

ADSORPTION OF PYRIDINE *N*-OXIDE ONTO MONTMORILLONITE

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Abstract—Pyridine *N*-oxide and montmorillonite form interlamellar complexes with basal spacings of 14.7 and 21 Å. The former corresponds to a monolayer with a tilted orientation of the pyridine ring; the latter comprises a double layer of molecules between the clay sheets. Infrared spectra show that pyridine *N*-oxide bonds through the NO group; in the 21 Å complexes it is coordinated to the exchangeable cations through water molecules acting as bridges which themselves are directly coordinated to the cations. In the 14.7 Å complexes a splitting of the $\nu(\text{NO})$ band occurs with the more polarizing cations Mg and Ca; the two bands correspond to pyridine *N*-oxide molecules directly coordinated to the cation and to other molecules coordinated through bridging by water molecules. Cs montmorillonite forms complexes with a basal spacing of approximately 14.7 Å which also shows a splitting of the $\nu(\text{NO})$ band.

INTRODUCTION

A BETTER understanding of the interactions of organic materials with soil clays may be gained through a study of the adsorption of simple organic compounds. During an investigation of the interaction between montmorillonite and highly polar organic compounds the montmorillonite-pyridine *N*-oxide system was examined. Pyridine-*N*-oxide (PNO) is a polar compound with a large dipole moment (4.24 D) which originates in part from resonance of the NO group with the pyridine ring (Linton, 1940; Kida, Quagliano, Walmsley and Tyree, 1963). It is a strong ligand, forming coordination complexes with numerous metal ions (Kida *et al.*, 1963; Kakiuti, Kida and Quagliano, 1963) and a good electron donor readily forming strong hydrogen-bonds (Hadzi, 1965; Hadzi and Kobilarov, 1966). It also participates in dipole-dipole interactions and other association reactions, in which the oxygen of the NO group is the donor species. Montmorillonite has a high cation exchange capacity and usually contains some cation hydration water; the ion-dipole and other interactions of this system with PNO were thus examined, particularly with regard to the nature of the exchangeable cation on the clay.

EXPERIMENTAL

The Na⁺ saturated form of the < 2 μm e.s.d.

fraction of a montmorillonite was prepared following the method Posner and Quirk (1964). The montmorillonite originated from the John C. Lane tract, Upton, Wyoming (Ref. No. 25b of the American Petroleum Institute project No. 49). Other homo-ionic forms were prepared by washing the Na⁺ form several times with molar solutions of the appropriate chloride salt; excess salt was removed by repeated washing with distilled water and centrifuging.

Pyridine *N*-oxide was synthesized by oxidation of pyridine according to Ochai (1953) and purified by distillation at reduced pressure.

For X-ray diffraction the air dry montmorillonite powders were outgassed at 150°C and 4×10^{-4} mm of Hg pressure for at least 16 hr to remove the sorbed water. The dry powder was then quickly immersed in solutions of PNO in dry chloroform in airtight tubes. The intercalation of PNO into montmorillonite was rapid and the expansion was complete within 2 hr. The suspensions in chloroform were spread onto unglazed porous ceramic tiles to form a thin layer. Any lumps of clay were spread out with a spatula and the tile covered with thin polythene film to minimize moisture sorption. A Philips PW 1049/50 goniometer and Fe filtered Co K α radiation were used to record the diffraction patterns of the complexes. The basal spacings were obtained from graphs of *d* values against 2 θ given by Parrish and Mack (1963).

The aggregates of clay, formed on air-drying of the montmorillonite suspensions, do not disperse

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in the chloroform solutions and are therefore unsuitable for recording the i.r. spectra. Uniform thin films were prepared by evaporation of dilute montmorillonite suspensions on AgCl windows over several days at room temperature. The films were outgassed under the same conditions used for the air-dried powders described above. Dry clay films on the AgCl windows were immersed in PNO solutions and kept in small desiccators over P_2O_5 . After intercalation, excess solution on the films was removed with filter paper and the samples subjected to continuous evacuation for 5 min to remove the chloroform. Infrared spectra were recorded on a Perkin-Elmer model 337 Infracord, a grating spectrometer. Wavelength check was provided by the polystyrene film supplied. Basal spacings were also determined on the samples on the AgCl windows during the stages of removal of the intercalated PNO.

