

## Absorption of Pyrimidines, Purines, and Nucleosides

by Co-, Ni-, Cu- and Fe(III)-Montmorillonite (Clay-Organic Studies XIII)

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## ABSTRACT

The absorptions of various pyrimidines, purines and nucleosides by Co-, Ni-, Cu- and Fe(III)-montmorillonite have been studied using aqueous solutions in the pH range 2-12, and organic concentrations between 0.8 and 1.4 m.molar. Under acidic conditions, absorption takes place by cation exchange and the absorption characteristics are similar to those of Ca-montmorillonite. In the weak acidic, neutral, and weak alkaline range, absorption is due to complex formation. At higher pH values, absorption decreases as formation of hydroxides takes place. The strength of absorption due to complex formation decreases in the order  $Cu \gg Ni > Co$  and  $adenine \geq hypoxanthine > purine \gg 6\text{-chloropurine}$ . These four compounds form complexes with positions N-3 and N-9 as shown by comparison of their absorption isotherms with those of 7- and 9-methyladenine. Depending on the pH, divalent and (stronger) monovalent complexes may be formed.

With adenosine no absorption due to complex formation was observed whereas 9-methyladenine formed weak complexes. Both compounds can form complexes with the amino group and N-7.

Weak complexes were observed with cytosine, cytidine, inosine, and guanosine. Thymine, uracil, and their nucleosides were not absorbed under the experimental conditions.

Fe-montmorillonite behaves somewhat differently from Co-, Ni- and Cu-montmorillonite. With purines and pyrimidines, the absorption characteristics resemble those of Ca-montmorillonite, but strong absorption extends to a higher equilibrium pH and then decreases more rapidly with increasing pH. The absorption of the nucleosides is very different with Fe-montmorillonite than with both Ca-montmorillonite and with the other transition metal montmorillonites. Inosine is not absorbed, guanosine shows very limited absorption which decreases slowly with increasing pH. Adenosine and cytidine show high absorption maxima at about pH5 and pH6 respectively.

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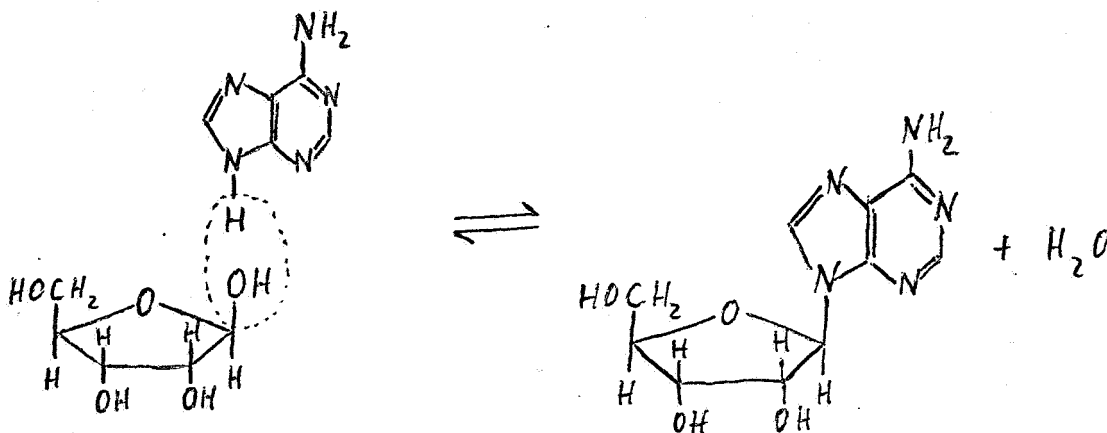
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## INTRODUCTION

The investigations reported in this and the preceding paper were undertaken to obtain fundamental knowledge on the absorption of nucleic acid derivatives by montmorillonite and on the nature of the resulting complexes. This knowledge is necessary for any studies which aim at showing a catalytic influence of clay minerals in the original synthesis of living forms, in this case in the synthesis of nucleosides from purines or pyrimidines and ribose, under possible conditions of the primitive earth, as emphasized by Bernal (1951).

The reaction between the bases and ribose to form nucleosides is a dehydration-condensation reaction as shown with the example of the adenosine formation:



The dehydration takes place more easily the more acidic is the imino group. Therefore it is relatively easy to form the glycosidic bond with chlorinated purine but most difficult to get a reaction at all with adenine. The only results of this kind are reported by Ponnampereuma (1963, 1964) who obtained small yields by UV-irradiation of solutions containing adenine and ribose or deoxyribose. The effect of UV-light is not too surprising since the  $pK_a$

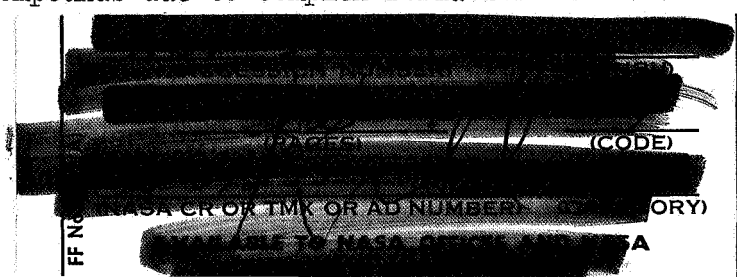
of the imino group of adenine in the excited state is stated to be 7.3 (Sukhorukov, Poltev, and Blyumenfel'd, 1963) in comparison with 9.8 in the ground state.

