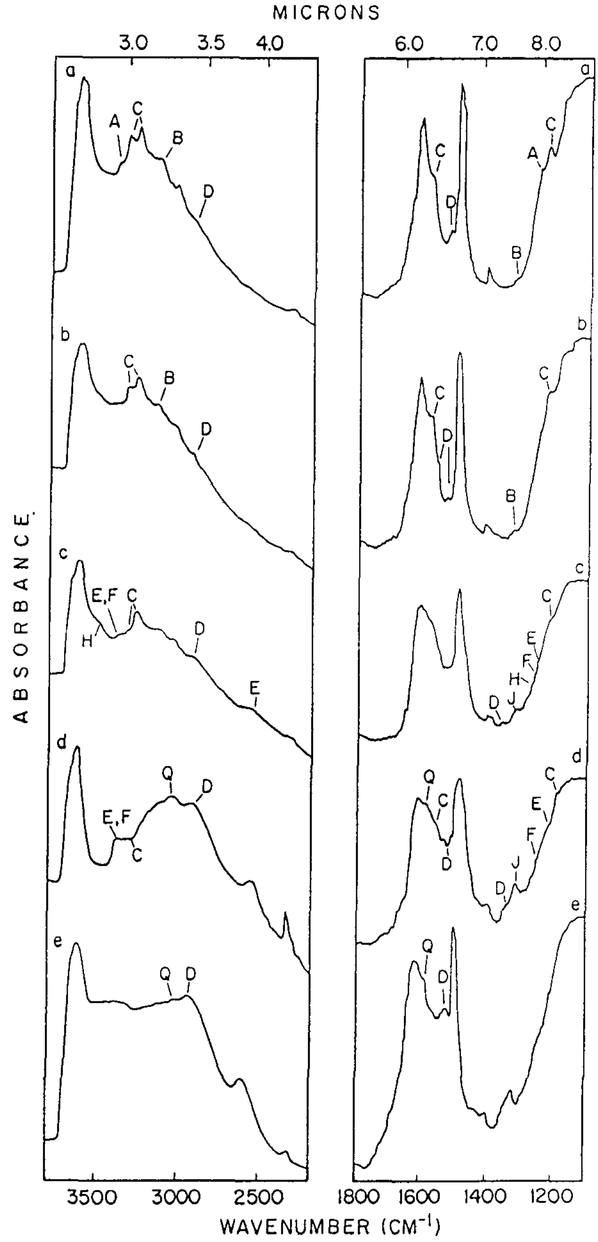


Fig. 3 IR spectra of a film of Cd-MONT saturated with BEN (a) air dried; (b) heated at 50°C under vacuum; (c) heated at 100°C under vacuum; (d) heated at 200°C under vacuum; (e) rehydrated (72 h – ambient conditions). When spectra b, c and d were recorded, the sample was kept in the vacuum cell

Table 4 Assignments and wavenumbers (cm^{-1}) of principal absorption bands in the spectra of Co-, Ni-, and Cd-MONT saturated with benzidine, recorded at room temperature, after thermal treatments under vacuum and after rehydration

Cation	T/ °C	Benzidine Assignments											Associations
		NH_2 stretching			NH_2^+	NH_2	C=N	NH_2	Ring	CN stretching			Relative amounts
					stret.	def.	stret.	def.	vib.				expressed by +
		I	II	III		V		VI		VII	VIII	IX	( ) small amounts
Co	r.t.	–3400br	3335	3280	–	1612	–	1576	1503	1314w	1250sh	1228	A++, B++, C++++, D++
	50	3470sh	3330vbr	3270		1622–1612		1576	1495	1320vw	–	1223	C+++++, D++, (H,J)
	100	3460sh	3370br	–	–	1622	1595	1576	1495	1320vw	–	1223sh	C+++++, D++, (H,J)
	150	–	3375br	3220–3050br		1620	1595	1580	1492	1330w	1250–1225vw		D+++, Q++ (E,F,J)
	200	3375–3335		3200sh	3050	1620	1595	–	1492	1325	1275–1210sh		D+++, Q+++ (E,F,J)
	rehy	3420br (HOH)		3200vbr	3050(Q)	1623	1595	–	1500	1320br	1245–1210sh		B++, D++++, Q+++
Cd	r.t.	3400sh	3335	3275		1614	–	1575	1503	1336sh	1254sh	1226	A+, B+, C+++++, D++
	50	–	3330	3270		1610	–	1575	1500	1320vw	–	1220	B+, C++++++, D++
	100	3380sh	3335	3270		1610	–	1575	1494	1325w	1280sh 1250sh	1226sh	C+++++, D+++ (E,H,J)
	150	3380–3325		3275–3040		1613	1590	1575	1494	1322	1270–1250sh	1226sh	C++, D+++, Q+ (E,F,J)
	200	3370		3250–3150, 3040		1620br	1590	–	1490	1320	1275sh	1220sh	C+, D+++, Q++ (E,F,J)
	rehy	3470–3350 (HOH)		3200–3050vbr		1620br	1595sh	–	1500	1320			B++, D+++++, Q++