Partial removal of PNO from the complexes could be achieved by immersing the samples, deposited on the AgCl windows, in dry chloroform for selected times. After the leachings the samples were evacuated for 5 min to remove the chloroform prior to recording the i.r. spectra and diffraction patterns.

RESULTS AND DISCUSSION

X-ray diffraction

Intercalation of PNO into montmorillonite results in two types of complexes. In concentrated solutions of PNO in chloroform (3.46 M) complexes with basal spacings around 21 Å are formed (Table 1); in dilute solution (0.1 M) complexes with basal spacings of about 14.7 Å result. The clay films deposited on the AgCl windows in concentrated solution, also form complexes with similar basal spacings. The 21 Å complexes (except the Cs complex) all give sharp diffraction peaks with integral higher orders. The 14.7 Å complexes can also be formed on the AgCl windows by leaching the 21 Å complexes with chloroform. Similar $d(001)$ spacings are observed for those complexes prepared from dilute solution (Table 1); however, the existence of higher orders for the 14.7 Å complexes was not investigated.

On a ceramic tile Cs montmorillonite gives a complex with $d(001)$ spacings less than 21 Å; the diffraction peak, though of low intensity is relatively symmetrical. On an AgCl window however, the peak is broad and of low intensity and appears at approximately 15 Å with a high low angle background and a broad shoulder at approximately

19.9 Å. Upon evacuation of the complex over P_2O_5 the intensity of the 15 Å peak increases and the 19.9 Å shoulder decreases; the 15 Å peak gradually becomes more symmetrical and attains a $d(001)$ spacing of 14.7 Å after evacuation for 50 min. In water Cs montmorillonite expands only to 13.2 Å (Edwards, Posner and Quirk, 1965) due to the very low hydration energy of the Cs cation.

The $d(001)$ spacings of complexes examined on the ceramic tile were always found to be less than those for complexes on the AgCl windows (Table 1). It was found that the addition of several drops of water to a Mg-montmorillonite suspension in 3.46 M PNO solution increased the $d(001)$ spacing from 20.2 to 21.0 Å. Precautions to minimize sorption of water by the complexes failed to eliminate the difference; i.r. spectra of the complexes, except the Mg complex, still showed a broad water band at approximately 3300 cm^{-1} . Preparation of the complexes for X-ray examination on ceramic tiles involved longer exposure to air and atmospheric water vapor, than preparation of the samples on AgCl windows for i.r. examination. Furthermore, since the clay powder and oriented films were outgassed under the same conditions, it appears that factors other than water are responsible for the differences in $d(001)$ spacings.

Greene-Kelly (1955); Farmer and Mortland (1966); Serratos (1966) and van Olphen (1968) found that pyridinium ions assume a flat orientation in montmorillonite to give a basal spacing of 12.5 Å. Pyridine gave spacings of 14.7 and 23 Å; the 14.7 Å spacing also corresponded to a monolayer, but with an almost perpendicular orientation of the pyridine ring to the clay surface. Nitrobenzene and benzoic acid also gave spacings around 15.2 Å as well as 12.4–12.8 and 15.1 Å respectively (Yariv, Russell and Farmer, 1966) which correspond to one of the above orientations for the molecule. The flat orientation of the pyridine ring may thus be an unfavourable one for PNO in montmorillonite, since spatial considerations could keep the coordination requirements of PNO around the cation from being fulfilled.