It is hoped that the electron distribution of the purine and pyrimidine bases may be changed due to their absorption on montmorillonite in such a way that the imino group becomes more acidic. The limitations for a possible reaction are discussed in the preceding paper.

Another possible way to change the electron distribution of absorbed molecules is through complex formation with the interlayer cations. It would certainly increase the acidity of adenine if the complexing cations could be bonded by the amino group and N-7, as has been suggested several times (Frieden and Alles, 1958; Harkins and Freiser, 1958; Freisder, Cheney and Fernando, 1959). However, since Weiss and Venner (1963, 1965) have shown that N-3 and N-9 are possibly the more important positions for the complex formation of the purine bases with  $Cu^{2+}$ , it seemed worthwhile to study the absorption due to complex formation with  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  as interlayer cations of montmorillonite in more detail before any synthesis experiments were conducted. Fe(III)-montmorillonite also has been included because of the common occurrence of iron in nature. The results of these investigations are reported in this paper.

EXPERIMENTAL

The preparation of the montmorillonite samples has been reported in the preceding paper as well as the properties and origin of the used organic compounds which are listed in Table 1 of that paper. The experimental procedures are the same as before. A possible change of the UV- extinction coefficients of the organic compounds due to complex formation with the



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exchanged interlayer cations could not be observed under the experimental conditions. Only for the alkaline samples of Fe(III)- montmorillonite was a modification of the procedure necessary for the UV- spectroscopic measurements of the equilibrium concentrations of the organic compounds since under alkaline conditions a Fe(III)- hydroxide sol was formed which was not removed from the solutions by centrifugation. However, after adding pH2- buffer (HCl-KCl) to the supernatant, sedimentation of a gel took place within a few minutes. The clear supernatant solutions were then used for the spectroscopic measurements. Due to this gel, the probable error of the pH- measurements in these samples is increased.

#### Infrared Spectroscopic Investigations

The infrared spectra of various clay-adenine complexes were obtained in the following manner: After centrifugation of the equilibrated clay suspensions, the supernatant solution was decanted and the clay with a little water stirred to a smooth paste. The paste was spread on a piece of nylon stocking, air dried and then dried for two days over  $P_2O_5$ . A piece of the same stocking was used as reference sample. The spectra were obtained with a Perkin-Elmer Model 621 infrared spectrophotometer.

### RESULTS

#### Absorption Isotherms

The absorption isotherms have been plotted in "% absorbed" against equilibrium pH for the reasons which are discussed in the preceding paper; as before, "100% absorbed" means that the available organic molecules are completely absorbed but only 25 meq/100g of the exchangeable cations are replaced by organic cations. (With larger ratios of organic molecules to montmorillonite larger amounts were absorbed. The shape of the absorption isotherms changed gradually with increasing amounts of the organic compounds.)

The absorption isotherms are given in Fig. 1-4. Thymine, uracil, and their nucleosides were not absorbed under the experimental conditions.

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Characteristic color changes due to pH and complex formation with the absorbed organic compounds have been observed with Co-, Cu-, and Fe(III)-montmorillonite. The intensity of the pale pink color of Co- montmorillonite increased from pH2 to pH7 according to the increasing amount of  $\text{Co}^{2+}$  ions remaining in the montmorillonite. Above pH7 the color changed to reddish pink if 7- methyladenine, purine, adenine, and hypoxanthine were absorbed. Above those alkaline pHs where the absorption isotherms begin to drop down rapidly, in all samples the color of the clay changed through pale blue to a dirty yellow. With 9- methyladenine, 6- chloropurine, cytosine, and the nucleosides this color change appeared between pH8 and pH8.5.

During the absorption by Cu- montmorillonite the color of the montmorillonite changed with the pH in the following order:

pH:	2	3	4-5	6-9	9-11	>11
Color:	white	pale blue	blue	darker blue	greenish blue	dark brown

The intensity of the blue color in the pH range 4 to 9 depended on the absorbed organic compounds. If the absorption was weaker the blue color was lighter and the change to greenish blue and dark brown, respectively, appeared at lower pHs.

In the case of Fe(III)- montmorillonite, the color changes were almost exclusively determined by the pH. From pH2 to pH4 the intensity of the yellow color of the clay increased in the same way as the concentration of  $\text{Fe}^{3+}$  in solution decreased. The more organic cations were absorbed the lighter appeared the clay. From pH4 to the pHs where the absorption isotherms begin to descend the color changed from yellow to yellowish brown. In this pH range, very few  $\text{Fe}^{3+}$  ions were in the supernatant solutions. In the following pH range the suspensions appeared brown and after centrifugation there remained a brown sol as supernatant.

All color changes, except the change of the blue color of Cu-montmorillonite to dark brown, took place within a few minutes after adding the clay suspensions to the organic solutions. This indicates that these reactions took place rapidly at least to a certain degree.

#### X-Ray Data

After absorption of adenine by Co-, Ni- and Cu- montmorillonite at pHs lower than 5, the formation of two phases took place in the same way as reported in the preceding paper for Ca- montmorillonite. At higher pHs, there was observed only a strong  $19\text{\AA}$  basal spacing if amounts up to 0.26 molecules adenine per unit cell were absorbed by Co- and Ni- montmorillonite. In one sample of Ni- montmorillonite with 0.2 molecules adenine absorbed per unit cell at pH8 in addition to the  $19\text{\AA}$  reflection, two weak 'texture' reflections were observed corresponding to a  $12.5\text{\AA}$  basal spacing.