r.t. – room temperature; rehy – *rehydrated* 72 h in ambient atmosphere
v – very, w – weak band, m – medium band, sh – shoulder, br – broad

atmosphere, the absorption at 3150 cm^{-1} disappears and the intensity of the band at 2925 cm^{-1} increases relative to that recorded before the thermal treatment. Associations *A*, *B* and *C* are present but only in small amounts.

Above 100°C, in addition to the protonation of BEN, thermal reactions similar to those occurring with Mn- or Zn-BEN-MONT also occur (Table 2). This includes π interactions between the aromatic ring and the oxygen plane and the formation of associations *E*, *H* and *J*. These associations are obtained by the partial decomposition of association *C*. It should be noted that associations *E*, *H* and *J* are present only in trace amounts and most of BEN which is released from association *C*, appears as BENH$^+$.

Thermal treatment of Co- and Cd-BEN-MONT

Figure 3 brings IR spectra of Cd-BEN-MONT before and after heating the film to different temperatures. In general, the films of Co- and Cd-BEN-MONT show a similar thermal behaviour (Table 4). In the first stage of the treatment the thermal behaviour is similar to that of Mn and Zn clays, and associations *A* and *B* are dehydrated being transformed into association *C*. Above 100°C the thermal behaviour becomes similar to that of Ni-MONT and a great fraction of association C is converted to association *D*, in part, directly and in part through associations *E*, *F*, *H* or *J*. In addition to the protonation of BEN, new bands are gradually developed in the spectra of Co- and Cd-MONT, at 1595 and 3040 cm^{-1}. These bands persist after rehydration of the clay which is carried out at ambient conditions after the thermal treatment. A similar phenomenon was observed previously with BEN adsorbed by Cs- or Al-MONT and it was concluded that BEN was oxidized to a semiquinone and a quinoidal cation type *Q)*. The new bands were attributed to C=N (with a double bond) and hydrogen bonded NH_2^+ . However, with Cs and Al the NH_2^+ absorption was located at about 2850 cm^{-1}. It is possible that different oxidation products are obtained. It is also possible that the oxidation is accompanied by polymerization and that different polymerization products are obtained which determine the location of the NH_2^+ absorption. It should be noted, however, that in these samples the oxidation products appear in addition to association *D* which is present in great amounts.

Thermal treatment of Hg-BEN-MONT

The spectrum of a film of Hg-MONT saturated with BEN, shows the presence of association *A*, and to a very small extent also *B* and *D* (Tables 1 and 3). After the thermal treatment, when the film is rehydrated the amount of these two associations highly increases. At room temperature association *C* is not formed. At 100°C a weak absorption at 3300 cm^{-1} accompanied by a shoulder

Table 5 Basal spacings of BEN treated monoionic montmorillonites (pm) air-dried and rehydrated after heating at 200°C

Interlayer cation	Untreated MONT			BEN saturated MONT	
	Air dried	Hydrated at 40% relative humidity	After heating at 200°C under vacuum	Air dried	Rehydration after heating at 200°C under vacuum
BENH	1308	1320	1244–1280	–	–
BEN·H·BEN	1448*; 1591**	–	1 497–1577	–	–
Mn	1448	1440	900	1484	1497
Co	1590	1470	1000	1577	1448
Ni	1424	1470	1020	1666	1510
Zn	1424	1370	1020	1424	1510
Cd	1522	1480	990	1698	1502
Hg	1271	1320	960	1253	1460