It is also plausible that the strong bonding of PNO to cations results in a substantial packing of PNO around the exchangeable cations in the complex even when prepared from 0.1 M PNO solution. To satisfy this and the coordination requirements of the cation, the pyridine ring of PNO orients itself almost perpendicular to the surface resulting in a 14.7 Å spacing. Only in more

Table 1. Basal spacings (Å) of montmorillonite-PNO complexes

Na ⁺	Cs ⁺	Mg ⁺⁺	Ca ⁺⁺	Preparation or treatment
On ceramic tile				
21.04	~ 14.7-15.3	20.18 14.75	20.43 ~ 14.8	in 3.46 m PNO solution in 0.106 PNO solution
On AgCl window 3.46 m PNO solution				
21.57	~ 19.9 sh* ~ 14.9-15.3b ~ 14.7	21.33	21.5	evac. total of 50 min evac. over P ₂ O ₅ total 13 hr
		19.5 } ~ 15.1d }	~ 20.6b	overlapping peaks leached 15 min
14.63		14.74		leached 17 min leached further 15 min total 30 min after evac. leached 30 min
	~ 14.1d		14.84	after evac. leached 32 min
14.62		14.74		leached total of 39 min leached total of 2 hr
	12.75			leached total of 4½ hr
14.5 } 13.1 sh } ^b				leached total of 6¾ hr
			14.85	total leaching of 30 hr

*sh—shoulder; b—broad; d—diffuse.

dilute solutions, when the activity of the PNO would be less giving a smaller level of adsorption, might the 12.5 Å complex be formed. Evidence in support of this comes from the work of van Olphen (1968) on the pyridine complexes. The projected area of the pyridine ring in a flat orientation is about 40 Å² while the area per exchange site is approximately 70 Å² which leads to a relatively small packing density of pyridinium ions in the 12.5 Å pyridinium complex. In the 14.7 Å complex the packing density would be similar.

Consideration of the dimensions of the PNO molecule and the Δ -value (MacEwan, 1948) of 5.1-5.3 Å for the 14.7 Å complexes [assuming a montmorillonite layer thickness of 9.5 Å] (Greenland, Laby and Quirk, 1962) indicates a tilted orientation of the PNO molecule. To avoid unduly large deviations from the calculated Δ -values and maintain coordination of PNO through the NO group, the *z*-axis (along the C...N-O direction) must lie parallel to the clay surface. The *x*-axis (in the plane of the ring and at right angles to the *z*-axis) is tilted at least at about 60° to the surface, depending on the cation and the amount of contraction and keying of PNO into the surface. This orientation with the NO group midway between the lamellae may be compared to the pyridinium ion in the 14.7 Å complex which is supposed to have the nitrogen directed towards the negative

silicate layers (Serratosa, 1966; van Olphen, 1968).

It should be noted that the 21 Å spacing for the PNO complexes lies between the values of 19.4 Å and approximately 23 Å reported by van Olphen (1968) and Greene-Kelly (1955) and Farmer and Mortland (1966) respectively, for the anhydrous and hydrated pyridine complexes. The increase in spacing to 23 Å was attributed by van Olphen (1968) to uptake of water by the 2 layer 19 Å complex and is confirmed by the infrared spectra of Farmer and Mortland (1966). The 21 Å spacing of the PNO complexes is considered to arise from the greater size of PNO in the *z*-axis direction as compared to pyridine, although the presence of water in the complexes may affect the orientation of PNO and the basal spacing.

I.R. spectra

The i.r. spectra of adsorbed PNO in the 21 Å montmorillonite complexes are all similar to each other; the spectrum of the 21 Å Na-montmorillonite complex is shown in Fig. 1a. The $\nu(\text{NO})$ band is at a lower frequency (~ 1235 cm⁻¹) than in a dilute solution of PNO in a non-polar solvent (1265 cm⁻¹) (Table 2). This difference shows that PNO bonds through the oxygen of the polar NO group and is in accord with the mechanism of bonding of PNO (Kida *et al.*, 1963; Hadzi and Kobilarov, 1966). The spectra however, (Table 2)

Table 2. Frequencies (cm^{-1}) and assignments of the montmorillonite-PNO complexes