More varied results were obtained from suspensions of Cu- and Fe(III)-montmorillonite after absorption of adenine. The results are listed in Tables 1 and 2.

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Table 1

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Table 2

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### Infrared Spectroscopic Data

Since the infrared spectra of the investigated organic compounds are very complex and only a few of the bands are assigned (Angell, 1961), no attempt has been made so far to obtain detailed information from the IR spectra of the clay-organic complexes. The intensities of many bands are very sensitive to the orientation of the molecules as shown by comparison of a sublimated sample of adenine with a KBr pellet. Further changes of the intensity and also some band positions are possibly due to the influence of the silicate layers on the electron distribution of the absorbed organic molecules. However, by comparison of the infrared spectra of various adenine-montmorillonite complexes, differences could be observed due to pH and the various interlayer cations.

Most of the absorption bands of adenine are located in the range from 700 to  $1750\text{ cm}^{-1}$ . However, since montmorillonite is strongly absorbing below  $1250\text{ cm}^{-1}$ , only bands in the range from 1250 to  $1750\text{ cm}^{-1}$  were available for the comparison.

The frequencies and relative intensities of the absorption bands of adenine (Angell, 1961), adenine hydrochloride (Angell, 1961), and some of the adenine-montmorillonite complexes are set out in Table 3.

### DISCUSSION

#### Absorption by Co-, Ni-, and Cu- Montmorillonite

##### Reaction Mechanisms:

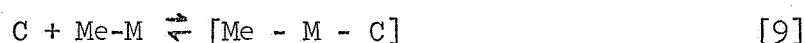
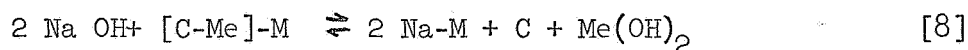
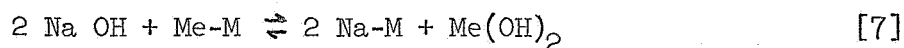
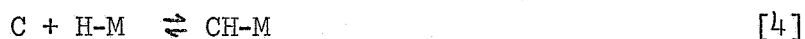
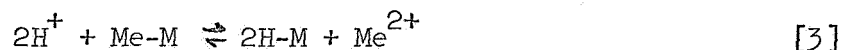
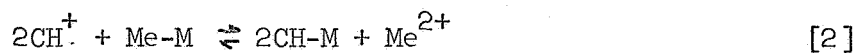
If absorption takes place under strong acidic conditions, the mechanisms involved are probably mainly cation exchange reactions as discussed in the preceding paper and expressed by the equations [1] to [5] (see later). This is suggested by the similarity of the absorption isotherms of Co- and Ni-montmorillonite with those of Ca- montmorillonite.

The differences between the IR spectra of adenine-Ca-montmorillonite and adenine-Cu-montmorillonite prepared at pH2 suggest that some complex formation between adenine and  $\text{Cu}^{2+}$  took place (compare Weiss and Venner, 1963, p. 170). The contribution of the complex formation between the organic molecules and the transition metal interlayer cations to the absorption (equation [6] ) becomes increasingly important as the pH rises, since the concentration of the metal ions remaining in the interlayer region increases with the pH. The strength of these complexes increases in the order  $\text{Co} < \text{Ni} \ll \text{Cu}$  as shown by the differences between the absorption isotherms of Co-, Ni-, and Cu-montmorillonite compared with those of Ca-montmorillonite, as well as by the IR spectra of the adenine complexes. Complexes different from those formed under acidic conditions are certainly formed in the alkaline range by the compounds adenine, hypoxanthine, purine, 6-chloropurine, inosine, and guanosine. Unfortunately, it was not possible to prepare the complexes of the various compounds with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  under the various pH conditions in aqueous solution and to absorb the complexes from these solutions e.g. by Ca-montmorillonite, since  $\text{Cu}^{2+}$  complexes could be isolated from aqueous solutions only under quite extreme conditions (Weiss and Venner, 1963, 1965). They were insoluble in cold water and in acid.

The formation of the hydroxides of the transition metals took place at lower pHs the weaker the absorption due to complex formation (equations [7] and [8]). 7- and 9- methyladenine are then still absorbed due to van der Waals attraction (equation [9]) as discussed in the preceding paper.

The following equations describe the reactions mentioned in the text:





where: C = organic compound;  $CH^+$  = organic cation; Me-M represents Co-, Ni-, and Cu- montmorillonite, respectively; CH-M = montmorillonite with absorbed organic cations;  $Me^{2+}$  represents  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$ , respectively; [C-Me]-M = montmorillonite with absorbed complex cations; Na-M = Na-montmorillonite; [Me - M - C] represents montmorillonite with physically adsorbed organic molecules.