* sample obtained by the immersion of BENH-MONT for 1 day in BEN solution

** sample obtained by the immersion of BENH-MONT for 14 days in BEN solution at 3130 cm^{-1} and a very weak shoulder at 1245 cm^{-1} indicates that small amounts of association C are formed. As well, weak shoulders at 3480 and 1280 cm^{-1}, first appearing at this temperature, indicate the presence of type *H*. At higher temperatures a very weak shoulder is developed at 1320 cm^{-1} which may be attributed to BEN hydrogen bonded to the oxygen plane or to HgO (types *H* and *J*, respectively). At 150°C very weak absorptions at 2850 and 2600–2500 and a shoulder at 1265 cm^{-1} indicate the formation of very small amounts of associations *E* and *F*. These associations are not observed after the rehydration of the film.

X-ray diffraction

The basal spacings of Mn-, Co-, Ni-, Zn-, Cd- and Hg-MONT, air-dried and after a thermal treatment and of the same clays saturated with BEN, are given in Table 5. Non-integral series of diffraction are obtained and the peaks of the BEN-clay complexes are broad. Spacings obtained after heating the films of BEN saturated clays at 200°C are always higher than those of the thermally treated non-saturated montmorillonites, proving that the adsorbed organic molecules are located in the interlayer space. For comparison the basal spacings of BENH- and BEN·H·BEN-MONT are also given in the Table.

The spacings of air-dried BEN saturated samples are similar to those of air-dried non-saturated montmorillonites, indicating that in these clays the spacing is determined by their initial hydration state. Only in the case of Ni- and Cd-MONT, where great amounts of BEN are adsorbed by the clay, the spacings are higher than those of air-dried non-saturated clays.

In part II of this series [12] we showed that after thermal treatment the spacing is determined by the type of association which is obtained in the interlayer space. For association *A* a spacing of ≈1,300 pm is required whereas for association *B* a spacing of ≈1,500 pm is required. The IR thermospectrometry study shows that during the rehydration of the thermally treated samples considerable amounts of association *B* are obtained from association *A* and consequently the resulting basal spacing should become ≈1,500 pm. Attention should be paid to the spacing of Hg-MONT which increases due to the transformation of association A to B during the rehydration of the thermally treated sample.

* * *

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Zusammenfassung — Übergangsmetall-Montmorillonite wurden mit Benzidin (BEN) gesättigt und in einer Vakuumzelle mit KBr-Fenstern nach und nach bis 200°C erhitzt. Vor, während und nach der thermischen Behandlung wurden bei verschiedenen Temperaturen IR-Spektren aufgezeichnet. Vor und nach der Wärmebehandlung wurden auch Röntgendiffraktionsaufnahmen angefertigt. Hg-Tonerde zeigt ähnliche Eigenschaften wie Mg- und Ca-Tonerde. In der Grenzschicht wird BEN an Hg über eine Wassermolekülbrücke gebunden, entweder durch Protonenaufnahme (Typ *A*) oder Protonenabgabe (Typ *B*). Einige BEN-Moleküle werden ebenfalls protoniert (Typ *D*).

Zuerst überwiegt Typ A, jedoch nimmt nach der thermischen Behandlung, wenn der Film rehydratiert ist, der Anteil der Typen *B* und *D* zu. Mit Mn-, Co-, Zn- und Cd-Montmorillonit wird neben geringen Anteilen von Typ *A*, *B* und *D* eine direkte Koordinierung von Benzidin durch dehydratierte Metallkationen beobachtet (Type *C*). Während der thermischen Behandlung wird Wasser freigesetzt und die Assoziate *A* und *B* werden vollständig in *C* umgewandelt. Bei höheren Temperaturen wurden Spuren folgender Assoziate identifiziert: Ammonium-Amin, an nicht strukturiertes Wasser gebundenes BEN, hydrophob absorbiertes BEN und an Sauerstoffebenen gebundenes BEN (Typ *E*, *F*, *H* und *J*). Bei der thermischen Behandlung von Co- und Cd-Tonerde wird ein Teil des Benzidins oxidiert, wahrscheinlich zu Semiquinon und quinoidalen Kationen.