	Na ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	PNO* (dil. soln)	
21-57	14-62	15-08	21-33	21-5	14-74	X-ray spacing (Å)
3614	3614	3610	3610	3612	3615	Montmorillonite $\nu(\text{OH})$
~3360	~3300-3500	~3340-3400	~3260-3340	~3300-3380	3320-3500	Water $\nu(\text{OH})$
3100 w†	~3113 w	3104	3105	3104	3100 vw	$\nu(\text{CH})$
		3080 sh	3080	3080		Water $\delta(\text{OH})$
1623-1663	1623	1647	~1622-1653 w	1622-1663	1622 w	$\nu_{8a}(A_1)$ ring stretch
1605	1608 sh	1605	1602 w	1604 w	1604 vw	$\nu_{19}(A_1)$ ring stretch
1464	1468	1466	1466	1468	1468	
~1457 sh	1457 sh		sh	sh	1456 sh	
		1390 w				
		1253 sh				
1233		1232	1230	1234	1248	$(A_1)\nu(\text{NO})$
	1220	1236			1213	
1170	1170 sh	1215	1171	1170	1176	$\nu_{15}(B_1)$ in-plane CH def.
837	837	1168	838	838	844	(A_1) in-plane N-O def.
794 w	795	835				
769	767	796	769	769	769	(B_2) CH out of plane def.
	756 sh	768	766		755 sh	
733					734 w	
676	673	676	675	734 w	734 w	$\nu_{11}(B_2)$ out of plane CH def.
		550 sh	550 sh	675	674	$\nu_{8a}(A_1)$ in-plane ring def.
		548		675	549	

*Kida *et al.* (1963)

†w - weak; v - very; sh - shoulder.

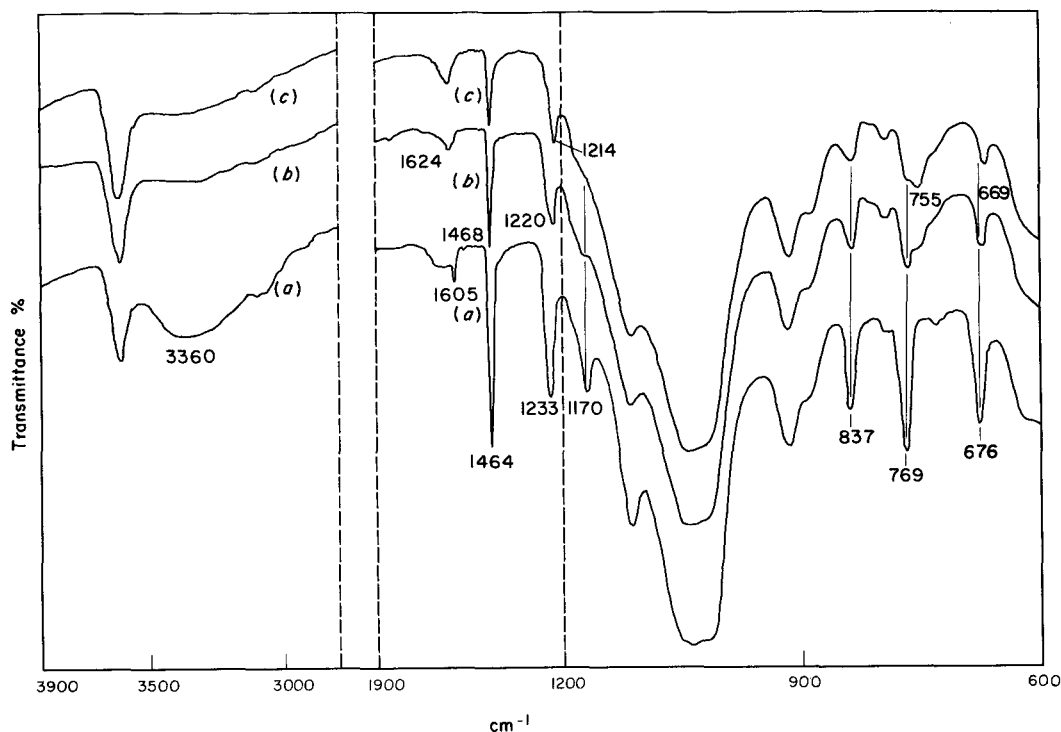


Fig. 1. I.R. spectra of Na-montmorillonite-PNO complexes (a) $d(001) = 21.6 \text{ \AA}$; (b) sample (a) leached with CHCl_3 for 39 min.; $d(001) = 14.6 \text{ \AA}$ and (c) sample (a) leached for total of $6\frac{3}{4}$ hr, $d(001) = 13.1\text{--}14.5 \text{ \AA}$. See Table 2 for band assignments.

show no significant variation of the $\nu(\text{NO})$ frequency with type of cation on the clay.