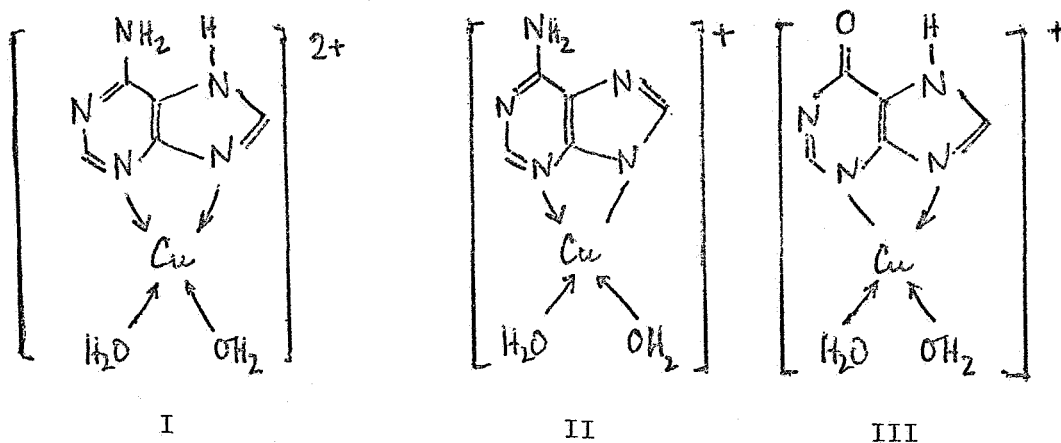
#### Complex Structures:

The absorption isotherms of Figures 1 and 2 can be divided into three groups, namely those of:

- (1) adenine, hypoxanthine, purine, and 6-chloropurine,
- (2) 7-methyladenine,
- (3) cytosine and 9-methyladenine.

Under the assumption that the purine derivatives are bidentate ligands, as reported by Weiss and Venner (1963, 1965), only the positions N-3 and N-9 are common to all four compounds of group (1) as possible positions for complex formation. If complex formation takes place, the molecules must be in a tautomeric form with the proton of the imino group bonded to N-7

(structure I). Structure I is suggested for complexes of the compounds of group (1) formed under acidic and neutral conditions. Since the ratio of interlayer cations to organic molecules is at least 2:1 it seems reasonable to assume that only 1:1- complexes will be formed. The acidity of the imino group of complex I depends on the acidity of the imino group of the organic compound and on the strength of the complex. If the pH rises, the proton of the imino group dissociates, and a stronger complex is obtained (structure II) causing an increased absorption by the montmorillonite. The formation of two complexes with different structures in the weak acidic and alkaline pH range, respectively, is indicated also by the IR spectra of the adenine-Cu-montmorillonite complexes.



The relative proportions of the complexes formed by the four compounds of group (1) are determined mainly by the basicity of N-3 and N-9 which depends on the substituent in position 6. The influence of these substituents on the basicity of the imino group has been discussed previously by Cheney, Freiser, and Fernando (1959). The supply of electrons by the amino and the hydroxy group via + M effect (Ingold, 1953) is comparable whereas the weak + M effect of chlorine is supercompensated by its strong electron withdrawing field effect. The strength of the formed complexes should therefore decrease in the order adenine  $\geq$  hypoxanthine  $>$  purine  $>$  6-chloropurine which is true

for the complexes formed by Cu-montmorillonite. The fact that purine is more strongly absorbed than adenine and hypoxanthine by Co- and Ni-montmorillonite may be due to steric relations between the inorganic cations and the purine derivatives since the bond lengths and angles in the purine ring system depend somewhat on the substituents.

To take into account the conclusion of Cheney, Freiser, and Fernando (1959) that the  $pK_a = 8.94$  of hypoxanthine is due to dissociation of the hydroxy group, structure III is suggested as an alternative for structure II.

Complexes with structure I can be formed also by 7-methyladenine. Due to the inductive effect of the methyl group, which substitutes for the imino hydrogen, the basicity of N-9 and possibly of N-3 is increased and stronger complexes are formed than with the compounds of group (1). Since no change of the complex structure is possible due to dissociation of the imino group, the absorption isotherms do not rise in the alkaline pH range.

The similarity between the absorption isotherms of cytosine and 9-methyladenine (group (3)) by Cu-montmorillonite suggests similar complex structures. These structures would have bonded the complexing cation to the amino group and N-3 of cytosine or N-1 of 9-methyladenine. However, cytosine has been discussed by Wang and Li (1966) as a monodentate ligand with the complex bond to N-3. Weiss and Venner (1963) have shown that 9-methyladenine is a bidentate ligand in its complex with  $Cu^{2+}$ . Since complex formation could not be observed with 6-amino - 2,4-dimethyl - pyrimidine similar to that of purine derivatives, they concluded that in 9-methyladenine complexes the cation must be bonded to the amino group and N-7. The similarity of the absorption isotherms may be interpreted, therefore, as an expression of the comparable strength and stability ranges with regard to pH of two different complex structures.

The most important fact, however, is that 9-methyladenine complexes are much weaker than complexes formed by 7-methyladenine or adenine (Fig. 2). The question whether in the complexes of adenine and hypoxanthine a five-membered ring is formed by the amino group and N-7 (Harkins and Freiser, 1958; Chency, Freiser, and Fernando, 1959; Frieden and Alles, 1958), or a four-membered ring by N-3 and N-9 (Weiss and Venner, 1963, 1965) must be decided in favor of the second possibility.

In adenosine the position 9 is blocked as in 9-methyladenine. Since the inductive effect of the methyl group is missing, weaker complexes would be expected with adenosine, and in fact, no absorption has been observed due to complex formation with the interlayer cations. A very weak complex between  $\text{Cu}^{2+}$  and adenosine has been reported (Frieden and Alles, 1958; Fiskin and Beer, 1965). This significant difference between adenine and adenosine could not be explained on the assumption that both compounds form complexes of the same structure, since the IR spectra of adenine and adenosine show that the ribose ring has only a small influence on the ~~electron distribution of the~~ adenine part of adenosine (Angell, 1961), and the complex formation constants therefore should be comparable.

For the observed complex formation of guanosine and inosine, the stronger influence of the ribose ring on the heterocyclic ring system could be responsible; this has been shown by IR spectroscopy for guanosine (Angell, 1961). The slight rise of the absorption isotherms in the alkaline pH range, which has been observed with these molecules in two cases, may be due to dissociation of the hydroxy group.

It should be mentioned that the similarity between the absorption isotherms of 6-chloropurine and pyridine by Cu-montmorillonite is certainly accidental and not due to similarity of the complex structures. If 6-

chloropurine could occur as a monodentate ligand like pyridine, its complex would be much weaker than the complex of pyridine, since the nitrogen of pyridine is much more basic than any nitrogen of 6-chloropurine.

#### Absorption by Fe(III)-Montmorillonite

The absorption characteristics of Fe(III)-montmorillonite have some outstanding features. An explanation cannot be given since even the properties and structures of Fe(III)-montmorillonite itself under the various pH conditions are still under investigation.

The absorption at low pHs is probably due to cation exchange according to equations [2] to [5] (p. 8). The equilibria of reactions [2] and [3] will be markedly influenced by the stronger bonding of  $\text{Fe}^{3+}$  by montmorillonite. As the pH rises, reaction [5] becomes less important, but also reactions [3] and [4]. Above pH 3 either successive hydrolysis of the  $\text{Fe}^{3+}$ -montmorillonite takes place providing an increasing number of exchange sites to be saturated by protons and organic cations and at higher pH by  $\text{Na}^+$  ions, or complex formation must take place between  $\text{Fe}^{3+}$  and the organic compounds, since in spite of the strong absorption of most of the organic compounds nearly no Fe(III) ions were detected in solution.

The question whether complex formation between Fe(III) ions and the organic compounds is involved in the absorption cannot be answered from the present experimental results. The IR spectra show that such complexes must have a structure very different from those formed with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ . The increase of the intensity of the IR absorption band at  $1420\text{ cm}^{-1}$  in the spectra of adenine - Fe(III)-montmorillonite complexes with increasing pH suggests absorption of neutral adenine. With other adenine-montmorillonite complexes this band has been observed only if free adenine, which was left in

the supernatant solution, contaminated the samples. The absorption isotherm of adenine by Fe(III)-montmorillonite shows that the appearance of the  $1420\text{ cm}^{-1}$  band in the IR spectra of adenine - Fe(III)-montmorillonite complexes cannot be due to contamination since all the adenine is absorbed. The suggestion that the  $1420\text{ cm}^{-1}$  band is due to absorbed neutral adenine is confirmed by the shift of the  $\text{NH}_2$  deformation vibration from  $1701$  to  $1690\text{ cm}^{-1}$  (Angell, 1961). This absorption may be due to a change of the properties of the montmorillonite layers by Fe(III) hydrolysis products, or to direct absorption on these products.

At the pHs where the absorption decreases, there has also been observed a separation of the Fe(III) hydroxides from the clay. The experimental procedure does not allow any answer to the question whether or not these hydroxides absorb the organic compounds under the given conditions. Experiments to separate the supernatant from the clay and the Fe(III) hydroxide sol with dialysis tubing did not give reproducible results.

Along with the hydrolysis of the Fe(III)-montmorillonite goes a change in its swelling behavior which becomes somewhat similar to that of Na-montmorillonite. This could explain some of the features of the absorption isotherms in the pH range above 6, especially the strong absorption of cytidine, since the pH measured in the supernatant does not give much information about the pH existing close to the absorbing surface.

#### SUMMARY AND CONCLUSIONS

The absorption characteristics of pyrimidines, purines, and nucleosides by Co-, Ni-, and Cu-montmorillonite in the acidic pH range are very similar to those observed with Mg- and Ca- montmorillonite, which are discussed in the preceding paper. With rising pH complex formation with the interlayer cations becomes increasingly important for many of the organic compounds.

The strength of the complexes decreases generally in the order  
 $\text{Cu} \gg \text{Ni} > \text{Co}$ .

It has been shown that complex bonding most probably takes place with  
of  
N-3 and N-9 adenine, hypoxanthine, purine, 6-chloropurine, and 7-methyl-  
adenine as suggested by Weiss and Venner (1963). The first four compounds  
at higher pHs develop a second type of complex due to dissociation of the  
imino group. Complex formation of these compounds is therefore not favorable  
for experiments to synthesize nucleosides since N-9 is blocked by the  
complexing cation.

9-methyladenine, guanosine, and inosine form much weaker complexes in  
which the cation probably is bonded to the substituent in position 6 and to  
N-7. The complexes of adenosine (Frieden and Alles, 1958; Fiskin and Beer,  
1965) are too weak to cause any absorption by montmorillonite due to  
complex formation. Weak complexes have been observed also between cytosine  
and cytidine, respectively, and  $\text{Cu}^{2+}$ .