Evacuation of the Ca-montmorillonite-PNO complex over P_2O_5 for almost 13 hr results in a decrease of the diffraction peak intensity and a basal spacing collapse from 21.5 to approximately 20.6 \AA with development of considerable high angle asymmetry of the diffraction peak. Further removal of intercalated PNO by subsequent evacuation or leaching intensifies and sharpens the diffraction peak and gradually shifts the $d(001)$ spacing to 14.8 \AA . Accompanying this, the i.r. spectrum of the complex shows a broadening of the $\nu(\text{NO})$ band ($\sim 1235 \text{ cm}^{-1}$) followed by a splitting into two overlapping bands. Cs-montmorillonite, however, at $d(001)$ spacings above 15 \AA forms a relatively unstable interstratified complex which collapses when evacuated to a more stable and definite 14.7 \AA complex. The $\nu(\text{NO})$ band also splits into overlapping bands at 1236 and 1215 cm^{-1} (Fig. 2a).

Generally 15 min leaching only partially collapses the $d(001)$ spacing from 21 to about 14.7 \AA and gives a diffraction peak with considerable low

angle asymmetry. A further 15 min leaching intensifies the 14.7 \AA peak and eliminates the asymmetry. The splitting of the $\nu(\text{NO})$ band ($\sim 1232 \text{ cm}^{-1}$) initiated by evacuation, heating, or the first 15 min leaching is completed during the second leaching. Table 2 lists the assignments of the 14.7 \AA complexes. In the Na-clay complex there is a lowering of the $\nu(\text{NO})$ frequency (1233 to 1220 cm^{-1}) from the 21 \AA complex (Fig. 1b) with a slight further lowering to 1214 cm^{-1} as more PNO is removed (Fig. 1c), whereas there is a splitting in other complexes (Fig. 2). Leaching the complexes for still longer periods results in further removal of intercalated PNO and collapse of the basal spacing; the relative ease of this however is governed by the exchangeable cation (Table 1).

Farmer and Mortland (1966); Yariv *et al.* (1966) and Parfitt and Mortland (1968) proposed that water acts as a bridge between the cation and organic compound in the adsorption of certain organic compounds onto montmorillonite. A similar bridging function of water is also envisaged for the PNO complexes, particularly as the spectra showed the PNO complexes to contain