Fe(III)-montmorillonite absorbs strongly most of the investigated  
compounds. The absorption isotherms indicate that below pH 3 the strong  
bonding of  $\text{Fe}^{3+}$  by montmorillonite influences the equilibrium constants of  
the cation exchange reactions significantly. Above pH 3 strong absorption  
occurs with progressive hydrolysis of the  $\text{Fe}^{3+}$ -montmorillonite. IR spectra  
suggest that with rising pH increasing amounts of neutral molecules of the  
organic compounds are absorbed. This could provide favorable conditions for  
synthesis experiments provided a separation did not take place into a 12.5 Å  
phase, characteristic for the organo-clay, and an expanded phase similar to  
Na-montmorillonite.

It must therefore be concluded that the synthesis of nucleosides from  
bases and ribose with transition metal montmorillonites as catalysts will be  
hindered by the nature of the complex formation with the cations Co, Ni, and

and Cu, but the situation as regards Fe(III)-montmorillonite is less certain.

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Table 1. X-ray data of complexes of adenine with  
Cu-montmorillonite in aqueous suspensions

Absorbed Compound	Molecules per unit cell	Equilibrium pH	Basal Spacing [Å]	Intensity relative to (020)
(HCl)	--	2.02	19.2	very strong
adenine	0.215	1.95	10.2	medium to weak
			12.5	medium to strong
--	--	5.11	19.2	very strong
adenine	0.223	5.25	< 18.5 diffuse	weak
			15.8	strong
adenine*	0.437	5.00	15.7 sharp	very strong
(NaOH)	--	9.00	> 40.0 diffuse	very strong
adenine	0.353	9.45	10.0	very weak
			29.2 (001)	very strong
			14.6 (002)	weak
			9.7 (003)	very weak

\*This sample, when air dried, gave a relatively poor pattern in which a basal spacing of 13.0 - 13.3 Å was measured.

Table 2. X-ray data of complexes of adenine with  
Fe(III)-montmorillonite in aqueous suspensions

Absorbed compound	Molecules per unit cell	Equilibrium pH	Basal Spacing [Å]	Intensity Relative to (020)
(HCl)	--	2.12	21.0 broad	very strong
adenine	0.097	2.25	21.0	strong
			10.5-12.5 diffuse	weak
adenine	0.205	2.40	20.0	very weak
			12.6 sharp	medium to strong
--	--	4.80	21.0 broad	very strong
adenine	0.120	4.90	20.0	strong
			12.4 diffuse	weak
adenine	0.236	5.60	>28.00 diffuse	weak
			12.5 sharp	strong
(NaOH)	--	6.91	>28.0 diffuse	very strong
adenine	0.091	7.25	>28.0 diffuse	strong
			>12.8 diffuse	medium
adenine	0.131	7.65	>28.0 diffuse	strong
			>12.5 diffuse	medium to strong

Table 3 IR absorption bands of adenine, adenine·HCl, and various adenine montmorillonite complexes in the range of 1250 - 1750 cm<sup>-1</sup>.






















\* band appears as a shoulder; ] plateau between these frequencies

adenine	adenine-HCl		adenine-Ca-montm.		adenine-Co-montm.		adenine-Ni-montm.		adenine-Cu-montm.		adenine-Fe(III)-montm.		
		pH2.0	pH4.6	pH5.5	pH9.1	pH2.0	pH5.1	pH9.1	pH2.1	pH5.2	pH9.3	pH2.2	pH4.9
(Angell, 1961)													
1250m	1258s	1280*	1240*	1240*	1270*	1235*	1240*	1230*	1235*	1270*	1280*	1280*	1240*
1305m		1310w	1310w	1310m		1310m	1310m	1310w	1312m	1300m			1310*
	1319w									1315*			
1333m		1330m	1338m	1337m	1330m	1338m	1338w	1330m	1336m	1345m	1325m	1330m	1340m
1368w	1381m	1389s	1395s	1395s	1390s	1393s	1390s	1395s	1396s	1400s	1385s	1390s	1395*
1418m	1425w		1420w			1420w	1420w					1420s	1420s
1451w	1441w	1450s	1449m	1450m	1452s	1450s	1448s	1450	1445*	1460m	1445m	1455*	1450*
			1460*	1460*		1460*	1460*	m					
			1480*	1480*		1480*	1480*	1480	1480s	1475m			
1510w	1500m	1505s	1505w	1505w	1505m		1510*	1500*	1510*		1505s	1510m	
			1550*	1550*		1550*	1540*		1550*	1540m			1540*
							1570*	1560*	1570*	1565m			
	1597m	1600*			1590*								
1605m	1623s	1617vs	1620vs	1620s	1615vs	1615s	1600*	1620s	1610s	1600*	1612vs	1618vs	1620s
				1650]s			1645vs			1650s			
									1670*				
1672s	1712s	1701vs	1700vs	1700vs	1701vs	1700vs	1688vs	1703vs	1700s		1700vs	1701vs	1690vs
									1720*				

Captions to Figures

Absorption of Pyrimidines, . . . by Co-, Ni-, Cu-, and  
Fe<sup>(III)</sup>-Montmorillonite (Clay-Organic Studies XIII)

by G. E. Lailach, T. D. Thompson and G. W. Brindley.

- Figure 1. Absorption by (a) Ca-; (b) Co-; (c) Ni-; (d) Cu-  
montmorillonite. Absorbed compounds: adenine  ;  
hypoxanthine  ; purine  ; pyridine  ; 6-chloropurine  .
- Figure 2. Absorption by (a) Ca-; (b) Co-; (c) Ni-; (d) Cu-  
montmorillonite. Absorbed compounds: adenine  ;  
7-methyladenine  ; 9-methyladenene  ; cytosine  .
- Figure 3. Absorption of nucleosides by (a) Ca-; (b) Co-;  
(c) Ni-; (d) Cu-montmorillonite. Adenosine  ;  
inosine  ; guanosine  ; cytidine  .
- Figure 4. Absorption by Fe(III)-montmorillonite. (a) adenine  ;  
hypoxanthine  ; purine  ; cytosine  ; (b) adenosine  ;  
inosine  ; cytidine  ; guanosine  .

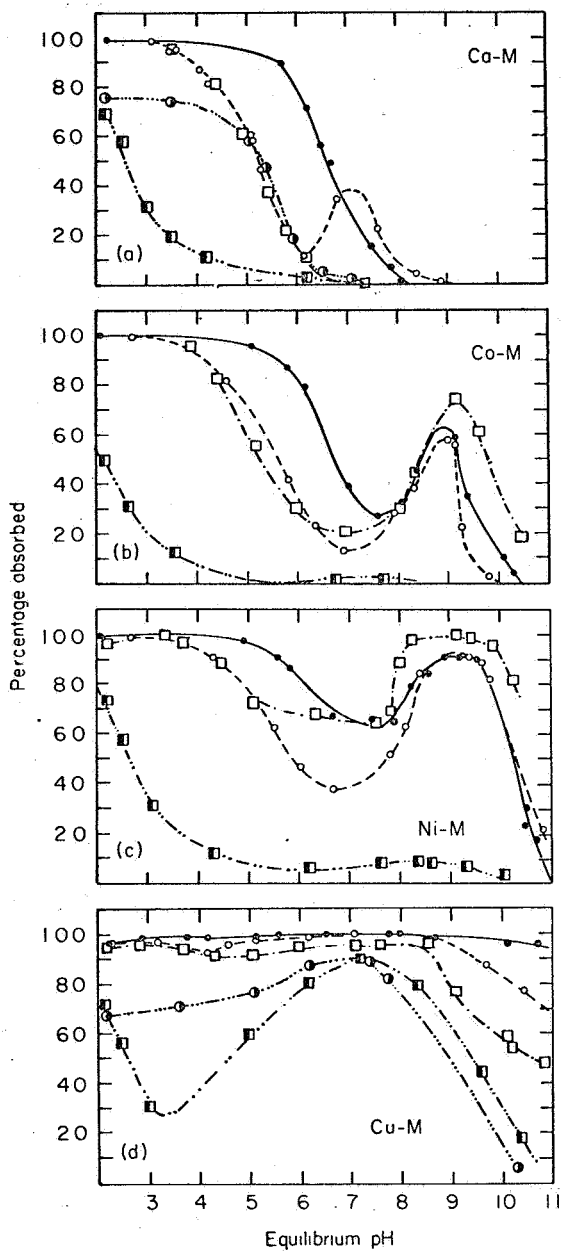


Figure 1

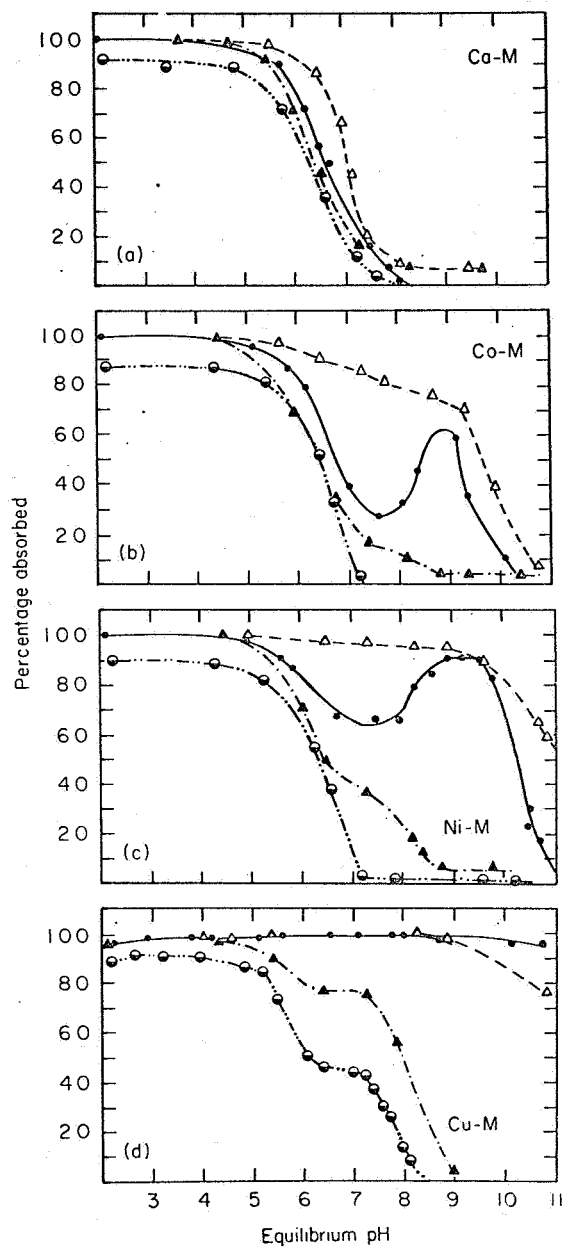


Figure 2

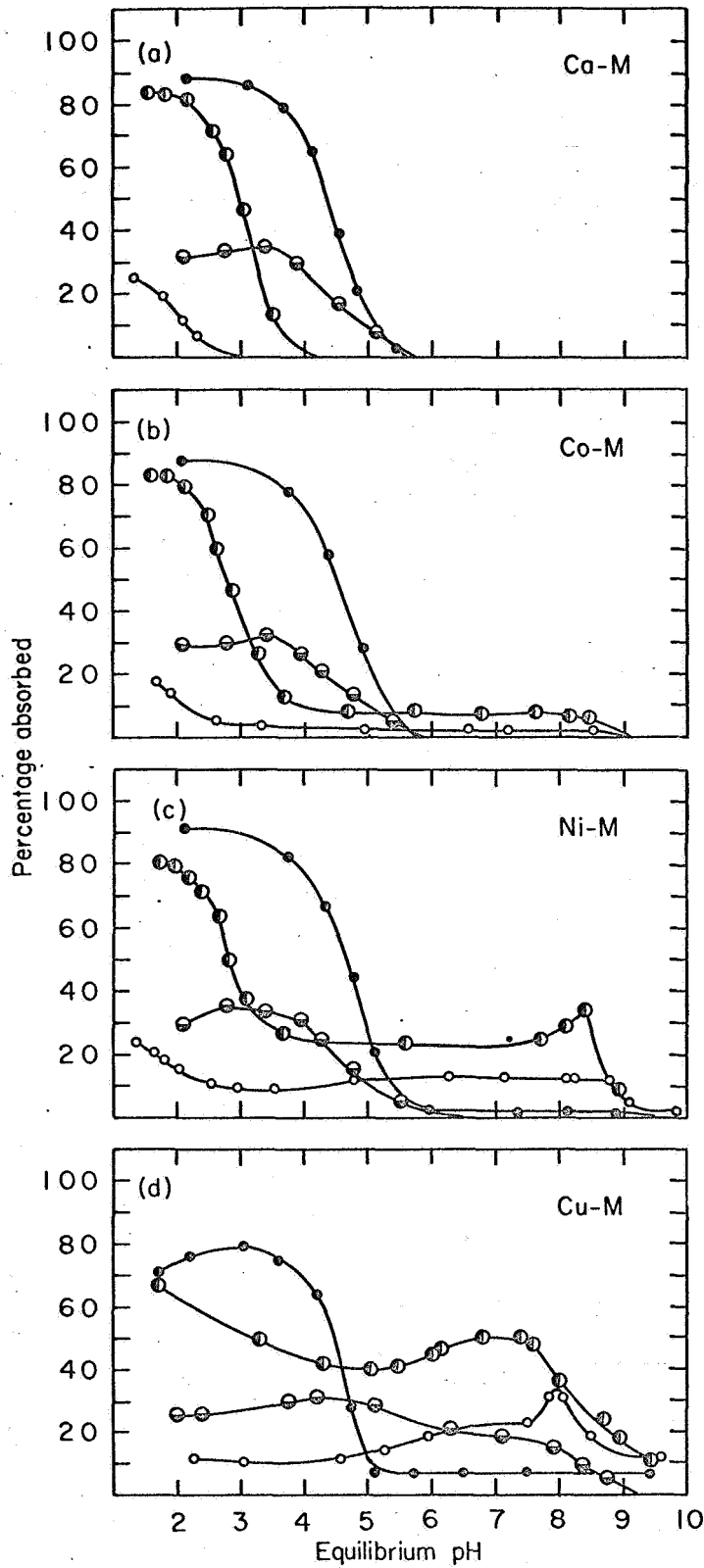


Figure 3

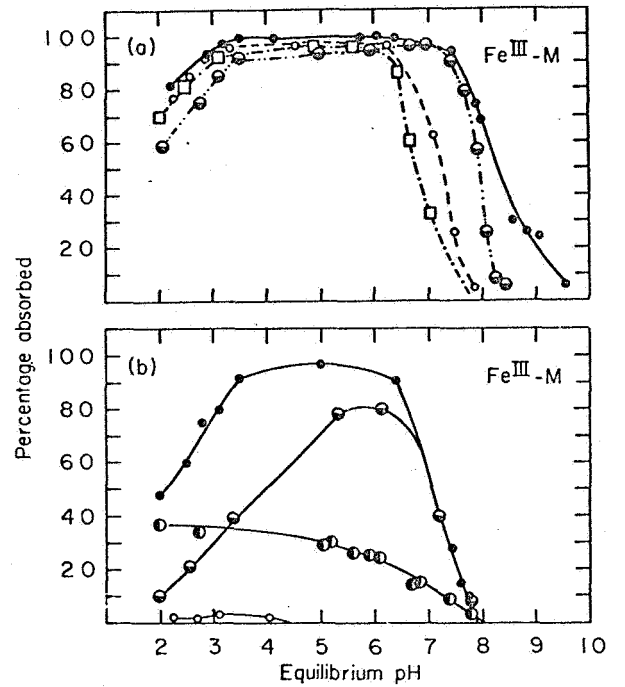


Figure 4