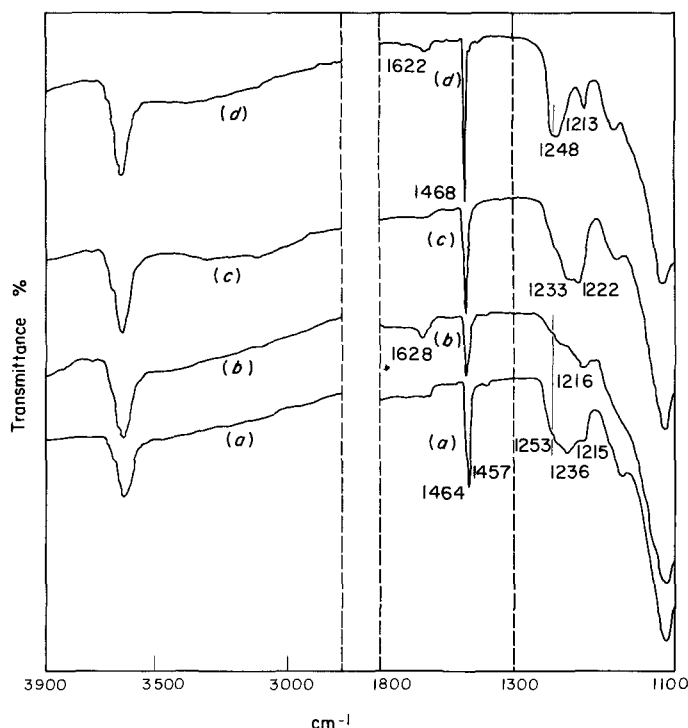


Fig. 2. I.R. spectrum of (a) Cs-montmorillonite-PNO complex evacuated over P_2O_5 for 50 min, $d(001) = 14.8 \text{ \AA}$; (b) sample (a) leached with $CHCl_3$ for 30 min, $d(001) = 14.1 \text{ \AA}$; (c) Mg-montmorillonite-PNO complex leached for 30 min, $d(001) = 14.7 \text{ \AA}$; and (d) Ca-montmorillonite-PNO complex leached for 32 min, $d(001) = 14.8 \text{ \AA}$. See Table 2 for band assignments.

water. Thus the 1232 cm^{-1} $\nu(\text{NO})$ band in the 21 \AA complexes is considered to arise from PNO in the second coordination sphere hydrogen-bonding to the OH of water in the hydration shell around the cation. This water is in turn directly coordinated to the cation. This circumstance may thus explain the invariance of the $\nu(\text{NO})$ frequency ($\sim 1235 \text{ cm}^{-1}$) with exchangeable cation on the clay (Table 2) and the difficulty of removing water. It is also likely since the $d(001)$ spacings for complexes formed on the AgCl windows are larger than those complexes examined on a ceramic tile, especially when water was added to the system.

With a decrease of the basal spacing and a lessening of water in the complexes a reorganization occurs which leads to a splitting of the $\nu(\text{NO})$ bands ($\sim 1235 \text{ cm}^{-1}$). It is suggested that in the 14.7 \AA Mg and Ca complexes the higher frequency band, at 1233 and 1248 cm^{-1} respectively, arises from the $\nu(\text{NO})$ of PNO water bridged to the cation as these are in the region of the $\nu(\text{NO})$ frequency (1235 cm^{-1}) in the 21 \AA complexes (Table 2). The lower frequency bands, at 1222 and 1214 cm^{-1}

respectively, are interpreted as being due to PNO directly coordinated to the cation, in keeping with similar observations on other complexes (Farmer and Mortland, 1966; Yariv *et al.*, 1966; Parfitt and Mortland, 1968). The absence of a $\delta(\text{OH})$ band at 1622 cm^{-1} in the spectrum of the Mg complex (see Figs. 2c and d) indicates a lower water content for the Mg than for the Ca complex. This could contribute to the smaller and less distinct splitting of the $\nu(\text{NO})$ band ($\sim 1230 \text{ cm}^{-1}$) in the Mg complex (Fig. 2c).

The Cs-montmorillonite-PNO complex also shows a splitting of the $\nu(\text{NO})$ band (1232 cm^{-1}) in the 14.7 \AA complex (Fig. 2a) and appears to be an exception in that the Cs cation is usually considered to be unhydrated. The band at 1216 cm^{-1} persists at $d(001)$ spacings of 14.1 \AA after removal of considerable PNO and virtual disappearance of the 1253 and 1236 cm^{-1} bands (Fig. 2b). Hence by analogy with the Mg and Ca complexes, the 1216 cm^{-1} band is interpreted as the $\nu(\text{NO})$ vibration of PNO directly coordinated to the Cs cation. The higher frequency $\nu(\text{NO})$ bands could arise from the strong hydrogen-bonding between

water and PNO which effectively results in PNO bonding to the Cs cation via a bridging water molecule.

The entrained water in the PNO complexes reveals some interesting features. The water in the 21 Å complexes is difficult to remove by evacuation over P₂O₅ without also the simultaneous removal of some interlamellar PNO and partial collapse of the *d*(001) spacing. The $\nu(\text{OH})$ frequency of water in the complexes varies slightly from cation to cation (Table 2); it occurs at a somewhat lower frequency, 3415 cm⁻¹, than if PNO were absent (Russell and Farmer, 1964) yet higher than the water $\nu(\text{OH})$ bands (3060 cm⁻¹) in montmorillonite-pyridine complexes (Farmer and Mortland, 1966). However in the Mg and Ca pyridine complexes (Farmer and Mortland, 1966) the water band at 3060 cm⁻¹ shifts to about 2780 cm⁻¹ for the Mg complex, when the *d*(001) spacing collapses to 14.7 Å. From this shift they concluded that water strongly hydrogen-bonded to pyridine in the complexes, which were stronger in the 14.7 Å than the 23 Å complexes and stronger in the Mg than the Ca complexes. The water however could be removed from the 14.7 Å complexes by evacuation or evacuation and heating, with pyridine then coordinating directly to the cation. It would thus appear that bonding of water in the PNO complexes differs from that in the montmorillonite-pyridine complexes; this could well be due to the high polarity of PNO.

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Résumé—Le *N*-oxyde de pyridine et la montmorillonite forment des complexes interlamellaires avec des espacements basaux de 14,7 et 21 Å. Le premier correspond à une monocouche avec une orientation inclinée du noyau pyridine; le second correspond à une double couche de molécules entre les feuillets d'argile. Les spectres infrarouges montrent que le *N*-oxyde de pyridine est lié par le groupe NO; dans les complexes à 21 Å, il est coordonné aux cations échangeables par l'intermédiaire de molécules d'eau agissant comme des ponts qui sont eux-mêmes directement coordonnés aux cations. Dans les complexes à 14,7 Å on observe un dédoublement de la bande ν (NO) avec les cations très polarisants Mg et Ca; les deux bandes correspondent à des molécules de *N*-oxyde de pyridine directement coordonnées aux cations et à d'autres molécules coordonnées par l'intermédiaire des molécules d'eau. La montmorillonite Cs forme des complexes avec un espacement basal de 14,7 Å environ, qui montrent aussi un dédoublement de la bande ν (NO).

Kurzreferat—Pyridin-*N*-oxyde und Montmorillonit bilden Zwischenschicht-Einlagerungskomplexe mit Basisebenenabständen von 14,7 und 21 Å. Ersterer entspricht einer einmolekularen Schicht mit Schrägstellung der Pyridin-Ringe. Letzterer enthält eine Doppelschicht der Moleküle zwischen den

Silicatschichten. Infrarotspektren zeigen, daß das Pyridin-*N*-oxid über die NO-Gruppe gebunden wird. Es ist im 21 Å-Komplex mit den austauschbaren Kationen koordiniert und zwar über Wassermoleküle, die ihrerseits eine direkte Zuordnung zu den Kationen aufweisen. Im 14,7 Å-Komplex tritt mit den stärker polarisierbaren Kationen Mg und Ca eine Aufspaltung der $\nu(\text{NO})$ -Bande auf. Die beiden Banden entsprechen Pyridin-*N*-oxid-Molekülen, die direkt mit dem Kation und solchen, die über Wassermolekülbrücken koordiniert sind. Cs-Montmorillonit bildet Komplexe mit einem Basisenabstand von annähernd 14,7 Å, die ebenfalls Aufspaltung der $\nu(\text{NO})$ -Bande zeigen.

Резюме — *N*-окисный пиридин и монтмориллонит образуют интерламнарные комплексы с постоянной кристаллической решетки 14,7 и 21 Å. Первый соответствует мономолекулярному слою с наклонной ориентацией пиридинового кольца; последний заключает в себе двойной слой молекул между пластинами глины. Инфракрасная область спектра показывает, что *N*-окисный пиридин связан по группе NO; в комплексах 21 Å он координационно присоединен к катионам посредством молекул воды, образующих мостиковые связи, которые в свою очередь вступают непосредственно в координационную связь с катионами. В комплексе 14,7 Å расщепление полосы $\nu(\text{NO})$ происходит с более поляризуемыми катионами Mg и Ca; обе полосы соответствуют молекулам *N*-окисного пиридина непосредственно координированных с катионом и с остальными молекулами координационно присоединенными мостиковой связью к молекулам воды. Cs монтмориллонит образует комплексы с постоянной кристаллической решетки примерно 14,7 Å, также проявляющей расщепление полосы $\nu(\text{NO})$.